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SCIENTIFIC AND TECHNICAL ASSESSMENTS
OF ENVIRONMENTAL POLLUTANTS

Nitrates:
An Environmental Assessment

A report prepared by the
Panel on Nitrates
of the Coordinating Committee for Scientific and Technical
Assessments of Environmental Pollutants

Environmental Studies Board
Commission on Natural Resources
National Research Council

NATIONAL ACADEMY OF SCIENCES
Washington, D.C. 1978

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PREFACE

In early 1975, the Office of Research and Development of the U.S. Environmental Protection Agency (EPA) asked the Environmental Studies Board of the National Research Council to undertake a series of studies to assess current knowledge on specific environmental contaminants. The objective of each study was to prepare a comprehensive document summarizing and assessing the scientific and technical information that EPA would need to consider in taking a regulatory action or actions with respect to the particular substance or class of substances.

The Environmental Studies Board established the Coordinating Committee for Scientific and Technical Assessments of Environmental Pollutants (STAEP) in the summer of 1975, and appointed panels to conduct assessments of the individual pollutants. The substances or classes of substances to be studied were chosen by mutual agreement between the Coordinating Committee and EPA. The agency's chief interest was in the selection of pollutants for which regulatory action was likely to be required, but for which such requirements were not immediately pending. The Coordinating Committee sought to choose subjects on which the scientific issues were challenging and controversial, where the expert judgment of the National Academy of Sciences could be most usefully applied. The substances chosen for panel studies in this series were (1) low molecular weight halogenated hydrocarbons; (2) mercury; (3) kepone, mirex, and hexachlorocyclopentadiene; and (4) nitrates.

The panels established under the STAEP Committee were charged with conducting a comprehensive review and assessment of their assigned pollutant substances or classes of substances, encompassing: (1) physical and chemical properties of the compound; (2) methods for analysis and measurement; (3) sources, environmental transport and transformations, and the occurrence and distribution of the substance in the various compartments of the environment; (4) environmental exposures and the effects of those exposures on human health, plants, animals, other organisms, and the inanimate environment; (5) control techniques and control strategies; and (6) economic costs and benefits of possible control measures. The panels were instructed to use a mass-balance approach to the study of problems, insofar as this was feasible. Each report on a particular pollutant was to reach judgments on scientifically controversial issues, and to identify areas in which information was inadequate to resolve important uncertainties.

In its charge to the Panel on Nitrates, EPA identified several areas in which regulatory actions for nitrates might be required, such as the establishment of national drinking water standards and the management of runoff from non-point sources. The STAEP Coordinating Committee was interested in a number of critical scientific questions, such as the magnitude of the contribution made by nitrates to exposures to nitrosamines, or (through production of nitrous oxide) to depletion of the ozone layer. The Committee also sought an assessment of the problems encountered in attempting to differentiate between human impacts and the natural variations in the biogeochemical cycle of an element.

The Panel on Nitrates was appointed late in 1975. Because of the comprehensive scope of the task assigned to the panel and the need for an integrated scientific, technical, and economic assessment of issues, a multidisciplinary team was assembled. The panel met three times during the initial phase of the study to identify critical issues, define its approach, draft an outline of its report, and assign writing responsibilities. The next stage of the study was devoted to information-gathering and included three meetings held in different parts of the country to discuss current research with investigators working on nitrate-related environmental problems. Members of the panel then prepared sections of the panel's draft report, which were discussed at a meeting in the fall of 1976, and after revision were compiled into a first draft of the report. That draft was circulated to selected scientists for peer review, and the panel held a week-long meeting in February, 1977, at which reviewers' comments were received and further revisions were made.

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The consultants to the panel assembled and evaluated information, and in some cases prepared drafts of sections

of the report. Jay J. Messer contributed substantially to the mass-balance studies in Appendix A and to the discussion of nitrogen mass balances in Chapter 5. Ian R. Fillery assisted in compiling information on the soil nitrogen cycle and on impacts of agricultural uses of nitrogen. James P. Heaney prepared an initial draft of the discussion of controls for nonpoint sources of nitrogen in surface runoff. Reza Pazand and Berry C. Ives compiled information to support the economic analysis in Chapter 11. We are also grateful for the assistance of Dr. David P. Hoel, of the National Institute of Environmental Health Sciences, who made the quantitative extrapolation of the estimated risk of liver cancer from dimethylnitrosamine, presented in Appendix C.

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Patrick L. Brezonik
Chairman
Panel on Nitrates

CHAPTER 1

EXECUTIVE SUMMARY

SCOPE OF THE STUDY

Environmental problems that involve nitrates are only part of a larger set of environmental issues related to the complex web of biogeochemical processes that are known collectively as the nitrogen cycle. While the focus here is on nitrates, (that is, nitrate ion and certain organic nitrate compounds), issues associated with these substances can be treated most effectively when examined in the context of the nitrogen cycle as a whole. It was beyond the scope of this study, however, to examine all human impacts on the nitrogen cycle. Furthermore, environmental issues related to two other important forms of nitrogen, ammonia and nitrogen oxides, have been assessed in other recent reports by the National Research Council (NRC 1977a, 1977b).

The Panel on Nitrates concentrated on some specific environmental issues related to nitrates, including:

(1) impacts of nitrates on human health:

- specific contributions of nitrates from environmental sources to human exposures to nitrosamines, and the related risk of cancer;
- nitrate in water and foods and its effects on health, especially the risk of methemoglobinemia;
- possible health hazards of atmospheric exposures to nitrates and nitric acid;

(2) ecological effects of nitrates:

- impacts of nitrogen fertilizers on the productivity of managed (agricultural) ecosystems;
- impacts of anthropogenic nitrogen fluxes on productivity in other terrestrial and aquatic

systems, including the role of nitrogen in the eutrophication of lakes and coastal waters;

  - contributions of nitrate (as nitric acid) to the acidity of precipitation, and consequent impacts on organisms and ecosystems;
  - direct toxic effects of nitrates and related compounds on plants and animals;

(3) potential depletion of the stratospheric ozone layer by human activities that fix nitrogen, and subsequent effects of such depletion of ozone on man, ecosystems, and climate.

Each of the above issues centers on concern about actual or potential effects on health or the environment. This assessment, however, encompasses a full range of related topics, including environmental exposures, processes of transport and transformation that link sources of fixed nitrogen to such exposures, and techniques that can mitigate or prevent adverse impacts, either through control of sources or by intervention at some point in the processes that link sources to effects. The assessment also includes an economic analysis of some nitrate-related environmental problems, and a brief examination of the implications of the scientific and economic data base, including the gaps and uncertainties in each, for policy decision making.

As a basic framework for analyzing the environmental issues, the panel used mass-balance approach, wherever possible. This approach examines reservoirs of fixed nitrogen and routes and rates of transfers among reservoirs of the nitrogen cycle, on scales appropriate to each of the problems (see Chapter 5). Because capabilities for analyzing or measuring different nitrogen forms or environmental processes often may determine our ability to know what occurs in the environment, a review of the state-of-the-art of measurement techniques is also part of the assessment (see Chapter 4).

Two kinds of findings are presented in this report. The first type of finding concerns the scientific and technical grounds for judgments as to, for example, the effects on health of exposure to nitrates and related compounds. Such findings include both judgments that the evidence does not permit precise definition of a relationship, as in the case of nitrosamines and human cancer, and judgments that a relationship has been established with some confidence, as in the case of nitrate in drinking water and infant methemoglobinemia. These judgments are likely to change only as new evidence is obtained by research. The second type of finding, in contrast, involves both scientific judgment and some weighing of social values; an example is the Panel's conclusion that our projection of the effect of nitrogen fixation on the stratospheric ozone layer does not represent a hazard that demands immediate action to implement control measures. Judgements of this second type are not subject to scientific verification; instead, they are the subjective views of the Panel, and where they occur, they are presented as such. These findings may change both as new evidence is produced and as the goals and values of society evolve.

NITRATES AND HUMAN HEALTH

Nitrate per se is relatively nontoxic to humans. The health hazards that are associated with nitrate result chiefly from the bacterial conversion of ingested nitrate to nitrite. Nitrite can induce methemoglobinemia (a reduction in the oxygen-carrying capacity of the blood), especially in infants. Nitrite also can react with other substances, such as amines, to form N-nitroso compounds. Most N-nitroso compounds are carcinogenic at high doses in animal tests; although no human tumors have yet been conclusively attributed to nitrosamines, it is reasonable to assume that exposure to these compounds might pose a risk of human cancer. However, assessment of the contribution of nitrate to that potential carcinogenic hazard and of the magnitude of the risk is a difficult task.

Human exposures to nitrates also include inhalation of organic and inorganic nitrates (including nitric acid). Even in a heavily polluted urban atmosphere, the nitrate absorbed by this route is unlikely to be a significant fraction of the total daily intake of nitrate. Some of the nitrate compounds, however, especially the peroxyacyl nitrates (PANs), are eye irritants and may be toxic at ambient levels.

Nitrates, Nitrosamines, and Cancer

The N-nitroso compounds, and in particular N-nitrosamines, are an important class of chemical carcinogens that have induced tumors in every species of laboratory animal tested, and in virtually every vital tissue (see Chapter 9). Many N-nitroso compounds also have been identified as mutagens in bacterial tests, but few data are available on their mutagenicity in mammalian cells.

Human exposures may result from inhalation or ingestion of preformed nitrosamines or from reactions of precursors to form nitrosamines in the stomach or, perhaps, in the lung (see Chapter 2). Very few data are available to support quantitative estimates of the magnitude of exposures by each route. Monitoring of the air in several cities has not detected nitrosamines except near industrial sources that emit nitrosamine compounds (see Chapter 2). Preformed nitrosamines also may be present in tobacco smoke, and in certain foods, such as bacon, sausages, and some fish products (see Chapter 9), but too few samples have been analyzed to estimate either the frequency of such contamination or the average exposure by this route.

Even fewer data are available on exposures to nitrosamines formed in vivo. Although the process has been demonstrated to occur in laboratory animals and in humans given relatively high doses of precursors, the extent to which nitrosation occurs in humans at typical levels of ingestion of nitrate, nitrite, and amines in unknown. However, because the average person in the United States ingests about 100 mg of nitrate, 11 mg of nitrite, and varying amounts of amines in a typical daily diet, in vivo formation of nitrosamines could be the largest source of exposure to these carcinogens for the general population (see Chapter 9 and Appendix C).

Several epidemiological studies have associated elevated incidence of cancer with the presence of nitrosamines in the diet; however, none of the studies accurately measured exposures, and few of the studies used adequate analytical methods to determine nitrosamines. It cannot be stated unequivocally, therefore, that any human cancer has been positively attributed to nitrosamines. A small number of studies also correlated elevated exposure to nitrate with increased incidence of stomach cancer, but the hypothesized etiology (involving in vivo conversion of nitrate to nitrite and subsequent nitrosation reactions) has not been demonstrated. Similarly, a statistical analysis of environmental variables and geographic patterns in cancer mortality showed a strong positive correlation between exposure to nitrite in the diet during the 1950s and total cancer mortality in 1972 (see Appendix B). However, once again biological evidence of the purported causal process is lacking, and correlations alone are insufficient to prove a causal relationship.

Although many N-nitroso compounds have induced tumors in laboratory animals, few studies provide adequate data to define detailed dose-response relationships (see Chapter 9 and Appendix C). The inadequacy of dose-response data from either epidemiologic or toxicologic studies precludes a determination of whether the exposures to N-nitroso compounds that might result from dietary nitrate and nitrite are "safe," or of how large a risk of human cancer such exposures may represent. Based on limited data on the incidence of liver cancer in rats given relatively large doses of dimethylnitrosamine, the Panel estimated the risk of cancer at much lower doses (see Appendix C). Such extrapolations, however, require many assumptions that lack scientific support. In particular, the estimated range of doses of nitrosamines used in the risk estimate was derived from arbitrary assumptions, and the upper estimate exceeds by a wide margin any human exposure that has actually been shown to occur. The numerical results in Appendix C therefore cannot be accepted as reliable approximations of the risk of human cancer from nitrosamines.

In the absence of more definitive information on the magnitude of the health hazard, we believe that the most prudent course of action is to take reasonable measures to minimize human exposure to N-nitroso compounds. Such measures as reduction of emissions of preformed nitrosamines from industrial sources and restriction of the amounts of nitrate and nitrite added to meat products are now being pursued (see Chapters 10 and 12). Exposures to nitrate and nitrite from vegetables and drinking water would be much more difficult to control. Addition of ascorbic acid to products that contain nitrate and nitrite may also reduce the risk of cancer, since ascorbate reacts with nitrite and inhibits nitrosation reactions in the stomach. The lack of more quantitative estimates of the hazard of cancer, however, precludes determining what level of control effort is justified (see Chapter 11).

Nitrate in Drinking Water and Methemoglobinemia

The most notable acutely toxic effect of nitrate likely to result from environmental exposures is infant methemoglobinemia. Methemoglobinemia occurs when an oxidizing agent such as nitrite, which is formed in the stomach from nitrate, combines with hemoglobin, reducing the oxygen-carrying capacity of the blood. Infants in the first three months of life are particularly susceptible to nitrite-induced methemoglobinemia, for a number of physiological reasons. Adults normally are not susceptible to the disease. Although some individuals with predisposing conditions could be at risk, we know of no confirmed reports of adult methemoglobinemia. A few cases of the disease have been associated with foods high in nitrate or nitrite, but nearly all cases reported in the United States have resulted from ingestion of nitrate in private well water used to make infant formula. Mortality from methemoglobinemia is extremely rare, but the presence of high levels of nitrate in drinking water supplies poses a health hazard that is a valid concern in some regions of the United States (see Chapter 9).

Many surveys of the incidence of methemoglobinemia in several countries have indicated that the disease is quite rare when water supplies contain less than 10 mg NO_3^--N/l. Although the available data do not fit an exact dose-response curve, it is evident that the risk of methemoglobinemia increases measurably as nitrate concentrations increase above 10 mg/l. Insufficient knowledge exists to determine whether subtle or chronic toxic effects might occur at levels of exposure below those that produce clinically obvious toxicity.

Methemoglobinemia is rarely fatal, is readily diagnosed, and is rapidly reversible with clinical treatment. Furthermore, infants that are breast-fed or given whole cow's milk rather than formula reconstituted with water are unlikely to be at risk. Nevertheless, the existence of a 10 mg/l drinking water standard for nitrate has been a useful policy instrument (see Chapter 12). There is no convincing scientific evidence to indicate that a more stringent standard would confer additional health protection; however, as noted, a less stringent standard that permitted higher exposures would entail a greater risk.

Nitrate concentrations above 10 mg/l are rare in public water supplies in the United States (see Chapter 3). High levels of nitrate are more likely to occur in well water, especially in regions where soil and hydrologic conditions favor accumulation of nitrate in groundwater; some private wells on small farms contain up to several hundred mg/l of nitrate.

Controls for Nitrate Water Pollution

Society may wish to avoid the risk of methemoglobinemia (or other possible effects of nitrate in water supplies), but prevention of nitrate contamination of ground or surface waters is complex and often difficult. The nitrate in water may come from a number of sources, including mineralization of soil organic nitrogen, fertilizers, sewage, and livestock manures; even at well-studied sites, the complexities of soil water and nitrogen cycles have frustrated attempts to determine the quantitative contributions of specific sources to nitrate pollution (see Chapters 4 and 6). On a national scale, soil characteristics, climatic factors, and agricultural practices are so heterogeneous that no quantitative general conclusions about the impact on water quality of a single factor, such as fertilizer application rates, can be supported (see Chapter 6).

The lack of more accurate information about sources and transport processes makes it extremely difficult to devise general control strategies to reduce nitrate levels in water supplies, particularly in cases of runoff or leaching from agricultural croplands. Control programs are already being implemented to reduce pollution by sewage and livestock wastes (see Chapter 10), and many available agricultural management practices can reduce the amount of nitrogen lost to the environment. The techniques include soil and water conservation measures, crop rotations, use of cover crops to remove residual nitrogen, and some well-tested and some more theoretical methods for improving the efficiency of crop use of fertilizers. In general, the combination of practices that could minimize losses of fertilizer nitrogen can be determined best at the level of individual watersheds or even individual farms (see Chapter 10). In some cases, such as nitrate contamination of groundwater beneath heavily fertilized irrigated croplands in certain regions, it is unlikely that any effective control measures could be compatible with productive, economically feasible agriculture using current cropping techniques.

Another possible control approach is the imposition of statutory limits on fertilizer application rates. This option has been considered in Illinois; however, the lack of credible quantitative information on the relationship between fertilizer use and water quality makes it impossible to predict accurately the environmental effects of any particular level of restriction, and no such policies have been shown to be warranted (see Chapter 10).

Removal of excessive nitrate from drinking water is technically feasible, although the advanced techniques that are available, such as anion exchange methods, are probably prohibitively expensive. A more feasible option is to avoid the use of high-nitrate water supplies for drinking, and especially to avoid using such supplies in infant formulas. This might be accomplished through provision of alternative water supplies (bottled or piped) to families or communities where drinking water came from nitrate-contaminated wells; or it might be approached through educational and health care delivery programs that could reach parents of infant children (see Chapters 10 and 11).

Health Hazards of Atmospheric Nitrates and Nitric Acid

Relatively little is known about the direct toxicity of the nitrate component of urban air pollution, which includes organic compounds such as peroxyacyl nitrates (PANs) and alkyl nitrates, inorganic nitrate aerosols, and nitric acid vapor. Some unpublished data from EPA's Community Health and Environmental Surveillance System (CHESS) studies suggested a link between high levels of suspended nitrates and increased incidence of asthma attacks, but other pollutants also present could be involved as well. In another case, respiratory illness was associated with nitrogen oxides, but could have been caused in part by nitrates (see Chapter 9). One Czechoslovakian study attributed elevated methemoglobin levels in children to high atmospheric nitrate levels.

Nitric acid vapor is an irritant, with a threshold limit value (TLV) for industrial exposure of 5 $\mu g/m^3$. In one preliminary report, acute inhalation exposure to nitric acid mist at approximately seven times the TLV exposure produced osteosarcomas in 4 of 58 rats. Further investigation of this possible link between nitric acid and cancer is desirable. In general, the data base is both too limited and too ambiguous (because nitrates are almost always present with many other pollutants) to provide any definite indication of the health hazards of ambient levels of atmospheric nitrates (see Chapter 9).

Most airborne nitrates are formed in the atmosphere from nitrogen oxides and other precursors, which are for the most part products of combustion. The reactions that produce PANs, inorganic nitrate and nitric acid aerosols, and nitric acid vapor are discussed in Chapter 2 (see Table 2.8). Evidence that nitric acid vapor is present at significant levels in the atmosphere has only recently become available. It now appears, however, that some of the nitrate measured by hi-vol filters is gaseous HNO_3, rather than particulate nitrate (see Chapters 3 and 4). Some recent data suggest that measured "nitrate" levels are one-tenth to one-third as high when quartz filters (which trap particulate nitrates but not HNO_3 vapor) are used instead of glass fiber filters (which trap HNO_3).

Typical levels of nitrates in urban and rural air are summarized in Chapter 3. Most of the nitrate fraction in urban air during daylight hours is composed of PANs, while at night and in rural areas inorganic nitrate aerosols predominate. Data from the National Air Surveillance Network show average annual inorganic nitrate concentrations of about 1.1 $\mu g/m^3$ at rural sites and 3.1 $\mu g/m^3$ at urban sites, and trend data indicate that levels have approximately doubled in the last 10 years. (The uncertainty created by knowledge that the samplers may have measured nitric acid as well, discussed earlier, must be noted in regard to the NASN data.) Fewer data are available on levels of PANs in ambient air, but in heavily polluted areas such as Los Angeles, average hourly concentrations on the order of 5 to 10 ppb are common. Virtually no data are available on typical levels of alkyl nitrates or nitric acid vapor.

In the absence of more positive evidence of a risk to health, other effects of atmospheric nitrates, such as corrosion of materials and contribution to the acidity of precipitation, provide the primary impetus for control efforts. The need for and feasibility of controls and emissions of nitrogen oxides are discussed later in this summary, in the section on nitrates in precipitation (also, see Chapter 10).

ECOLOGICAL EFFECTS OF NITRATES

Ecological effects of nitrate can be beneficial or detrimental. Nitrogen is an essential nutrient for biotic productivity, and in managed agricultural ecosystems nitrogen fertilizer enhances crop yields. However, in some natural ecosystems, such as lakes and estuaries, the addition of nitrogen can contribute to eutrophic conditions that are considered undesirable. Nitrate (as nitric acid) also contributes to the acidity of rainfall and to corrosion of materials, and some nitrates and related compounds are toxic to plants, animals, or microorganisms.

Nitrogen Fertilizers and Crop Production

The most widespread effect of anthropogenic inputs of nitrogen on biological systems is the increased yield of agricultural crops in response to fertilizers. The responses of various crops to different forms, amounts, and application schedules of nitrogen fertilizer have been thoroughly studied because of their obvious agronomic and economic importance. Knowledge of crop responses is also critical for sound environmental management, since efficient use of fertilizer can help minimize losses of excess nitrogen to the environment. The general relationship between nitrogen fertilizer application rates and crop yields is well known qualitatively; however, the growth of a crop in a given location and the efficiency of the crop's use of available nitrogen depend on soil properties, weather and climate, and many cultivation and management practices in addition to those that involve fertilizer. This complexity makes it impossible to predict how much nitrogen fertilizer a given crop at a given location needs or to determine the amount of residual nitrogen lost to the environment (see Chapter 8). The lack of an accurate quantitative relationship between fertilizer application rates and crop yields also precludes accurate determination of the marginal economic benefit of incremental applications of fertilizer, an important measure needed to estimate some of the costs of possible control strategies (see Chapters 10 and 11).

Even in the absence of more exact knowledge of crop nitrogen needs, many techniques can be employed to improve the efficiency of fertilizer use and to minimize the potential environmental impacts of overfertilization, where this occurs. These techniques are reviewed in Chapter 10.

Nitrogen Inputs and Productivity of Terrestrial Ecosystems

In most nonagricultural terrestrial ecosystems, the major processes that provide nitrogen for plant growth are mineralization of soil organic nitrogen and biological fixation of atmospheric nitrogen. When fluxes of nitrogen enter such systems as a result of human activities, the added inputs in many cases represent a significant fraction of total nitrogen inputs. On the basis of such mass-balance considerations, it seems likely that such fluxes are important nutrient sources that could support increased biotic productivity.

Except in ecosystems that receive fertilizer or nitrogenous wastes, the most important anthropogenic inputs are likley to be from atmospheric pathways. Total (inorganic plus organic) nitrogen loadings in wet and dry precipitation may be equivalent to from 8 to 25 percent of the nitrogen used by plants in different natural ecosystems (see Chapter 6, Chapter 8, and Appendix A, Section 3). Even in heavily managed ecosystems, annual atmospheric fluxes may be substantial; for instance, calculated total nitrogen inputs from precipitation and from gaseous deposition over the Florida peninsula exceed by a factor of two the amount of nitrogen applied as fertilizer to the agricultural land area within the region (see Appendix A, Section 6).

Determination of the response of an ecosystem to such nitrogen inputs is probably impossible. The same complex interactions among numerous factors that were discussed in relation to the response of agronomic crops to fertilizer nitrogen apply in this case. In addition, quantitative information about the nitrogen cycle at specific sites is lacking. If emissions of fixed nitrogen to the atmosphere were reduced, one consequence might be a reduced flow of nutrients that support potentially beneficial ecosystem productivity; however, the magnitude or extent of such effects cannot be estimated with current knowledge.

Nitrogen Inputs to Aquatic Ecosystems and Eutrophication

The overenrichment of surface waters, usually lakes, with nutrients is termed eutrophication. This process results in an array of water quality changes that are generally regarded as undesirable (see Chapter 8). Phosphorus and nitrogen are the most important nutrients that stimulate eutrophication, and in most lakes phosphorus is considered the more critical of the two. In coastal and estuarine ecosystems, however, nitrogen is more often the limiting nutrient, and nitrogen inputs may control eutrophication. Furthermore, in many already-eutrophic lakes, biotic productivity is controlled by nitrogen, because the N/P ratios of pollutants from many cultural sources (e.g., domestic sewage) are far below the ratios needed for plant growth. The role of nitrogen in cultural eutrophication therefore appears to be important, although it is complex and poorly quantified relative to the role of phosphorus (see Chapter 8).

The sources of anthropogenic nitrogen inputs to surface waters include sewage, industrial wastes, animal manures, surface runoff and sub-surface transport of nutrients from urban and agricultural lands, and atmospheric fluxes. Estimates discussed in Chapter 6 indicate that more than 90 percent of the nitrogen entering surface waters comes from nonpoint sources, and that more than 80 percent of that portion is from agricultural lands (including livestock feedlots). Because nitrogen forms in aquatic systems are readily interconvertible, all nitrogen inputs, rather than nitrate per se, must be considered (see Chapters 6 and 8).

The average atmospheric input of 10 to 20 kg N/ha-yr that is typical for most of the United States is also a sufficient nutrient loading to support a moderate increase in biotic productivity in some lakes, especially shallow, oligotrophic lakes that may be nitrogen-limited. Atmospheric nitrogen fluxes may contribute to slight eutrophication in such cases; however, it is unlikely that these inputs alone would induce serious water quality problems (see Chapters 6 and 8).

Prevention of eutrophication requires the elimination of excessive nutrient inputs to lakes and coastal waters. Many sources of nitrogen, such as sewage outfalls, are now subject to controls, and effective reduction of nitrogen discharges from such sources appears technically feasible (see Chapter 10). The control of nitrogen pollution from nonpoint sources is more complex and difficult; the sources and control techniques that are involved were discussed, in relation to nitrate in drinking water, in an earlier section of this summary (also, see Chapter 10). Atmospheric sources also pose a difficult control problem (see discussion of nitrate in precipitation, below). An important part of the fixed nitrogen in precipitation enters the atmosphere by ammonia volatilization, chiefly from animal wastes; such inputs cannot be effectively controlled as long as land disposal of manures is the most common measure employed to prevent more immediate (runoff) impacts on water quality.

The levels of nitrogen that can stimulate moderate increases in biotic productivity in surface waters are at least an order of magnitude lower than the levels that pose hazards to human health. Effective elimination of the risk of eutrophication, at least insofar as nitrogen is a controlling factor in the process, could therefore require much more stringent control measures than are needed to meet the 10 mg N/l drinking water standard for nitrate. However, it has not been demonstrated that such complete prevention of nitrogen pollution is necessary. Scientific and economic assessments of problems at specific sites would be required to determine the benefits and costs of measures that could be used to reduce the risk of eutrophication in any given case.

Atmospheric Nitrates and the Acidity of Precipitation

Precipitation that has a pH of less than 5.6 is considered acidic. The principal agents of acidity in precipitation are acid sulfates and nitrates, formed in the atmosphere from emissions of sulfur oxides and nitrogen oxides. Recent data indicate that almost all of the United States east of the Mississippi River receives rainfall with a pH of less than 5.0, and the average pH of precipitation over New York state and lower New England is between 4.0 and 4.2. There is general agreement that acid rainfall is a man-caused problem with potentially severe adverse ecological effects; however, several aspects of the problem remain controversial because the existing scientific information is inadequate or ambiguous.

The effects of acidic precipitation on organisms and ecosystems have been studied extensively in North America and in Scandinavia. Prolonged leaching by acid rainfall produces numerous changes in soils, and vegetation may suffer direct or indirect adverse effects. It is suspected that acid rainfall has had adverse impacts on the long-term growth of forests; however, current data are inadequate to establish any convincing trends in this regard for the United States, or to separate the effects of rainfall acidity from those of other variables, such as weather, that affect the productivity of forests (see Chapter 8). Many aquatic organisms are sensitive to pH changes, and the pH of many lakes in northern Europe and in parts of the eastern United States has been declining in recent decades. For instance, about half of the lakes in the Adirondack Mountains in New York have a pH of 5.0 or less; and 90 percent of those lakes are devoid of fish (see Chapter 8). The economic value of losses of forest productivity and sport fisheries in the United States may exceed $100 million per year (see Chapter 11).

Although serious adverse ecological effects of acid rainfall are likely, a number of critical scientific issues related to the problem remain to be resolved. It is well established that both the acidity of rainfall and the geographic extent of the area receiving acid rain have increased in the past two decades; however, uncertainties about the accuracy of historical pH values and the limited number of locations with adequate data preclude firm estimates of the rate of change of either aspect. Also, the exact causes of the increasing acidity have not been determined. Various changes in fuel use patterns and increasing use of tall stacks that disperse pollutants over wider areas have occurred concurrently with the declining pH, and it is not clear which of these (or perhaps other factors) has had the greatest impact on rainfall acidity.

The relative importance of nitrate and sulfate contributions to the acidity of precipitation, while critical for the design of effective control strategies, is difficult to quantify (see Chapter 6). Best estimates are that from 25 to 30 percent of the acidity of rainfall in the eastern United States is derived from nitrate, and trend data for the past two decades indicate that the proportional contribution of nitrate is increasing. Furthermore, limited data suggest that the trend of increasing annual input of acidity correlates well with the nitrate input, but not with sulfate fluxes. To date, control measures for stationary combustion operations have emphasized reduction of sulfur oxides and not restricted nitrogen oxide emissions, except from new sources; as a result, emissions of SO_x have declined in recent years, but NO_x emissions have increased. If this pattern persists, the nitrate fraction of rainfall acidity will continue to grow.

Acidic Nitrate Aerosols and Damage to Materials

A substantial fraction of the nitrate in precipitation is in dry fallout of aerosol particles; at some sites, inputs from dry precipitation are several times greater than those from wet precipitation (see Chapter 6). It is not known whether dry deposition of acidic aerosols between rainfall events aggravates the ecological damage caused by acid rainfall, but acidic aerosols have relatively well-established adverse effects on materials (see Chapter 8). Only a few studies on the corrosion of metals and weathering of calcareous materials by acidic air pollutants have attempted to determine the effects of individual compounds; however, a small number of instances of damage specifically attributed to nitrates have been reported. Estimates of the costs of corrosion by air pollutants suggest that the NO_x-related portion of such damages may be from $135 to $542 million per year for the United States. These damages substantially exceed those estimated for measurable ecological effects of acid rain, and are an important element in arguments for further control of NO_x emissions (see Chapter 11).

Controls for NO_x Emissions

The nitric acid and acidic nitrate aerosols that fall out in precipitation are formed in the atmosphere, and the only effective control is to reduce emissions of NO_x precursors. Although much remains to be learned about the rates of formation and residence times of atmospheric nitrates, the available evidence suggests that emitted NO_x may be transported as much as 300 to 1500 km downwind before they are deposited as nitric acid in rainfall (see Chapter 6). The long-distance nature of the impacts suggests that if controls are to be attempted, they should be regional or national measures rather than local or statewide control strategies.

Three basic approaches are available to reduce NO_x emissions from combustion sources: modification of the combustion process to reduce the amount of NO_x formed; removal of NO_x from the exhaust stream; and use of fuels with a lower nitrogen content. (Because most of the NO_x emitted is formed from atmospheric N_2, the importance of this third approach is limited.) Control measures now in effect will require progressive reductions in NO_x emissions from motor vehicles (see Chapter 10). On the other hand, NO_x emissions from stationary sources currently exceed those from mobile sources, and seem likely to increase in the next decade. Furthermore, the emissions from tall stacks of stationary sources are more likely to be transported long distances and to contribute to the acid rain problem than ground-level emissions from auto exhausts (see Chapter 6).

The most promising techniques for the control of NO_x emissions from stationary combustion sources are discussed in Chapter 10. In general, the technical and economic feasibility of such measures is more favorable for large operations than for small ones, and for new units than for existing units. Most available control techniques for NO_x emissions have been tested at the laboratory or pilot-plant scale, but the effectiveness and the costs of such controls have not been adequately evaluated for full-scale applications (see Chapter 10).

From an economic perspective, the costs and benefits of controls of NO_x emissions encompass a wider range of issues than the acid rainfall problem alone. In addition to contributing to biotic productivity and potential effects on materials and ecological damages of acid rain, NO_x emissions also pose a potential hazard to health, and have quantifiable aesthetic effects (on visibility). The expected benefits of control of NO_x emissions are substantial, but vary widely from one region of the country to another. Cost/benefit analyses and assessments of the need for additional emission controls therefore should be conducted for specific regions (see Chapter 11).

Direct Toxic Effects of Nitrates and Related Compounds in Ecosystems

While the major known ecological effects of nitrates are those related to nutrient enrichment of ecosystems or acidification of precipitation, direct toxic effects of nitrates, nitrites, or nitrosamines on plants and animals warrant some concern. There is little information available from which to assess such hazards quantitatively; however, none of the risks currently appears to be large (see Chapter 8).

Elevated concentrations of nitrite rarely occur in the environment; the exceptions usually are situations in which large amounts of ammonia are rapidly undergoing nitrification, as in streams that receive heavy loads of nitrogenous wastes. Nitrite is toxic to some species of fish at concentrations of less than 1.0 mg N/l, and may pose a localized hazard to aquatic life. High levels of nitrite in soils (>10 ppm NO_2^-) can retard plant growth, especially in acid soils; however, since nitrite accumulates only in alkaline soils, nitrite toxicity is not likely to be a widespread problem. Peroxyacyl nitrates (PANs) are phytotoxic products of urban air pollution; but PANs are less important as hazards to vegetation than other photochemical oxidants, such as ozone. Some nitrosamines are emitted directly from industrial sources, and the possibility exists that amines and nitrite could react in the environment to form carcinogenic N-nitroso compounds. However, virtually no data are available on exposures of wildlife to N-nitroso compunds, and whether there is any hazard of cancer from such potential exposures is a purely speculative question.

If future research should indicate that the toxic effects of any of these substances are ecological hazards that require preventive action, control measures discussed in earlier sections of this summary would be applicable to these problems as well.

NITROGEN FIXATION, NITROUS OXIDE, AND DEPLETION OF STRATOSPHERIC OZONE

Concern has grown in the past decade over certain human activities that could result in depletion of the stratospheric ozone layer, which shields the biosphere from harmful exposures to ultraviolet radiation. Increased ultraviolet irradiation of the earth's surface would probably lead to increased incidence of human skin cancer, could have adverse effects on plants, animals, and microorganisms, and might lead to changes in climate (see Chapters 8 and 9).

Ozone is formed in the stratosphere by photolysis of molecular oxygen; this process is not influenced by human actions. The chief natural mechanism that removes ozone from the stratosphere is a catalytic cycle involving nitrogen oxides (NO_x, = NO_2 + NO) (see Chapter 2), and the principal source of NO_x in the stratosphere is nitrous oxide (N_2O). N_2O is unreactive in the troposphere, and is transported by turbulent diffusion to the stratosphere, where it undergoes photolysis and forms some NO_x; this is the only known atmospheric sink for N_2O. The total amount of N_2O in the global atmosphere therefore is a major determinant of the rate of destruction of stratospheric ozone; and processes that increase the global pool of N_2O ultimately will lead to some depletion of the ozone layer (see Chapter 7).

The most important source of N_2O is denitrification in soils and sediments; some N_2O is also produced in combustion, but this appears to be a minor source (see Chapter 2). Any human activities that increase the amount of fixed nitrogen available for denitrification, therefore, are likely to increase the rate of production of N_2O. The major anthropogenic sources of fixed nitrogen are fertilizer production and the cultivation of nitrogen-fixing legumes; in 1976, these two activities combined produced an estimated 84 million metric tons (Mt) of fixed nitrogen globally (see Section 7 of Appendix A). Combustion also fixes nitrogen, and in 1976, known fuel uses accounted for emissions of 21 Mt of NO_x-N. It is also possible that combustion of wood, both as fuel and in land clearing, releases a substantial additional amount of fixed nitrogen to the atmosphere (see Chapter 6 and Appendix A, Section 7). Human activities therefore account for about 105 Mt of a total estimated global rate of nitrogen fixation of 259-359 Mt/year, or 29 to 41 percent of known sources, plus an uncertain but possibly significant contribution from combustion of biomass. Furthermore, it is likely that nitrogen-fixing activities related to agriculture and energy use will increase in the future. The potential anthropogenic increase in the atmospheric pool of N_2O is therefore substantial.

Quantitative prediction of the magnitude of possible impacts of N_2O from human activities on the ozone layer is highly uncertain, because current knowledge is insufficient to determine accurate values for several critical variables. The fate of anthropogenically fixed nitrogen, and particularly the fraction that is denitrified promptly (within decades), is one variable about which much uncertainty remains (see Chapter 7). A second critical variable is the fraction of the products of denitrification that is N_2O, as opposed to N_2. Available measurements on agricultural soils are insufficient to provide an accurate global average value for the N_2O/N_2 ratio; and less is known of either the rates or the ratios of the gaseous products of denitrification in most of the world's oceans. A third critical variable of uncertain magnitude is the atmospheric residence time (τ) of N_2O; various estimates indicate that τ could be anywhere from 5 to 160 years, although recent data may have narrowed the range to 10 to 40 years. A final critical variable is the sensitivity factor that relates an increase in NO_x in the stratosphere to a decrease in ozone. The best current estimate is that a doubling of stratospheric NO_x probably would reduce the ozone content of the stratosphere at most by 1/10; however, the factor could be as large as 1/5 or as small as 1/15, and estimates of its value have changed markedly as knowledge of stratospheric chemistry has expanded (see Chapter 2).

The interrelated uncertainties combine to make projections of N_2O-related impacts on the ozone layer only educated guesses. The range of uncertainty can be narrowed, however, because current understanding of the global nitrogen cycle makes certain combinations of the variables implausible. Although the absolute size of the projected effect is subject to revision as research data accumulate, our current understanding suggests that N_2O from human-induced nitrogen fixation could lead to decreases in ozone of from 0.1 to 13 percent, with a "most probable" range of 1.5 to 3.5 percent. The change could occur as early as the year 2000, or might not be fully felt for 500 years, but seems most likely to occur by about the beginning of the 22nd century (see Chapter 7).

The analysis also leads to certain additional conclusions. First, it is unlikely that N_2O could produce a large depletion of the ozone layer in the near future; if an impact occurs soon, it is likely to be very small, and if a large impact occurs, it is likely to develop only over a period of several centuries, assuming continued major human contributions to global nitrogen fixation. Second, on the basis of current information, the "most probable" estimate of the N_2O-related threat to the ozone layer is approximately one quarter as large as the impact projected from current use of chlorofluorocarbons, or one half of the projected effect of a commercial fleet of 500 stratospheric aircraft (see Chapter 7).

In short, understanding of the global nitrogen cycle is firm enough to support the validity of concern over impacts of anthropogenic nitrogen fixation on the ozone layer. However, despite some very important uncertainties, it appears that any effect that occurs will develop slowly over decades, and that no immediate corrective action is required. If continued research demonstrates a need for preventive measures, the only effective control on N_2O production appears to be to limit the contribution of human activities to global nitrogen fixation. Although some reduction in industrial fixation might be achieved through more efficient recycling of nitrogenous wastes, it is likely that growing world demands for food and energy will lead to continued increases in the rate of nitrogen fixation for agricultural use and from fuel combustion, unless measures could be devised and implemented that would reverse those global trends.

An economic analysis presented in Chapter 11 indicates that, because of the distant nature of the projected impacts on the ozone layer, the present discounted value of damages is small. We did not attempt a broad-scale assessment of the full costs and benefits of current or projected patterns of global food production and energy use. Nevertheless, in our opinion, the current value to society of those activities that contribute to global nitrogen fixation far exceeds the potential cost of any moderate (e.g., up to a decade) postponement of action to reduce the threat of future ozone depletion by N_2O. This issue should, however, be the subject of renewed analysis as the information base is enlarged.

INTERCONNECTIONS OF PROBLEMS AND SOLUTIONS

Each of the major issues examined in this report can be viewed as a perturbation in some phase of the nitrogen cycle. The "solutions" to some of the resulting problems, however, may lead to other perturbations. For example, to prevent pollution of surface waters by the nitrogen in sewage or livestock manures, these wastes can be processed through treatment systems or spread on land. Waste treatment, however, can increase losses to the atmosphere of ammonia or nitrous oxide; and land spreading can lead to ammonia volatilization, denitrification with some evolution of N_2O, and leaching of nitrate into groundwater. Little quantitative information is available to assess such trade-offs. However, in order to minimize untoward consequences of the kind suggested here, nitrate-related environmental problems are best evaluated within a comprehensive framework that can take into account the complex, interwoven processes of the nitrogen cycle.

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CHAPTER 2

THE NITROGEN CYCLE

GENERAL ASPECTS

Although nitrate problems are the focus of this report, it is not possible to discuss nitrate without reference to other forms of nitrogen. The major nitrogen species in the biosphere are interrelated by a complicated series of reactions that collectively comprise the "nitrogen cycle." A more accurate description might be "nitrogen web," since the image of a simple loop of compounds through which nitrogen successively passes bears little relation to reality.

The literature contains numerous diagrams of the nitrogen cycle, with varied formats reflecting the different perspectives and purposes of the authors. Figure 2.1 illustrates the nitrogen cycle in the biosphere, with emphasis on those sources and transfers of nitrogenous materials that are most affected by human activities. Figure 2.2 indicates the quantitative flows of major nitrogen forms among the atmospheric, terrestrial, and aquatic phases of the global nitrogen cycle. Although the biospheric nitrogen cycle is driven primarily by biological transformations, the atmospheric reactions in the cycle (shown in Figure 2.1) are chemical and photochemical.

In terrestrial and aquatic systems, the major nonbiological processes of the nitrogen cycle involve phase transformations rather than chemical reactions. These transport processes include volatilization of ammonia and other gaseous forms of nitrogen; sedimentation of particulate forms of organic nitrogen; and sorption (e.g., of ammonium ion by clays). Understanding of the biospheric nitrogen cycle and of the factors that control the cycle depends primarily on an understanding of biological principles, especially those of microbial ecology.

Although the diagrams of the nitrogen cycle in Figures 2.1 and 2.2 appear to be highly dissimilar and complex, the biological transformations of nitrogen shown in these diagrams are comprised of only six major processes (Figure 2.3): (1) <u>assimilation</u> of inorganic forms (primarily

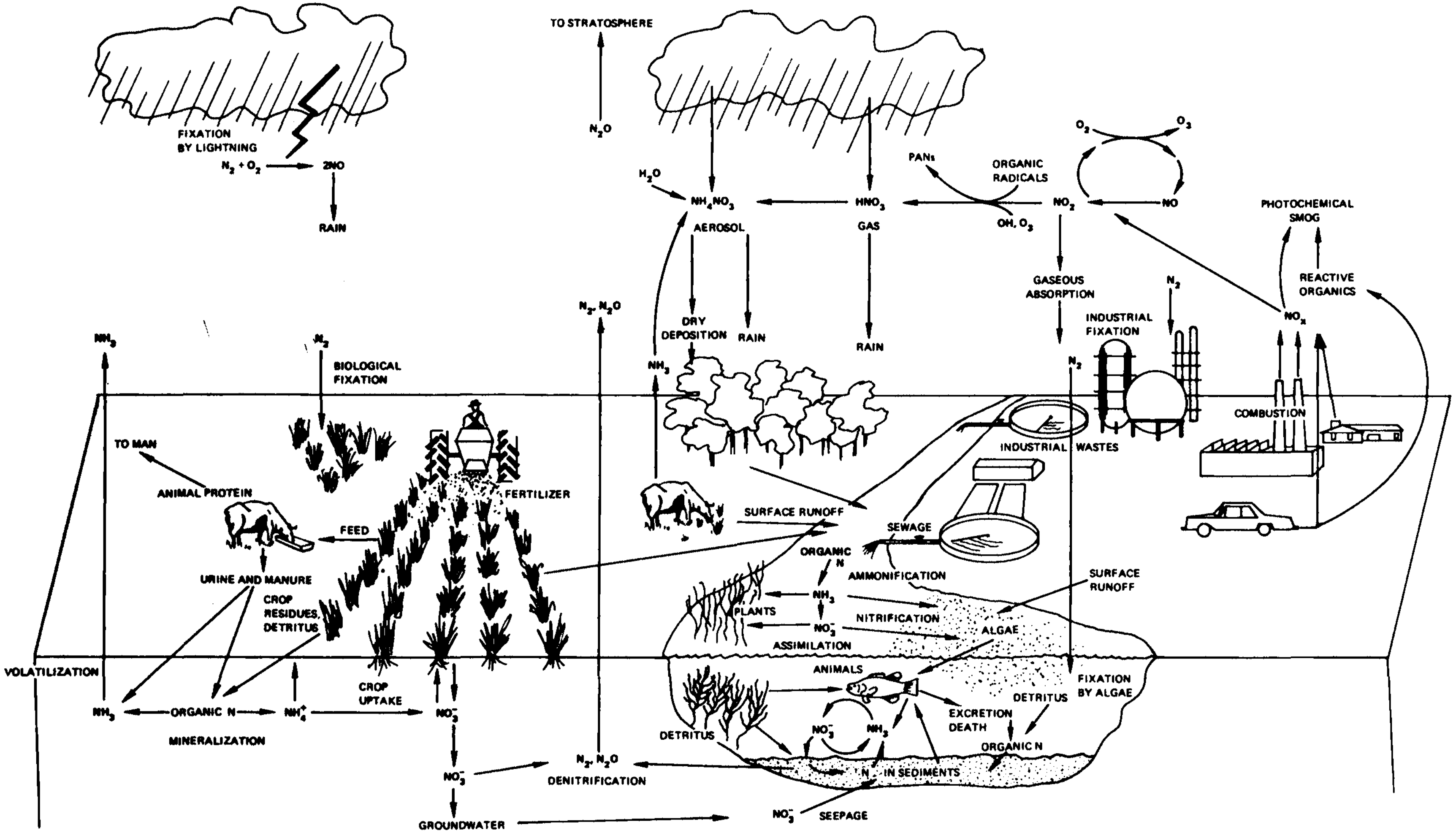
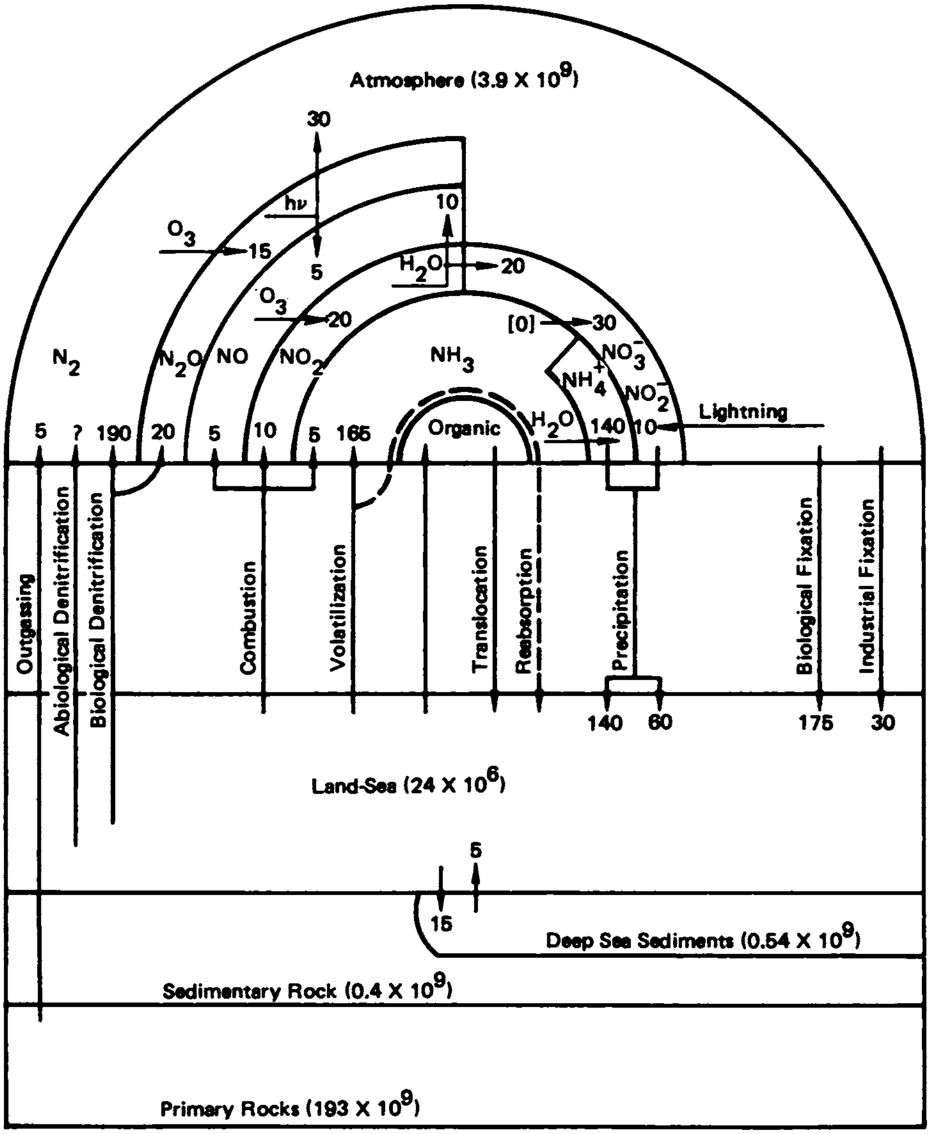


FIGURE 2.1 Schematic representation of the nitrogen cycle, emphasizing human activities that affect fluxes of nitrogen.



Estimates of movements and conversions are annual rates, in millions of metric tons per year. Inventory values for the major reservoirs and sinks are shown in parentheses.

SOURCE: Modified from Burns and Hardy (1975).

FIGURE 2.2 Global cycling of nitrogen.

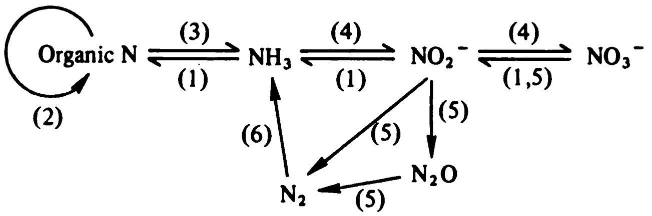


FIGURE 2.3 Simplified biological nitrogen cycle, showing major molecular transformations. Numbers in parentheses correspond to numbered processes discussed in text: (1) assimilation; (2) heterotrophic conversion; (3) ammonification; (4) nitrification; (5) denitrification; (6) nitrogen fixation.

ammonia and nitrate) by plants and microorganisms to form organic nitrogen, e.g., amino acids, proteins, purines, pyrimidines, and nucleic acids (Note: In this report the term ammonia is used for gaseous NH_3 and collectively for NH_4^+ plus NH_3, when there is no need or intention to distinguish between these forms. Ammonium (ion) is used specifically to indicate the cationic form NH_4^+.); (2) heterotrophic conversion of organic nitrogen from one organism (food or prey) to another organism (consumer or predator); (3) ammonification, i.e., the decomposition of organic nitrogen to ammonia; (4) nitrification, the oxidation of ammonia to nitrite and nitrate; (5) denitrification, the bacterial reduction of nitrate to nitrous oxide (N_2O) and molecular nitrogen (N_2) under anoxic conditions; and (6) nitrogen fixation, the reduction of nitrogen gas to ammonia and organic nitrogen by various microorganisms.

The predominant agents of assimilation in water and on land are autotrophic algae and higher plants. In soils, bacteria are important agents of assimilation of inorganic nitrogen. Heterotrophic conversions (e.g., of organic nitrogen in plants to animal protein) are highly complicated processes involving numerous steps, but are not treated in any detail here, or in most descriptions of the nitrogen cycle at the ecosystem level.

Ammonification and nitrification together constitute the process of mineralization. Bacteria and fungi are the principal agents of ammonification in soils; autolysis of cells and excretion of ammonia by zooplankton and fish are also important processes in aquatic systems. Ammonification is important in renewing the limited supply of inorganic nitrogen for further assimilation and growth by plants. Nitrification is mediated primarily by aerobic bacteria that obtain their energy by oxidizing ammonia to nitrite and nitrate. Nitrification converts ammonia, which is volatile but highly sorbable, into nitrate, a nonvolatile but easily leached form.

On an ecosystem scale, denitrification is considered a nitrogen sink since the products (N_2 and N_2O) are readily lost to the atmosphere; furthermore, most organisms cannot use nitrogen in these gaseous forms. Denitrification is carried out by a ubiquitous group of bacteria that use nitrate as their terminal electron acceptor in the absence of oxygen.

Nitrogen fixation is important as a source of available nitrogen for plant growth in both natural and managed agricultural ecosystems. On a global scale and over millions of years, nitrogen fixation balances the losses by denitrification; on time scales of decades to thousands of years, the two processes may be out of phase without significantly affecting the nitrogen content of the global atmosphere.

Numerous texts, monographs, and papers review the nitrogen cycle (Brezonik 1972; Bartholomew and Clark 1965; Delwiche 1970; Hutchinson 1944, 1954, 1957; Keeney 1973; Söderlund and Svensson 1976), and other reviews cover specific aspects of the cycle in detail. This chapter emphasizes the processes of the nitrogen cycle that are important to an understanding of the accumulation of nitrate and its transformations in the biosphere. Because the literature dealing with nitrate and the nitrogen cycle is so extensive, no attempt has been made to provide exhaustive documentation here.

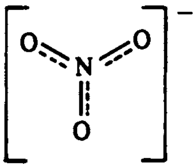
After brief discussions of the chemical properties and chemical reactions of nitrate and nitrite, this chapter focuses on biological processes related to nitrate. For terrestrial and aquatic ecosystems, the principal source of nitrate is nitrification, and the principal sinks are assimilation and denitrification. Nitrogen fixation is only an indirect source of nitrate in the biosphere, but this process is important in global nitrogen balances, reviewed later in this report, and in the current controversy over the depletion of stratospheric ozone by N_2O, formed by denitrification of nitrogen in fertilizer. Consequently, biological nitrogen fixation is also reviewed in this chapter. For each process, the chapter reviews the microbial agents and biochemistry of the reactions involved, the environmental factors affecting the rates of the process, and the occurrence and rates of the process in various compartments of the biosphere.

Because ammonia assimilation, ammonification, and heterotrophic conversions (reactions 1, 2, and 3 in Figure 2.3), do not result directly in a gain or loss in nitrate, these processes are not reviewed here. Nitrate assimilation also is not explicitly reviewed in this report, although it is the major sink for nitrate in the biosphere. The process is well understood and there do not appear to be any important policy issues that would necessitate a review. The assimilation of nitrate by plants or microbes and its conversion into biomass are described in texts on plant physiology, for instance Bonner and Varner (1965), Lewin (1962), and Stewart (1973).

Various photochemical and thermal reactions are involved in the production of nitrate compounds from gaseous nitrogen oxides in the atmosphere. These reactions are intimately involved in the production of photochemical smog, a complicated process that has received much study in the past two decades (see NRC 1977a, 1977b). The nitrogen oxide precursors are formed by a variety of processes, especially from atmospheric N_2 in high-temperature combustion processes, but also from combustion of nitrogen in fuels, from oxidation of ammonia in the air, and from fixation of N_2 by lightning. The final section of this chapter reviews the basic tropospheric processes related to the formation of atmospheric nitrates, and summarizes reactions of nitrogen oxides in the stratosphere, emphasizing the effect on stratospheric ozone of the nitrogen oxide catalytic cycle and the relationship between N_2O (a product of denitrification) and that catalytic cycle.

PHYSICAL AND CHEMICAL PROPERTIES OF NITRATE AND NITRITE

Nitrogen exists in nature in oxidation states ranging from -3 (ammonia, amines) to +5 (nitrates). The nitrate ion (NO_3^-) is the most oxidized form of nitrogen and has a planar and symmetrical structure:



The nitrogen atom forms σ bonds with the three oxygen atoms using sp^2 hybrid orbitals. Other p orbitals of the nitrogen and oxygen atoms combine to yield a π bond that is shared among the three sites.

In dilute aqueous solution, nitrate is chemically unreactive, and nearly all of the transformations involving nitrate in natural waters are mediated biochemically. The nitrate salts of all common metals are quite soluble in water. Nitrate has little tendency to form coordination complexes with metal ions in dilute aqueous solution.

Nitrate ion is the conjugate base of nitric acid (HNO_3), a colorless liquid at room temperature. Nitric acid is a strong acid, which is about 93 percent dissociated in 0.1 molar (M) solution (Cotton and Wilkinson 1966). Since the conjugate bases of strong acids are very weak bases, solutions of nitrate salts are neutral in pH. Although concentrated nitric acid is a powerful oxidizing agent, its oxidizing power is highly dependent on its concentration, and dilute solutions (<1 M) of the acid or of nitrate salts have virtually no oxidizing power.

Nitric acid can react with many organic compounds, especially in concentrated sulfuric acid, to add the $-NO_2$ group; this process is called nitration, and the reactive species is the nitronium ion, NO_2^+, produced by dissociation of nitric acid under strongly acidic conditions: ($2NHC_3$ -->

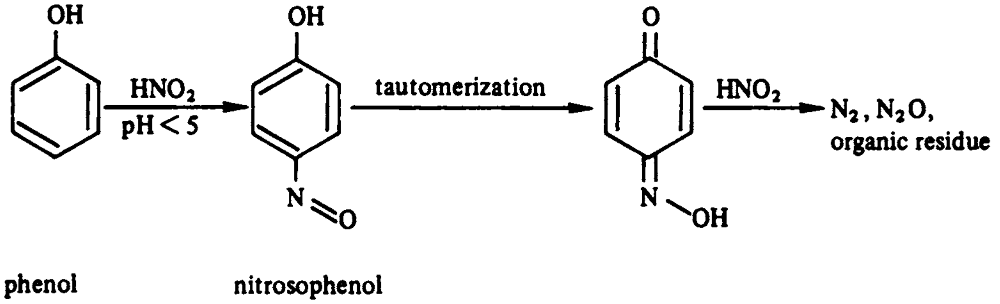
$NO_2^+ + NO_3^- + H_2O$). However, the nitration reaction does not take place in dilute aqueous solution.

Nitrate can be reduced to nitrite by microbial action, and many of the deleterious effects of nitrate in the environment result from its conversion to nitrite. Nitrite ion contains nitrogen in an intermediate and relatively unstable oxidation state (+3). Both chemical and biological processes can result in the further reduction of nitrite to various products, or in oxidation back to nitrate.

Nitrite salts are also quite soluble, although they are uncommon compared to nitrate salts. Nitrite, in contrast to nitrate, forms strong complexes with many transition metals. However, because nitrite concentrations in natural waters are typically very low (parts per billion), such complexation is not likely to be important in the environmental chemistry of nitrite.

The nitrite ion is the conjugate base of a weak acid, nitrous acid (HNO_2), $K_a = 4.36 \times 10^{-4}$, $pK_a = 3.36$. In most natural waters, the acid is dissociated, but in acidic environments (mine drainage waters, bogs, swamps, and acid soils), a significant fraction can exist as the undissociated species. Nitrite is a weak reducing agent and is oxidized to nitrate only by strong chemical oxidants or by nitrifying bacteria. Nitrite oxidizes many reduced substances, including iodide, sulfide, and sulfite. Aqueous solutions of nitrous acid are unstable, and decompose by disproportionation (i.e., self-oxidation and reduction). Spontaneous decomposition of nitrous acid is reported to occur in acidic soils by the reaction: $2HNO_2 \text{ ---> } NO + NO_2 + H_2O$ (Bremner and Nelson 1968).

Nitrous acid also reacts with phenolic substances, including lignins and tannins, to form nitrosophenols, which eventually decompose to N_2 and N_2O:

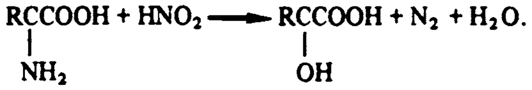


(2-1)

This reaction is said to be responsible for the decomposition of nitrite in acidic soils (Bremner and Nelson

1968), but the reaction has not been widely studied and its quantitative importance as a sink for nitrite remains unknown.

Nitrous acid reacts with amino acids (the Van Slyke reaction) to yield N_2:



$$\underset{\displaystyle NH_2}{RCCOOH} + HNO_2 \longrightarrow \underset{\displaystyle OH}{RCCOOH} + N_2 + H_2O. \qquad (2-2)$$

This reaction is of historical interest as the basis for the analysis of amino acids, by measurement of the volume of N_2 produced. The occurrence of the Van Slyke reaction in acidic lakes and soils has been conjectured (e.g., Hutchinson 1957), but several lines of evidence (reviewed by Brezonik 1977) indicate that the reaction is unimportant in the natural environment. The reaction of nitrous acid with sulfanilic acid to form diazonium ions, which further react with aromatic amines to form diazo dyes, is of analytical and commercial interest, but it is doubtful that this reaction occurs in the environment.

Finally, the reaction of nitrous acid with secondary amines to form N-nitrosamines is presently a great environmental and public health concern because many nitrosamines are carcinogenic (see Chapter 9). Mechanisms for the formation of nitrosamines are discussed below.

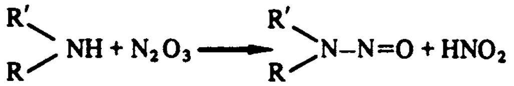
Nitrosation Reactions

Several nitrosating agents can react with secondary amines (RR'NH) to form nitrosamines in the environment or *in vivo*. In aqueous systems, nitrous acid is the precursor of the most important agent, nitrous acid anhydride (N_2O_3). In acid solution, nitrite is converted to nitrous acid:

$$NO_2^- + H^+ \rightleftharpoons HNO_2, \qquad (2-3)$$

Two molecules of nitrous acid reversibly form one molecule of nitrous acid anhydride, which subsequently reacts with nonionized secondary amines (Ridd 1961) to form N-nitrosamines:

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O \qquad (2\text{-}4)$$

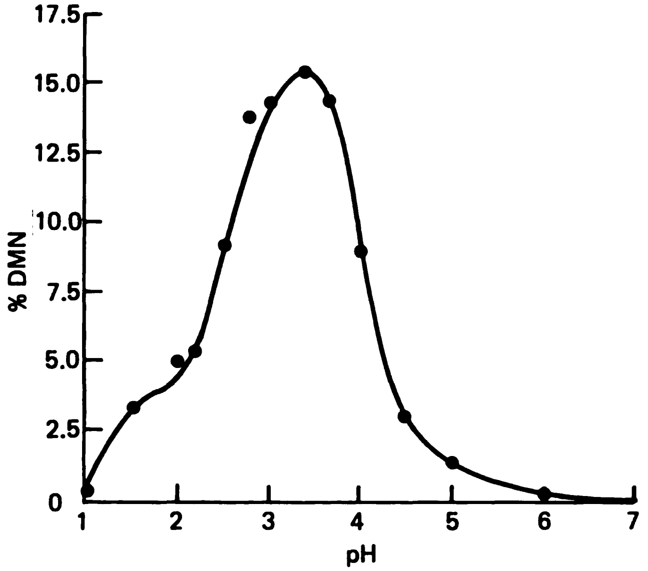


$$R'RNH + N_2O_3 \longrightarrow R'RN{-}N{=}O + HNO_2 \qquad (2\text{-}5)$$

The rate of nitrosation depends on the basicity of the amine and on pH; the maximum rate occurs near the pH at which nitrous acid is 50 percent ionized, i.e., at pH = pK_a = 3.36 (Figure 2.4). The mechanism described in Equations (2-4) and (2-5) implies that the rate of nitrosation is proportional to the concentration of nitrous acid anhydride, and is thus proportional to the square of the concentration of nitrous acid (and nitrite). Results by Mirvish (1970) for nitrosation of dimethylamine support this mechanism. The effect of pH on nitrosation (Figure 2.4) is also explained by the above mechanism. As the pH decreases toward pK_a for nitrous acid, the concentration of HNO_2 increases tenfold for each unit decrease in pH, and the concentration of nonionized dimethylamine (pK_1 = 10.7) decreases by a like amount. Because the concentration of nitrous acid is squared in the rate equation, the net effect is an increase in the rate of nitrosation until pK_a for HNO_2 is reached. Below this pH, the concentration of HNO_2 becomes essentially constant, and equal to the total nitrite. Further decreases in pH lower the rate of nitrosation because of the continuing decrease in the concentration of nonionized amine.

Although acid conditions promote the formation of nitrosamines, Mills and Alexander (1976) found that dimethylnitrosamine was formed from dimethylamine and nitrite at pH values as high as 7.7 in samples of soil, sewage, and lake water. The samples, however, contained unrealistically high concentrations of the precursors. For a series of amines at a given pH and total amine concentration, the fraction of the amine that is present in nonionized form is inversely proportional to amine basicity. Consequently, less basic aromatic amines are nitrosated up to a thousand times more rapidly than the more basic dimethylamine (Mirvish 1970).

Mirvish et al. (1972) reported that ascorbic acid acts effectively to block nitrosation by reacting directly with nitrite (or with nitrous acid), thus eliminating the nitrosating precursor. Addition of ascorbic acid to foods that have been preserved with nitrite has been proposed to minimize the possibility of nitrosamine formation (see Chapter 9). On the other hand, thiocyanate, which is commonly found in human saliva, catalyzes the nitrosation reaction (Boyland et al. 1971); thus, the presence of saliva



SOURCE: Mirvish (1970). Reproduced by permission of *J. Nat. Cancer Inst.* and by the author.

FIGURE 2.4 Dependence of dimethylnitrosamine formation on pH.

in the stomach may result in more rapid in vivo formation of nitrosamines than was previously thought.

Other nitrosating agents besides nitrous acid anhydride include nitrosyl chloride (NOCl), nitrous acidium ion ($H_2NO_2^+$, i.e., protonated nitrous acid), and nitrosyl thiocyanate (ON•NCS). Not all nitrosatable compounds follow the kinetic pattern described above; tertiary amines, amides, and ureas have different pH optima and rate laws. The kinetics for nitrosation of various secondary amines and other nitrosatable substances in aqueous systems has been reviewed in the U.S. EPA STAR document on nitrosamines (U.S. EPA 1977).

N-Nitroso compounds also can be formed by transnitrosation, the direct transfer of the nitroso group from one N-nitrosamine to another secondary amine, forming a new N-nitroso compound in the absence of nitrite or nitrous acid. Consequently, the formation in the environment of a noncarcinogenic nitrosamine may lead ultimately, by transnitrosation, to the formation of a carcinogenic N-nitroso compound. For example, the noncarcinogenic compound N-nitrosodiphenylamine transnitrosates N-methylaniline to form a carcinogen, N-nitrosomethylaniline.

Three mechanisms have been proposed for the formation of nitrosamines in the atmosphere (U.S. EPA 1976):

(1) formation of nitrosamines from homogeneous (gas phase) reaction of nitrous acid and secondary amine vapors;

(2) heterogenous generation of nitrosamines in the atmosphere in acid aerosols;

(3) free radical generation of nitrosamines by reaction of gaseous amines with hydroxyl (HO•) radicals that are formed photochemically in urban air.

Evidence for the occurrence or importance of these reactions is sketchy at present. A study by the Science Advisory Board of EPA (U.S. EPA 1976) concluded that the homogeneous mechanism, (1), is likely to be a minor source of nitrosamines in the atmosphere because of slow kinetics and because of the photolysis of nitrous acid during daylight hours.

An important aspect of mechanism (2) is that uv light absorbed by nitrosamines is highly attenuated in acidic solutions as a result of protonation of the -N-N=O group. The absorbtion of uv leads to rapid decay of gaseous nitrosamines in sunlight; for example, the half life of dimethyl nitrosamine is approximately 30 minutes near noon in full sunlight (Hanst et al. 1977). Nitrosamines that are generated in an acidic aerosol such as H_2SO_4 and $(NH_4)HSO_4$, (which are important aerosols in urban atmospheres) tend to be protected against photochemical decomposition.

The free radical mechanism, (3), involves reaction of secondary amines with HO• radicals to form amino ($R_2N\bullet$) radicals, which can react with oxygen to form various products, or with nitric oxide to form nitrosamines, e.g., with dimethylamine:

$$(CH_3)_2\,NH + HO\cdot \longrightarrow (CH_3)_2\,N + H_2O \tag{2-6}$$

$$(CH_3)_2\,N\cdot + O_2 \longrightarrow CH_2{=}N{-}CH_3 + HO_2\text{, or} \tag{2-7}$$

$$(CH_3)_2\,N\cdot + O_2 \longrightarrow (CH_3)_2\,NO_2 \longrightarrow \text{other products}$$

$$(CH_3)_2\,N\cdot + NO \longrightarrow (CH_3)_2\,N{-}N{=}O \tag{2-8}$$

A kinetic model was developed for this mechanism, which also involves several other reactions (U.S. EPA 1976), but experimentally-derived rate constants are not available to permit accurate estimates of the rate of nitrosamine formation and the equilibrium concentration of dimethyl nitrosamine as a function of solar irradiation. Preliminary calculations, using estimated rate constants and typical concentrations for NO in polluted urban and unpolluted atmospheres, suggest that the free radical mechanism would result in maximum dimethylnitrosamine levels of less than 1/100th to 1/1000th of the initial dimethylamine concentrations, depending on NO levels.

In addition, nitrosamines could be formed *in vivo* from ingested amines and from nitrous acid formed in the respiratory tract by reaction of inhaled NO, NO_2, and H_2O. This mechanism is theoretically possible, but its occurrence has not been demonstrated definitively.

Nitrosamines have been detected in ambient air near sources of emissions of preformed dimethylnitrosamine (DMN) (see Chapter 9 and Appendix C). In an effort to determine whether atmospheric formation is also a significant source of exposure, EPA has sampled the air near sources of amine emissions in several locations. Only two air samples contained detectable amounts of DMN. Surveillance of urban atmospheres for nitrosamines is continuing (J. Bachmann, U.S. EPA, Reserach Triangle Park, N.C., personal communication, 1977).

In conclusion, information on nitrosamine formation in the atmosphere at present is primarily qualitative. Nitrosamines can be formed from precursors in the atmosphere, but they also decompose in sunlight. The relative importance of the various reactions and of the environmental factors affecting these processes are not well understood.

MAJOR BIOLOGICAL PROCESSES

Nitrification

Nitrification, the microbial oxidation of ammonia to nitrite and nitrate, is of great environmental significance for many reasons. Except for certain chemical reactions that form nitrate from oxides of nitrogen in the atmosphere, biological nitrification is the sole natural source of nitrate in the biosphere. Nitrification in soils, natural waters, and sewage has been reviewed by Alexander (1965), Keeney (1973), Focht and Chang (1975), and Focht and Verstraete (1977).

Nitrification is a two-step process, with both steps mediated primarily by obligate aerobic bacteria (Table 2.1). The chemoautotrophic nitrifiers obtain their energy by oxidizing reduced forms of nitrogen, and obtain their carbon by reducing carbon dioxide. Nitrosomonas is by far the most commonly mentioned agent of the first step, which produces nitrite from ammonia:

$$NH_4^+ + 3/2\ O_2 \dashrightarrow NO_2^- + H_2O + 2H^+,\ \Delta G^\circ = -65\ \mathrm{Kcal/mol} \quad (2\text{-}9)$$

Contrary to popular belief, Nitrosomonas is not a true autotroph, in that its growth is stimulated by pyruvate and amino acids (Clark and Schmidt 1967; see Focht and Verstraete [1977] for further review of this subject). Reaction (2-9) proceeds via the endergonic oxidation of ammonia to the intermediate, hydroxylamine (NH_2OH). Oxidation of the latter to form nitrite is a multistep process involving unconfirmed intermediates and a respiratory cytochrome system. Soriano and Walker (1973) suggested that Nitrosospira multiformis is the predominant agent in some soils, rather than the usually cited Nitrosomonas. Nitrosococcus oceanus (formerly Nitrosocystis oceanus), a common, obligate marine species (Watson 1965, 1974), may be the principal agent of ammonia oxidation in the sea.

Oxidation of nitrite to nitrate is the second step in nitrification:

$$NO_2^- + 1/2\ O_2 \dashrightarrow NO_3^-,\ \Delta G^\circ = -20\ \mathrm{Kcal/mole} \qquad (2\text{-}10)$$

This step is mediated by a separate group of bacteria, the best known and most common of which is Nitrobacter. This organism is also capable of heterotrophic growth (Smith and Hoare 1968). Nitrite usually does not accumulate during nitrification but is oxidized as rapidly as it is formed.

TABLE 2.1 Microbial Agents of Nitrification

Chemoautotrophs	(Habitat)	Heterotrophs*
Ammonia oxidizers		Bacteria
Nitrosomonas	(soil, marine and fresh water)	*Arthrobacter spp.*
Nitrosospira	(soil)	*Azotobacter sp.*
Nitrosococcus	(soil, marine and fresh water)	*Pseudomonas fluorescens*
Nitrosolobus	(soil)	*Aerobacter aerogenes*
		Bacillus megaterium
Nitrite oxidizers		*Proteus sp.*
Nitrobacter	(soil, marine and fresh water)	
Nitrospira	(marine)	Fungi
Nitrococcus	(marine)	*Aspergillus flavus*
		Neurospora crassa
		Penicillium spp.
		Yeasts
		Rhodotorula
		Candida
		Actinomycetes
		Streptomyces
		Nocardia
		Algae
		Chlorella sp.
		Ankistrodesmus sp.

*Not an exhaustive list of heterotrophic nitrifiers.

SOURCE: Derived from Focht and Verstraete (1977).

Nitrifying bacteria are rather fastidious organisms. The optimum pH for nitrification is 8.0, and activity decreases rapidly below pH 7. Nitrifiers also are sensitive to various organic compounds, especially to amino compounds, and this probably accounts for the absence of nitrification in activated sludge sewage treatment plants until most of the organic waste has been oxidized. Although nitrifiers are mesophilic (optimum temperature: approximately 30°C; maximum temperature: 37°C), nitrification can occur even under ice in lakes. Nitrite oxidizers have narrower temperature and pH tolerances than do ammonia oxidizers, and nitrite tends to accumulate under extreme conditions. At high pH, nitrite oxidation is inhibited, in part because free ammonia is toxic to nitrite oxidizers.

Nitrifying organisms are widely distributed in soils and aquatic systems. In fact, nitrite-oxidizing bacteria have been isolated in low concentrations from rainwater (Visser 1964), lending partial support to the still unproven hypothesis that the oxidation of ammonia to nitrate in the atmosphere is mediated biologically. Presumably, the organisms grow on aerosols and dust particles.

Growth kinetics of nitrifying bacteria conform to the Monod equation (Monod 1942). Knowles et al. (1965) found half-saturation constants (K_M) for Nitrosomonas that ranged from 0.2 to 8.0 mg $NH_4{}^+$-N/l (14-570 μM), depending on temperature. Suzuki et al. (1974) found decreasing K_M values with increasing pH for the oxidation of ammonia by Nitrosomonas, and they interpreted the trend to indicate that undissociated NH_3, rather than $NH_4{}^+$, is the substrate for oxidation. K_M values (at 25°C) ranged from 56 mg N/l (4000 μM) at pH 7.0 to 1.96 mg N/l (140 μM) at pH 9.1. Srinath et al. (1976) found a pH optimum of 7.4 to 7.9 for ammonia oxidation and reported zero-order kinetics (rate independent of concentration) at ammonia levels above 10 mg N/l.

By comparison, half-saturation constants for the assimilation of ammonia by phytoplankton are in the range 1.4 to 140 μg $NH_4{}^+$-N/l (0.1-10 μM) (Eppley et al. 1969; also, see Chapter 8). Since maximum specific growth rates for the two kinds of organisms are similar (1 to 3 doublings per day), nitrifiers are not successful competitors for ammonia in the euphotic zone of lakes and oceans, where ammonia concentrations are typically below 100 μg N/l (Goering 1972). Brezonik (1972) and Goering (1972) were unable to detect nitrification in surface waters by ^{15}N tracer methods, which provides some verification that phytoplankton have the competitive advantage. In lake hypolimnia, nitrification exerts a significant oxygen demand during early summer, and the nitrate produced by nitrification is denitrified as the water becomes anoxic.

The sequential nitrification-denitrification thus acts as a sink for fixed nitrogen in lakes.

Difficulties in isolating autotrophic nitrifiers from surface waters and the finding that significant rates of oxidation of ammonia occur in acidic environments, in which nitrifying bacteria should be inhibited, led to the discovery of heterotrophic nitrification. Various bacteria, fungi, and actinomycetes are capable of oxidizing organic nitrogen and ammonia to a variety of inorganic and organic nitrogen compounds, including hydroxylamine, nitrite, nitrate, N-nitroso compounds (R_2N-NO), hydroxamic acids (RCONHOH), amine oxides (R_3NO), and nitro compounds (RCH_2-NO_2) (Alexander 1965, Focht and Verstraete 1977). Verstraete and Alexander (1972) found that heterotrophic nitrification by a strain of Arthrobacter resulted in significant releases of hydroxylamine (NH_2OH), a potent mutagen, and 1-nitrosoethanol ($CH_3CH(CH)NC$). Verstraete and Alexander (1973) reported the same patterns in samples of sewage, river and lake water, and soils to which ammonia and acetate had been added.

Heterotrophic nitrification differs from autotrophic nitrification both in the variety of products formed and in that it typically is not associated with cell growth, whereas autotrophic nitrifiers use nitrification as their source of energy for growth. Although the importance of heterotrophic nitrification cannot be assessed accurately, present evidence indicates that the dominant nitrifying populations in soil, water, and sewage are autotrophic (Alexander 1971). Isirimah et al. (1976) concluded that nitrification in the surface sediments of shallow, eutrophic Lake Wingra, Wisconsin, was autotrophic. (See Appendix A for discussion of the mass balance for nitrogen in this lake.) Nitrification in stirred aerobic sediments was completed inhibited by nitrapyrin [2-chloro-6-(trichloromethyl) pyridine], an inhibitor of autotrophic ammonia oxidizers (see Chapter 10). No autotrophic nitrifiers could be detected in samples of the lake water, leading the authors to conclude that nitrification in the lake itself was conducted by heterotrophs.

Although nitrite is the principal product of the oxidation of ammonia by nitrifying bacteria, the production of NO and N_2O by cell-free extracts and whole cell preparations of Nitrosomonas has been reported (Hooper 1968; Yoshida and Alexander 1970; Ritchie and Nicholas 1972, 1974). Apparently, the production of these gases is associated with the oxidation of hydroxylamine coupled to enzymatic reduction of nitrite. Although this activity has been found in whole cells grown both aerobically and anaerobically, Ritchie and Nicholas (1972) reported that the enzyme that catalyzed the reduction was most active under anoxic conditions. Ritchie and Nicholas (1974) suggested that the reductase system may act to remove nitrite that has accumulated within cells during the oxidation of ammonia. The activity of nitrite reductase may account for the poor recovery of nitrite in studies of the oxidation of hydroxylamine by cell-free preparations of nitrifiers (Nicholas and Jones 1960); the nitrite reductase activity in nitrifiers could act as a direct sink for fertilizer ammonia, thus eliminating the remaining nitrification and denitrification steps. Bremner and Blackmer (1978) recently reported evidence that N_2O is released from soils during nitrification of added ammonium or urea fertilizer. Although the emissions are insignificant in terms of fertilizer loss (only 0.04 to 0.45 percent of the added nitrogen was released as N_2O), they are rougly comparable to the rates of N_2O production by denitrification in cropped soils (about 1 kg/ha-yr). Thus nitrification could be an important source of N_2O to the atmosphere. Further studies are needed for an accurate evaluation of the significance of this process.

Nitrification has practical implications in environmental systems that are managed or affected by man. The oxidation of ammonia to nitrate requires about 4.5 mg of oxygen per mg of nitrogen; consequently, streams receiving high loadings of ammonia from sewage effluents have considerable demands for oxygen (i.e., a so-called nitrogenous biochemical oxygen demand [NBOD]). Because nitrate is mobile and readily leached from soil, and is susceptible to denitrification, nitrification can result in large losses of nitrogen from ammonia fertilizers applied to soils. In neutral and alkaline soils, ammonia is nitrified in a few days or weeks. The use of urea fertilizer delays oxidation, but ureases hydrolyze urea to ammonia relatively rapidly.

Methods of inhibiting nitrification, therefore, have considerable practical importance. The compound nitrapyrin [2-chloro,6-(trichloromethyl) pyridine] selectively inhibits ammonia-oxidizing bacteria, and has recently become commercially available under the trade name "N-Serve" (Mullison and Norris 1976). The compound seems promising for agricultural use; management implications of the widespread application of nitrapyrin are discussed in Chapter 10.

Denitrification

Nitrate may be used by microorganisms either assimilatively, as a source of nitrogen for growth, or dissimilatively, as a terminal electron acceptor in respiration. Approximately 45 genera of bacteria and fungi can reduce nitrate dissimilatively to nitrite (or, in some cases, to ammonia [Payne 1973]), but reduction to these products does not result in a loss of fixed nitrogen. Of primary interest are the 17 genera (Table 2.2) of denitrifying bacteria that are capable of reducing nitrate to the gaseous forms N_2 and N_2O, which may be easily lost from the ecosystem.

Mechanism and Products of Denitrification

Denitrification is carried out by bacteria that can use nitrate as a terminal electron acceptor when oxygen has been depleted. In this process, nitrate is reduced ultimately to molecular nitrogen (N_2):

$$\underset{\text{nitrate}}{NO_3^-} \text{ ---> } \underset{\text{nitrite}}{NO_2^-} \text{ ---> } \underset{\substack{\text{nitric}\\\text{oxide}}}{NO} \text{ ---> } \underset{\substack{\text{nitrous}\\\text{oxide}}}{N_2O} \text{ ---> } \underset{\substack{\text{molecular}\\\text{nitrogen}}}{N_2}$$

Nitric oxide normally is not a significant product of denitrification. However, according to Robinson and Robbins (1971), cases have been reported in which NO_2 reached toxic levels in silos (Lowry and Shuman 1956), apparently from the oxidation of NO that was produced by denitrification, or, possibly, by chemodenitrification.

Nitrous oxide also usually is not considered a major product of denitrification, but few good quantitative estimates of its importance are available. The relative production of N_2O compared to N_2 during denitrification is currently a matter of great interest and investigation because of the role of N_2O in the destruction of stratospheric ozone (see below in this Chapter, and Chapter 7). Some bacteria apparently produce N_2O as their major or perhaps sole product of denitrification (see Brezonik [1977] and Focht and Verstraete [1977] for reviews). Those factors that favor an increase in the ratio of N_2O to N_2 in the products of denitrification also tend to have a negative effect on the rate of denitrification. For example, temperatures below 5°C result in high $N_2O:N_2$ ratios, but the absolute rate of denitrification drops off rapidly below about 10°C (Stanford et al. 1975). Similarly, the proportion of N_2O increases at pH values below about 5 to 6 (Focht 1974), while the rate of denitrification drops rapidly at pH values that are less than 7.

According to Cady and Bartholomew (1960), N_2O is the main product of denitrification in soils with a low but finite level of oxygen, whereas in truly anoxic soils N_2 is the main product. However, any extrapolation of such findings to the situation that generally prevails in natural soils needs to be done cautiously, because incubation

TABLE 2.2 Taxonomy of Denitrifying Microorganisms[a]

Organism	Comments
Achromobacter liquefaciens	Oxidize CH_4 with NO_3^-
Alcaligenes sp.	Oxidize CH_4 with NO_3^-
Bacillus	Many species known to denitrify
Chromobacterium	
Corynebacterium nephridii	Produces only NO and N_2O
Fusarium spp.	Two species of this fungus reduce NO_2^- (but not NO_3^-) to N_2O
Halobacterium	
Hydrogenomonas spp. (=*Alkalingenes sp.*)	
Hyphomicrobium sp.	Oxidizes methanol with NO_3^-
Micrococcus denitrificans	Chemolithothroph; oxidizes H_2
Moraxella	
Propionibacterium	
Pseudomonas spp.	Many well-known denitrifying species
Spirillum	
Thiobacillus spp.	Chemolithotrophs; oxidize S and $S_2O_3^{-2}$ with NO_3^-
Veillonella alcalescens	Strict anaerobe; both assimilatory and dissimilatory NO_3^- reduction
Xanthomonas	

[a] Not all species within a genus may be capable of denitrification.

SOURCE: Reprinted with permission from P. L. Brezonik, Denitrification in Natural Waters, Progress in Water Technology 8:373-392 (1977), Pergamon Press, Ltd.

conditions in batch-type, laboratory studies of denitrification frequently have not been comparable to the conditions in environmental situations. The Council for Agricultural Science and Technology (CAST 1976), Hahn and Junge (1977), and Crutzen and Ehhalt (1977) have reviewed the literature on production of N_2O by denitrification in agricultural soils. CAST (1976) estimated that production of N_2O accounts for about 6 percent of the nitrogen loss in denitrification.

The extent to which N_2O produced by bacteria is absorbed in soils and reduced further to molecular nitrogen is an open question, but Blackmer and Bremner (1976) recently demonstrated that uptake of N_2O from the atmosphere occurs in enclosed soil systems.

Biochemistry of Denitrification

In closed aqueous systems where there is an excess of organic matter, microbes use molecular oxygen (O_2), nitrate (NO_3^-), sulfate (SO_4^{2-}), and carbon dioxide (CO_2) as electron acceptors in a preferential sequence that generally follows the order of their thermodynamic energy yield in organic oxidation. However, of greater relevance than free energy changes are the ATP (adenosine triphosphate) yields with various electron acceptors. While the yields depend upon available free energy, some latitude exists in the efficiency of cells in trapping energy.

The determination of energy yields in the reduction of nitrate to nitrous oxide or molecular oxygen is complicated because the reduction is a multi-step process that involves several distinct terminal enzymes. ATP yields may differ in the several reduction steps (e.g., see Cox and Payne [1973]). However, Koike and Hattori (1975b) reported evidence supporting a hypothesis that ATP yields are similar for each two-electron reduction step. Recent literature indicates that the efficiency of ATP production varies according to species, phase of growth, and electron donor (see Brezonik [1977] for further details). Cell yield (g cells/g substrate utilized) is lower in the presence of nitrate under anoxic conditions than under oxygenated conditions. Koike and Hattori (1975a) found cell yields with denitrification were about half those under aerobic conditions.

In summary, the energetics of denitrification is complicated and is not fully understood. While oxidative phosphorylation, the synthesis of ATP in the respiratory chain, has been linked clearly to denitrification, the points of linkage and the efficiency of ATP production (hence the growth or yield efficiencies) still are open questions.

Studies of denitrification have shown that the process commonly involves a buildup of nitrite preceding gas production, but a distinct two-step process does not always occur. Goering and Cline (1970) found two stages in laboratory incubations of seawater, with most of the nitrite reduction (gas production) occurring after nitrate was depleted, and Brezonik and Lee (1966) found a similar lag between nitrate reduction and the production of N_2. Although these observations seem at odds with the fact that synthesis of all the denitrifying enzymes begins simultaneously (Payne and Riley 1969), the anomaly can be explained by the fact that nitrate inhibits the activity of enzymes that are associated with nitrite reduction.

Environmental Factors Affecting Denitrification

Oxygen. The long-standing controversy over the occurrence of denitrification in the presence of oxygen has been reviewed by Delwiche (1956), Painter (1970), and Brezonik (1977). Most evidence indicates that denitrification is essentially an anoxic process and that its onset requires complete oxygen depletion, at least in the immediate cell environment. Reported cases of aerobic denitrification can be explained by transient effects; by microanoxic zones, which are common in soils; or by overestimates of the transfer rates of oxygen into active microbial cultures. However, the aerobic denitrification of nitrite apparently has been demonstrated in several species of bacteria (Skerman et al. 1958, Mechsner and Wuhrman 1963).

It is not surprising that the role of oxygen in denitrification is controversial. Denitrification does not require or result in a highly reducing environment, as do the reduction of sulfate and the formation of methane. Most denitrifiers are aerobic organisms, whereas those that reduce sulfate and form methane are obligate anaerobes. Furthermore, the possibility of denitrification at low oxygen levels is not merely an academic matter; many aquatic and soil systems, including certain oceanic areas, marshes, and waste treatment plants, have just such conditions.

Substrate, Temperature, pH, and Trace Minerals. The growth requirements of denitrifiers are rather simple. The organisms can oxidize a wide variety of organic substrates, including aromatic compounds. Denitrification occurs at temperatures from less than 5°C (Goering and Dugdale 1966) to 60°C (Nommik 1956), but individual species have narrower temperature limits (Konishi 1969). Stanford et al. (1975) reported a Q_{10} of about 2 between 15°C and 35°C for soil denitrification (i.e., with each 10°C increase in temperature the rate of denitrification doubled). The optimum pH is apparently 7 to 8 (Delwiche 1956), and rates decline rapidly under acidic conditions (Bremner and Shaw 1958, Broadbent and Clark 1965). Molybdenum is required for nitrate reductase, but no other unusual mineral requirements are known. Since most denitrifiers are aerobes, they may be metabolically active over a wide range of oxygen pressures and of oxidation-reduction (redox) potentials. The cosmopolitan habits of the denitrifying bacteria give them potential importance as a nitrogen sink in a variety of systems.

Nitrate Concentrations. Broadbent and Clark (1965) state that the rate of denitrification is independent of the concentration of nitrate, but at some concentration, diffusion or enzymatic affinity clearly will begin to affect the rate of reaction. The lack of a correlation between the concentration of nitrate and the rate of denitrification in many studies probably reflects the unrealistically high additions of nitrate that are commonly made in such studies. Koike et al. (1972) demonstrated that the concentration of nitrate had a significant effect on denitrification in a brackish Japanese lake; they estimated half-saturation values of about 110 and 55 μg N/l (4 and 8 μM) for nitrate and nitrite reduction, respectively. Vanderborght and Billen (1975) reported data from sediment cores that support a model they developed in which the rate of denitrification is first order in nitrate concentration.

Other Mechanisms for Production of Nitrogen Gases

Over the years it has been proposed that various non-enzymatic reactions and other biological processes produce gaseous nitrogen compounds (N_2, N_2O, NO) from nitrate or nitrite, but there is evidence for only a few of these schemes. Direct oxidation of ammonia to molecular nitrogen by O_2 or NO_3^- has been proposed by various workers. Richards (1965) suggested that the ammonia released from organic matter during denitrification also could be oxidized to nitrogen gas. However, several workers who used ^{15}N as a tracer found that all the N_2 in denitrification was derived from nitrate and that there was no evidence to support a direct oxidation mechanism (for a review, see Brezonik [1977]). Mechanisms for the formation of N_2 and gaseous N oxides from nitrite by non-enzymatic chemical reactions (i.e., chemodenitrification) were discussed earlier in this chapter.

Nitrate Reduction and Immobilization

Immobilization occurs when nitrate, which is very mobile in soil, is reduced to organic nitrogen as a result of anoxic assimilation. There is disagreement about the environmental importance of nitrate immobilization and of respiratory reduction of nitrate to ammonia as compared to denitrification. Originally, immobilization and nitrate reduction to ammonia were thought to be insignificant compared to denitrification in soils (Nommik 1956) and in lakes (Goering and Dugdale 1966). More recent studies have shown that the reduction of nitrate to ammonia or to organic nitrogen accounts for up to about 40 percent of the nitrate lost in rice paddy soils (MacRae et al. 1968), and in the water (Brezonik and Lee 1966) and sediments (Keeney et al. 1971, Chen et al. 1972) of Lake Mendota. Larsen (1977) found that 30 to 40 percent of the nitrate in lake sediments was converted to ammonia or organic nitrogen, and Isirimah et al. (1976) found that 20 percent was converted to these forms in such sediments. Van Kessel (1977), however, reported that only 2.8 to 5.5 percent of nitrate was immobilized in irrigation ditches in Holland.

Respiratory reduction of nitrate to ammonia and immobilization of nitrate is aparently a common occurrence during denitrification. Normally, the rates of these processes are lower than the rates of denitrification, but the percent of nitrogen converted to organic forms and ammonia is somewhat variable. The factors controlling the relative importance of these two reactions are not well understood, although the carbon/nitrogen ratio of the substrate appears to be an important factor. Additional studies are needed in order to predict the extent of immobilization and ammonia formation from nitrate as a function of environmental conditions.

Denitrification in Natural Environments

Interest in denitrification stems from its roles as a sink for fixed nitrogen, and as a source of N_2O. Quantitative estimation of the amount of denitrification is important to geochemists constructing global nitrogen balances, water quality specialists making nitrogen budgets for lakes, agronomists who are concerned about losses of fertilizer, and atmospheric scientists studying the global balance of N_2O. Relatively little is known about the significance of denitrification in aquatic environments or on the scale of the global nitrogen cycle, and the extent of denitrification in these cases cannot be accurately quantified.

Denitrification in Soils. Major factors that affect the amount of denitrification losses in soils are: (1) the availability of an organic carbon substrate, (2) the moisture content of the soil (and therefore, the extent of microanoxic zones in the soil), (3) the presence or absence of a cover crop, and (4) the type of fertilizer applied (ammonia must be nitrified in aerobic portions of the soil before denitrification can occur).

Denitrification occurs rapidly and completely in soils under conditions of complete anaerobisis and high availability of organic matter. Under most farming practices and weather conditions, prolonged flooding and anaerobiosis rarely occur; however, a continual but slow loss of nitrogen may occur in moist, fine-textured soils that have anoxic microenvironments (Broadbent and Clark 1965, Greenwood 1968). Denitrification in flooded soils that are exposed to atmospheric oxygen has been relatively well studied (Patrick and Tusneem 1972, Patrick and Gotoh 1974, Dijksoorn and Ismunadji 1973). For example, the last of these authors reported that up to half of the nitrogen supplied as fertilizer to a rice crop was lost through nitrification when the soil was aerobic and subsequent denitrification when the soil became flooded.

More experimental evidence is needed to evaluate the significance of anoxic microsites. Preliminary analysis by Flühler et al. (1976a) indicated a high spatial variability for these sites in an undisturbed Hanford sandy loam soil. Flühler et al. (1976b) also found considerable heterogeneity in the aeration of soils and concluded that the amounts and sizes of anaerobic microsites in soils cannot be measured directly.

As Allison (1955) has pointed out, most studies of nitrogen balances have indicated a large deficit of nitrogen that can be attributed only to denitrification. These losses range from 1 to 75 percent of the added nitrogen fertilizer (Broadbent and Clark 1965), but commonly are between 10 and 20 percent. Some values reported by investigators who directly measured losses by gas evolution or in ^{15}N balance experiments are presented in Table 2.3. It should be noted, however, that pretreatment and preparation of samples greatly affect results obtained in laboratory studies of denitrification in soils, and much of the research published to date can be criticized because of unrealistic pretreatment or incubation conditions that produce widely differing results.

Stefanson (1976) investigated the effect of plants on denitrification, as measured by the evolution of N_2 in a sealed growth chamber. Soil moisture was at field capacity, yet significant amounts of N_2 were formed regardless of where the nitrate was placed. Assuming that this experiment duplicated field conditions, the nitrogen loss was equivalent to about 40 kg/ha in 36 days. In a recent study of two irrigated fields of ryegrass in California, Rolston et al. (1976) found that from 20 to 70 percent of the applied nitrate fertilizer was lost through denitrification. Hauck (1971) summarized the literature on denitrification losses and crop recovery in various terrestrial systems (Table 2.4) and estimated the average loss from denitrification on cropland to be about 19 kg/ha-yr.

TABLE 2.3 Losses of Nitrogen by Denitrification

Experiment	Loss (mg N/kg soil/day)	Reference
Sealed chamber, gas evolution	0.3- 3.2	Stefanson and Greenland (1970)
Laboratory incubation, ^{15}N	4.2- 7.7	Nommik (1956)
Laboratory incubation, ^{15}N	14.6-64.0	Cady and Bartholomew (1960)
Sealed chamber	0.4- 1.0	Stefanson (1976)

TABLE 2.4 Denitrification Losses and Crop Recovery of Nitrogen in Various Terrestrial Systems

Ecosystem	N Loss by Denitrification (% of applied N)	Crop Recovery of N (% of applied N)	N Balance (% N accounted for)
Cropland	0-40	50-75	60-111
Pasture	25-35	50-70	70- 90
Forest	–[a]	–[a]	(79- 90)[a]
Paddy	20-50	26-45	–

[a] No data available on denitrification or crop recovery in forests; percent of N balance is estimated.

SOURCE: Derived from Hauck (1971).

In summary, although considerable efforts have been made in recent years to determine the significance of denitrification in soil systems, it still is not possible to make accurate generalizations from the results of individual field or lysimeter studies to determine the amounts of nitrogen lost by this process in the world's agricultural systems.

Denitrification in Lakes and Sediments. Denitrification was proposed as the mechanism for nitrate depletion in the bottom waters of stratified lakes by Hutchinson in 1957. The first measurements of denitrification, however, were made by Goering and Dugdale (1966), who used ^{15}N to measure denitrification rates of 15 μg N/l-day under the ice in Smith Lake, Alaska. Brezonik and Lee (1968) determined the rates of denitrification in Lake Mendota, Wisconsin, and compared the losses due to denitrification to the lake's nutrient budget. Rates of denitrification ranged from 8 to 26 μg N/l-day, and the total nitrogen lost from the hypolimnion in 1966 was calculated to be 2.8×10^7 g, or an average loss of 0.7 g/m^2-yr. Based on an existing nitrogen budget for the lake, the authors concluded that about 11 percent of the annual nitrogen imputs were lost by denitrification. A more recent nitrogen budget for this lake (see Appendix A) indicates that denitrification in the hypolimnion accounts for about 5 to 7 percent of the nitrogen inputs. Larsen (1977) found rates of denitrification ranging from 3 to 74 μg N/l-day in the hypolimnia of five Danish lakes; anoxic conditions prevailed long enough in four of these lakes to deplete all of the nitrate in the anoxic zone.

Lake sediments provide an ideal habitat for denitrifying flora. Carbonaceous substrates usually are in ample supply, and there is a band of anoxic sediment within a few cm of the surface at the proper redox potential for denitrification to occur (-0.10 to +0.20 V). Nitrate may be transported to this zone by upward seepage in groundwater (Keeney et al. 1971), or it may diffuse downward to the anoxic sediment zone from the overlying water or from the zone of nitrification in aerobic surface sediments (Barnes et al. 1975, Vanderborght and Billen 1975).

Nitrate transport to anoxic sediments by the upward seepage of groundwater may be important in many lake systems, but this mechanism has not been studied in detail. Keeney et al. (1971) hypothesized that this process may be an important sink in the nitrogen budget of Lake Mendota, Wisconsin. Chen et al. (1972) found lower rates of denitrification in laboratory incubations of sediments from a soft water lake than in the calcareous sediments of a hardwater lake. Bouldin et al. (1974) presented a simple model to express the rate of nitrogen loss from small ponds as a function of the rate of nitrate diffusion into the sediment. Vollenweider (1968), Anderson (1974) and Larsen (1977) used a mass balance approach to estimate denitrification in the water and sediments of lakes (see Chapter 4 and Appendix A). Vollenweider estimated that denitrification caused the loss of 45 to 81 percent of the nitrogen retained annually in six Swiss lakes; some of the lakes develop anoxic hypolimnia in which denitrification undoubtedly occurs. Anderson (1974) found that denitrification eliminated up to 54 percent of the nitrogen inputs to six shallow, unstratified Danish lakes, and Larsen (1977) found denitrification accounted for 23 and 61 percent of the annual nitrogen inputs to two Danish lakes. Denitrification in sediments accounted for over 90 percent of the loss in the lake with a 61 percent loss of nitrogen, whereas losses from the water column were more important in the other lake.

Denitrification in Oceans. Richards and Benson (1961) first demonstrated the occurrence of denitrification in marine waters. Using N_2/Ar and natural N_2 isotope ratios, they found evidence of denitrification in anoxic waters of the Cariaco Trench off Venezuela. Denitrification in the ocean has been studied most intensely in an oxygen-depleted region of the eastern tropical North Pacific, off Mexico and Central America. Goering et al. (1973) estimated the annual loss of nitrogen from the 3×10^7 km^2 area to be approximately 10 Mt (million metric tons = 10^{12} g), while Cline and Richards (1972) calculated the loss to be 230 Mt. More recently, Codispoti and Richards (1976) estimated the rate of denitrification as 20 Mt N/yr for the eastern tropical Pacific Ocean. In these mass-balance studies, order-of-magnitude estimates probably are the best that can be expected because of questions about water movements, the rates of nitrate diffusion into the anoxic zone, and the downward transport of oxidizable substrate.

Other areas in which denitrification has been measured include the Black and Arabian Seas, the eastern tropical South Pacific off Peru, and the South Atlantic shelf off southwest Africa. Goering (1976) recently reviewed studies on oceanic denitrification. He estimated the total annual denitrification in all areas of the open ocean to be 30 Mt N/yr and, on the basis of a single datum for sediments of the continental shelf, he calculated the rate of denitrification for such sediments to be 300 Mt N/yr, for a total oceanic rate of 330 Mt N/yr.

The global rate of denitrification cannot be estimated directly with any confidence, given the present uncertainties about the rates in oceans and sediments and the paucity of information on terrestrial rates. Most global nitrogen balances have estimated the denitrification rate by the difference between known sources and sinks of nitrogen. Because of the large uncertainties that are inherent in each of the components of a balance, estimates of this kind must be regarded as highly uncertain. Table A.25 of Appendix A, Section 7 lists global estimates of denitrification from a variety of studies. The rates range from 43 to 390 Mt/yr for terrestrial denitrification and from 0 to 330 Mt/yr for oceanic denitrification; and total global estimates range from 83 to 510 Mt/yr. These estimates are discussed further in the Appendix.

Other Sites of Denitrification. Considering the importance of denitrification as a global sink for fixed nitrogen, it is surprising that many areas that provide ideal habitats for denitrifying microbes, such as wetland sediments, have received virtually no research attention. Detailed studies on wetlands systems currently are being conducted, however, at several sites in the United States. Both freshwater and estuarine wetlands are detritus-based systems, and the high concentrations of oxidizable substrate and the anoxic sediments in these systems should lead to significant denitrification. Lee et al. (1975) observed denitrification in a freshwater marsh based on indirect nitrogen mass balance evidence. In estuarine wetlands, tidal exchange should continually supply nitrate-bearing water to anoxic sediments, and the repeated exposure and wetting of mudflats may induce a nitrification-denitrification process in the surface sediments. A similar phenomenon may occur with a seasonal periodicity in marshlands and in the surface sediments of shallow lakes.

Nitrogen Fixation

Biological nitrogen fixation involves the reduction of molecular nitrogen (N_2) to ammonia, which is directly incorporated into organic nitrogen compounds. Nitrogen fixation is not a direct source of nitrate, but it does add to the global pool of fixed nitrogen, and ultimately it can result in increased production and concentrations of nitrate in the environment.

The process of nitrogen fixation is essential in maintaining a nitrogen balance in the biosphere, which otherwise would become depleted of nitrogen through denitrification, over millions of years. In natural waters, nitrogen fixation is important because it allows organic production to continue after the supply of inorganic fixed nitrogen is exhausted. In agricultural systems, it is important in maintaining soil fertility, and crop rotation that involves nitrogen-fixing legumes has been practiced at least since early Roman times.

Numerous recent reviews treat the biology, biochemistry, and ecology of nitrogen fixation in an authoritative and thorough fashion (e.g., Burns and Hardy 1975; Dazzo and

Hubbell 1974; Evans and Barber 1977; Hardy et al. 1971; Skinner 1976; Stewart 1966, 1968, 1969, 1973). The agents and sites of nitrogen fixation, the environmental factors affecting the rate of fixation, and the quantitative significance of fixation as an internal source in the nitrogen budgets of ecosystems are examined here.

Agents of Nitrogen Fixation

The agents of nitrogen fixation have been termed "diazotrophs" by Burns and Hardy (1975). Table 2.5 lists the major classes of diazotrophs and gives specific examples of each class. The agents of fixation can be grouped into three major categories: (1) free-living organisms, (2) associative symbioses, and (3) obligatory symbioses involving bacteria or actinomycetes and higher plants. In the nitrogen-fixing associations involving higher plants, only the microbial partner is capable of synthesizing the nitrogen-fixing enzyme, nitrogenase, and it is highly probable that the synthesis of nitrogenase is limited to procaryotic cells. Free-living nitrogen-fixing organisms include certain blue-green algae, apparently all genera of photosynthetic bacteria, and various anaerobic, facultative, and aerobic bacteria.

The list of nitrogen-fixing species of blue-green algae (Cyanophyta) is still growing; for example, evidence that <u>Aphanizomenon</u> <u>flos-aquae</u>, an important bloom-forming alga in eutrophic lakes, fixes nitrogen was reported first by Stewart et al. (1968). Most nitrogen-fixing blue-green algae are filamentous and have heterocysts (large empty-looking cells), the abundance of which is related to the nitrogen-fixing capacity of the algal sample. Heterocysts lack photosystem II, the source of oxygen in photosynthesis. Since nitrogenase is highly susceptible to inhibition by oxygen, heterocysts seem an obvious location for nitrogen fixation. Van Gorkom and Donze (1971) and Thomas and David (1972) found that during aerobic culture, fixation occurs only in heterocysts, but under anaerobic conditions, it can also occur in vegetative cells.

Seven genera of photosynthetic bacteria are well-established nitrogen fixers, and 17 untested genera also are thought to have this capability. The habitat of photosynthetic bacteria is limited, however, by their simultaneous requirements for light and anoxic conditions, and the global input of fixed nitrogen from these bacteria is therefore probably small.

Among heterotrophic bacteria, at least 18 genera are known or probable nitrogen-fixers, including both cosmopolitan groups and species with specialized metabolic roles (e.g., methane oxidizers, sulfate reducers, and

TABLE 2.5 Summary of Nitrogen-Fixing Organisms and Associations

Kinds of Organisms	Examples
Free-Living Organisms	
Photosynthetic bacteria	*Rhodospirillum, Chromatium, Chlorobium*
Aerobic bacteria	*Azotobacter, Beijerinckia, Derxia, Spirillum, Thiobacillus*
Facultative bacteria	*Klebsiella, Bacillus, Vibrio* (methane oxidizers)
Obligate anaerobic bacteria	*Clostridium, Methanobacterium, Desulfovibrio*
Actinomycetes	*Mycobacterium, Nocardia, Actinomyces*
Blue-green algae:	
Heterocystous:	*Anabaena, Aphanizomenon, Gloeotrichia, Nostoc, Calothrix, Shizothrix*
Nonheterocystous:	*Gloeocapsa, Oscillatoria, Plectonema*
Non-Obligatory Associations*	
Animal associations (bacteria)	Termites, sea urchins, cattle, sheep
Aquatic macrophytes (blue-green algae)	*Azolla (Anabaena); Sargassum (Dichothrix,* blue-green algae); *Codium,* a macro-green alga *(Azotobacter)*
Leaf surfaces of angiosperms (bacteria)	Various tropical plants
Leaf nodules (bacteria)	*Psychotria,* a tropical plant *(Klebsiella)*
Lichens (blue-green algae and fungi)	*Peltigera aphthosa (Nostoc)*
Root nodules of tropical gymnosperms (blue-green algae)	*Podocarpus, Macrozamia, Cycas*
Obligatory Symbioses	
Non-leguminous angiosperms (root nodules)	Alder tree–*Alnus sp., Myrica, Elaeagnus, Coriaria, Dryas*
Legume root nodules *(Rhizobium spp.)*	Beans, peas, alfalfa, clover, soybeans, lentils, peanuts

*Nitrogen-fixing agent in parentheses.

SOURCE: Modified from Burns and Hardy (1975).

sulfide oxidizers). Facultative bacteria fix nitrogen only under anoxic conditions. In many of the genera, only some species or strains within a species are capable of nitrogen fixation. Several genera of mold-like bacteria (order Actinomycetales) also are probable nitrogen-fixers.

A variety of non-obligatory associations between free-living nitrogen-fixers and other organisms has been found in nature, and probably many more of these associations are still to be detected. These associations have received only limited attention and their global significance is unclear. They range from loose interactions between a nitrogen-fixer and another microorganism to more intimate symbioses, and include: (1) phylloplane associations, involving bacteria on leaves, especially of tropical plants; (2) rhizosphere associations, involving bacteria in the root zone of terrestrial and aquatic plants; (3) leaf nodules, primarily on tropical plants, that contain either nitrogen-fixing bacteria or blue-green algae, (4) lichens, i.e., morphologically distinct associations of fungi and nitrogen-fixing blue-green algae; (5) root nodules containing blue-green algae in certain tropical gymnosperms; and (6) bacterial associations in the intestinal flora of animals having a high carbon-to-nitrogen ratio in their diet, e.g., termites, sea urchins, and ruminants (cattle, sheep, deer).

Two classes of obligate symbioses are known, those involving non-legume angiosperms and those involving legumes and bacteria in the genus Rhizobium. Fixation apparently does not occur in the free-living form of these bacteria, but only in root nodules, where they are converted into physiologically altered forms known as bacteroids.

Burns and Hardy (1975) listed 14 genera of non-leguminous angiosperms in which root-nodule fixation occurs; the best known of these genera are the alder tree (Alnus) and the myrtles (Myrica spp.). Nodule-bearing, non-leguminous angiosperms such as Myrica play important pioneering roles in vegetating nitrogen-impoverished soils, e.g., in dredged and mine spoil areas and in natural, sandy scrubland (Silver 1969). Attempts to isolate the endophyte of alder-type symbioses have been unsuccessful thus far, but actinomycetes are thought to be the agents of fixation. Until the endophyte is isolated, it cannot be determined whether symbioses of the alder type are indeed obligatory for fixation; however, similarities of alder-type and legume symbioses suggest that they are obligatory (Burns and Hardy 1975).

Because of the importance of legumes in agriculture, legume-Rhizobium symbioses have been studied intensively. Important crop legumes include soybeans, peanuts, peas, beans, alfalfa, and clovers. The processes of root infection by Rhizobium and the consequent formation of nodules on the roots are known in considerable detail (Stewart 1966, Dixon 1969, Bergersen 1971, Burns and Hardy 1975). Legume infection by rhizobia is to a large extent species specific. For example, *R. trifolii* infects clover, while *R. japonicum* usually infects soybeans. Rhizobia are widely distributed in soils as free-living cells, but these cells do not fix nitrogen, most probably because of inhibition of the process by oxygen. Under anaerobic conditions, free-living rhizobia recently have been found capable of fixing nitrogen.

Biochemistry of Nitrogen Fixation

Knowledge of the biochemistry and molecular biology of nitrogen fixation has expanded greatly in the past decade or so, but understanding of the exact mechanisms of reduction has remained elusive (Burris 1969, Burns and Hardy 1975). Fixation involves the transfer of six electrons to molecular nitrogen, forming two ammonia molecules. The process involves several steps, probably with two electrons transferred at a time, but the presumed intermediates never have been isolated nor identified despite numerous efforts, implying that the nitrogen remains tightly bound to the active site of the enzyme (Burris 1969, Burns and Hardy 1975).

Nitrogen fixation requires a source of energy (ATP) and a reducing agent. Ferredoxin, a low molecular weight plant protein that contains iron, usually is the agent that transfers electrons from various donors to nitrogenase; under iron-deficient conditions, a flavoprotein (flavodoxin) apparently serves the same purpose. Several electron donors, including pyruvate and molecular hydrogen (via hydrogenase), can reduce ferredoxin. In blue-green algae, the reduced form of nicotinamide-adenine dinucleotide phosphate, NADPH, produced in the photoreduction of water, may act as the reducing agent for ferredoxin, thus providing a close link between photosynthesis and nitrogen fixation. ATP is required in large amounts for nitrogen fixation and is obtained by normal cellular breakdown of organic substances.

Nitrogenase systems that have been isolated from all major classes of nitrogen-fixers over the past 15 years have been shown to exhibit great similarities in structure and function (Burns and Hardy 1975), and it is commonly held that the fundamental mechanism of nitrogen fixation is essentially the same in all agents. The nitrogenase enzyme is made up of two proteins, a molybdenum-iron (Mo-Fe) protein, and an iron (Fe) protein, which can be separated and recombined to yield active nitrogenase. In most cases, cross-recombination of Mo-Fe protein from one species and Fe protein from another also yields a functional enzyme, thus substantiating the similarity of the nitrogenase systems of various agents.

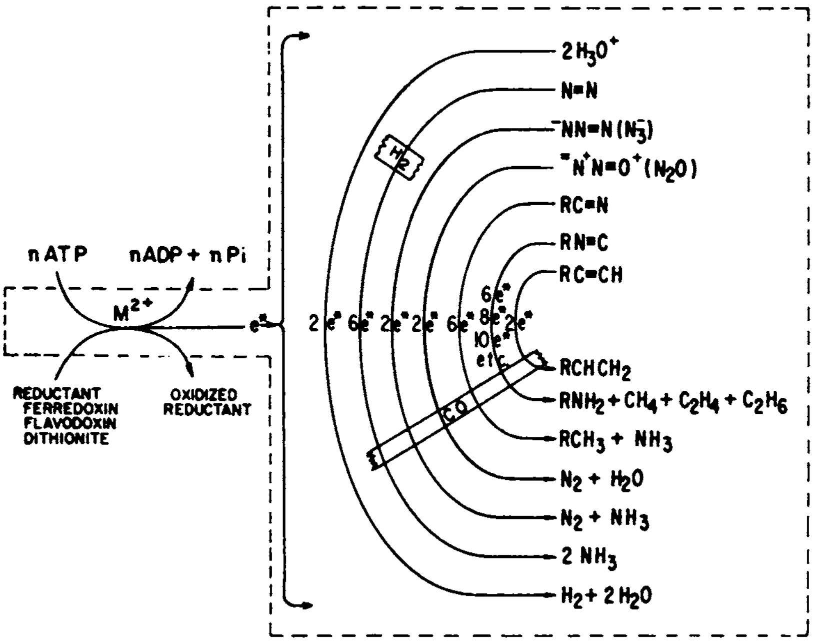
Nitrogenase is a unique enzyme in its ability to reduce triple bonds. In addition to reducing its physiological substrate, molecular nitrogen, the enzyme reduces the triple bonds in a variety of other compounds: acetylene, terminal alkynes, azides, nitrous oxide, cyanide, and nitriles (Figure 2.5). The enzyme behaves differently with N_2 than with the other substrates; for example, H_2 inhibits only the reduction of nitrogen. The reduction of acetylene ($HC\equiv CH$) to ethylene ($H_2C=CH_2$) by nitrogenase is the basis for a rapid and sensitive, although indirect, assay of fixation (Stewart et al. 1967; also see Chapter 4 of this report). Reported K_M values (the pressure of N_2 at which the enzymatic reaction is half its maximum rate) are in the range 0.05 to 0.20 atm for cell-free systems and 0.02 to 0.03 atm for cultures of whole organisms (Burns and Hardy 1975).

Nitrogenase is inhibited by carbon monoxide and hydrogen gas (Figure 2.5), and by nitric oxide. All three gases bind at the active site but do not undergo reduction. Inhibition is competitive and reversible, and in the case of H_2, it is relatively weak. The alternative substrates also inhibit the reduction of other reducible substrates, usually in a competitive fashion.

Burns and Hardy (1975) have thoroughly discussed the biochemistry of nitrogen fixation, and Skinner (1976) has reviewed current research on this subject.

Factors Affecting Nitrogen Fixation

Inorganic Nitrogen. Nitrogen fixation is an adaptive process that occurs at significant rates only when the supply of fixed nitrogen is low and apparently growth-limiting. Fixation of nitrogen requires a considerable input of energy; consequently, nitrogen-fixing heterotrophs must respire large amounts of organic substrate, and nitrogen-fixing algae must divert large amounts of their reducing power from carbon fixation to nitrogen fixation. In situations in which other forms of nitrogen are available, the energy requirements of nitrogen fixation result in a considerable competitive disadvantage to organisms that fix nitrogen compared to organisms that use ammonia or nitrate. Thus, all agents of fixation use ammonia or nitrate when they are available, and synthesis of nitrogenase in organisms that are capable of nitrogen fixation occurs only when sources of fixed nitrogen are depleted.



SOURCE: Burns and Hardy (1975).

FIGURE 2.5 The reactions of nitrogenase, based on utilization of ATP for formation of a strong reductant, or activated electron, e*, which can reduce H_3O^+, or N_2 and the other indicated species, subject to the H_2 and CO inhibition shown.

Ammonia and possibly nitrate repress the synthesis of nitrogenase; the nitrate ion may act indirectly by increasing the concentration of ammonia in the cell. It is not known whether the synthesis of nitrogenase is directly inducible (e.g., by N_2), or whether it is controlled simply by the repression by ammonia. Furthermore, the concentrations of ammonia that are required to repress the synthesis of nitrogenase are not known precisely, but they appear to be relatively high. Organisms probably vary in their sensitivity to ammonia, however, and the intracellular concentration of ammonia would seem to be more important than its concentration in the surrounding medium.

Rapid growth of nitrogen-fixing blue-green algae can result in leakage of fixed nitrogen into lake water, and ammonia levels as high as 500 µg N/l have been observed in blooms of Aphanizomenon (Brezonik 1973) and Anabaena (Horne and Goldman 1972). Reports in the literature conflict, but it appears that enzymatic activity is not directly inhibited by ammonia and that nitrogen fixation can continue for some time in the presence of relatively high levels of ammonia. On the other hand, nitrogen fixation does not normally begin to occur in lake waters until concentrations of inorganic nitrogen are highly depleted (i.e., typically less than 50 µg/l); possibly this reflects the inhibition of heterocyst formation by relatively low concentrations of ammonia and nitrate.

Nitrogen fixation in soils and submerged sediments occurs at low rates in the presence of rather high levels of ammonia (e.g., Brooks et al. 1971; Macgregor and Keeney 1973; Torrey and Lee 1976). But high concentrations of ammonia in the overall environment are not necessarily available to nitrogen-fixing organisms, which may exist in nitrogen-limited microenvironments within a sediment.

Based on the statistical analysis of data from a bloom of Anabaena in Clear Lake, California, Horne et al. (1972) proposed that nitrogen fixation requires high levels of phosphate and of dissolved organic nitrogen. This hypothesis agrees with the known association of nitrogen-fixing blue-green algae with eutrophic lakes. However, there is little experimental support for the hypothesis concerning dissolved organic nitrogen, and the absence of high rates of nitrogen fixation from oligotrophic lakes more likely is related to deficiencies of phosphorus and possibly other mineral nutrients in such environments.

Mineral Factors. Molybdenum is a constituent of nitrogenase, and also of the reductase enzymes involved in the assimilation of nitrate and in denitrification. Vanadium can substitute for the molybdenum requirement, however, in some nitrogenases. Low concentrations of molybdenum in natural waters could limit the occurrence of nitrogen fixers, but this is unlikely to occur because the amounts needed in nitrogenases are small. However, in Castle Lake, California, low levels of molybdenum apparently limit primary production (Goldman 1960). In some agricultural regions, the natural abundance of available molybdenum is considered suboptimal. The addition of as little as 70 g Mo/ha resulted in improved growth and nitrogen fixation by legumes in some Australian soils (Anderson 1956; also see Stewart [1966:120]).

Nitrogen fixers also require cobalt and iron. Whether cobalt plays a direct role in nitrogen fixation is still unknown, but it is known that nitrogen fixers have a greater need for cobalt than do nonfixers. Nitrogen fixers also have higher requirements for iron than do plants that employ fixed nitrogen for growth. Iron is a constituent of both nitrogenase and ferredoxin, as well as of the hemoglobin in the root nodules of legumes. Because iron occurs only at low concentrations in oxygenated waters, plant growth may be limited by iron deficiency more often than is commonly supposed (e.g., Goldman et al. 1975).

Physical Factors. Other important environmental factors that affect nitrogen fixation are temperature, light, pH, and dissolved oxygen.

As a group, the nitrogen fixers are adapted to wide extremes in temperature and can grow in harsh environments. *Nostoc* growths are found in Antarctica, where they contribute significantly to the meager supply of fixed nitrogen (Holm-Hansen 1963). Nitrogen-fixing blue-green algae are also the primary colonizers of islands formed by volcanic activity. For example, blue-greens were important in re-vegetating the island of Krakatoa after the massive volcanic eruption there in 1885 (Treub [1888], cited in Stewart [1966]). Schwabe (1970) reported that *Nostoc* and *Anabaena* colonized the Icelandic island of Surtsey within two years after the eruptions there had ceased, and Henriksson et al. (1972) measured the nitrogen fixation rates of these colonizers. *Nostoc* and *Anabaena* also are common in the soil of Death Valley, California (Cameron and Fuller 1960). These are examples of adaptation to extreme temperatures, but it should be recognized that individual species or strains have temperature ranges and optima, which may be exceeded in specific environments.

In temperate eutrophic lakes, nitrogen fixation usually occurs during the period of maximum water temperature in late summer. However, factors such as nutrient availability are probably more important than temperature in regulating the timing of nitrogen fixation in lakes.

Light is an important factor in fixation by blue-green algae; when algal cultures are placed in the dark, fixation declines rapidly. Several field studies have correlated nitrogen fixation with light intensity and with photosynthesis, but the optimal conditions for each process do not necessarily occur simultaneously. Most studies of nitrogen fixation in lakes have assumed that nighttime fixation is negligible, but recent data from A.J. Horne (University of California, Berkeley, personal communication, 1977) and others suggest that this may not be true in all cases. Up to one third of the nitrogen fixation in Clear Lake, California occurs at night.

Light also is an important factor in nitrogen fixation by the root nodules of symbiotic plants. Lie (1974) indicated that within certain limits a relationship can be obtained between light intensity and nitrogen fixation. The primary effect of light results from its effect upon photosynthesis and the supply of photosynthates to the nodules. The rate of nitrogen fixation is invariably negligible in plants that have been exposed to 24 hours of darkness (Virtanen et al. 1955, Wheeler 1971, and Lawrie and Wheeler 1973). Other experimental treatments that reduce the translocation of photosynthates to the nodules also decrease nitrogen-fixing activity. These treatments include defoliation (Chu and Robertson 1974), destruction of alder bark by stem ringing (Wheeler 1971), and detachment of plant nodules (Bergersen 1970).

As a group, nitrogen-fixing organisms tolerate a wide range of pH values, but individual species often have narrow pH limits. At low pH, molybdenum tends to become unavailable to plants. Blue-green algae favor alkaline environments, and the soil bacterium Azotobacter cannot fix nitrogen below pH 6.0. On the other hand, Beijerinckia, an aerobic bacterium, can fix nitrogen at pH 3.0 (Stewart 1966). Legumes are generally capable of fixing nitrogen in the pH range of 5 to 8, but liming of soil is commonly practiced with legumes to insure a neutral to slightly alkaline pH for fixation. Non-legumes such as Alnus and Myrica generally grow in acid soils and can fix nitrogen at soil pH values as low as 3.3.

Oxygen is another important factor in fixation by both bacteria and algae. Photosynthetic bacteria are strict anaerobes, which are inhibited by even small amounts of oxygen, and facultative bacteria fix nitrogen only under anoxic conditions. In blue-green algae, nitrogen fixation apparently takes place in heterocysts, which lack the ability to produce oxygen. These facts suggest that oxygen inhibits nitrogenase, and studies on cell-free nitrogenase extracts from aerobic bacteria such as Azotobacter bear this out. Aerobic organisms have developed a variety of mechanisms to avoid inhibition of nitrogenase while maintaining an otherwise aerobic metabolism. These mechanisms include the heterocysts of algae and the extraordinarily high respiration rates of Azotobacter; in legumes, leghemoglobin may function as a reservoir and transport agent for oxygen, thus maintaining a constant but tolerably low concentration of oxygen at the bacteroid surface.

Occurrence and Significance of Nitrogen Fixation

Field studies using the popular acetylene reduction assay for nitrogen fixation (see Chapter 4) have permitted more detailed assessment of the role of nitrogen fixation in ecosystem nitrogen budgets. Furthermore, recent research has revealed that nitrogen fixation occurs not only in soils and lakes, as is widely known, but also in lake and estuarine sediments, and in the intestinal flora of certain animals that have high-carbon, low-nitrogen diets (Benemann 1973, Hardy et al. 1968), in shipworms (Carpenter and Culliney 1976), and in sea urchins (Guerinot and Mann 1977). Nitrogen fixation also has been reported in the intestinal flora of humans (Bergersen and Hipsley 1970).

Lakes. The contribution of nitrogen-fixing blue-green algae to the nitrogen supply in surface waters of lakes was suggested by Hutchinson in 1941, but actual measurements of fixation were not made until many years later.

Table 2.6 summarizes available estimates of the contributions of nitrogen fixation to the nutrient budgets of lakes. The reliability of these estimates is variable, and in some studies sampling was infrequent or of short duration. In most lakes in which fixation occurs, it makes relatively low contributions to the annual input of nitrogen (<15 percent), but in a few well-studied cases (e.g., Clear Lake, California), fixation accounts for 30 to 50 percent of the total annual input. However, even when only low contributions are made to the total loadings of nitrogen, the process is still ecologically significant because it stimulates blue-green algal blooms.

Dugdale et al. (1959) first reported measurements of nitrogen fixation in lakes by ^{15}N tracer techniques. Dugdale and Dugdale (1962, 1965), Goering and Neess (1964), Horne and Fogg (1970), Billaud (1968), and Horne and Viner (1971) have also used ^{15}N methods to measure rates of nitrogen fixation in lakes. In these studies, nitrogen fixation was correlated with the occurrence of blue-green algae, most commonly Anabaena spp.; all of the lakes studied were eutrophic and thus had high nutrient levels and frequent algal blooms. In temperate lakes, fixation was found most commonly in late summer, and some of the studies found that the uptake of $^{15}NH_3$ and $^{15}NO_3^-$ occured concurrently with nitrogen fixation. Although most of the studies estimated the contributions of fixation to the

TABLE 2.6 Contributions by Nitrogen Fixation to the Nutrient Budgets of Ten Lakes*

Lake	Location	Total N Fixed (g/m^2-yr)	Percent of Annual Total N Input	Reference
Lake George	Uganda	4.4	33	Horne and Viner (1971)
Lake Windermere	England	0.04-0.29	<1	Horne and Fogg (1970)
Esthwaite Water	"	0.06-0.13	<1	"
Smith Lake	Alaska	~0.4	–	Billaud (1968)
Lake Wingra	Wisconsin	~2.0	–	Goering and Neess (1964)
Lake Erken	Sweden	0.5	40	Granhall and Lundgren (1971)
Clear Lake	California		30-50	Horne and Goldman (1972)
Newnans Lake	Florida	0.3	5	Brezonik (1973)
Bivins Arm Lake	"	1.0	7	"
Lake Mendota	Wisconsin	0.24	3.8	Stewart et al. (1971) Lee et al. (1966)
Lake Mendota	"	0.025	0.4	Goering and Neess (1964)
Lake Mendota	"	0.96	7	Torrey and Lee (1976)
Lake Mendota	"	data insufficient to quantify		Rusness and Burris (1970)
Lake Mendota	"	–	5-10	G. P. Fitzgerald (estimate cited by Torrey and Lee [1976])

******Anabaena* **and/or** ***Aphanizomenon*** **were the most common N-fixing algae in nearly all of these lakes.**

annual nitrogen budgets of the lakes (Table 2.6), factors affecting the nitrogen fixation rates and the spatial and diurnal variations in fixation could not be measured because of limitations in the ^{15}N methodology.

The acetylene reduction technique developed by Stewart et al. (1967) has simplified the collection of data on nitrogen fixation activity, but the quantitative relationship between nitrogen fixation and acetylene reduction remains questionable (see Chapter 4). Stewart et al. (1971) used the acetylene method to survey nitrogen fixation in some Wisconsin lakes and found rapid fixation in three eutrophic lakes but only low rates in four oligotrophic lakes. Brezonik (1973) found active fixation at least once over the period of a year in 15 of 55 Florida lakes. Brezonik and Harper (1969) and Keirn and Brezonik (1971) found evidence of bacterial nitrogen fixation in two lakes with high levels of humic coloration. This finding is unusual; algae are normally the only significant agents of fixation in lake waters.

Detailed studies of nitrogen fixation over an entire growth season have been conducted on relatively few lakes. In studies of Clear Lake, California, Horne and Goldman (1972) found two periods of rapid nitrogen fixation, a spring bloom of _Aphanizomenon_ and a fall bloom of _Anabaena_. Brezonik (1973) found that a winter bloom of _Aphanizomenon_ fixed most of the nitrogen in one Florida lake, while summer activity of _Anabaena_ predominated in a nearby lake. Torrey and Lee (1976) concluded that nitrogen fixation by blue-green algae in Lake Mendota, Wisconsin occurred primarily during the late summer, when inorganic nitrogen was depleted in the surface waters.

At least five separate estimates of annual nitrogen fixation rates have been reported for Lake Mendota, as shown in Table 2.6. The disparities in the findings of these studies can be attributed in part to differences in sampling programs, but there also are annual variations in the algal flora of the lake. The range of rates shown in Table 2.6 for Lake Mendota indicates the imprecisions inherent in measurements of large-scale environmental processes.

There are several recent reports of bacterial fixation of nitrogen at low rates in lake sediments (e.g., Brezonik 1973, Macgregor and Keeney 1973, Torrey and Lee 1976), but the significance of this activity either as a source of nitrogen to the overlying lake water or in relation to the total global rate of nitrogen fixation appears to be relatively minor.

Oceans and Estuaries. Dugdale et al. (1961, 1964) discovered nitrogen fixation associated with the blue-green alga _Trichodesmium_ (now called _Oscillatoria theibautii_) in the Sargasso Sea. Recent thorough studies by Carpenter and McCarthy (1975) found that measured rates of nitrogen fixation were negligible, however, compared to other nitrogen inputs to surface waters of the west Sargasso Sea. On the other hand, Carpenter and Price (1977) reported high populations of *Oscillatoria* and high rates of nitrogen fixation in the Caribbean; they concluded that fixation is a significant source of nitrogen input to those waters. Carpenter and Price (1976) found that *Oscillatoria theibautii* fixes nitrogen at significant rates only when it grows in clumps; single filaments lose their ability to fix nitrogen apparently because of oxygen inhibition. Nitrogen fixation by this organism probably is limited to calm seas, where clumping can occur. Because the species is found in great abundance and throughout large areas of the tropical seas, oceanic fixation represents a potentially large source of fixed nitrogen for the global budget, but studies on a large geographical scale are needed for better assessment of this contribution.

Nitrogen fixation by *Dichothrix*, a heterocystous blue-green epiphyte on *Sargassum* in the Sargasso Sea and in the Gulf Stream, was reported by Carpenter (1972). Rates of 0.10 to 0.26 μg N/m^2-day were measured over a three-month period. Head and Carpenter (1975) found that symbiotic nitrogen fixation was associated with the marine macroscopic green alga, *Codium fragile*; *Azotobacter* isolated from the surface of *Codium* was identified as the agent. According to Head and Carpenter, fixation could be significant both to *Codium* and to some shallow bays of the Atlantic in which *Codium* has proliferated in recent years.

In estuarine and coastal areas, nitrogen fixation has been associated with blue-green algal mats on rocks (Jones and Stewart 1969) and on the tidal flats of salt marshes (Whitney et al. 1975, Jones 1974); anaerobic bacteria in shallow sediments (Brooks et al. 1971, Whitney et al. 1975, Jones 1974); the rhizosphere of seagrasses (Patriquin and Knowles 1972); epiphytes of seagrasses (Goering and Parker 1972, McRoy et al. 1973); and the blue-green flora associated with coral reefs (e.g., Burris 1976). Reports sometimes disagree about the significance of some of these processes; for example, extensive nitrogen fixation by sea grass epiphytes and mangrove detritus has been found in Biscayne Bay, Florida (J.H. Carpenter, University of Miami, personal communication, 1977) and Patriquin and Knowles (1972) concluded that nitrogen fixation by bacteria in the root zone of turtle grass (*Thalassia sp.*) supplies the inorganic nitrogen needs of that plant, while McRoy et al. (1973) found only negligible rates of fixation in the rhizosphere and epiphytic material of *Thalassia*.

Terrestrial Nitrogen Fixation. Nitrogen fixation by legumes has been well studied because of its role in agricultural productivity. Bergersen (1971), Burns and Hardy (1975), Dixon (1969), Evans and Barber (1977), and Stewart (1966) have published important reviews on the occurrence and significance of nitrogen fixation by legumes.

Legumes can obtain up to 80 percent of their nitrogen needs by fixation; even in highly developed agricultural lands, fixation by legumes accounts for a significant portion of the nitrogen supply. For example, reports cited by Burns and Hardy (1975) indicate that legumes supply 42 percent of the agricultural nitrogen in England, with the balance coming from fertilizer (27 percent) and manure (31 percent).

Nitrogen fixation rates tabulated in Burns and Hardy range from about 50 to 300 kg/ha-yr for legume fields; in computing global rates of nitrogen fixation, these authors used an average value of 140 kg/ha-yr for all types of legumes. Symbiotic fixation by non-legumes in terrestrial systems has not been so well studied. Burns and Hardy cited four studies on nitrogen fixation by Alnus in which reported rates ranged from 56 to 156 kg/ha-yr and the mean rate was 112 kg/ha-yr. Goldman (1961) reported that nitrogen-fixing alder trees growing around Castle Lake, California supplied significant amounts of nitrogen to the lake via leaf litter and the leaching of nitrate from the soil. Other studies of nitrogen fixation by non-leguminous symbiotic angiosperms have found rates that range from 2 to 270 kg/ha-yr (see Stewart [1966] and Burns and Hardy [1975]); about 50 kg/ha-yr seems a reasonable average rate for nitrogen fixation by terrestial non-legume symbionts.

Fixation by blue-green algae may be an important source of nitrogen in rice paddies. The addition of about 1.1 to 5.5 kg of Tolypothrix per hectare of rice paddy has been calculated to be equivalent to the addition of 29 kg/ha of ammonium sulfate fertilizer (Stewart 1966). Data tabulated in Stewart indicate annual contributions of >15 to 54 kg/ha-yr by algal fixation in rice paddies, and data tabulated in Burns and Hardy (1975) indicate a range of 10 to 55 kg/ha-yr from this source.

Recent evidence indicates that nitrogen fixation by free-living terrestial organisms is more common than was previously thought. Jones et al. (1974) found fixation on the leaves and in the soil associated with Douglas fir. Total annual rates in the soil, litter, and canopy at two sites were estimated to be about 7.5 and 20 kg/ha-yr, or about half of the annual needs for the growth of the trees. Bormann et al. (1977) used a mass balance to estimate by difference the nitrogen fixed in Hubbard Brook Forest in New Hampshire. Their model produced an estimated rate of fixation of 14 kg N/ha-yr, but no corroborating direct measurements were made. Nitrogen fixation by blue-green algae has been found in wet mountain meadows (Porter and Grable 1969), and by *Azotobacter* in grassland soils (Kass et al. 1971); natural meadows and grasslands also contain a wide range of leguminous species. Burns and Hardy (1975) estimated the annual fixation rate to be 15 kg N/ha-yr for such lands. Finally, recent studies have shown that nitrogen fixation may be widespread in tropical grasses; the bacterium *Spirillum lipoferum* has been found to be the agent (Smith et al. 1976, Skinner 1976).

Potential for Enhanced Nitrogen Fixation in Agricultural Systems

There is much interest currently in applying recent findings on the biochemistry and microbiology of nitrogen fixation to the enhancement of nitrogen fixation rates in agricultural systems. Although many of the proposed applications require additional research before they will have practical use, they do offer hope for decreased needs for chemical fertilizers. In a review of research on these and other possible enhancement techniques, Skinner (1976) reported that the possible ways of enhancing biological nitrogen fixation range from simple improvements in crop rotations involving legumes to the transfer of the *nif* gene that controls fixation from organisms that can fix nitrogen to those that cannot. Some success has been achieved in transferring the *nif* gene from *Klebsiella pneumoniae* to the common intestinal bacterium *Escherichia coli*, and from *K. pneumoniae* to a non-fixing strain of *Azotobacter vinlandii*; transfer of the ability to fix nitrogen from prokaryotic cells to eukaryotic cells of higher plants, however, is a much more difficult problem. Other proposals for the enhancement of nitrogen fixation include: (1) the discovery and use of more effective symbiotic combinations of legumes and rhizobia and the use of newly-found symbiotic combinations of microorganisms with grasses and cereals; (2) increasing the efficiency of fixation in bacteria by selecting strains that use energy more efficiently (in many bacteria, hydrogen ions compete with nitrogen for electrons in nitrogenase, and up to half of the electrons go into the production of H_2, which is wasted, rather than to the reduction of N_2); (3) improved techniques for inoculating (coating) seeds with nitrogen-fixing bacteria.

Global Contributions of Nitrogen Fixation

As indicated above, nitrogen fixation is widespread in terrestrial and aquatic habitats, but quantitative information on the contributions of fixation to the global nitrogen budget is still too sparse to permit accurate calculations to be made.

A wide range of estimates of global fixation rates has been published in the past several decades. Hutchinson (1944) estimated biological nitrogen fixation to average 0.01 to 0.07 mg N/cm^2 of land surface, or a total of 1.5 to 10 x 10^{13} g N/yr (15 to 100 Mt N/yr). Delwiche and Stout (1964) estimated nitrogen fixation on land at 75 Mt N/yr. Delwiche (1965) considered the average rate to be 0.1 mg N/cm^2 of land surface, or approximately 150 Mt N/yr, but he later revised this estimate to 44 Mt N/yr for fixation on land and added 10 Mt N/yr for fixation in oceans, for a total global rate of 54 Mt N/yr (Delwiche 1970). More recent estimates of global fixation are higher, reflecting greater knowledge about fixation obtained since the development of the acetylene reduction technique.

The Burns and Hardy (1975) estimates of nitrogen fixation rates are probably the most comprehensive summary now available. These authors concluded that biological fixation from all sources totals 175 Mt N/yr. Burns and Hardy considered nitrogen fixation in oceans to be the least well-defined factor in global nitrogen fixation; their estimate of 36 Mt N/yr for fixation in oceans is a noteworthy increase over earlier estimates. A recent review of the global nitrogen cycle by Söderlund and Svensson (1976) used Burns and Hardy's estimates for nitrogen fixation on land; however, Söderlund and Svensson gave a range of 20-120 Mt N/yr for aquatic fixation and 10 Mt N/yr for fixation in marine sediments, yielding a total of 169 to 269 Mt N/yr for global biological nitrogen fixation (see Appendix A-7).

To put these rates into perspective, they can be compared with total rates of nitrogen fixation by all natural and man-made sources. Söderlund and Svensson (1976) estimated non-biological fixation to amount to 76 Mt N/yr in 1975, of which 53 Mt is industrial fixation of nitrogen for fertilizer and 23 Mt is from combustion (see Chapter 6). These authors regarded fixation of nitrogen by lightning as negligible, but recent studies by Chameides et al. (1977) suggest that lightning may fix up to 30 to 40 Mt N/yr. The total annual fixation estimated by Söderlund and Svensson amounts to 245 to 345 Mt, and biological processes predominate, accounting for 69 to 78 percent of the 1975 total. If an additional 30 Mt of nitrogen is fixed per year as a result of lightning, the fraction of the total fixation attributable to biological processes decreases to 61 to 71 percent. However, it should be noted that much of the nitrogen fixation that is attributed to legumes (35 Mt/yr; see Table A.23, Appendix A, Section 7) is anthropogenic. Assuming that leguminous fixation would be negligible in the absence of human activities, natural fixation represented only 49 to 62 percent of the total fixation from all sources (including lightning) in 1975. Hardy (cited in Skinner [1976]) estimated total global nitrogen fixation at 255

Mt/yr, of which 69 percent (175 Mt) is from biological fixation (including that from legumes). Global rates of nitrogen fixation are described further in Appendix A, Section 7.

MAJOR ATMOSPHERIC REACTIONS RELATED TO NITRATE

Natural processes inject nitrous oxide (N_2O), ammonia (NH_3), and nitric oxide (NO) into the atmosphere. Human activity can lead to an increase in the rate at which these gases and other nitrogen oxides are introduced into the atmosphere. The principal atmospheric reactions involving each of these gases and the formation of nitrate from these gases are reviewed here.

Tropospheric Processes: Nitrous Oxide and Ammonia

Nitrous oxide (N_2O) is produced in soils and waters largely by bacterial action. Human activity can form additional nitrous oxide by increased fixation of nitrogen, followed ultimately by denitrification. The time between fixation and denitrification probably is quite different, depending on whether fixation is by commercial production of inorganic fertilizer, by bacteria in the root nodules of cultivated legumes, or by combustion followed by precipitation as nitrate or nitric acid. Also, human activity directly produces N_2O as a by-product of the combustion of organic nitrogen in fuel oil and coal (Rasmussen et al. 1976, Pierotti and Rasmussen 1976, Weiss and Craig 1976).

At present there are no known reactions involving N_2O as a reactant in the troposphere, and this gas can be considered separately from higher nitrogen oxides, which react photochemically and ultimately form nitrate in the lower atmosphere. The principal atmospheric sink for N_2O is photolysis in the stratosphere to form molecular nitrogen (N_2), oxygen, and nitric oxide (NO); see Johnston and Selwyn (1975). Nitric oxide eventually forms nitric acid and is removed from the atmosphere by rain in the troposphere. There is indirect evidence (based on estimates of short residence times) for the destruction of N_2O in the troposphere or on the surface of land or sea by some unknown process or processes (Schutz et al. 1970, Junge 1974, Hahn 1974, Hahn and Junge 1977). At present, this topic is a matter of active research and controversy (see Chapter 3). Also, soils may act as sinks as well as sources for N_2O; uptake of atmospheric N_2O by soil microorganisms has recently been demonstrated (Blackmer and Bremner 1976).

Ammonia (NH_3) may be released into the atmospere from decaying organic matter or from alkaline soils or waters.

The principal human activities leading to increased atmospheric ammonia are the production of animals for food, especially in cattle feedlot operations (see Chapter 6) and the use of ammonia fertilizer, especially on alkaline soils. Atmospheric aerosols are often found to contain ammonium nitrate or ammonium sulfate, presumably formed by the reaction of gaseous ammonia and gaseous nitric acid on the surface of particulate matter in the atmosphere and by the reaction of ammonia with sulfuric acid aerosols:

$$NH_3 + HNO_3 \text{-----}> NH_4NO_3\ (s), \qquad (2\text{-}11)$$

$$NH_3 + H_2SO_4 \text{-----}> NH_4HSO_4\ (s). \qquad (2\text{-}12)$$

Ammonia can be oxidized by ozone via hydroxyl (HO•) radicals. The troposphere contains small concentrations (10^6 to 10^7 radicals cm^3) of HO•, which are produced primarily from the reaction of water with singlet oxygen, which is produced from photolysis of ozone:

$$O_3 + h\nu(\lambda < 310\ nm) \text{---}> O_2 + O(^1D), \qquad (2\text{-}13)$$

$$O(^1D) + H_2O \text{---}> 2\ HO\bullet\ . \qquad (2\text{-}14)$$

Hydroxyl radicals attack ammonia,

$$HO\bullet + NH_3 \text{---}> H_2O + NH_2\bullet, \qquad (2\text{-}15)$$

and the $NH_2\bullet$ radical undergoes further reactions with oxygen via unknown mechanisms, presumably forming nitric oxide and eventually nitric acid (de Pena et al. 1973, Olszyna et al. 1974).

The importance of chemical oxidation of ammonia in the atmosphere is controversial. Robinson and Robbins (1971) regarded the ammonia-ozone reaction as extremely slow and inconsequential, but evidence for the process is now firm. Chameides et al. (1977) estimated that this reaction accounts for 20 to 40 Mt of NO_x-N per year, or about 25 to 50 percent of the annual global production of NO_x. Microbial oxidation of atmospheric ammonia to nitrite and nitrate in aerosols and in dust particles also has been conjectured, but there is little evidence to support this idea.

Tropospheric Reactions of NO_x: Smog Formation

Nitric oxide (NO) is produced in the troposphere as a minor product of denitrification under acidic conditions, from oxidation of ammonia by free radicals, and from several processes for which the net reaction is

$$N_2 + O_2 = 2NO. \tag{2-16}$$

Nitric oxide is produced in the atmosphere via reaction 2-16 by lightning and by ionizing cosmic radiation (Chameides et al. 1977).

Human activity adds NO to the troposphere principally by combustion, for instance in automobiles, power plants, and jet aircraft. Above 2000°K, nitrogen and oxygen are rapidly converted to nitric oxide by a complex mechanism involving oxygen and nitrogen atoms. The reverse reaction also occurs rapidly at this temperature, with the equilibrium concentration of NO about 0.1 percent. The equilibrium concentration of NO increases only slowly with temperature, but the rates of reaction are extremely sensitive to temperature. The differences in the rates of formation and decomposition at different temperatures result in a "thermal fixation" of NO when high temperature exhausts, as from internal combustion engines and furnaces, are rapidly cooled. Ultimately NO is converted to nitrogen dioxide (NO_2), nitric acid (HNO_3), and nitrate aerosols by a complex series of photochemical reactions; the nitrate is removed from the troposphere by rainfall and dry fallout.

In non-metropolitan areas, the concentration of NO_2 in the troposphere is probably less than one part per billion. The fraction of NO_2 in the stratosphere is 1 to 10 parts per billion. Thus the gradient is such that turbulent diffusion moves NO_2 from the stratosphere to the troposphere, and little NO_x from combustion in the troposphere reaches the stratosphere. If NO is released into the stratosphere by high-flying aircraft, it adds to the natural NO_x there and is eventually transported to the troposphere as HNO_3.

Nitrogen dioxide and, to a much lesser extent, nitric oxide, are absorbed from the atmosphere by plants (Hill 1971). Nitrogen dioxide is highly soluble in water and reacts with water ultimately to form nitric acid. The importance of these processes as sinks for NO and NO_2 is not well understood. (Chapter 6 treats the subject in greater detail).

The oxides of nitrogen (NO and NO_2) play a principal, albeit complex, role in photochemical smog. The most important processes involving NO_x in smog formation are summarized in Table 2.7, and are described in greater detail

TABLE 2.7 Important Reactions Involving Nitrogen Oxides (NO_X) and Smog Formation

1.	Oxidation of nitric oxide		
	$2NO + O_2 \longrightarrow 2\,NO_2$	(slow)	(2-17)
2.	NO -NO_2 null cycle		
	$NO_2 + h\nu\ (385\ nm < \lambda < 435\ nm) \longrightarrow NO + O$		(2-18)
	$O + O_2 + M \longrightarrow O_3 + M$	$M = O_2$ or N_2	
	$NO + O_3 \longrightarrow NO_2 + O_2$		
NET:	no reaction		
3.	Hydrocarbon attack by hydroxyl free radicals		
	$RH + HO\cdot \longrightarrow R\cdot + H_2O$		(2-19)
	$R\cdot + O_2 \longrightarrow ROO\cdot$	(peroxyl free radicals)	
4.	Peroxyl -NO_X catalytic cycle of ozone formation		
	$ROO\cdot + NO \longrightarrow RO\cdot + NO_2$		(2-20)
	$NO_2 + h\nu \longrightarrow NO + O$		
	$O + O_2 + M \longrightarrow O_3 + M$		
NET:	$ROO\cdot + O_2 \longrightarrow RO\cdot + O_3$		
	Further reactions of RO radical form aldehydes, which are strong promoters of the smog reaction.		
5.	Carbon monoxide oxidation (simplest smog reaction)		
	$HO\cdot + CO \longrightarrow CO_2 + H\cdot$		(2-21)
	$H\cdot + O_2 + M \longrightarrow HOO\cdot + M$		
	$HOO\cdot + NO \longrightarrow HO\cdot + NO_2$		
	$NO_2 + h\nu \longrightarrow NO + O$		
	$O + O_2 + M \longrightarrow O_3 + M$		
NET:	$CO + 2\,O_2 \longrightarrow CO_2 + O_3$		
6.	Destruction of chain-carrying radicals		
	$HO\cdot + NO_2 + M \longrightarrow HNO_3 + M$		(2-22)
	$HO\cdot + HOO\cdot \longrightarrow H_2O + O_2$		(2-23)
	$HOO\cdot + HOO\cdot \longrightarrow H_2O_2 + O_2$		(2-24)
7.	Formation of PANs (peroxyacyl nitrates)		
	$RCO\,(OO) + NO_2 \longrightarrow R\overset{O}{\overset{\parallel}{C}}OONO_2$		(2-25)
8.	Nitrous acid formation		
	$NO + NO_2 + H_2O \longrightarrow 2HNO_2$		(2-26)
9.	Nitrous acid photolysis		
	$HNO_2 + h\nu \longrightarrow HO + NO$		(2-27)
10.	Nitrogen dioxide/ozone reaction		
	$NO_2 + O_3 \longrightarrow NO_3 + O_2$		(2-28)
	$NO_3 + NO_2 \longrightarrow N_2O_5$	(nitric acid anhydride)	(2-29)

in the EPA report on atmospheric nitrates (U.S. EPA 1974), the report of the National Research Council's Committee on Medical and Biologic Effects of Environmental Pollutants, Panel on Nitrogen Oxides (NRC 1977a), and in many texts on air pollution.

The major reactants in the formation of smog are unburned hydrocarbons from auto exhaust and NO_x; the major products are ozone and more oxidized nitrogen species, including PANs (peroxyacyl nitrates) and inorganic nitrates. Nitric oxide (NO) is the major oxide of nitrogen in auto exhaust. It is oxidized slowly to NO_2 in the air by thermal reactions involving oxygen (e.g., Equation 2-17 in Table 2.7), and the reaction is accelerated by several chain processes involving hydroxyl (HO•) radicals (e.g., the first reaction in Equation 2-20, the third reaction in Equation 2-21). Nitrogen dioxide is a key intermediate species in the formation of smog, and, as discussed below, it reacts via photodissociation mechanisms to produce ozone and PANs.

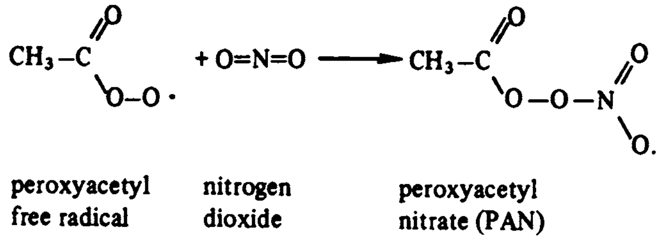
Nitrogen dioxide dissociates by absorbing light in the actinic uv range (385 to 435 nm) to produce NO and ground state oxygen atoms, $O(^3P)$ (see Table 2.7: the first reaction in Equation 2-18, the second reaction in Equation 2-20, the fourth reaction in Equation 2-21). The oxygen atoms react with oxygen molecules (O_2) and a third body ($M = O_2$ or N_2) to produce ozone (see Table 2.7: the second reaction in Equation 2-18, the third reaction in Equation 2-20, the fifth reaction in Equation 2-21). This reaction is the only known source of ozone in urban air (Finlayson and Pitts 1976). In turn, ozone can react with the NO formed in the photodissociation of NO_2, again forming NO_2 plus O_2, thus inducing a null cycle (see Table 2.7: reaction sequence 2-18). This cycle results in a steady state mixture of NO, NO_2, and O_3.

In order to obtain a net yield of NO_2 and O_3, oxidizable (consumable) substrates must be present to drive the process. Unburned hydrocarbons from auto exhaust are the usual source of this driving power in urban air, and reaction sequences 2-19 and 2-20 in Table 2.7 describe the basic mechanisms involved. However, not all hydrocarbons are equally reactive. Olefins and aromatic compounds react more rapidly than do alkanes; a scale for the relative reactivity in smog formation of classes of organic compounds has recently been devised (Bufalini et al. 1976).

In general, hydrocarbons can be attacked by ozone and ground state oxygen atoms, but the combined rates of decay are insufficient to account for losses of hydrocarbons observed in chamber studies and in ambient air (Finlayson and Pitts 1976). The role of hydroxyl (HO•) and hydroperoxyl (HOO•) free radicals as the major oxidizing agents in photooxidation of hydrocarbons was recognized only about 10 years ago. Reaction sequence 2-19 in Table 2.7 shows that hydroxyl radicals attack hydrocarbons to yield organic radicals, which in turn react with oxygen to yield reactive organic peroxyl radicals. These oxidize NO to NO_2 (reaction sequence 2-20), ultimately resulting in a net formation of ozone. Note that NO and NO_2 behave in a cyclic or catalytic manner in hydrocarbon oxidation and ozone production.

Reaction sequence 2-21 in Table 2.7 describes the simplest smog reaction, in which carbon monoxide (CO) acts as the oxidizable reservoir. As in the hydrocarbon sequence of Table 2.7 (2-19, 2-20), NO and NO_2 behave in a cyclic manner, and the net reaction involves the formation of ozone by the oxidation of CO to CO_2. This reaction is believed to be of lesser importance than the hydrocarbon sequence, but Westberg et al. (1971) found that CO does accelerate ozone formation in chamber studies with isobutene and NO_x.

Peroxyl organic radicals also react with NO_2 to produce PANs; for instance, peroxyacetyl free radical plus NO_2 yields peroxyacetyl nitrate:



(2-30)

PAN and its higher analogs are among the most damaging ingredients of photochemical smog; they are both eye irritants and phytotoxicants.

As Equation 2-22 in Table 2.7 shows, nitrogen dioxide also quenches the hydroxyl free radical that initiates the smog reactions (i.e., Equations 2-19, 2-21):

$$NO_2 + HO\bullet + M \dashrightarrow HNO_3 + M. \qquad (2\text{-}22)$$

Thus, by this reaction, NO_2 tends to inhibit or to delay the onset of photochemical smog reactions. On the other hand, NO_2 is the essential ingredient in forming the two major detrimental smog products, ozone and PAN (Equations 2-20, 2-25). Finally, NO_2 also is removed from the catalytic cycle by reaction with ozone, ultimately to form nitric acid anhydride (N_2O_5) (Equations 2-28, 2-29, Table 2.7). The principal end product of NO_x in smog reactions is nitric acid; the mechanisms involved in this process are described below. Although literally hundreds of reactions have been identified in photochemical smog, the processes described above and in Table 2.7 are believed to be the most important aspects of this exceedingly complex system.

Formation of Nitric Acid and Nitrate Aerosols

A variety of processes and reactions are responsible for the conversion of NO_x into nitric acid vapor, nitric acid aerosols, and nitrate aerosols; the major reactions are listed in Table 2.8. The quantitative importance of the various mechanisms remains controversial and conjectural.

The volatility of nitric acid is such that it is not appreciably taken into water droplets in the atmosphere unless the droplets contain neutralizing reactants. Thus, homogeneous nucleation (reaction 2-32, Table 2.8) is not an important mechanism for nitrate aerosol formation (U.S. EPA 1974, NRC 1977a). By comparison, sulfuric acid has a low vapor pressure and undergoes rapid homogeneous hydration.

Until recently, there was no firm evidence for the existence of nitric acid vapor in the atmosphere, and all of the nitrate measured by Hi-Vol filters was assumed to be in particulate (aerosol) form. Nitric acid vapor has been detected in the stratosphere by infrared spectroscopy (Murcray et al. 1969), and direct measurements of gaseous nitric acid have been reported very recently for the troposphere (Pitts et al. 1977). Several other recent studies that used different kinds of filter materials indicate the existence of gaseous HNO_3 in both the troposphere (Okita et al. 1976, Spicer 1976) and lower stratosphere (Lazrus et al. 1972; also, see Chapter 3). Present data are insufficient to quantify the relative amounts of gaseous and particulate nitrates in typical rural atmospheres or in urban atmospheres as a function of time during episodes of smog.

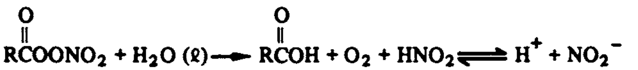
Aerosols that contain basic or neutral substances may absorb and neutralize atmospheric nitric acid, and volatile products may be released as a result. For instance:

$$NaCl\ (l) + HNO_3(g) \longrightarrow NaNO_3(l) + HCl\ (g), \qquad (2\text{-}41)$$

$$CaCO_3(l) + 2HNO_3(g) \longrightarrow Ca(NO_3)_2(l) + CO_2(g). \qquad (2\text{-}42)$$

There is some evidence that nitric acid forms stable compounds or complexes in solutions of sulfuric acid (Castleman 1974); the importance of removal of nitric acid by sulfuric acid aerosols needs further evaluation. Presumably, these mixed aerosols are neutralized by

TABLE 2.8 Nitric Acid and Nitrate Aerosol Formation Reactions

1. Nitrogen dioxide – hydroxyl free radical reaction		
$NO_2 + HO\cdot + M \longrightarrow HNO_3 + M$		(2-22)
(same as first chain breaking reaction 2-22 of Table 2.7).		
2. Nitric acid anhydride reaction		
$NO_2 + O_3 \longrightarrow NO_3 + O_2$	same as reactions 2-28 and	
$NO_3 + NO_2 \longrightarrow N_2O_5$	2-29, respectively, Table 2.7.	
$N_2O_5 + H_2O \longrightarrow 2HNO_3$		(2-31)
3. Homogeneous conversions of nitric acid to aerosol		
$HNO_3\ (g) + H_2O\ (g) \longrightarrow HNO_3$ aerosol		(2-32)
$N_2O_5\ (g) + H_2O\ (\ell) \longrightarrow HNO_3$ aerosol		(2-33)
$NH_3\ (g) + HNO_3\ (g) \longrightarrow NH_4NO_3$ aerosol		(2-34)
4. NO_x absorption into aerosol droplets		
$2\,NO_2 + H_2O\ (\ell) \longrightarrow HNO_3 + HNO_2$	(aqueous solution)	(2-35)
$NO + NO_2 + H_2O\ (\ell) \longrightarrow 2HNO_2$	(aqueous solution)	(2-36)
HNO_2 (aq.) $\longrightarrow H^+ + NO_2^-$	(aqueous solution)	
$NO_2^- + \frac{1}{2}O_2$ (in aerosol solution) $\longrightarrow NO_3^-$		(2-37)
$NO_2^- + O_3$ (in aerosol solution) $\longrightarrow NO_3^- + O_2$		(2-38)
5. Hydrolysis of PANs		
 $R\overset{O}{\overset{\Vert}{C}}OONO_2 + H_2O\ (\ell) \longrightarrow R\overset{O}{\overset{\Vert}{C}}OH + O_2 + HNO_2 \rightleftharpoons H^+ + NO_2^-$		(2-39)
$NO_2^- + \frac{1}{2}O_2 \longrightarrow NO_3^-$	(aqueous solution)	
6. Methyl nitrate formation		
$CH_3O\cdot + NO_2 \longrightarrow CH_3NO_3$		(2-40)
Methoxy radical — methyl nitrate		

absorption of gaseous ammonia to form ammonium nitrate and ammonium sulfate aerosols.

Direct reaction of gaseous nitric acid and gaseous ammonia to form ammonium nitrate (Equation 2-34, Table 2.8), either homogeneously or on dust surfaces, may be a significant source of nitrate aerosol at high concentrations of NH_3; however, further studies are needed to evaluate the rate of this reaction and the diurnal patterns of gaseous ammonia concentrations in urban atmospheres. Nitric acid vapor is readily adsorbed on surfaces, especially on metal surfaces, but gaseous deposition is of unknown importance as a sink for atmospheric nitric acid.

The role of nitric acid anhydride in the formation of nitric acid and nitrate aerosols (Equation 2-31, Table 2.8) is somewhat controversial. The EPA report on atmospheric nitrates (U.S. EPA 1974) described this as the major source of nitrates in atmospheric aerosols, but the National Research Council's report on nitrogen oxides (NRC 1977a) regarded this reaction as less important than the hydroxyl-nitrogen dioxide reaction (2-22). Using reaction rate constants from the recent literature and typical concentrations for NO_x-hydrocarbon-polluted atmospheres, the NRC (1977a) report concluded that reaction (2-22) would form nitric acid at a rate of 2 to 6.6×10^{-5} ppm/min and that reaction 2-31 would yield nitric acid at a rate much less than 1.6×10^{-5} ppm/min. According to calculations by W. Chameides (University of Florida, Department of Physics, personal communication, 1977), reaction 2-22 proceeds about 100 times as fast as reaction 2-31 in unpolluted (background) atmospheres (i.e., 6.7×10^{-7} ppm/min for reaction 2-22 compared to 6.7×10^{-9} ppm/min for reaction 2-31). However, Chameides' calculations for urban or polluted areas suggested that the N_2O_5 path could be competitive with the NO_2-OH path.

The extent to which NO_x absorption into aerosols (Equations 2-35, 2-36, Table 2.8) is responsible for nitrate and nitrite aerosols is not known (NRC 1977a), but Hidy (1973) believes that these reactions may be rapid enough to account for all observed nitrate formation.

In urban atmospheres, PANs (which are present as vapors) are the major organic nitrate forms, and are present in higher concentrations than inorganic nitrates during the late afternoon (U.S. EPA 1974). Simulation models described in the NRC (1977a) report predict that a large fraction of NO_x ultimately ends up as PANs; however, hydrolysis of PANs at night (Equation 2-39) continues, and inorganic nitrates become the major portion of the atmospheric nitrates. Similarly, as a polluted air mass moves away from an urban center, the ratio of inorganic nitrate to organic nitrate (primarily PANs) will increase. Limited data from

Riverside, California, about 100 km downwind from Los Angeles, support this contention (U.S. EPA 1974; T. Mischke, University of California at Riverside, personal communication, 1976).

Because the amount of nitrite in rainfall is low compared to nitrate levels, it appears that the ratio of nitrite to nitrate in aerosols also should be low; however, few data are available on the nitrite content of atmospheric aerosols. Apparently the rate of oxidation of nitrite to nitrate (Equations 2-37, 2-38, Table 2.8) is quite rapid. Methyl nitrate (Equation 2-40) is presumed to represent a smaller fraction of the organic nitrates in polluted air than do the PANs, but according to E.R. Stevens (University of California at Riverside, personal communication, 1977), confirmed measurements of methyl nitrate in polluted air are lacking. Photolysis and hydrolysis of methyl nitrate and other alkyl nitrates are probably slow, and the ultimate fate of these compounds is not well known.

Stratospheric Reactions

The reactions of nitrogen oxides in the stratosphere are important because they affect the stratospheric ozone layer, which serves as an effective barrier to the transmission of damaging uv radiation to the lower atmosphere. Ozone (C_3) is formed in the stratosphere by photolysis of molecular oxygen by far uv radiation (Table 2.9: Equation 2-43). The wavelengths of light capable of photolyzing molecular oxygen do not penetrate to the lower atmosphere; thus, ozone formation by photolysis of oxygen is limited to the stratosphere. The rate of photochemical formation of C_3 is relatively constant on an annual basis, but it varies diurnally and seasonally as a function of altitude and latitude. Similarly, the rates of removal of stratospheric ozone by its major natural sinks are relatively constant on an annual basis, but they vary with altitude and latitude. The net effect of these competing and spatially varying processes of ozone formation and decay is a "shield" of ozone in the stratosphere that exhibits complicated patterns of spatial distribution, relatively large short-term variations in concentration, and relatively small variations from year to year. Figure 2.6 illustrates the vertical distribution of O_3 in the stratosphere as a function of latitude. At mid-latitudes, a maximum O_3 concentration of about 6 to 8 ppm (v/v) occurs at an altitude of 25 to 40 km. Figure 2.7 shows that the short-term oscillating pattern of ozone concentrations in the stratosphere can be averaged on a yearly basis to yield relative constant mean annual O_3 levels in the stratosphere over the past several decades.

Several potential threats to the integrity of the ozone layer have been the subject of controversy and have

TABLE 2.9 Important Reactions of Ozone, Nitrogen Oxides, and Water Vapor in the Stratosphere

1. Ozone formation	
$O_2 + h\nu\ (\lambda < 242\ \text{nm}) \longrightarrow O + O$	(2-43)
$(O + O_2 + M \longrightarrow O_3 + M)$, twice	
NET: $3O_2 + h\nu \longrightarrow 2\,O_3$	
2. Ozone photolysis	
$O_3 + h\nu \longrightarrow O_2 + O$	(2-44)
A. $O + O_2 + M \longrightarrow O_3 + M$	
NET: null reaction	
B. $O + O_3 \longrightarrow O_2 + O_2$	(2-45)
NET: $2\,O_3 \longrightarrow 3O_2$	
3. Nitrous oxide photolysis	
$N_2O + h\nu\ (\lambda < 240\ \text{nm}) \longrightarrow N_2 + O$	(2-46)
4. Nitrous oxide – singlet oxygen reaction; formation of NO_X	
$O_3 + h\nu\ (\lambda < 310\ \text{nm}) \longrightarrow O_2 + O\,(^1D)$	(2-13)
$N_2O + O(^1D) \longrightarrow N_2 + O_2$	(2-47)
$N_2O + O(^1D) \longrightarrow 2\,NO$	(2-48)
5. NO_X – Ozone decomposition cycle	
$NO + O_3 \longrightarrow NO_2 + O_2$	(2-49)
$O_3 + h\nu \longrightarrow O_2 + O$	
$NO_2 + O \longrightarrow NO + O_2$	
NET: $2O_3 + h\nu \longrightarrow 3O_2$	
6. NO_X – ozone null cycle	
$NO + O_3 \longrightarrow NO_2 + O_2$	(2-50)
$NO_2 + h\nu \longrightarrow NO + O$	
$O + O_2 + M \longrightarrow O_3 + M$	
NET: null reaction	

TABLE 2.9 (continued)

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7. Water – hydroxyl – ozone catalytic decomposition cycle

$O_3 + h\nu\ (\lambda < 310\ \text{nm}) \longrightarrow O_2 + O(^1D)$ (2-13)
$O\ (^1D) + H_2O \longrightarrow 2HO\cdot$ (2-14)
$HO\cdot + O_3 \longrightarrow HOO\cdot + O_2$ (2-51)
$HOO\cdot + O_3 \longrightarrow HO\cdot + O_2 + O_2$

NET: (bottom two reactions): $2O_3 \longrightarrow 3\ O_2$

$HO\cdot + O_3 \longrightarrow HOO\cdot + O_2$ (2-52)
$HOO\cdot + O \longrightarrow HO\cdot + O_2$

NET: $O + O_3 \longrightarrow 2O_2$

8. NO_x – hydroxyl null reaction

$$\left.\begin{array}{l} HO\cdot + O_3 \longrightarrow HOO\cdot + O_2 \\ HOO\cdot\ NO \longrightarrow HO\cdot + NO_2 \\ NO_2 + h\nu \longrightarrow NO + O \\ O + O_2 + M \longrightarrow O_3 + M \end{array}\right\} \text{(2-53)}$$

NET: null reaction

9. NO_2 removal by nitric acid formation

$HO\cdot + NO_2 + M \longrightarrow HNO_3 + M$ (2-22)

10. Nitric acid photolysis

$HNO_3 + h\nu\ (\lambda < 350\ \text{nm}) \longrightarrow HO\cdot + NO_2$ (2-54)

11. Chlorine - ozone decomposition cycle (2-55)

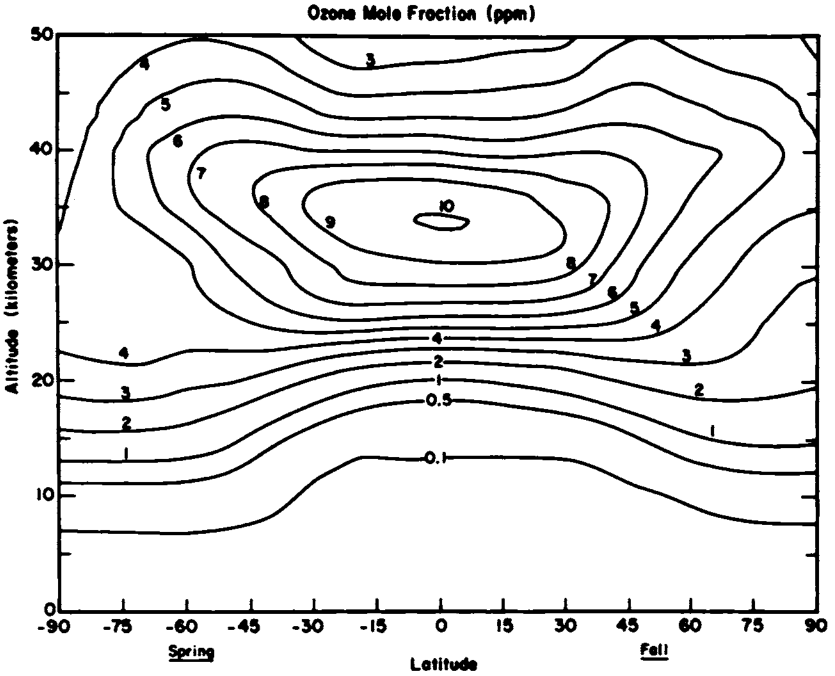
$Cl\cdot + O_3 \longrightarrow ClO\cdot + O_2$
$O_3 + h\nu \longrightarrow O_2 + O$
$ClO\cdot + O \longrightarrow Cl\cdot + O_2$

NET: $2O_3$ $3O_2$

12. Chlorine - ozone - NO_x null cycle (2-56)

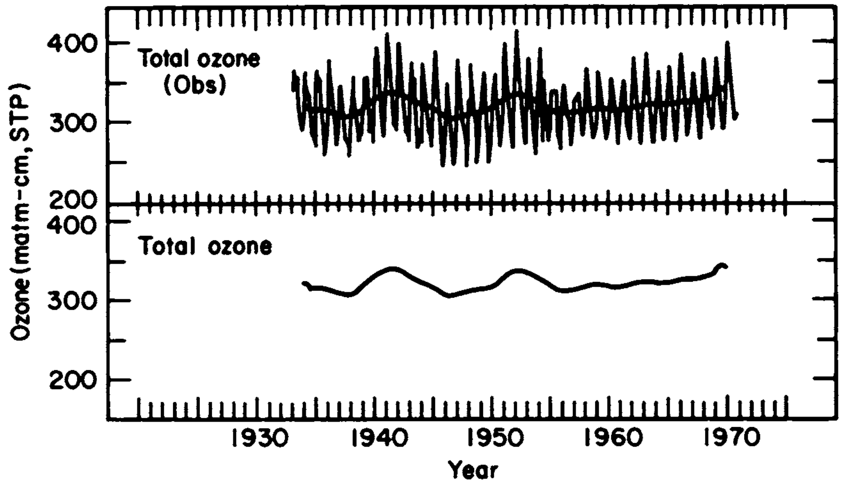
$Cl\cdot + NO \longrightarrow ClO\cdot + O_2$
$ClO\cdot + NO \longrightarrow Cl\cdot + NO_2$
$NO_2 + h\nu \longrightarrow NO + O$
$O + O_2 + M \longrightarrow O_3 + M$

NET: null reaction



SOURCE: NRC (1975).

FIGURE 2.6 Average (March 22) ozone mole fractions or mixing ratio by volume (ppm). Because of large decreases in total atmospheric pressure with increasing elevation, the distribution of ozone on a concentration basis (molecules/cm^3) is quite different in appearance from the distribution of mixing ratios presented above.



SOURCE: NRC (1975).

FIGURE 2.7 Long-term variations in total ozone in the northern hemisphere. The sharp seasonal variations are shown in the top panel. An 11-year running mean is inscribed in the top panel and repeated in the bottom panel. A possible 11-year cycle is indicated before 1960. An increasing trend is indicated for 1960-1970, but the 1970 high value is still less than high values before 1960. It is generally recognized that the data base before 1960 is too sparse to offer firm support to these suggested long-term trends.

stimulated much research on stratospheric chemistry within the last decade. These potential threats include water vapor and NO_x from SSTs, chlorofluorocarbons (Freons) used as aerosol propellents, and, most recently, increased production of nitrous oxide (N_2O) from an increase in the global rate of denitrification. This last is thought to result from increased industrial fixation of nitrogen for fertilizer. Studies prompted especially by the SST and chlorofluorocarbon controversies have resulted in a much clearer understanding of the processes regulating ozone levels in the stratosphere. Current evidence indicates that four main sinks balance the natural rate of ozone formation in the stratosphere: (1) ozone photolysis (Table 2.9: reaction sequence 2; known as the Chapman reactions); (2) reactions of ozone with hydroxyl and perhydroxyl radicals formed from photolysis of water (Table 2.9, reaction sequence 7); and (3) the NO_x-ozone catalytic cycle (Table 2.9, reaction sequence 5); and (4) the ClX-ozone catalytic cycle (Table 2.9, reaction sequences 11 and 12). The relative importance of these processes is shown in Table 2.10. Anderson et al. (1977) reported surprisingly high concentrations of ClO in the stratosphere. If these values turn out to be representative of the global average, chlorine is now an important agent in the global ozone balance.

<u>Ozone - NO_x - H_2O Reactions</u>. The main cycle involving nitrogen oxides in the stratosphere is illustrated in Figure 2.8, and important reaction sequences involving NO_x in the stratosphere are listed in Table 2.9. Whereas ozone is present at a few parts per million in the stratosphere, nitric oxide and nitrogen dioxide concentrations are a few parts per billion, and the processes involving ozone and nitrogen oxides are somewhat different from those that prevail in the troposphere.

Nitrous oxide is transported from the troposphere into the stratosphere by turbulent diffusion and undergoes photolysis (Equation 2-46, Table 2.9) by absorbing uv radiation (<240 nm: Johnston and Selwyn 1975); the photolysis produces molecular nitrogen (N_2) and singlet oxygen. Singlet oxygen, which also is produced by ozone photolysis, reacts with more nitrous oxide to produce two sets of products (Equations 2-47, 2-48, Table 2.9):

$$N_2O + O(^1D) \longrightarrow N_2 + O_2 \qquad (2\text{-}47)$$
$$N_2O + O(^1D) \longrightarrow NO + NO. \qquad (2\text{-}48)$$

The predominant products, which account for about 90 percent of the reacted N_2O in Equations 2-47, 2-48 are N_2 and O_2, but the NO that is formed is sufficient to serve as the major sink for stratospheric ozone (via reaction

TABLE 2.10 Mechanisms for the Decomposition of Stratospheric Ozone

Mechanism	Percent of Total O_3 Destruction Rate
Photolysis (Chapman reactions)	20*
Transport to troposphere	0.5
Hydroxyl and hydroperoxyl radicals from photolysis of water	10*
NO_X catalytic cycle	50-70*
Chlorine from natural and man-made sources (present effect)	10-40*

*These loss processes represent an average over the ozone formation region between about 25 and 40 km altitude.

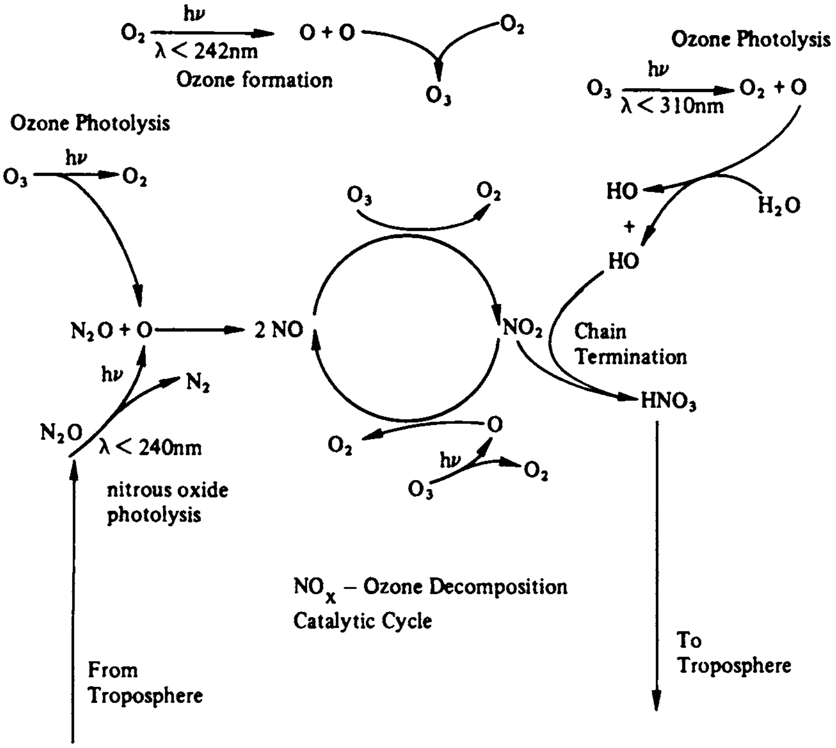


FIGURE 2.8 Main cycle of nitrogen oxides in the stratosphere emphasizing catalytic destruction of ozone.

sequence 2-49, Table 2.9). Nitric oxide reacts with ozone to form nitrogen dioxide and oxygen, and the NC_2 reacts with oxygen atoms from ozone photolysis to produce more NO plus O_2:

$$\begin{array}{ll} & NO + O_3 \longrightarrow NO_2 + O_2 \\ & O_3 + h\nu \longrightarrow O_2 + O \\ & NO_2 + O \longrightarrow NO + O_2 \\ \hline \text{NET:} & 2O_3 + h\nu \longrightarrow 3O_2. \end{array} \tag{2-49}$$

This reaction sequence is a catalytic cycle in which ozone is destroyed, but NO_x is not. The third step in sequence 2-49 is the rate-limiting step for the cycle; photolysis of NO_2 to NO and oxygen atoms is more rapid than the reaction of NO_2 with oxygen atoms. In the former case, there is a net null reaction, as the oxygen atoms react with molecular oxygen to form ozone (see reaction sequence 2-50, Table 2.9). The null reaction sequence is important in quantifying rates of ozone decomposition; in effect the null cycle competes with the catalytic destruction cycle, and thus it is important to have accurate information on the rates of reactions in both cycles.

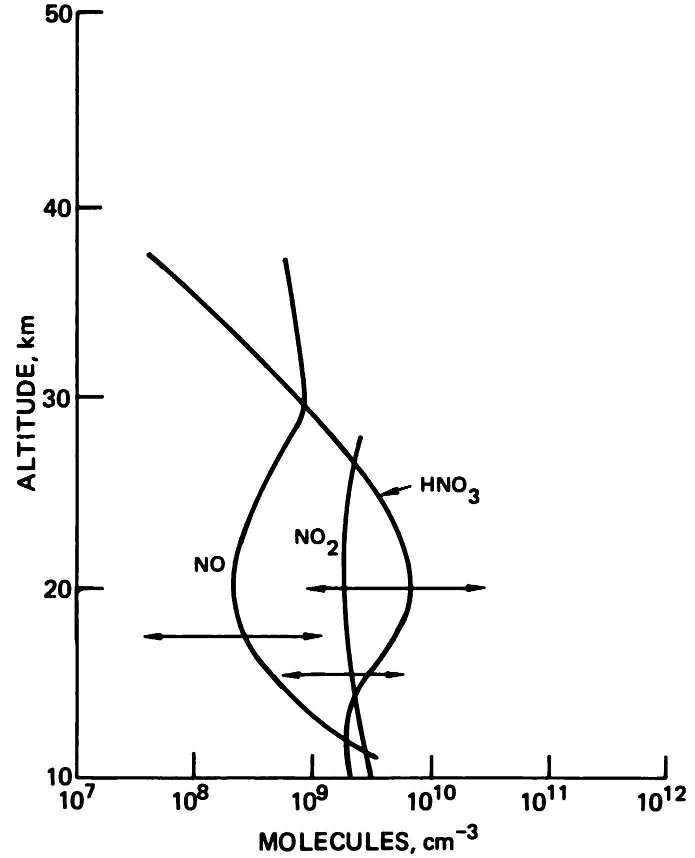
The catalytic cycle of destruction of ozone by NO_x is terminated by the reaction of NO_2 with HO• radicals to form nitric acid; this is the same reaction that produces nitric acid in the troposphere(Equation 2-22, Tables 2.8 and 2.9):

$$NO_2 + HO \longrightarrow HNO_3. \tag{2-22}$$

Nitric acid can be photolyzed back to NO_2 and HO• radicals by uv radiation in the stratosphere (Equation 2-54, Table 2.9).

At the elevation of the maximum concentration of ozone in the stratosphere, (25 to 30 km), NO, NO_2, and HNO_3 occur in comparable amounts (see Figure 2.9). Below the ozone maximum, HNO_3 predominates, and NO_x is removed from the stratosphere primarily by transport as HNO_3 into the troposphere, where it is removed by rainfall in a matter of days. Above the ozone maximum, nitric acid is largely photolyzed, and NO_2 is the predominant species in the mid-stratosphere. In the upper stratosphere, NO is the principal form. The average residence time for NO_x in the stratosphere between formation from N_2O and loss to the troposphere as HNO_3 is about three years.

Hydroxyl radicals are formed from the reaction of singlet oxygen atoms with water vapor (Equation 2-14) and



SOURCE: Derived from NRC (1975).

FIGURE 2.9 Concentrations of nitric oxide, nitrogen dioxide, and nitric acid in the stratosphere.

also are involved in catalytic, ozone-destroying cycles (sequences 2-51 and 2-52, Table 2.9). The hydroxyl (HO•)-hydroperoxyl (HOO•) cycle of ozone depletion also has a competing null cycle (reaction sequence 2-53) analagous to the null cycle for NO_x. Because the hydroxyl null cycle involves NO and NO_2, it provides an important link between the two ozone-depleting cycles. The rate-limiting step in the hydroxyl null cycle is the reaction between HOO• and NO to form HO• and NO_2 (the second reaction in sequence 2-53). Recent direct measurements (Howard and Evenson 1977) indicate that the rate constant for this reaction is much larger than previous indirect techniques had estimated. The net effect of this new information is three-fold. First, the stratospheric ozone content is made less sensitive to the levels of NO_x. The new rate constant for the HOO• + NO reaction shifts the predicted ratio of HOO• to HO• in the direction of more HO•. (Direct measurements of the concentrations of these radicals in the stratosphere are not available.) Since HO• tends to tie up NO_2 as unreactive HNO_3 (reaction 2-22), the effectiveness of the catalytic NO_x cycle thus is diminished. Second, since the HOO• + NO reaction is the rate-determining step in diverting HO_x into its null cycle reactions, the larger value for the rate constant increases the relative importance of the HO_x null cycle over the catalytic ozone destruction cycle. Third, as discussed below, HO reacts with HCl to yield chlorine radicals (Cl•), which also react to destroy ozone in a catalytic cycle. With an increased ratio of HO• to HOO•, the chlorine catalytic cycle becomes about twice as important as previous calculations indicated it to be. Similarly, the new value for the HOO• + NO rate constant decreases the effect of added NO_x on stratospheric ozone by a factor of about two. Previously (up to 1977), it was thought that a doubling of stratospheric NO_x would decrease the stratospheric ozone content by about 1/5 (see Chapter 7). At present, the best estimate for the reduction in ozone associated with a doubling of NO_x is 1/10, with an estimated range of about 1/5 to 1/15.

The full family of stratospheric reactions involving ozone, the oxides of nitrogen, and the free radicals derived from water numbers about sixty. The above discussion focuses on the NO_x catalytic cycle, but Table 2.9 gives more details on the mechanisms of ozone formation and destruction in the stratosphere.

Other Mechanisms for Ozone Depletion. Although the processes described above are the major natural mechanisms for destruction of ozone in the stratosphere, several other natural catalytic cycles are potentially important because human activities release the reactants to the atmosphere. Most significant are the chlorofluoromethanes Freon 11 ($CFCl_3$) and Freon 12 (CF_2Cl_2), which have been widely used in recent decades as aerosol propellants. These substances are chemically and biologically inert in the biosphere and troposphere (NRC 1976). Transported by turbulent diffusion to the stratosphere like N_2O, the chlorofluoromethanes are photolyzed and react with singlet oxygen to produce chlorine (Cl•) and chlorine monoxide (ClO•) radicals. These products react in a catalytic cycle analogous to the NO_x-O_3 cycle that destroys ozone (Table 2.9, reaction sequence 2-55). Nitric oxide plays a role in the chlorine-ozone cycle, reacting with ClO to induce a null cycle (Table 2.9, reaction sequence 2-56). The effect of reaction sequence 2-56 is to lessen the destructive effect of chlorine, hence of chlorofluoromethanes, on the ozone layer. NO_x is cycled, rather than destroyed, in sequence 2-56; consequently, this cycle has no effect on the NO_x-ozone cycle.

The chlorine released by photolysis is reversibly tied up as hydrochloric acid:

$$Cl\bullet + CH_4 \text{ -----> } HCl + CH_3 \qquad (2\text{-}57)$$

$$HCl + HO\bullet \text{ -----> } H_2O + Cl\bullet \qquad (2\text{-}58)$$

In the lower stratosphere, HCl is the predominant chlorine-containing species, and it is transported to the troposphere where it is removed by rainfall. In the upper stratosphere ClO• and Cl• are the predominant forms of chlorine. The role of HCl as a reservoir for active chlorine forms is comparable to that of HNO_3 in the NO_x family of reactions, with one important difference: hydroxyl radicals tie up the catalytically active form of NO_x (see Equation 2-22), but release the active form of chlorine (Equation 2-58). As discussed above, recent measurements of the rate constant for the reaction between HOO• and NO to form HO• plus NO_2 (Howard and Evenson 1977) have increased the predicted ratio of HO•/HOO• in the stratosphere, thus enhancing the importance of chlorine and reducing that of NO_x in the catalytic destruction of ozone.

In summary, the chemical processes in the stratosphere that destroy ozone may be qualitatively understood, but major quantitative uncertainties remain. It appears that the natural NO_x catalytic cycle is the largest mechanism of ozone removal, but the sensitivity of the statospheric ozone layer to increased levels of NO_x is still a matter of debate. Nitrous oxide, produced chiefly by denitrification, is the main source of NO_x in the stratosphere. Chapter 7 of this report examines the possible impacts on the ozone layer that might result from an increase in the global rate of denitrification of nitrogen fixed by human activities.

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CHAPTER 3

OCCURRENCE AND TRANSPORT OF NITRATES IN THE ENVIRONMENT

INTRODUCTION

This chapter summarizes typical levels and ranges of nitrates and related nitrogenous compounds found in the major compartments of the environment--soil, water, air, and vegetation. It is not intended, however, as an exhaustive review of the extensive data on the geographic distribution and temporal variations of nitrate levels in the environment.

Nitrate is transported within a single phase of the environment by two general processes: advective movement of water or air containing nitrate, and diffusion. Nitrate is transported between phases by leaching and water-driven erosion of soil particles (from soil to water); by wind erosion (from soil to air); and by rainfall and dry deposition (from air to land and surface water). Because nitrate is a nonconservative substance, mass-balance calculations of the distribution and amounts of nitrate in a given phase must account not only for the effects of transport processes but also for the effects of *in situ* formation and decomposition processes (nitrification, denitrification, assimilation, and atmospheric chemical reactions) described in Chapter 2. Most of the transport processes mentioned above (e.g., advective movement of surface water) are relatively simple to understand and are mentioned only briefly here. The movement of nitrate from soils to ground and surface waters, however, is more complicated and is of major importance in the distribution of nitrate in the environment. Consequently, the factors affecting nitrate movement in soils are described in this chapter.

DISTRIBUTION IN SOILS

Only a small fraction (usually < 1 percent) of the total nitrogen in surface soils is present as nitrate, but this fraction can undergo rapid changes. The concentration at any one site depends on both environmental conditions and external sources.

Nitrate concentrations (expressed on the basis of soil solids[1]) often are nil in flooded soils, in highly leached infertile soils, and in acid forest soils. Nonfertilized fallow soils often have 5 to 10 mg/kg of NO_3^--N in winter and around 50 mg/kg in spring and summer, while organic soils may have several hundred mg/kg (Harmsen and Kolenbrander 1965). High concentrations also are found in the vicinity of banded fertilizer application zones. Table 3.1 lists nitrate concentrations in a variety of soils.

Moisture and temperature are major factors affecting the amount of nitrate in soil, and the nitrate concentrations vary seasonally, often in a complicated and unpredictable fashion. In humid temperate climates, nitrate is usually depleted in the winter as a result of leaching by late fall rains and negligible mineralization and nitrification. Nitrate concentrations increase as the soil warms in spring, and nitrate may accumulate during summer if rainfall is low and leaching or denitrification does not occur. In the fall, rains will leach much of the nitrate not used by vegetation.

Harmsen and Kolenbrander (1965) discussed the numerous factors influencing nitrate levels in the soils of several climatic zones. Essentially, nitrate distribution in a soil profile is a function of the water balance of the soil system. Rainfall and irrigation move nitrate downward, while evaporation moves nitrate back towards the surface. The latter process is usually important only in the upper 30 cm of the soil profile (Thomas 1970). Temperature also plays a role, because water drains more slowly through cold soils, and freezing essentially stops downward nitrate movement.

Nitrate generally does not accumulate under grasslands; in these soils, nitrate is assimilated as rapidly as it is formed. Tillage stimulates ammonification and nitrification, and most row cropping practices leave the land bare at least part of the year, leading to increased nitrate loss. Many other agricultural practices also affect nitrate distribution in soil, including the application of manure and other fertilizers, artificial drainage, and irrigation and cropping practices (see Chapter 6 for discussion).

SPATIAL VARIABILITY IN SOILS

Soils are heterogeneous, and even units classified as homogeneous as to soil type have large variations in chemical and physical properties (Peterson and Calvin 1965).

TABLE 3.1 Nitrate Concentrations in Some Soils and Soil Solutions

	Nitrate-N		
System Sampled	mg/l	mg/kg	Reference
Alfalfa-soil profile	–	<1.9	Shertz and Miller (1972)
Alfalfa-water table	1 - 44	–	Stewart et al. (1967)
Virgin grassland	0.1- 19	–	
Wheat fallow	5 - 9.5	–	
Irrigated land	0 - 36	–	
Cattle feedlots	0 - 41	–	
Marsh soil	0 - 0.14	–	Isirimah and Keeney (1973)
Unfertilized wheat	–	1- 30	Cooke et al. (1957)
Fertilized wheat	–	5- 40	
Bare fallow	–	10-120	Simpson (1962)
Subterranean clover	–	2- 15	
Potato field drainage	12 - 56	–	Saffigna and Keeney (1977)
Permanent pasture	–	2- 12	Thompson and Coup (1940)
Urine-affected area	–	120-640	
Anhydrous NH_3 band	–	35-710	Chalk et al. (1975)
Corn root zone	–	1- 30	
Asparagus	38 -439	1- 30	Ayers and Branson (1973)
Celery	525	–	
Sugarbeets	264	–	
Potatoes	175 -536	–	
Irrigated lands	10 -215	–	Pratt et al. (1975)
Corn-300 cm	2 - 35	–	
Tile drains	6 - 18	–	Kohl et al. (1971)
Tile drains	1 - 62	–	Johnston et al. (1965)

This variability extends to microsites (Flühler et al. 1976a, 1976b) and to leaching characteristics. For example, Biggar and Nielsen (1976) found that 100 observations were required to estimate mean pore velocity to 50 percent of its true value, and that the estimates were log-normally distributed. P.F. Pratt (University of California, Riverside, personal communication, 1976) estimated that up to 500 cores per hectare may be required to obtain a reliable mean value for the nitrogen that leaches below the root zone in some California soils. Saffigna et al. (1976, 1977a, 1977b) noted large variability in solute leaching in a sand due to nonuniform infiltration under irrigated potatoes and in uncropped soil. Rible et al. (1976) and Middleton et al. (1975) have noted wide variability of nitrate distribution in results for vertical soil cores. Samples of soil leachate obtained from a single field by porous ceramic cups also show wide variations in nitrate (Hansen and Harris 1975). This extreme heterogeneity greatly increases the number of samples of soil required to obtain valid estimates of nitrate leaching. Estimates based on averages of only a few samples must be treated with caution unless information is provided to prove that relatively homogeneous conditions exist.

MOVEMENT OF NITRATE FROM SOIL TO GROUND AND SURFACE WATERS

Movement of Water and Solutes in Soils

The main processes involved in the movement of nitrate and other solutes in soil are advective transport of substances dissolved in soil water, and molecular and eddy diffusion resulting from concentration gradients (Gardner 1965).

The flow of water through soil is caused by a driving force that results from an effective potential gradient (Hillel 1971). The rate of flow is proportional to the gradient and is affected by the geometry of the pore channels of the soil. In water-saturated soils, gravity dominates, and the soil water has a positive pressure potential compared to a reference body, usually a free water body. The potential energy of water in soils is expressed in bars (equivalent to the pressure exerted by a 10.2 m column of water). The term mbar (1.02 cm water) also is commonly used.

In a soil that is less than saturated with water (i.e., some of the soil pores contain air), water is held between soil particles by adhesion and cohesion. These forces create a negative pressure potential of the soil water with respect to a free water body. The term "matric potential" (expressed in bars or mbars) is now commonly used to describe this phenomenon, but other terms such as tension, matric suction, and soil water suction also are used (Hillel 1971).

Most water in soils is under a matric potential (Ψ_m) and also is acted on by gravity (Ψ_g) and osmotic forces (Ψ_o). (The sum of these three terms, Ψ_{tot}, integrates the forces acting on soil water.) The osmotic potential reflects the interaction between water molecules and salts dissolved in the water and is not a factor in water movement in soils, but it is involved in water movement from soils to the roots of plants. The water stress that plants suffer in moist but saline soils is a result of an osmotic potential that prevents uptake of water by the roots.

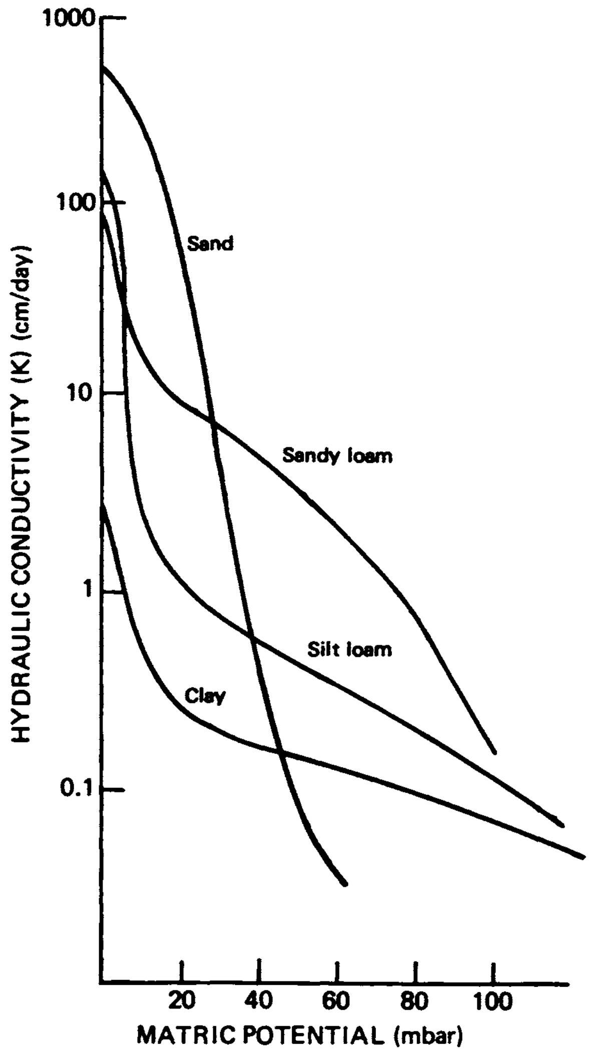
The rate of water flow in soils depends on two factors: (1) a driving force, expressed as the change in water potential per unit of distance, and (2) the hydraulic conductivity (K), which describes the ability of a soil to transmit water. These factors are related by a form of Darcy's law:

$$q = \frac{K\Delta\Psi_{tot}}{L}$$

where q = rate of flow and L is the distance between two locations.

In water-saturated soil, the matric and solute potentials are zero and gravity is the sole driving force. Thus, the main factors limiting movement of water are the size and continuity of pores in the soil. Hydraulic conductivity increases as pore size increases; as a result, saturated sandy soil can transmit water much faster than a saturated clay soil (Figure 3.1). Saturated hydraulic conductivities for sands can be 200 to 300 times greater than corresponding values for clays, because of differences in soil texture and structure.

As soils become unsaturated, matric potential becomes the more dominant term in Ψ_{tot}, and both the rate of soil water flow and the hydraulic conductivity of a soil drop off rapidly. Larger soil pores empty first, leaving only the finer pores to transmit water. Consequently, as soils become drier and the matric potential increases, hydraulic conductivity decreases. At tensions of about one bar (about one atmosphere), the hydraulic conductivity of a soil can be as little as 10^{-5} of the value for the saturated soil. In porous (e.g., sandy) soils, the water transmission rate declines much faster than it does in soils that have a finer texture. In very dry soils, the matric potential is very



SOURCE: Bouma et al. (1972).

FIGURE 3.1 Hydraulic conductivity (K) as a function of soil matric potential. Increasing matric potential values represent increasingly dry soil.

high (up to 10^3 to 10^4 bars), and water flow is negligible. The point at which water movement approaches zero (about 200 to 500 mbar) is commonly termed "field capacity." Only in the moist soil region (0 to about 100 mbars) is there significant leaching of solutes.

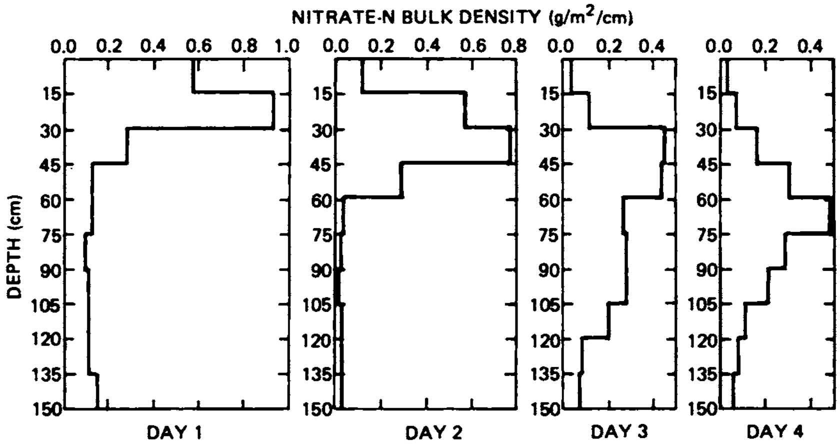
Prediction of the rate of nitrate movement in unsaturated soils is particularly complex. While Darcy's law applies to both unsaturated and saturated flow, hydraulic conductivity is constantly changing under unsaturated conditions, making flow prediction difficult.

The extent and direction of nitrate movement by convection depends on both the concentration of nitrate in solution and the direction and rate of water flow. The concentration of nitrate in soil solution is not necessarily homogeneous throughout the solution. Nitrate can move at different rates through soil than does the bulk water (Thomas 1970, Krupp et al. 1972). Qualitatively, this can be explained either by anion repulsion (negative adsorption) of nitrate by negatively charged soil surfaces, or conversely by anion sorption. In most soils of the United States, however, neither process is important, and as a first approximation, nitrate movement can be described by water movement.

A thin band of nitrate, applied to the surface of soil, will have an increasingly broad concentration peak as it moves with water through a soil. This spreading is caused by diffusion and hydrodynamic dispersion (nonuniform velocity of water flowing through soil pores). Figure 3.2 illustrates the effects of diffusion and dispersion on nitrate profiles in an irrigated soil column. The peak in the nitrate profile after one day (equivalent to 2.5 cm of applied water) was at 15 cm. The peak moved downward about 15 cm per day, and gradually became less sharply defined as a result of diffusion and dispersion.

A practical result of diffusion and dispersion in soils is that more than one pore volume must be leached to remove a solute peak completely from a given depth of soil. Hence, water requirements for irrigation in semi-arid and arid regions are greater than would be predicted on the basis of the water needs of plants because of the need to remove excess salts from the soil. Conversely, rainfall in humid regions does not move fertilizer nitrate downward as rapidly as might be predicted solely on the basis of water movement (Hillel 1971).

The nitrate concentration of a soil solution and the rate of nitrate leaching in a soil depend on climate and irrigation and on the net nitrogen leached below the root zone (Keeney and Gardner 1975). Thomas (1970) discussed general geographical trends in the leaching of nitrate. In



SOURCE: Adapted from F.J. Endelman, et al., Journal of Environmental Quality, Vol. 3. page 297 (1974), by permission of the American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America.

FIGURE 3.2 Movement of fertilizer through sandy loam soil. KNO_3 was applied on the surface of a Plainfield sandy loam soil at the rate of 20 g N/m^2 and irrigated with 2.5 cm of water each day. Data are expressed in density units: 1 g N/m^2/cm is equal to 625 mg N/kg soil.

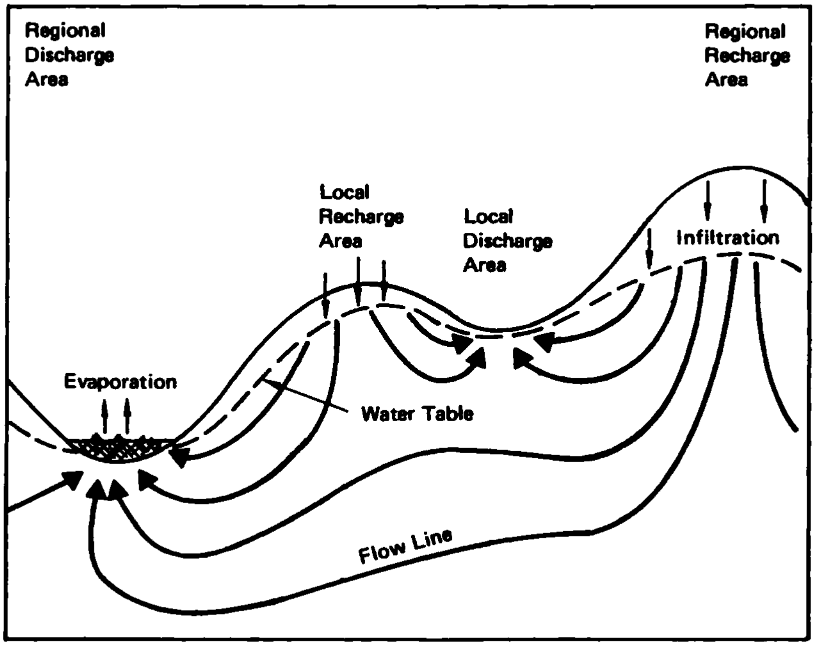
the South and Southeast, high rainfall during periods of low evaporation in the winter rapidly move nitrate downward in the soil, while the high evapotranspiration rate in the summer may prevent leaching even when there is much precipitation. In the Northeast, lower rates of evapotranspiration and the relatively high rates of precipitation during the summer and fall result in considerable leaching. In the Midwest, high rates of rainfall in the spring and early summer promote considerable leaching. In the Great Plains, high evaporation and low average rainfall result in low leaching from soils that are not irrigated, but summer storms of high intensity may move nitrate rapidly out of the root zone of the soils. Frozen soils minimize nitrate movement in the Northeast, Midwest, and Great Plains in the winter.

The seasonal nature of evaporation from land results not only in the intermittent leaching of most soil profiles, but often results in annual maxima and minima in the concentration of ions in the soil solution. In general, there is not sufficient mixing from diffusion and dispersion to obliterate these peaks of ions before they reach the water table. The vertical distance between peaks is expressed by the net percolation for any one season, divided by the water content of the soil between peaks (Saffigna 1976).

Tile drainage systems tend to integrate many of the variables that create uneven distributions of nitrate in soil profiles. In theory, then, nitrate levels in tile-drain effluents can provide a more accurate indication of nitrate leaching than can the analysis of soil profiles. However, the movement of water to tile systems is itself an extremely complex process (Gardner 1965). Leaching patterns are not uniform, and tiles may not intercept all of the water. Nitrate may accumulate between the tiles, adding further uncertainty in efforts to estimate mass flow of nitrate on the basis of drainage effluent values. Moreover, in many older drainage systems the flow patterns and areas drained by a given line are unknown.

The speed and direction of nitrate movement below the water table is determined by the groundwater flow. Figure 3.3 shows a hypothetical flow system within a homogeneous soil area. Groundwater originates largely as precipitation, a portion of which percolates through the soil to the water table. It moves along flow lines and obeys Darcy's law in the same way that water flows in saturated soils (Hillel 1971).

Accurate mapping of groundwater flow requires that the flow network and the permeability of the soil be known with at least a modest degree of accuracy. Such knowledge makes it possible to predict both the residence times for peak



SOURCE: Stephenson and Clark (1974). Used with permission of the author.

FIGURE 3.3 Hypothetical groundwater flow system within a homogeneous soil area, showing a variety of possible flow paths and discharge and recharge areas.

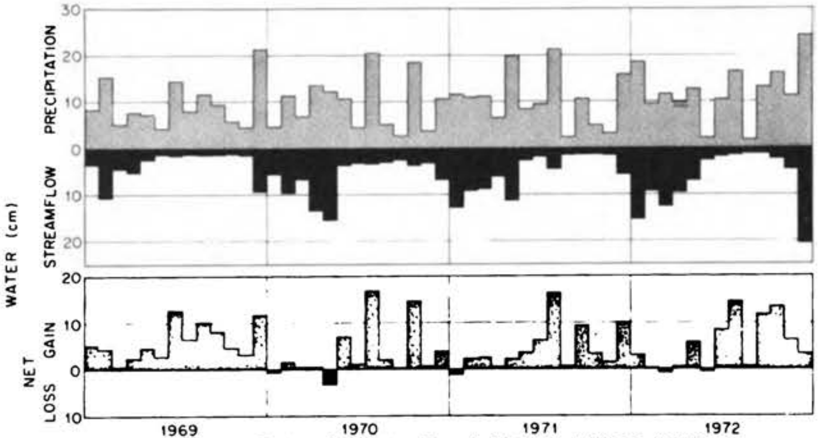
concentrations of nitrate or other solutes and the actual paths that are taken from the point of entrance to the groundwater and to the points of return to surface water. Random sampling of groundwater without regard to flow paths, however, can be expected to obscure the picture.

Precipitation and Nitrogen Losses from Terrestrial Ecosystems

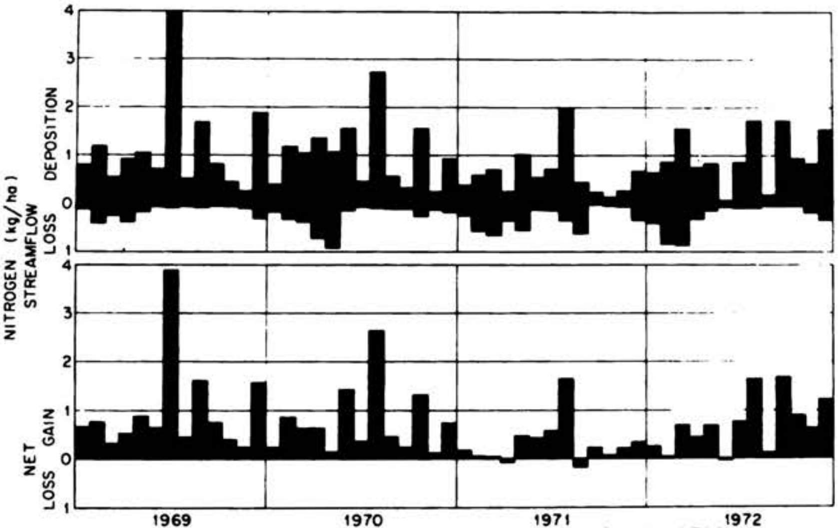
While terrestrial ecosystems tend to conserve nutrients, they are not totally efficient at this, especially for highly soluble species such as nitrate. Losses of nitrogen from land depend strongly on the movement of water, which transports nitrogen in both dissolved and particulate forms. Most such losses occur during storms rather than in dry weather; the amount and form of the nitrogen losses is influenced by the intensity of a storm and the characteristics of the terrestrial ecosystem. In undisturbed ecosystems such as forests, most nitrogen losses result from the transport of particulates (e.g., leaves, litterfall, detritus, soil particles); nitrate is then formed in streams or lakes by nitrification. In perturbed ecosystems, such as clearcut forests, use of nitrogen by plants is decreased, and nitrification is greatly enhanced. The result is enhanced nitrate loss from the soil in such areas (Likens et al. 1969, 1978).

Some general relationships between precipitation and nitrogen losses from terrestrial ecosystems are illustrated in a study of a small (97.5-ha) watershed, Walker Branch, in a deciduous forest of eastern Tennessee (Figure 3.4; Henderson and Harris 1975). Nitrogen loss in this watershed is highly dependent on runoff volume; consequently, it is important to assess these losses during individual storm events. Figure 3.5 summarizes results for typical summer and winter rain events. During one August rainstorm in the watershed, streamflow increased rapidly and then receded to near prestorm conditions within a few hours. In a less intense but longer-lasting rainstorm in November, streamflow increased less markedly and reached a plateau which lasted through the three days of sampling.

Changes in nitrogen concentrations in the stream were similar in both storms. Nitrogen levels initially were diluted by the large increases in streamflow, but then concentrations increased because of greater transport of fine particulate material during the period of high streamflow.. Subsequent lower concentrations reflected the decreased availability of material for transport after the initial scouring and flushing actions. Although concentrations varied during storms, the rate of discharge of total nitrogen in kg/hr (concentrations multiplied by



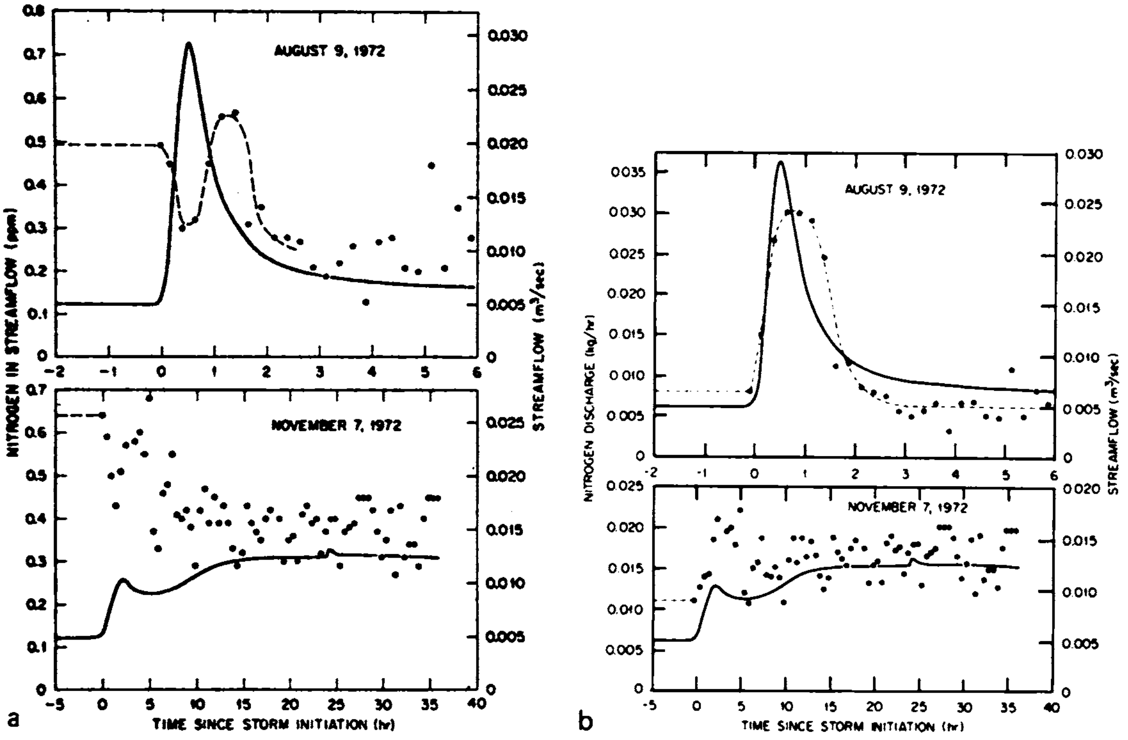
Hydrologic Budget for Walker Branch Watershed (1969-1972)



Nitrogen Budget for Walker Branch Watershed (1969-1972)

SOURCE: Henderson and Harris (1975). Excerpt from "Forest Soils and Forest Land Management", edited by B. Bernier and C.H. Winget, published by Les Presses de l'Université Laval, and reproduced with their permission.

FIGURE 3.4 Comparison of the hydrologic budget and nitrogen budget for the Walker Branch watershed, distributed by four-week intervals, from 1969 through 1972.



SOURCE: Henderson and Harris (1975). Excerpt from "Forest Soils and Forest Land Management", edited by B. Bernier and C.H. Winget, published by Les Presses de l'Université Laval, and reproduced with their permission.

FIGURE 3.5 Relationships between (a) nitrogen concentration (ppm) in streamflow, and (b) nitrogen discharge rate (kg/hr), and streamflow discharge rate (m^3/sec) for storms on August 9 and November 7, 1972 at Walker Branch Watershed in east Tennessee. Solid line is stream discharge rate, dashed line and points are nitrogen concentration and discharge rate, and dashed line to the point at time 0 is nitrogen concentration and nitrogen discharge rate prior to the onset of the storm. Nitrogen discharge rates were calculated by multiplying the volume of streamflow expressed on an hourly basis by the concentration in (a).

streamflow) followed the stream hydrographs closely for both storms (Figure 3.5).

As noted above, the bulk of nitrogen transport to streams in undisturbed terrestrial ecosystems occurs as coarse and fine particulate matter. For example, Henderson and Harris (1975) found that more than one kg/ha of nitrogen in the form of coarse particulates was lost from Walker Branch watershed during a single intense (15 cm) rainfall in December of 1975, and this loss was more than 30 percent of the total annual export of nitrogen from the watershed. Despite strong flushing action, nitrate (and ammonium) concentrations in the stream remained low during the storm. Low concentrations of nitrate in forest runoff also have been observed at the U.S. Forest Service Coweeta Hydrologic Laboratory in North Carolina and in an experimental forest in western Oregon (Henderson et al. in press). Loss of nitrogen in the streamflow of undisturbed forest ecosystems is equivalent to only 2.5 percent of the total nitrogen circulating annually in those systems, with the bulk of the loss in the form of organic nitrogen in particulate matter (suspended sediments).

Approximately 4 x 10^9 tons of sediment are transported to tributary streams in the United States each year (Wadleigh 1968). Assuming a nitrogen content in the range of 0.1 to 0.4 percent (Searsbrook 1965), between 4 x 10^{12} and 1.6 x 10^{13} g N/yr (4-160 Mt N/yr) is transported to U.S. streams in sediment. For harvested land, Stanford et al. (1970) estimated that erosion losses in the United States decreased from 5 x 10^6 tons in 1930 to 3 x 10^6 tons in 1969 as the result of improved land use and management practices. This still represents an input of at least 3 x 10^9 to 1 x 10^{10} g N to surface waters from croplands in the United States.

Table 3.2 illustrates the relative magnitude of sediment and solution fluxes of nitrogen to aquatic ecosystems from cropland in Minnesota. If some sources of nitrogen (e.g., coarse particulates, sediments, and dissolved organics) are not considered, potential nitrate levels in aquatic systems may be underestimated, since such inputs are readily nitrified.

In summary, stormwater runoff can be responsible for a substantial fraction of the annual nitrogen losses from terrestial ecosystems. In most unperturbed systems, the nitrogen is lost in the form of coarse and fine sediment particles, which, through subsequent nitrification, may increase nitrate levels in receiving waters.

TABLE 3.2 Average Annual Nitrogen Losses in Runoff Solution and Sediment Load at Morris, Minnesota, 1966 and 1967

Crop	Nitrogen Application kg/ha	Total Nitrogen		Ammonium (NH_4-N)		Nitrate (NO_3-N)	
		Solution	Sediment	Solution	Sediment	Solution	Sediment
					(kg/ha)		
Fallow	–	2.2	62.6	0.0	0.6	1.0	0.3
Corn-Continuous	112	0.3	12.6	0.0	0.2	0.4	0.0
Corn-Rotation	56	0.8	4.1	0.0	0.1	0.4	0.0
Oats-Rotation	18	0.2	5.2	0.0	0.1	0.6	0.0
Hay-Rotation	–	3.2	0.0	0.0	0.0	0.1	0.0

SOURCE: Derived from Timmons et al. (1968) and Kilmer (1974).

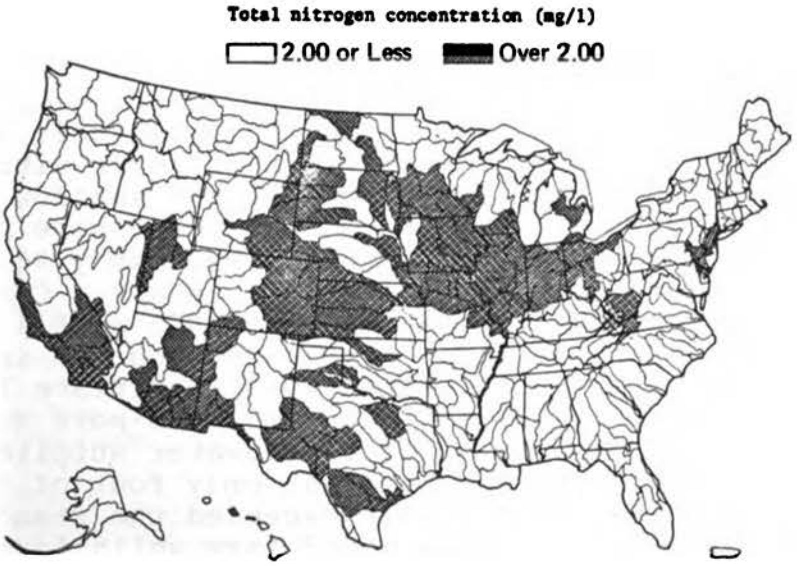
DISTRIBUTION OF NITRATE IN FRESH WATER

Concentrations of nitrate in surface waters are highly variable, commonly ranging over about four orders of magnitude (about 1 μg/l to 10 mg/l as N). Nitrite concentrations usually are much lower than those for nitrate, and concentrations above 25-50 μg N/l are relatively rare. High concentrations of nitrite indicate unstable conditions and the occurrence of nitrification or denitrification. Such conditions occur in streams where nitrification of sewage effluents is occurring, and in anoxic hypolimnetic waters of lakes at the onset of denitrification.

In natural waters, nitrate is a minor ionic constituent and seldom accounts for more than a few percent of the total anions (expressed in equivalents per liter). Nitrate levels in lakes seldom exceed 1 mg/l (expressed as N) and are typically less than 0.1 mg/l in surface waters during the summer. Nitrate concentrations higher than several hundred μg N/l in lake surface waters tend to stimulate algal blooms and indicate eutrophic conditions (see Chapter 8). Concentrations of several mg N/l may occur in streams receiving municipal wastes or runoff from urban or agricultural areas, but streams draining natural forest areas typically have concentrations ranging from 1 to 100 μg N/l. Data on relationships between land use and concentrations of various forms of nitrogen in adjacent waters have been examined in several recent reviews (e.g. Loehr 1972, Omernik 1976; also see Chapter 6). Nitrate is often a significant proportion of the total nitrogen in urban runoff and in agricultural areas where management practices effectively limit erosion. Figure 3.6 shows general patterns of nitrate levels in surface streams of the United States and suggests the importance of agricultural activity as a source of nitrate.

Because organic nitrogen and ammonia are relatively immobile in soils, nitrate is also the major nitrogen form in groundwaters. Again, concentrations are highly variable, ranging from tens of μg N/l to over 20 mg N/l in arid regions and in some intensively farmed regions. Nitrate levels typically are higher in groundwaters than in surface waters, in part because plants remove nitrate from surface waters.

Nitrate concentrations ranging from several hundred μg N/l to a few mg N/l are common in groundwater used for drinking water supplies in the United States. Durfor and Becker (1964) reported a range of 0 to 6.2 mg NO_3^--N/l (the median value was 0.15 mg N/l) for water supplies of the 100 largest American cities in 1962. A survey of 969 public water supplies in the United States in 1969 revealed that only about two percent of the systems, serving about one



Alaska, Hawaii, and Puerto Rico not drawn to scale.

SOURCE: Council on Environmental Quality (1976).

FIGURE 3.6 Levels of total nitrogen in U.S. streams, 1975. Annual mean values in mg N/1. Data from the U.S. Geological Survey's National Stream Quality Accounting Network, as analysed by CEQ.

percent of the total survey population, exceeded the 10 mg N/l standard for nitrate in drinking water recommended by the U.S. Public Health Service (McCabe et al. 1970, U.S. PHS 1970). The maximum concentration found was 20 mg NO_3^--N/l.

The National Research Council (1972) reviewed data from surveys of nitrate levels in well waters from several states. Table 3.3 summarizes these and several other studies. Some of the studies focused only on areas known to have high nitrate levels in groundwater or involved relatively small numbers of samples; consequently, the fraction of samples exceeding the 10 mg N/l standard in these cases is not a reliable index of the incidence of excessive nitrate in well water on a state or nationwide basis.

Data from a large number of wells in Illinois (Larson and Henley 1966) show a clear pattern of lower nitrate content in deeper wells; 28 percent of the shallow wells (less than 8 m in depth) had nitrate levels above 10 mg N/l. However, of all 8,844 wells in the survey, only 481, or 5.4 percent, exceeded the drinking water standard. Comly (1945) reported nitate concentrations of up to 125 mg N/l in well water in Iowa; similar values have been recorded in several other states (Walton 1951, Walker 1969). Nitrate levels that exceed the 10 mg N/l standard are much more common in private wells than in municipal groundwater supplies. For example, Walker (1969) reported that only four of 789 public groundwater supplies in Illinois exceeded the standard, but up to several thousand domestic and farm wells in the state were thought to do so. In many cases, the source of nitrate in private wells is thought to be a nearby barnyard or a septic tank rather than general nitrate contamination of the aquifer (see further discussion in Chapter 6).

OCCURRENCE AND TRANSPORT IN THE MARINE ENVIRONMENT

Nitrogen is an important limiting factor for primary production in estuaries and the oceans. Increased inputs of dissolved inorganic forms of nitrogen often stimulate plant growth, with resulting increases in total plant biomass and changes in dominant algal species (Goldman 1976, Pomeroy et al. 1972, Ryther and Dunstan 1971, Williams 1972). Numerous studies have assessed the impacts of human activities on the nitrogen cycle and on primary production and the eutrophication process in marine systems. The role of increased nitrogen loading on coastal eutrophication and estuarine water quality is reviewed briefly in Chapter 8.

TABLE 3.3 Nitrate Levels in Well Waters of Several States

State	Number of Wells Sampled	Number of Wells Exceeding 10 mg N/l	Percent Exceeding 10 mg N/l	Comments
Illinois	221	179	81	Dug wells;
(Washington County)	38	13	34	drilled wells
Illinois	480	134	28	Depth 0-8 m
	926	185	20	Depth 9-15 m
	1,568	78	5	Depth 16-30 m
	2,042	61	3	Depth 31-60 m
	3,828	23	0.6	Depth over 60 m
Total	8,844	481	5.4	
Missouri	>5,000	>1,350	27	
Nebraska	364	18[a]	5[a]	
New York (Nassau County)	370	20	5.4	
Wisconsin (central)	250	177	71	Area of known high nitrate levels. Exceeded standard at least once in biweekly sampling over one year.
		112	45	Consistently exceeded standard during year of sampling.

[a] Nebraska data were expressed as county-wide averages. In only one county (18 wells) was the average NO_3^--N level above 10 mg/l; the average for those wells was 14.0 mg/l in 1961, and 15.4 mg/l in 1971. Statewide averages were 2.43 mg/l in 1961 and 3.07 mg/l in 1971.

SOURCE: Data compiled in NRC (1972) from Illinois State Water Survey, Larson and Henley (1966) [Illinois]; Smith and Baier (1969) [New York]; Crabtree (1970) [Wisconsin]; and G. E. Smith (personal communication) [Missouri]. Olson et al. (1973) is source of Nebraska data.

Nitrate in Coastal Marine Environments

Several lines of evidence suggest that the fluxes of dissolved nitrogen discharged by rivers and streams of the United States into estuaries and coastal wetlands have been increasing in recent years (Ackermann et al. 1970, Council on Environmental Quality 1976, Wolman 1971). The predominant forms of nitrogen in river runoff are organic nitrogen and nitrate; significant concentrations of nitrite and ammonia occur only in the vicinity of heavily polluted or naturally deoxygenated areas. Nitrate fluxes to U.S. coastal marine waters are not likely to decrease until non-point sources of nutrients are more adequately controlled.

The annual global discharge of nitrate to the marine environment from rivers is approximately 8.1 Mt N/yr; about 85 percent of that is derived from agricultural runoff (Söderlund and Svensson 1976). It is reasonable to expect that future increases in fertilizer use will further increase the global flux of nitrate to the coastal marine environment, particularly from developing countries where potential agricultural areas often are in coastal plains.

In coastal areas where nitrogen limits plant growth, a significant portion of nitrate in river discharges is assimilated by plankton during transit through the estuarine environment. Studies on a North Carolina estuary (Hobbie et al. 1975) indicated that at least 50 percent of the incoming nitrate from the Pamlico River was transformed by phytoplankton into particulate organic matter and then deposited in the sediment.

The efficiency of nitrate removal from water during transport through the coastal environment depends on the flushing characteristics and residence time of water in the coastal area. Discharges from the major American rivers (the Mississippi, Hudson, and Columbia) move rapidly through their estuaries, and carry nitrate directly to the open ocean. The discharges of the smaller rivers draining from the eastern and southeastern coasts of the United States, on the other hand, move relatively slowly through coastal marshes and shallow estuaries.

In the highly productive coastal wetlands of the southeastern United States, river input of nitrate represents only a small percentage of the total nitrogen accumulated annually by primary producers (Windom et al. 1975). Estuarine vegetation thus appears to derive its nitrogen from a variety of sources, including internal recycling (from sediments) and nitrogen fixation.

The potential for the purification of partially-treated sewage wastes by passage through coastal marshes is currently being evaluated (Tourbier and Pierson 1976).

However, because municipal wastes differ in chemical and physical characteristics from natural waters, and because coastal marsh plants have evolved to derive most of their nutrients from sediments, rather than from the water, the efficiency of marsh communities in removing nutrients from effluents may be low, and increased export of nutrients to adjacent coastal waters may result. For example, Chalmers (1976) found that salt marsh plants did not respond proportionally to increased nitrogen loading applied as sewage sludge; the plants assimilated less than 10 percent of the nitrogen added annually.

The most complex and unresolved problems related to sources and cycling of nitrate in coastal systems are the transport mechanisms that control exchange across the sediment/water interface. The few available studies have demonstrated that nutrient fluxes to and from coastal sediments are highly variable and may have substantial impacts on nitrate levels in the overlying water (Pomeroy et al. 1972, Hale 1975, Gilbert and Loder 1976).

In summary, nitrate fluxes related to human activities can affect coastal marine ecosystems by producing increased plant growth and changes in the dominant species of the plant community, possibly leading to a deterioration in water quality. In planktonic communities, such changes in nutrient flux can result in particularly rapid shifts of dominant species. In the salt marsh community the sediment is the primary nutrient reservoir, and availability to plants is determined by rates of remineralization in the sediment matrix. The salt marsh community thus is not so responsive to variable inputs from outside nutrient sources as is the estuarine planktonic community.

Nitrate in the Ocean

A global inventory of nitrogen in the world ocean is presented in Table 3.4. Clearly, the major storage is as dissolved molecular nitrogen, but this pool is fairly independent of other pools. Among the inorganic fixed forms, nitrate is much more important than ammonia, by a factor of 80 times. The amount of nitrogen stored in biomass is small compared to the dissolved inorganic and organic nitrogen fractions.

The basic structure of the nitrogen cycle in the oceanic environment has been known at least since Cooper's (1937) classic paper. Biological processes are the primary control on sources and transport of nitrogen in the ocean through mechanisms such as nitrogen fixation, remineralization, and denitrification. Extensive reviews of the nitrogen cycle in the ocean have been published by Redfield et al. (1963),

TABLE 3.4 A Global Inventory of Nitrogen in the World Ocean

Reservoir	Storage (Mt N)[d]
Plant biomass[a]	300
Animal biomass[b]	170
Dead organic matter[a]	
(dissolved)	530,000
(particulate)	30,000-240,000
N_2 (dissolved)[b]	22,000,000
N_2O[a]	200
NO_3^-[c]	570,000
NO_2^-[a]	500
NH_4^+[a]	7,000

[a] Söderlund and Svensson (1976).
[b] Delwiche (1970).
[c] Emery et al. (1955).
[d] Million metric tons (10^{12} g).

Vaccaro (1965), Richards (1965), Goering (1972), and Söderlund and Svensson (1976).

Vaccaro (1965) reviewed the distribution of nitrogen forms in the oceans. Concentrations of nitrate in surface layers range from less than 1 μg N/l in oligotrophic areas like the Sargasso Sea to up to a few hundred μg N/l in upwelling areas, such as off the coast of Peru. Below the permanent thermocline, concentrations of nitrate range up to about 500 μg N/l, depending on depth and geographic area. Denitrification leads to the complete absence of nitrate in the bottom water of a few permanently anoxic basins (e.g., the Black Sea). Various areas of the ocean, such as the eastern tropical north Pacific, at depths of 200-800 m in oxygen minimum layers, are also nitrate poor, for the same reason.

There is no evidence that anthropogenic sources of nitrogen in river discharges have had a significant impact on nitrate concentrations in the open ocean, or that they are likely to do so in the next several decades. Studies of the nitrogen budget on the continental shelf off the southeastern United States (Haines 1975) indicate that the annual nitrogen input from land to ocean is less than 5 percent of the calculated yearly uptake of nitrogen by primary producers for this region, and that little nitrate or ammonia is exported from coastal waters to the ocean.

The Ocean and Nitrous Oxide

The role of the ocean as a source or sink for atmospheric nitrous oxide (N_2O) is of particular interest because of concern over the effects of N_2O on the stratospheric ozone layer, as discussed in Chapter 7.

The most likely oceanic source of N_2O is denitrification of nitrate, but the extent of marine denitrification and of associated N_2O production is still an open question (see Chapter 2). Another possible oceanic source of nitrous oxide is nitrification. The production of nitrous oxide has been detected in some laboratory studies of nitrification using cell-free preparations and soil samples, but the environmental significance of this process has not been evaluated (see Chapter 2).

Several investigators have measured nitrous oxide concentrations in sea water, calculated the flux of N_2O from the ocean to the atmosphere at specific sites, and extrapolated the flux estimates to obtain crude estimates of the global flux (Hahn 1974, Rasmussen et al. 1976). Hahn and Junge (1977) have provided a detailed review of the oceanic flux measurements reported in the literature. Recent estimates of the global flux of N_2O from the ocean to the atmosphere are summarized in Table 3.5. Because of the small number of measurements available and the extreme heterogeneity in the spatial distribution of N_2O in the oceans, substantial uncertainty exists in the estimates. Furthermore, various investigators used different assumptions, methods, and numerical constants to calculate the global flux values. The most recent of these estimates, by Hahn and Junge (1977), indicates a global net production of 45 Mt N_2O-N/yr, approximately half the amount estimated in an earlier study by Hahn (1974).

The possibility also exists that oceanic areas which exhibit undersaturation may act as sinks for N_2O. However, on the basis of a "stagnant film" gas exchange model, Hahn and Junge (1977) concluded that a substantially greater degree of undersaturation of N_2O would have to exist throughout the surface layer of the oceans than recent measurements indicate if the oceans were to act as a significant sink for N_2O.

NITRATE IN PRECIPITATION

In contrast to the situation in surface and groundwaters, where nitrate and ammonium are minor ionic constituents, both of these nitrogen forms are major ionic constituents of rainfall. As a result, concentrations of these inorganic nitrogen species have been measured frequently in atmospheric precipitation, and numerous data, some going back to the turn of the century, exist for levels of ammonia and nitrate in precipitation.

Unfortunately, the historical record is still inadequate for several reasons. First, nitrogen levels in rainfall are highly variable, both spatially and temporally, and the factors affecting these concentrations are not sufficiently well understood to provide a basis for quantitative predictive models. Second, some data, especially from early studies, are unreliable because of faulty analytical methods. Third, most rainfall sampling programs have collected bulk precipitation; that is, rainfall plus whatever portion of dry fallout is trapped by the sampling device. The efficiency of rainfall samplers in collecting dry fallout is variable but generally is less than 100 percent. Finally, in many past studies, rainfall samples were collected over periods of days or weeks, and inadequate attention was paid to preservation of samples. Microbial activity in collected rainfall could result either in uptake of nitrate or in oxidation of ammonia to produce nitrate.

Typically, concentrations of nitrate in rainfall range from about 100 to 700 µg N/l. Higher or lower values may occur in individual rain events and in certain locales. Chapin and Uttormark (1973) and Brezonik (1976) reviewed the

TABLE 3.5 Estimates of Global Fluxes of Nitrous Oxide (N_2O) from the Oceans to the Atmosphere

Estimated N_2O Flux (Mt N/yr)	Range	Reference
86	30-300	Hahn (1974)
26		Rasmussen et al. (1976)
45		Craig et al. (1976)
	20-80	Söderlund and Svensson (1976)
45	16-160	Hahn and Junge (1977)

literature on nutrients in rainfall and the factors affecting nutrient concentrations in precipitation. Chapin and Uttormark concluded that, because nutrient concentrations in rainfall vary so widely, individual or even average concentration values are relatively meaningless, and that rainfall contributions should be measured and reported as annual fluxes (g/m^2-yr or kg/ha-yr). Brezonik (1976) concluded that bulk precipitation contributes 10 to 20 kg/ha-yr (1 to 2 g/m^2-yr) of total nitrogen over large areas of the United States. Fluxes outside the range 5 to 30 kg/ha-yr were considered to be unusual and to reflect special conditions. Chapter 6 discusses nitrogen levels in rainfall in greater detail, and reviews the sources, historical trends, and factors affecting the occurrence of nitrate in rain.

NITROGEN OXIDES AND NITRATE COMPOUNDS IN THE ATMOSPHERE

Most nitrate compounds in the atmosphere are formed in situ by the processes described in Chapter 2; only a minor fraction of nitrate aerosol can be attributed to wind erosion of soil and fertilizer particles. Atmospheric nitrates, including peroxyacetyl nitrates (PANs), alkyl nitrates, and inorganic nitrate aerosols, are closely related to gaseous nitrogen oxides, and Table 3.6 summarizes the concentrations of these compounds in the atmosphere. Other recent reviews of atmospheric NO_x and nitrates have been compiled by the National Research Council (1975, 1977a, 1977b, 1977c), U.S. EPA (1974), and Söderlund and Svensson (1976).

Nitrous Oxide Concentrations

Nitrous oxide (N_2O) is unreactive in the lower atmosphere, and most texts list its concentration as 250 ppb (v/v) worldwide. However, recent unpublished measurements by various researchers suggest that the global average concentration of N_2O is in the range of 300 to 330 ppb (Pierotti and Rasmussen 1977; R.J. Cicerone, University of Michigan, personal communication, 1977).

Nitrous oxide concentrations in the atmosphere have not been routinely monitored as have the higher oxides, NO and NO_2, because until recently there were no known anthropogenic sources for this gas. Variations in atmospheric N_2O levels have been thought to be small and not attributable to human activity. Several recent reports indicate, however, that nitrous oxide is produced by automobile catalytic converters and by combustion of coal, oil, and to a lesser extent, natural gas (see Chapter 2). Weiss and Craig (1976) reported that the N_2O content of the atmosphere over the Pacific Ocean has increased by 1.5

TABLE 3.6 Summary of Some Levels of Gaseous and Particulate Forms of Nitrogen in the Atmosphere[a]

Site and Measurement Interval	NH_3	NH_4^+ Aerosol	N_2O	NO	NO_2	NO_3^- Aerosol[b]	PANs[c]	Alkyl Nitrates[c]
Non-Urban Air[d]								
Temperate land	2-6		300-330	2	4		–	–
Tropical land	6-15	2.0	"	2	4	0.1-0.4	–	–
Oceans	0.4	0.4	"	0.2	0.5	0.02	–	–
Annual average (U.S.)		0.19				1.10		
24-hour maximum (U.S.)		1.52				3.24		
Urban Air								
Annual average		0.32	300-330	50	<10	3.11	?	?
Annual 24-hour maximum		3.30		700	215	8.90		1-2
Monthly average							2-7	
Monthly average of daily 1-hour maximum							2-10	
Average of 1-4 hour samples	14-43							

[a] Concentrations of gases, PANs, and alkyl nitrates are in parts per billion (v/v); levels of aerosols are expressed in $\mu g/m^3$.

[b] Recent findings indicate that values for nitrate aerosols may include substantial amounts of nitric acid vapor. (See text for discussion.)

[c] No data were found for PANs and alkyl nitrates in uncontaminated air, but concentrations are thought to be negligible. Values in the table are taken from Figure 3.8.

[d] Background levels calculated by sources cited from available data, with measurements over various time intervals.

SOURCES:

1. NH_3: Values for non-urban air from Söderlund and Svensson (1976), NRC (1977c); values for urban air from NRC (1977c).
2. NH_4^+ Aerosol: Values for tropical and oceanic non-urban air from Söderlund and Svensson (1976). Non-urban annual average and 24-hour maximum values are calculated from NASN data for 18 sites for 1974, in Akland (1977). Values for urban air are four-year averages (1971-1974), calculated from NASN data for 144 sites, presented in Akland (1977).
3. N_2O: Pierotti and Rasmussen (1977).
4. NO and NO_2: Values for non-urban air from Robinson and Robbins (1971); values for urban air are six-year averages for five major U.S. cities in the U.S. EPA's Continuous Air Monitoring Program (data in NRC [1977a]); maxima are the averages of maxima at those sites.
5. NO_3^- Aerosol (see footnote b): Values for tropical and oceanic non-urban air from Söderlund and Svensson (1976). U.S. values calculated from NASN data on 22 non-urban and 144 urban sites, in Akland (1977), as in (2) above.
6. PANs: NRC (1977b).
7. Alkyl nitrates: U.S. EPA (1974).

percent in the past decade; during the same period, the CO_2 content of the atmosphere rose 2 percent as a result of fossil fuel combustion.

Measurements of N_2O concentrations in the marine atmosphere over the Pacific and Atlantic Oceans and the Caribbean Sea indicate relatively homogeneous distribution at a concentration of about 330 ppb (Hahn 1974, Yoshinari 1976, Rasmussen et al. 1976). The only variation consistently observed by several investigators has been slightly lower N_2O concentrations in air masses originating over northwest Africa (Junge et al. 1971, Rasmussen et al. 1976). The latter authors reported a mean of 332 ppb with a standard deviation of 9 ppb, or 2.8 percent of the mean, in a 6,500 km transect of the Pacific Ocean from southern California to Peru.

Junge (1974) used an empirically-derived relationship between atmospheric residence time (τ) and the observed relative standard deviation for concentrations of a trace gas to calculate τ for N_2O. He estimated τ_{N_2O} to be 8 years, with an uncertainty factor of two. More recently, Hahn and Junge (1977) refined the calculation and concluded that τ_{N_2O} could be as low as one year, but should not greatly exceed 11 years. On the other hand, Rasmussen et al. (1976) applied Junge's empirical relationship to continuous monitoring data from a site in northeast Washington State, and estimated τ_{N_2O} to be more than 30 years.

Variations in N_2O concentrations and residence times in the lower atmosphere have been reviewed in detail by Crutzen and Ehhalt (1977), Hahn and Junge (1977), and Pierotti and Rasmussen (1977). The last authors summarized the results of thousands of analyses of atmospheric N_2O levels that they have made over a large portion of the globe since 1975. Their results indicate a more homogeneous and constant distribution of N_2O in the troposphere than was reported by Schütz et al. (1970) and Hahn and Junge (1977). In general, the results obtained by Rasmussen, Pierotti, and co-workers suggest a relatively long atmospheric residence time for N_2O, on the order of several decades or more. The discrepancy between Hahn and Junge's very short estimates for τ_{N_2O} and the findings of Pierotti and Rasmussen is currently unresolved, and constitutes a major uncertainty in the fertilizer-stratospheric ozone controversy (see Chapter 7).

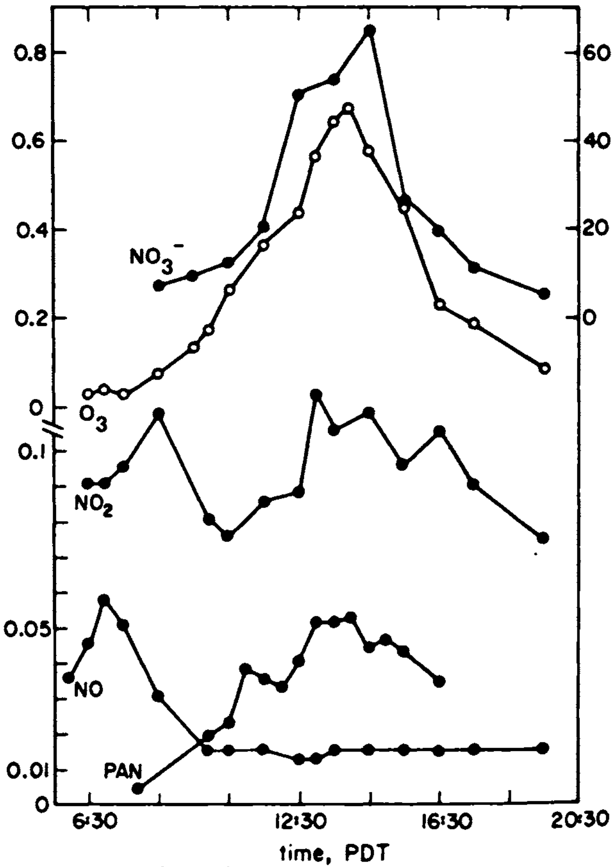
Nitric Oxide and Nitrogen Dioxide Concentrations

The background concentrations of nitric oxide (NO) and nitrogen dioxide (NO_2), are thought to be lower over the open ocean and tropical lands than over temperate lands (Söderlund and Svensson 1976), but data are sparse on concentrations of these gases in rural and remote areas. A large quantity of data has been collected in the past decade, however, on NO and NO_2 levels in urban atmospheres of the United States. Although some of these data are suspect because of faulty analytical methods (see NRC 1977a), there are sufficient reliable data to indicate diurnal and seasonal variations, as well as annual trends, for major cities. Both NO and NO_2 are highly dynamic gases, and their roles in forming photochemical smog produce large diurnal variations in their concentrations and large concentration gradients from urban to rural environments. Daily peak concentrations of NO in large urban areas typically may reach several hundred ppb in the early morning hours, but the levels decline rapidly with the onset of photochemical smog reactions (see Chapter 2). Typically, NO_2 exhibits an attenuated peak somewhat later in the day (Figure 3.7).

The NRC (1977a) report on nitrogen oxides reviews monitoring data on NO and NO_2 in considerable detail. The data reviewed there indicate a gradual (about 2 percent per year) increase of NO and NO_2 in five U.S. cities from 1962 to 1971. Five-year average concentrations of NO_x (as NO_2) ranged from 49 to 114 ppb for these cities, with grand means of 65 and 71 ppb over the periods 1962-1966 and 1967-71, respectively.

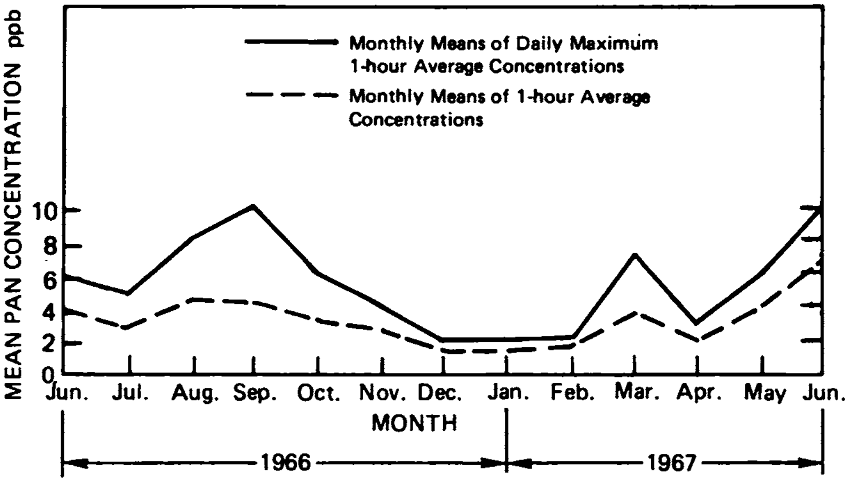
Organic and Inorganic Nitrate Concentrations

According to several reports, PANs constitute the largest fraction of atmospheric nitrate in cities during late daylight hours (NRC 1977b). Figure 3.7 indicates that the buildup of PANs occurs as NO_2 and O_3 reach their daily peaks. At night and in rural areas, inorganic nitrate aerosols predominate over organic nitrates. Because PANs are unstable and difficult to measure reliably, data on PANs in urban atmospheres are sparse compared to the large amount of monitoring information on nitrate aerosol obtained by the National Air Surveillance Network (NASN). More extensive data are available for some areas of California, however. Measurements taken in Los Angeles showed PAN levels that typically rose from about 6 to 8 ppb in the early morning to as much as 65 ppb in midafternoon, during one month (October, 1965) in the generally heavily-polluted autumn (NRC 1977b). Figure 3.8 shows monthly average and average maximum 1-hour PAN concentrations for one year in Riverside, California, and also indicates such a seasonal peak. Almost no data are available on the occurrence of alkyl nitrates in the atmosphere. Methyl nitrate is thought to be the major alkyl nitrate in urban atmospheres; limited information suggests that it occurs concurrently with PANs at concentrations of a few ppb (Table 3.6).



SOURCE: NRC (1977b).

FIGURE 3.7 Diurnal profiles of nitrogen compounds, Pasadena, California, July 25, 1974. NO, NO_2, O_3 and PAN in ppm; inorganic aerosol nitrates in $\mu g/m^3$.



SOURCE: Modified from NRC (1977b).

FIGURE 3.8 Monthly variation in PAN concentrations at the Air Pollution Research Center, Riverside, California, June 1966-June 1977.

Although theoretical models have long predicted the existence of nitric acid vapor in the atmosphere, direct measurements of $HNO_3(g)$ have been reported for ambient air only recently (Pitts et al. 1977). Routine analytical (hi-vol) techniques for inorganic nitrate can not differentiate unequivocally between gaseous and aerosol HNO_3. Recent measurements of nitrate "aerosol" by Spicer (1976), however, indicated that three to ten times as much nitrate was collected when standard glass fiber filters were used in hi-vol samplers than when quartz filters were used (also, see Chapter 6). Quartz filters are neutral and are thought to collect only particulate nitrate, but glass fiber filters contain basic sites and impurities that apparently extract at least some nitric acid vapor, increasing total nitrate readings.

Figure 3.9 summarizes mean annual nitrate aerosol concentrations at 55 urban and 17 nonurban sites from the NASN, (U.S. EPA 1974, Akland 1977). Values in urban air are substantially higher than in nonurban air. Although year-to-year variations are substantial, both urban and nonurban averages show upward trends. Because, as noted above, standard hi-vol samples may collect both gaseous nitric acid and nitrate aerosols, the values shown in Figure 3.9 and the NASN aerosol nitrate data are now considered to be an unreliable measure of particulate nitrate plus a variable amount of nitric acid vapor (J. Bachmann, U.S. EPA, Research Triangle Park, N.C., personal communication, 1977). Current analytical methods for aerosol nitrate also do not differentiate between neutral (e.g., NH_4NO_3) and acidic (HNO_3) nitrate aerosols. It is therefore not possible to estimate the relative importance of neutral and acid nitrates in aerosols.

ACCUMULATION IN VEGETATION

Comprehensive reviews of nitrate accumulation in vegetation are available (NRC 1972). Under normal cropping practices and in the absence of extreme environmental conditions, the levels of nitrate in plants generally are low. Levels of nitrate in vegetation vary considerably, however, among species. Becker (1967) reported values of nitrate ranging from 0.0045 to 0.05 percent (as N) for plant species receiving little or no added nitrate.

Total nitrogen levels in plants also vary seasonally. Typically, values rise sharply with the onset of growth in spring, reach a peak early in the growing season, and decline somewhat as vegetation matures. Internal redistribution of nitrogen occurs seasonally, particularly during fruit development. In perennial plants, nitrogen can be depleted from senescing plant parts and presumably is stored elsewhere in the plant.

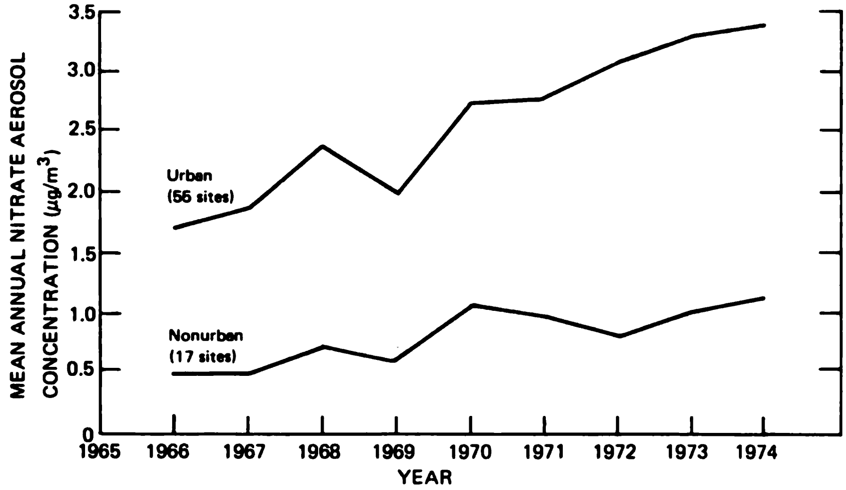


FIGURE 3.9 Mean annual nitrate aerosol concentrations in urban and nonurban air from the National Air Surveillance Network. Data up to 1970 from U.S. EPA 1974; data for 1971-1974 from Akland (1977).

A number of environmental factors can promote the accumulation of nitrate in plants. These are: (1) hot, dry, growing conditions, (2) decreased sunlight, (3) heavy manure or fertilizer treatments, (4) insufficient levels of other essential nutrients (e.g., phosphorus, potassium), or nutrient imbalance, (5) sharp and sudden temperature change, (6) frost, (7) injuries such as bruising, and (8) insect infestations that retard normal plant growth. Fertilizer applications beyond the point where yield continues to increase have been shown to coincide with nitrate accumulation (Griffith and Johnston 1961). Of the factors listed above, improved fertilizer use offers a practical means of reducing the hazard of nitrate accumulation in vegetation.

High nitrate levels are associated with high total nitrogen or crude protein content in vegetation. Griffith (1960) found that nitrate began to accumulate when crude protein in three grass mixtures approached 18 percent (2.85 percent N). He concluded that grass with greater than 21 percent crude protein should be used with caution because it will contain more than 0.07 percent NO_3^--N. Viets (1965) concluded that no precise relationships exist between total N and NO_3^--N and that none are likely to be developed because of the number of factors that influence the nitrate content of plants. He noted, however, that fodder with total nitrogen levels above 2.5 percent for nonlegumes and 3 percent for legumes may be toxic to livestock. An important related concern is the hazard to human health posed by accumulation of nitrate in vegetable crops. Nitrate levels in foods and associated risks to human health are reviewed in Chapter 9.

NOTE

1 Although nitrate-N concentrations in soils usually are expressed on the basis of soil solids (e.g., mg/kg [ppm] of NO_3^--N), they also can be given on the basis of soil solution concentration, assuming all of the NO_3^--N is dissolved in the soil water. Thus a soil containing 10 percent water and a NO_3^--N concentration of 10 mg/kg would have a soil solution NO_3^--N concentration of 100 mg/liter.

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CHAPTER 4

TECHNIQUES FOR THE ANALYSIS AND MEASUREMENT OF CRITICAL COMPOUNDS AND PROCESSES

INTRODUCTION

This chapter reviews analytical methods for nitrate and related nitrogen species in water, air, and soil, and discusses the principal methods that can be used to study the processes of the biological nitrogen cycle in natural and agricultural systems. Because the analytical methods for nitrate in the atmosphere and in soils generally involve extraction (dissolution of nitrate from the solid or gas medium and into water), there is a great similarity in the final measurement techniques for all three media. Although nitrate analyses have been done routinely for many years and a large number of chemical methods are available, problems still exist in measuring nitrate accurately, especially at low levels, in each medium.

Measurement of the dynamics of processes of the nitrogen cycle in terrestrial and aquatic systems is especially difficult because of the lack of suitable radioisotope tracers. In addition to methodological problems in determining rates of processes at specific sites, it also is difficult to extrapolate rates determined on a "micro" scale, involving milligram or microgram quantities of nitrate in gram or kilogram samples of soil or water, to entire ecosystems. Obviously the degree of spatial variability in the natural environment influences the reliability of extrapolations and the number of measurements needed to make reliable extrapolations. Because soil systems exhibit great spatial heterogeneity, measurement of the transport and transformation processes of the nitrogen cycle in agricultural systems is especially difficult (see Chapter 3).

CHEMICAL ANALYSIS

Water

Many methods are available for determining the amount of nitrate in water samples. None of them is satisfactory over the broad range of nitrate concentrations and water matrices (i.e., the combinations of ions present) encountered in environmental samples. In general, procedures for higher concentrations are subject to fewer problems than those for low or trace levels; manual methods for nitrate concentrations below about 0.1 mg N/l are tedious and often have poor reproducibility.

Nitrogen species, including nitrate, are highly labile, and unpreserved samples can undergo rapid changes during storage. Techniques that have been used to preserve nitrogen samples include refrigeration, freezing, and preservation with sulfuric acid (to pH 1-2) or mercuric chloride. Simple refrigeration is not an adequate storage method for periods longer than a day, because it slows down but does not stop biological activity. Freezing apparently is effective for preserving nitrate, but it causes cell lysis and thus can affect levels of other forms of nitrogen. Sulfuric acid is not a desirable nitrogen preservative because it accelerates nitrite loss, possibly by oxidation to nitrate (Brezonik and Lee 1966, Howe and Holley 1969), and promotes cell lysis and hydrolysis of organic nitrogen. The current edition of Standard Methods for the Examination of Water and Wastewater, published by the American Public Health Association (APHA 1976) recommends sulfuric acid for preservation of nitrogen; the 15th edition now in preparation will no longer recommend this preservative. Mercuric chloride is an effective preservative for nitrogen species, especially when coupled with refrigeration or freezing, but mercuric ion interferes with the commonly-used copperized cadmium reduction method for nitrate. The use of this preservative is discouraged in some manuals (e.g., U.S. EPA 1974b) because of the toxicity of mercuric ion.

Table 4.1 summarizes current analytical methods for nitrate in water. The nitrate ion absorbs strongly in the far uv (at 220-230 nm), allowing direct spectrophotometric measurement of nitrate in the absence of interfering substances (Armstrong 1963, Navone 1964). The method is sensitive to about 0.05 mg NO_3^--N/l under ideal conditions. However, because many organic compounds absorb strongly at the same wavelength as nitrate, this method can be used only on samples with low concentrations of organic matter, such as many groundwaters. The absorbance of organic matter at 220 nm generally is compensated for empirically by measuring the absorbance at 275 nm, at which nitrate does not absorb but many organic compounds do. However, the magnitude of

TABLE 4.1 Analytical Methods for Nitrate in Water

Method	Range[a]	Interferences	Comments	Reference
UV Absorbance	0.1-10	Organic matter, some inorganic ions	Use only in unpolluted (low organic) waters	APHA (1976)
Ion Electrode	0.2-1,400	Chloride, ionic strength	Must buffer samples to constant ionic strength	APHA (1976)
Nitration Reactions:				
Phenoldisulfonic acid		Chloride	Not recommended	APHA (1971)
Brucine	0.1-2.0		Poorly reproducible, toxic reagent	APHA (1976)
Chromotropic acid	0.1-5.0	Many, but all readily removed		APHA (1976)
Automated fluorometry with substituted benzophenone	0.005-1.0	Organic color, chloride, sulfide, but readily removed	Method not widely tested	Afghan and Ryan (1975)
Reduction Methods:				
Zinc	0.02-1.0	Sensitivity varies with age of column	Not recommended	O'Brien and Fiore (1962)
Amalgamated cadmium	<0.01-1.0		Columns are difficult to prepare	APHA (1976)
Copperized cadmium	<0.01-1.0		Columns are difficult to prepare; mercuric chloride preservative interferes with column	U.S. EPA (1974b) APHA (1976) Strickland and Parsons (1972)
Hydrazine-copper	<0.01-1.0	Reduction is pH sensitive	Used by oceanographers; method is slow and tedious	Mullin and Riley (1955)
Devarda's alloy	2->200		Reduction to NH_3 measured by titration or colorimetric method	APHA (1976)

[a] Concentrations in mg N/1.

the empirical correction depends on the nature of the organic matter and varies from one water sample to another.

Nitrate can be measured potentiometrically by means of nitrate ion selective electrodes (Langmuir and Jacobson 1970, Keeney et al. 1970). These electrodes operate on the same principle as pH electrodes, although construction details are different. While pH electrodes develop potentials across glass membranes as a function of H^+ activity, nitrate electrodes produce the same effect by means of a selective liquid ion exchange material held in the electrode by a thin porous membrane (Ross 1969). Ion electrodes have linear response over a broad range (many orders of magnitude) of concentrations. For example, the nitrate electrode exhibits Nernstian response (a 59 mv change in potential for each ten-fold change in concentration) over the range 10^{-5} to 10^{-1} M (0.14 mg N/l to 1.4 g N/l). Ion selective electrodes respond directly to activity rather than to concentration, and samples therefore must be buffered to a constant ionic strength (Milham et al. 1970). The nitrate electrode is relatively selective, but it does respond to chloride when the Cl^-/NO_3^- ratio is greater than about 10, and to other ions such as nitrite, bromide, sulfide, and iodide at concentrations above their normal levels in natural waters. Although response time of the electrode is normally less than one minute, the time required to achieve steady-state readings increases to several minutes as concentrations approach the detection limit. Because they are susceptibile to matrix interferences and are not adequately sensitive for many surface water samples, nitrate electrodes at the present stage of development have not yet achieved widespread acceptance.

Wet chemical methods for nitrate analysis generally fit into two major reaction types: (1) nitration, i.e., the substitution of the $-NO_2$ moiety onto an organic ring compound to form a colored product; and (2) nitrate reduction, usually to nitrite, with subsequent colorimetric analysis of the reduced nitrogenous product. Nitration reactions require a strong acid medium (e.g., 50 percent H_2SO_4), and usually a high temperature (see Table 4.1). The phenoldisulfonic acid method was widely used in the past, but it suffers from serious chloride interferences and is no longer recommended. Chloride interferences have been eliminated from the brucine procedures (Jenkins and Medsker 1964), but this method is difficult to reproduce. Brucine also is a highly toxic chemical, and although the method had widespread use in the past decade, most laboratories now prefer other procedures. In the chromotropic acid procedure, which is useful for moderate levels of nitrate, potential interferences from nitrite and chlorine can be readily eliminated (APHA 1976), and other potential interferences are not commonly found in natural waters.

This method tolerates less critical control of reaction conditions than does the brucine method. A number of other organic reagents (e.g., strychnine, 2,4 xylenol, benzidines) have been used in the past to determine nitrate by nitration reactions, but all suffer from interferences and poor reproducibility (Riley 1965).

Several recently developed nitration methods purport to offer improved precision and good sensitivity. In the method of Afghan and Ryan (1975), for example, nitrate is determined by measuring the fluorescence of the product of its reaction with a substituted benzophenone. The method has a detection limit of 5 µg N/l and appears best suited for automated analyses, but it has not been subjected to widespread evaluation and round-robin testing.

In contrast to analytical methods for nitrate, a highly sensitive, accurate, and simple colorimetric method has long been available for nitrite ion (NO_2^-). Nitrite is the anion of the weak acid HNO_2 (nitrous acid, pK = 3.36), which reacts with sulfanilic acid or sulfanilamide to form a diazonium salt. The latter couples with substituted naphthylamines to form stable red-pink azo dyes. Detection limits of 1 µg N/l or less can be readily obtained with this reaction. Consequently, many analytical procedures for nitrate have been based on its reduction to nitrite and subsequent analysis by the above reaction. Nitrate is readily reduced by a number of agents, including metallic zinc and cadmium, but quantitative recovery of NO_3^- as NO_2^- has proven difficult to achieve (Nydahl 1976). Early reduction methods used columns of zinc granules (e.g., O'Brien and Fiore 1962), but the efficiency of reduction changed rapidly in these columns with use, and they are no longer recommended.

Techniques using cadmium columns are currently favored by water analysts. Strickland and Parsons (1972) and the U.S. Environmental Protection Agency (U.S. EPA 1974b) use copperized cadmium columns; both copperized and amalgamated cadmium filings, are used in Standard Methods (APHA 1976). Some analysts have noted difficulties in preparing cadmium columns, but once a suitable column is prepared it can remain effective for up to several weeks. Reduction of nitrate to nitrite can be quantitative in cadmium columns (Nydahl 1976) but depends on sample pH, flow rate, and the rate of further reduction of nitrite. The sensitivity of nitrate analyses by reduction techniques is in the µg/l range.

Oceanographers also have used the Mullin and Riley (1955) method, which uses hydrazine in the presence of copper to reduce nitrate to nitrite. Henriksen (1965) adapted this procedure to automated analysis, but the reduction is not quite stoichiometric. More serious is the fact that the method is highly pH sensitive, leading to difficulties in analyzing samples with widely varying pH and buffer intensities, such as in estuarine samples. Kamphake (1967) automated this procedure for analysis of fresh water, and the revised edition of the EPA analytical manual (scheduled for publication in late 1977 or early 1978) will include a modification of the method (personal communication from M.E. Gales, Research Chemist, U.S. EPA, Cincinnati, Ohio).

Finally, nitrate can be reduced quantitatively to ammonia by use of Devarda's alloy (50 percent Cu, 45 percent Al, 5 percent Zn). The ammonia so formed can be analyzed by titration or colorimetry, using Nessler's reagant (APHA 1976). Because precision is poor at low levels, this method is useful only for relatively high concentrations (above 2 mg N/l).

Soils and Plant Tissues

Analysis of soils for nitrate is complicated by the wide range in concentrations encountered among various soils, and even from day to day in the same plot. Soil nitrate concentrations vary from nil to more than 50 mg N/kg of soil solids (up to several hundred mg N/l of soil solution). Numerous interferences also may be present, depending on the method used.

Measurement of nitrate in soil samples is made more difficult by the fact that concentrations can change rapidly because of immobilization, nitrification, and denitrification; rapid analysis or preservation of samples is therefore required. Improper handling or storage of soil samples and soil extracts probably is the source of most errors in soil nitrate analysis. Ideally, soil samples should be analyzed immediately after sampling, but because this is usually not practical, biocides (e.g., toluene, chloroform) have been used to prevent microbial activity. These reagents often are ineffective, however, and their use is not recommended (Bremner 1965b). Freezing at -10 to -15°C, is perhaps more satisfactory, but this also leads to changes in levels of inorganic nitrogen (Allen and Grimshaw 1962). Rapid air- or oven-drying is satisfactory for nitrate analysis, but not for ammonium ion or nitrite in soil (Bremner 1965b). Often the most suitable method is aqueous extraction of the soil sample as soon as practicable after sampling, and treatment of the extracts with phenylmercuric acetate to inhibit microbial growth, coupled with cold storage (0°C or below). Other preservatives such as strong acid are not acceptable if nitrite is present, since nitrite decomposes spontaneously in acid media.

Nearly all methods for the determination of nitrate in soils involve separation of nitrate from the soil sample by an extraction technique (Barker 1974). Nitrate is extracted quantitatively from most soils by water; however, most methods employ a salt solution, such as $CaSO_4$, K_2SO_4, or KCl, to provide a clear extract and to ensure that nitrate is removed (Bremner 1965b). Recent methods designed to determine ammonium ion, which is held on ion exchange sites in the soil and must be extracted by displacement with another cation such as K^+, have used neutral, 1 M or 2 M KCl almost exclusively.

Soil extracts often contain large amounts of turbidity and colored organic compounds, which must be removed before colorimetric analysis. Because nitrate and nitrite have little tendency to adsorb onto soil colloids, these interferences usually can be removed by flocculation, usually with calcium salts. Other methods of decolorizing soil extracts, such as activated charcoal, ion-exchange resins, or hydrogen peroxide, may cause changes in the nitrate content of the sample (Bremner 1965b).

Methods commonly used for analysis of waters also can be applied to soil extracts (Table 4.2), and many colorimetric techniques for soils are identical to or are slight modifications of methods listed in Table 4.1. However, the usual requirement that only one extraction be used for all forms of mineral nitrogen (ammonia, nitrite and nitrate) in a soil sample limits the choice to those methods that can tolerate the higher chloride content of the extracting solution. Some of the methods described in Bremner (1965b) are no longer recommended for soil extracts, mainly because of chloride interferences. The most popular method in recent years has been reduction of nitrate to ammonia by Devarda's alloy in a magnesium oxide-buffered medium while distilling with steam (Bremner and Keeney 1965). Ammonia is first removed from the sample by steam distillation with only magnesium oxide added, and nitrite is removed before distillation by treatment with sulfamic acid. This method has been found to give good results with a wide range of soils, and in most cases, filtration of the extract is not necessary. A method is also available which allows direct distillation of the soil without previous extraction (Keeney and Bremner 1966).

Automated analysis of soil extracts is most commonly conducted by reduction to nitrite on cadmium columns and colorimetric estimation of nitrite. The nitrate electrode has not achieved widespread acceptance for soil analysis, particularly with salt-affected soils, such as those that have received significant quantities of fertilizer. Bremner et al. (1968) noted interferences from nitrite, sulfate, chloride, and phosphate in measuring nitrate in soils by the liquid membrane nitrate electrode. Further, accuracy is

TABLE 4.2 Methods for Determination of Nitrate in Soils

Method	Range (mg/l)[a]	Interferences	Comments	References
Ion Electrode	2-1,400	Chloride, bromide, nitrite, iodide, sulfide, ionic strength	Less accurate than many methods, must buffer samples to common ionic strength	Carlson and Keeney (1971)
Phenoldisulfonic Acid	0.1-2	Chloride, organic matter, nitrite	Not recommended	Bremner (1965b)
Brucine	0.1-2		Poorly reproducible; toxic reagent	Bremner (1965b), APHA (1976)
Reduction to NO_2^- by Cd; Griess-Ilosvay method	0.02-0.1	None	Very sensitive, problems with reduction step	Bremner (1965b), APHA (1976)
Reduction to NH_3 by Devarda's Alloy, Steam Distillation of NH_3, or Conway Microdiffusion	1-1,000	Labile amides, phosphate, nitrite	Measure NH_3 by titration or colorimetric methods	Bremner (1965b)

[a] Range on soil basis varies widely, depending on soil: solution ratio of extractant.

poor below about 5 to 10 mg/l of nitrate-nitrogen (Carlson and Keeney 1971).

Analysis of plant tissues for nitrate involves essentially the same principles as those for soils, except that the concentration range is much higher; values up to 10,000 mg NO_3^--N/kg of dry plant material are not uncommon. Extremely rapid changes in nitrate concentration can occur if the plant sample is not handled properly. For convenience, rapid oven drying at 50-60°C in a forced air oven usually is recommended. Extraction of nitrate from the tissue matrix is essential, and salt solutions (KCl, NaCl, or $CaCl_2$) are most commonly used (Barker 1974).

Air

The discussion of the analysis of oxygenated nitrogen compounds in the air is more complicated than that for the other two media for several reasons:

1. Classical methods involve capturing nitrogen oxide gases in aqueous solution prior to wet chemical analysis, thereby adding another step that is difficult to control and is subject to error. Direct measurement of some of the nitrogenous compounds in the gas phase by physico-chemical techniques is a recent development.

2. Collection by scrubbing into aqueous solution complicates differentiation between aerosol and gaseous forms for some species such as ammonia and nitric acid. Aerosols usually are collected on glass fiber filters, but the efficiency of such filters in collecting submicrometer-sized particles (diameter $<$ about 0.3 μm) is open to question.

3. Analytical methods for most forms of nitrogen in air tend to be unsatisfactory and inadequate, especially at the low concentrations found in unpolluted atmospheres. Attempts to improve the principal methods have given rise to a confusingly large number of modified procedures based on a few common reactions.

4. In the field of air pollution, analytical reference manuals do not seem to have quite the widespread use enjoyed by the manuals for water (APHA 1976, U.S. EPA 1974b) and soil (Black 1965). There is no EPA manual for air pollutants comparable to the EPA (1974b) water manual, although EPA has published reference methods in the Federal Register (e.g., NRC 1977). An Intersociety Committee assembled a manual in 1972 for air sampling and analysis similar to that published by APHA for water and wastewater, but developments in analytical techniques soon made the manual outdated. A much revised edition of the air sampling

and analysis manual has recently been published (Intersociety Committee 1977).

5. Finally, there are many more forms of oxygenated nitrogen compounds of interest in the atmosphere than there are in soil and water (see Chapters 2 and 3). These include gaseous oxides of nitrogen, primarily nitrogen dioxide (NO_2), nitric oxide (NO), and nitrous oxide (N_2O), and the atmospheric nitrates: peroxyacyl nitrates (PANs), alkyl nitrates, and inorganic nitrate aerosols. NO and NO_2 are often determined together and the result is reported as NO_x. Other intermediates such as nitrosyl chloride (NOCl), nitrogen trioxide, (NO_3), nitric acid anhydride (N_2O_5), and gaseous nitric acid (HNO_3) are usually considered to represent insignificant atmospheric pools of nitrogen and are not routinely measured.

Table 4.3 lists the various nitrogen forms in the atmosphere and common analytical methods for each. Particulate inorganic nitrate usually is determined colorimetrically on aqueous extracts from glass fiber filters of hi-vol samplers. Apparently a considerable fraction of the nitrate collected on glass fiber filters is actually gaseous nitric acid, which is trapped by basic sites on the glass surface and thus is measured as particulate nitrate. The use of quartz filters has been suggested as a means of circumventing this problem (see Chapter 6; Spicer 1976). In normal monitoring programs hi-vol samplers are operated continuously for 24 hours, collecting particulates from 2000 m^3 of air. Analysis of the extracts is reasonably straightforward, but an EPA study concluded that methods commonly used for particulate nitrate suffer from "inadequate sensitivity, complexity and interferences" (U.S. EPA 1974a). These methods include nitration reactions with brucine and 2,4-xylenol (Intersociety Committee 1972), as well as reduction to nitrite and measurement by diazotization (Morgan et al. 1967). Currently EPA is using the copper-cadmium reduction technique (U.S. EPA 1974b) described in Table 4.1 for analysis of nitrate in both atmospheric particulates and natural water samples. The sensitivity of this method for air samples (about 0.03 $\mu g\ NO_3^-/m^3$ based on a 24-hr sampling period) is considered sufficient for routine ambient monitoring.

Appel et al. (1977) recently reported negative errors of up to a factor of three in analysis of nitrate in aerosols related to motor vehicle emissions using the 2,4-xylenol method (compared to the cadmium reduction technique as a reference method). A correlation was noted between the magnitude of error and the level of particulate lead, but concentrations of lead, halides, and peroxide in the extracts were insufficient to account for the interference, which remained unidentified.

TABLE 4.3 Analytical Methods for Oxidized Nitrogen Compounds in Air

Substance	Method	Comments	Reference
Nitrate Aerosols	Wet chemical analysis of extracts from filters of hi-vol samples using brucine, 2,4-xylenol, or cadmium reduction methods	Many of the techniques have poor sensitivity; the 2,4-xylenol method gives low response in samples with automotive exhaust	Intersociety Committee (1972, 1977), Appel et al. (1977)
PANs and Alkyl Nitrates	1. Direct injection of gas sample into gc, using electron capture detection	Controversy exists concerning effect of humidity on results; operating variables are critical for accurate response	Intersociety Committee (1977), Lonneman (1977)
	2. Chemiluminescence	Sensitive to ppb level. Applicable to continuous monitoring	Pitts et al. (1973)
NO_x (NO and NO_2)	1. Griess-Saltzman single reagent mixture; NO_2 reacts to form an azo dye	Calibrating or reference method	Intersociety Committee (1977), Saltzman (1960)
	2. Jacobs-Hochheiser absorption of NO_2 into alkaline solution; subsequent analysis of NO_2^- by diazotization; many variations on this approach	Variable efficiency of different absorbing solutions; controversy over reliability of various modifications	See text and NRC (1977)
	3. Chemiluminescence from reaction of NO and ozone	Federal reference method. Suitable for continuous monitoring; highly sensitive; PANs may interfere	Fontijn et al. (1970), Sigsby et al. (1973)
N_2O	Gas chromatography with thermal conductivity detectors or more sensitive helium ionization, ultrasonic, and electron capture detectors	Less sensitive detectors require cryogenic concentration for analysis of N_2O at ambient air concentrations	Rasmussen et al. (1976); Blackmer and Bremner (1977a)

In general there seems to be little communication between analysts of atmospheric nitrate and their counterparts in water analysis, although cooperation between the two groups would appear to be beneficial. Some of the recently developed procedures for analysis of nitrate in water samples (Table 4.1) may prove useful in analysis of atmospheric nitrates.

The chemical instability of PANs and their low (ppb) levels, even in polluted atmospheres, make analysis for these compounds difficult. No reliable means has been developed to store air samples containing PANs (U.S. EPA 1974a), but reference samples of PANs in helium or dry nitrogen are now available. PANs are explosive in air at relatively low concentrations, and caution should be observed in handling them. Direct injection of air samples into a gas chromatograph with highly sensitive electron capture detection has been used by various investigators (Stephens and Price 1973, Darley et al. 1963, Intersociety Committee 1977) to achieve separation and direct analysis of several PANs, such as peroxyacetyl and peroxypropionyl nitrates, at the ppb level in ambient air. However, operating variables must be chosen carefully because of the ready decomposition of these compounds. Chemiluminescent methods for PANs sensitive at the ppb level have recently been developed (Pitts et al. 1973) and offer promise for routine monitoring of atmospheric PAN.

Holdren and Rasmussen (1976) reported a water anomaly in PAN analysis by gas chromatograph-electron capture detectors. Reduced response to PAN was found in samples of low relative humidity (<30 percent). Lonneman (1977) disputed the generality of these results, and reported no water anomaly in gas chromatograph systems used by the U.S. EPA. Watanabe and Stephens (1978) confirmed some aspects of the moisture anomaly, however. They found consistent loss of sensitivity only in samples prepared in dry, acid-washed flasks, and attributed the loss to adsorption of PAN onto active sites of the container surfaces.

Peroxybenzoyl nitrate (PBzN) has been measured by bubbling air through alkaline methanol solution, trapping the PBzN and converting it to methyl benzoate. Gas chromatography with flame ionization detection is used for analysis of the methyl benzoate (Appel 1973).

The technique based on direct air injection into gas chromatographs with electron capture detectors can also be used to measure alkyl nitrates, and columns used to separate PANs also separate these compounds. For example, Lonneman (1977) showed separation of PAN and methyl nitrate within 30 minutes on a standard column used for PAN analysis.

The extensive literature on the analysis of oxides of nitrogen has been reviewed in detail by the NRC Subcommittee on Nitrogen Oxides (NRC 1977), and only a brief summary of this complex topic is presented here. Nitric oxide (NO) and nitrogen dioxide (NO_2) commonly have been determined by absorption into solution and analysis of the resulting nitrite by diazotization. In all the wet chemical methods, nitric oxide must be oxidized to NO_2; if ambient NO_2 is not first removed, the sum of the two gases is measured and reported as NO_x. Much research on NO_x analysis has focused on development of a suitable oxidant for NO. Ozone, acidified manganese dioxide, permanganate-sulfuric acid, periodate, persulfate, oxygen, nitrogen pentoxide, and chlorine dioxide have been used as oxidants, but each suffers from one or more disadvantages (Levaggi et al. 1974). In some cases the oxidation is incomplete; with other oxidants, such as ozone, there is a tendency for oxidation to proceed all the way to nitric acid. However, Levaggi and co-workers reported quantitative oxidation of NO to NO_2 using CrO_3 coated on a firebrick support, provided that the relative humidity of the air was maintained between 35 and 80 percent.

The Griess-Saltzman method (Intersociety Committee 1977) is based on direct reaction of NO_2 with a single reagent mixture to form an azo dye (Saltzman 1960). This technique formerly was considered the calibrating or reference method for NO_2, but according to Margeson and Fuerst (1975), the reliability of data obtained by the method before 1974 is questionable because of the use of a static calibration procedure.

Measurement of NO_2 by absorption into alkaline solution and subsequent analysis of the resulting nitrite is the basis for the Jacobs-Hochheiser (J-H) methods (Jacobs and Hochheiser 1958). The efficiency of NO_x removal from air and absorption in the collecting solution is a potentially large variable in this two-step approach. The old Federal Reference Method based on the J-H technique had a low and apparently variable collection efficiency (about 35 percent) (Hartwell et al. 1974), and results obtained by this method are considered questionable (NRC 1977). The U.S. EPA no longer considers this as a reference method. A chemiluminescent method has recently replaced the Jacobs-Hochheiser wet-chemical technique as the Federal Reference method for NO_2 in air (U.S. EPA 1976).

More recent developments apparently have overcome the problems of poor and variable recovery (Purdue et al. 1975). Modifications of the J-H technique using sodium arsenite and triethanolamine in the collecting solution have reported efficiencies of 85 and 100 percent, respectively (Beard and Margeson 1974, Hartwell et al. 1974), and the EPA now regards available methods as reliable (J.H. Margeson, U.S.

EPA, Research Triangle Park, N.C., personal communication, 1977). Kobayashi et al. (1977) recently explained the efficiency of NO and NO_2 absorption by aqueous solutions of inorganic and organic reagents as a function of the standard redox potentials of the half reactions in which the reagents participate.

Recently, continuous monitors have been developed for NO and NO_2 based on the chemiluminescence produced in the reaction of NO with ozone (Fontijn et al. 1970):

$$NO + O_3 \text{ ---> } NO_2{*} + O_2$$
$$NO_2{*} \text{ ---> } NO_2 + h\nu.$$

Catalytic reduction of NO_2 to NO using low temperature reactions with metal oxide catalysts or high temperature (>600°C) thermal decomposition of NO_2 permit determination of NO_2 and NO_x by this method (e.g., Sigsby et al. 1973), and several commercial analyzers are now available. Black and Sigsby (1974) reported a variation in which atomic oxygen (O, obtained from thermal decomposition of ozone) is used both to reduce NO_2 to NO and to produce a chemiluminesence by reacting with NO. Baumgardner et al. (1975) compared a number of instrumental methods to measure NO_2 and reported favorable results for chemiluminescent monitors. However, Winer et al. (1974) found that chemiluminescent monitors using molybdenum or carbon converters for reduction of NO_2 to NO also quantitatively measure PAN and other organic nitrates, and respond nonquantitatively to nitric acid and nitroethane. For most routine monitoring of ambient air quality, these interferences are not serious, since concentrations of NO_x generally are much higher than those of the interfering compounds; but for highly quantitative ambient air or smog-chamber studies, the interferences can be significant.

Because nitrous oxide (N_2O) is considered an unreactive, natural component of air rather than a primary or secondary pollutant, it is not commonly measured in air pollution studies. Recent concern about the role of N_2O in depletion of stratospheric ozone and interest in measuring the rates of production of N_2O by denitrification in soils and natural waters have stimulated interest in the measurement of N_2O at ambient levels (about 250-300 ppb). The analysis of N_2O involves gas chromatographic separation and detection by a variety of methods. Thermal conductivity detectors have been used in the past, but they have minimum detection limits of 2.5 to 3 ppm N_2O, and require laborious cryogenic concentration techniques to detect N_2O at the levels in ambient air (Hahn 1972). Improved methods for detection of trace amounts of N_2O have been reported recently. Delwiche and Rolston (1976) achieved a sensitivity of about 1 ppb N_2O

using a helium ionization detector and cryogenic concentration, while Blackmer and Bremner (1977a) and Rasmussen et al. (1976) respectively reported the use of an ultrasonic and hot-electron-capture detectors for direct determination of N_2O at levels of 10 ppb or less. Rasmussen et al. (1976) reported a precision of better than 1 percent on repetitive analyses of N_2O in ambient air (concentration about 300 ppb), using a ^{63}Ni pulsed electron capture detector operated at 350°C.

MEASUREMENTS OF PROCESSES

Isotopic Tracer Techniques

Studies With ^{15}N

Nitrogen has five radioisotopes (Table 4.4), but with the possible exception of ^{13}N, they have half-lives that are too short for practical application to most experiments on transport or biological transformations of N. Therefore, the stable isotopes (^{14}N and ^{15}N) are for practical purposes the only ones available. Compounds enriched in ^{15}N have been widely used in biological research since they became available in 1942 (see bibliographies by Hauck and Bystrom [1970], and Hauck and Bremner [1976]). Increased availability and lower costs of ^{15}N-enriched and ^{15}N-depleted compounds, combined with improvements in the methodology and instrumentation needed for their use, probably will result in even wider application in the future.

The natural abundance of ^{15}N in the atmosphere is 0.366 percent, and the absolute ratio of $^{14}N/^{15}N$ is 272 (Junk and Svec 1958). A wide range of ^{15}N-enriched inorganic and simple organic compounds is commercially available. Because the isotopes are separated by physical techniques, ^{15}N-enriched compounds are relatively expensive compared to those enriched with radioactive isotopes. Current prices range from about $60 to $150 per gram of ^{15}N, depending on source and difficulty of synthesis.

The high cost of ^{15}N-enriched compounds generally precludes their use in large-plot field studies. The major expenses in ^{15}N tracer research, however, are usually the high costs of instrumentation and the skilled labor needed to conduct the analyses and maintain the equipment. Precise determination of ^{15}N requires conversion of the nitrogen compounds to N_2 and analysis of the isotope ratio by low-mass resolution mass spectrometers that ideally are specially designed and restricted to elements of mass 3 to about 40. Current costs of these instruments range upward from about $50,000, depending on the degree of sophistication required. Less expensive, but less precise,

TABLE 4.4 Stable and Radioactive Isotopes of Nitrogen

Mass Number	Natural Abundance (%)[a]	Half-Life[b]
12	–	0.011 sec
13		9.97 min
14	99.63	–
15	0.37	–
16	–	7.2 sec
17	–	4.16 sec
18	–	0.63 sec

[a] Adapted from analyses of atmospheric nitrogen by Junk and Svec (1958) indicating that the absolute ratio of $^{14}N/^{15}N$ in atmospheric nitrogen is 272 ± 0.3 (% abundance of ^{15}N, 0.3663 ± 0.0004).

[b] Adapted from Weast (1976).

emission spectrographic methods for determining $^{15}N/^{14}N$ ratios are now used in a few laboratories (Keeney and Tedesco 1973).

Preparation of samples for ^{15}N analysis almost always requires conversion of the form of nitrogen under analysis to an ammonium salt. For nitrate, this usually involves conversion to ammonia, using Devarda's alloy and the steam distillation technique described earlier in this chapter. The sample is then evacuated at 10^{-5} to 10^{-6} mm Hg to remove all atmospheric nitrogen, and the ammonia is reacted with alkaline hypobromite to liberate nitrogen gas. The relative abundance of molecules of mass 29 ($^{15}N^{14}N$) and 28 ($^{14}N^{14}N$) is measured by a mass spectrometer, and the atom percent ^{15}N is calculated from the ratio of the 28/29 peaks (Bremner 1965c).

Errors that can occur during this analysis include incomplete conversion of the sample to ammonium ion or to N_2 gas, with some isotopic discrimination occurring in the conversion; contamination of the sample; and air leakage. However, when conducted properly, nitrogen isotope ratios determined by modern mass spectrometers can achieve precision of ± 0.0001 atom percent ^{15}N.

At least two commercially available emission spectrometers can be used for ^{15}N analysis. These instruments detect ^{15}N on the basis of the difference in emission bandheads of $^{14}N^{14}N$, $^{14}N^{15}N$, and $^{15}N^{15}N$ when an N_2 sample, under low pressure, is made to discharge in an electrical field. The primary advantages of emission spectrometry are lower initial cost ($10,000 to $15,000) and lower maintenance costs compared to mass spectrometry; furthermore, much smaller samples can be analyzed. However, emission spectrometry is not as precise as mass spectrometry, and at present it cannot be used for research with ^{15}N-depleted materials or for natural abundance ratio studies.

Hauck (1973) recently reviewed the benefits and problems associated with the use of stable nitrogen isotopes in studies of the nitrogen cycle. Other discussions of the use of ^{15}N techniques for soil and water research include those by Jansson (1958), Bremner (1965c), Hauck and Bremner (1964, 1976), Hauck and Bystrom (1970), Neess et al. (1962), and Dugdale and Dugdale (1965).

Recent developments in the separation of stable isotopes at the Los Alamos Scientific Laboratory in New Mexico (Hammond 1972) have resulted in the availability of relatively large quantities of highly purified ^{15}N-depleted ammonium sulfate (0.003 to 0.009 atom percent ^{15}N; Hauck and Bremner 1976). The low price of the ^{15}N-depleted compound (about $145/kg in 1975) makes it more attractive for field studies than the costly ^{15}N-enriched compounds. Several recent investigations have shown that ^{15}N-depleted ammonium sulfate is satisfactory for determination of plant recovery of fertilizer nitrogen during the first growing season (e.g., Edwards and Hauck 1974, Patrick et al. 1974, Starr et al. 1974). However, since the isotopic identity of ^{15}N-depleted material is lost after about 200 to 2000 dilutions, ^{15}N-enriched materials, which can be diluted up to 50,000 times, must be used for most long-term transformation and availability studies (Hauck 1973). The small differences in concentrations that must be measured when ^{15}N-depleted material is used require a highly sensitive mass spectrometer, and the potential for errors due to isotopic discrimination is much greater than when highly enriched ^{15}N compounds are used.

Two basic assumptions are involved in nitrogen isotope tracer research: (1) that the nitrogen isotopic composition of natural materials is constant, and (2) that isotopic discrimination does not occur within limits of experimental error (that is, that the reactions of the nitrogen cycle do not proceed at different rates for ^{15}N-containing samples than for ^{14}N-containing samples, because of the difference in mass between the two moieties). These assumptions are valid for most tracer experiments using ^{15}N-enriched materials, but they do not necessarily hold when measurements are made in a narrow range of detection in the vicinity of natural abundance. Variation in the nitrogen isotope abundance of biological materials is the rule rather than the exception (Table 4.5). The ^{15}N variations in materials usually are expressed as $\delta^{15}N$ units, where:

$$\delta^{15}N = \frac{(\text{At\% } ^{15}N \text{ of sample - At\% } ^{15}N \text{ of air})}{\text{At\% } ^{15}N \text{ of air}} \times 1000$$

Thus, one $\delta^{15}N = 0.00037$ atom percent (At%) ^{15}N. A positive $\delta^{15}N$ indicates a higher ^{15}N concentration, and a negative value a lower concentration than that in atmospheric N_2. In general, fertilizer materials have lower enrichments than does total soil nitrogen; however, the reported range of $\delta^{15}N$ in N fertilizers varies from -23 to +6, while values as low as -7 and as high as +18 have been reported for soils.

There may be sufficient differences in isotopic composition of many natural materials and some fertilizer materials to consider these materials as tracer substances with low levels of ^{15}N enrichment or depletion (see Table 4.5). However, the accuracy of the data they may provide as tracers depends on the ability to detect very small amounts of isotope enrichment or depletion in one form of nitrogen compared to the other nitrogen in the system under study.

TABLE 4.5 Variation in ^{15}N Abundance ($\delta\ ^{15}N$) of Various Materials

Material[a]	Average $\delta\ ^{15}N$	Range	Reference
Atmospheric N_2	0		By definition
NH_3 from coke gas	-9.0		Bokhoven and Theeuwen (1966)
Fertilizer NO_3^- (KNO_3)	-4.1		Blackmer and Bremner (1977)
Fertilizer NO_3^- (NH_4NO_3)	+2.3		Shearer et al. (1974)
Fertilizer NH_4^+ [$(NH_4)_2SO_4$]	-4.1		Black and Waring (1977)
Fertilizer NH_4^+ (NH_4NO_3)	-1.0		Freyer and Aly (1974)
Fertilizer NH_4^+ (NH_4NO_3)	-0.5		Shearer et al. (1974)
Fertilizer urea	-2.1		Black and Waring (1977)
Organic fertilizer	+15.0		Shearer et al. (1974)
Forest surface soil	-7.0		Riga et al. (1970)
Surface soils (16)	-0.2		Bremner and Tabatabai (1973)
Surface soils (69)	+2.6		Riga et al. (1970)
Surface soils (39)	+5.4		Delwiche and Steyn (1970)
Surface soils (28)	+6.3		Cheng et al. (1964)
Surface soils (6)	+8.5		Shearer et al. (1974)
Surface soils (11)	+8.8		Rennie et al. (1976)
Surface soils (139)	+9.2		Shearer et al. (1975)
Surface soil (1)	+13.0		Kohl et al. (1971)
Leaves, 5 species		-6.5 to +1.9	Hoering (1955)
Seaweed	+8.1		Hoering (1955)
Peat (Ireland)	+1.9		Hoering (1955)
Peat (New York)	-2.8		Hoering (1955)
Chilean nitrate	-2.6		Hoering (1955)
Rainwater NO_3^- - N (6)	-4.9	-12.4 to +2.7	D. H. Kohl, personal communication (1977)
Rainwater NH_4^+ - N (2)	-1.2		D. H. Kohl, personal communication (1977)
Rainwater total N (Kjeldahl N + NO_3^-) (5)	-3.3	-6.1 to +1.0	D. H. Kohl, personal communication (1977)
Rainwater NO_3^- - N (9)	-1.7	-7.2 to +3.4	Hoering (1957)
Rainwater NH_4^+ - N (9)	+4.4	-0.1 to +9.0	Hoering (1957)
Rainwater total N (Kjeldahl N + NO_3^-) (5)	-3.3	-6.1 to +1.0	Hoering (1957)

[a] Values in parentheses indicate number of samples.

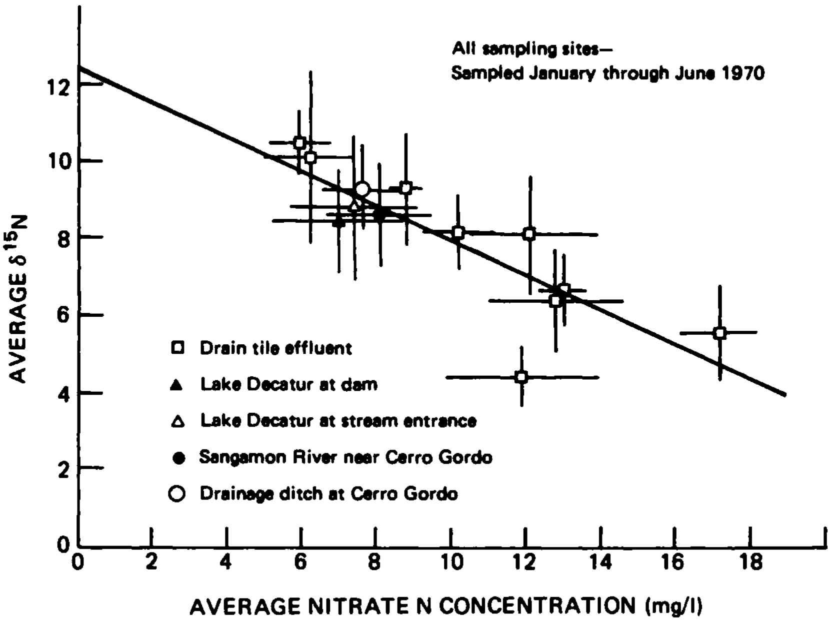
Isotopic discrimination and inherent variations in the isotopic abundance of the nitrogen in the system are more serious problems in natural abundance studies, mainly because of the extremely narrow range of detection required (Edwards 1973).

In one of the best-known examples of the application of this technique in field investigations, Kohl et al. (1971) used variations in the natural abundance of ^{15}N to estimate the fractional contribution of soil organic nitrogen and fertilizer nitrogen to the nitrate levels in surface waters in a 2331 km² watershed in central Illinois. The fertilizer used in the area had an estimated average $\delta^{15}N$ of +3; a sample of virgin soil from the area produced NO_3^--N of +13 $\delta^{15}N$ when incubated in the laboratory. The $\delta^{15}N$ of the nitrate in the surface waters was determined, and a linear interpolation between +13 and +3 was used to estimate the fertilizer contribution. A $\delta^{15}N$ of +8, for example, would result in an estimate of 50 percent of the nitrate-nitrogen coming from fertilizer. Results of the relative enrichment data obtained in the study are shown in Figure 4.1 (Kohl et al. 1971).

This report sparked considerable interest and debate on the applicability of the natural abundance approach to estimating the relative contributions of sources of nitrate reaching surface waters from a large watershed. While there is much conflicting data, the evidence indicates firmly that this approach cannot quantitatively differentiate between various sources of nitrate in biological systems where nitrogen turnover is considerable (Hauck 1973). When fertilizer nitrogen is added to soil, it rapidly loses its identity through the complex web of reactions of the nitrogen cycle.

Discrimination that results in depletion of ^{15}N in the product and enrichment in the remaining reactant has been observed during nitrification and denitrification (Delwiche and Steyn 1970, Chien et al. 1977, Blackmer and Bremner 1977b). In the last study, the authors found that discrimination during denitrification of anoxic soils amended with glucose and 100 mg/kg of NO_3^--N resulted in an increase in the $\delta^{15}N$ of the remaining nitrate from an initial value of zero to +16 to +20 by the time 67 to 78 percent of the nitrate was reduced. Even larger variations, both negative and positive, were found in the nitrite fraction.

Another major problem with the natural abundance approach is obtaining valid estimates of the $\delta^{15}N$ in the nitrate originating from the soil organic nitrogen. For example, a recent study by Black and Waring (1977) on a small uniform watershed in Queensland, Australia showed large variability in $\delta^{15}N$ of the soil organic nitrogen and



SOURCE: Kohl et al. (1971) Fertilizer nitrogen: contribution to nitrate surface water in a corn belt watershed. *Science* 174:1331-1334.

FIGURE 4.1 Relative $\delta^{15}N$ of drainage and surface waters compared to total amount of nitrate-nitrogen present.

of the mineralized nitrate. The subsoil of this site can adsorb nitrate by anion exchange processes (Black and Waring 1976), and isotope ratio analysis of nitrate-nitrogen in the soil profile below a fertilized area showed increasing $\delta^{15}N$ with depth. The authors attributed this to isotopic discrimination in favor of retention of ^{14}N, but denitrification seems a more likely explanation. The authors concluded that the natural abundance method was of doubtful value for providing even qualitative estimates of the contributions of various nitrogen sources to surface and ground waters in this watershed.

In addition to the wide variability in $\delta^{15}N$ of various soils, differences also have been observed in the $\delta^{15}N$ produced upon incubation of different soils (Bremner and Tabatabai 1973) or of the same soil for different lengths of time (Feigin et al. 1974). These findings also support the conclusion reached by Delwiche and Steyn (1970), Hauck (1973), Meints et al. (1975), and Shearer et al. (1975) that in fertilizer nitrogen studies the natural abundance method should be regarded as a qualitative or, at best, a semi-quantitative estimate of the relative contributions of nitrate sources.

On the other hand, isotope geochemists have used stable isotope variations for several light elements to obtain insights into many natural geochemical processes. For example, oxygen isotope ratios in marine carbonates have been used to determine long-term trends in oceanic temperatures and hence in global climate. Stable isotope ratios also have been used to measure impacts of human activity in cases where natural ratios have been altered by addition of material with a different isotopic ratio. For example, stable carbon isotope ratios have been used to differentiate pollutant organics of petrochemical origin from organic matter of recent biological origin.

Some applications of the ^{15}N abundance approach could provide information unobtainable by other means. The $\delta^{15}N$ of nitrogen fractions in the ocean may indicate the extent to which denitrification is occurring there. For example, Richards and Benson (1961) used variations in $^{15}N/^{14}N$ ratios in dissolved N_2 as corroborating evidence, along with N_2/Ar ratios, in the first published report on the occurrence of denitrification in the sea (see Chapter 2). Similarly, the relative magnitude of denitrification rates in terrestrial systems might be evaluated by comparing the $\delta^{15}N$ of soils with a range of drainage characteristics and moisture contents. The $\delta^{15}N$ of ammonium and nitrate in rain also may help to identify the sources of this nitrogen. Rennie et al. (1976) determined the $\delta^{15}N$ of soils, soil profile nitrate, fertilizers, and plants in the Canadian Great Plains, a region characterized by low precipitation. The authors suggested that, under the conditions of their study, variations in natural abundance could be used to differentiate between fertilizer and natural sources of nitrogen in crops. Hauck (1973) suggested that more detailed knowledge of the natural variations of nitrogen isotope ratios in various ecosystems could aid in evaluating the relative magnitude of nitrogen transformations.

Until sufficient data have been gathered on various ecosystems throughout the world, the usefulness of $\delta^{15}N$ methods for studying such questions will remain speculative. In addition, further research on the factors affecting the abundance of ^{15}N in natural pools of nitrogen and on the extent of isotopic discrimination in processes of the nitrogen cycle may ultimately increase the reliability of the use of ^{15}N as a tracer in agricultural and other systems.

Studies with ^{13}N

Gersberg et al. (1976) reported the first application of $^{13}N\text{-}NO_3^-$ to denitrification studies. They produced the short-lived radiotracer in a cyclotron and immediately vacuum-transferred the nitrate solution to soil samples. Tiedje et al. (1977) also recently demonstrated that ^{13}N can be used to study denitrification in soils. The major advantages of this approach are the use of low NO_3^- concentrations (μg/l), rapid kinetics (minutes), and high accuracy. This technique promises to provide information on rapid nitrogen transformations unobtainable by any other approach, but its applications are limited by its high cost, need for specialized equipment, and the requirement that field samples be brought to the cyclotron. Furthermore, many important processes of the nitrogen cycle, such as denitrification in sediments overlain by oxygenated and nitrate-containing water, are limited by mass transport rates; this would preclude the use of this radiotracer in establishing in situ reaction rates.

Denitrification

Because of the problems inherent in attempts to quantify the gaseous nitrogen products of denitrification, measurement of this process in soil systems under field conditions is a difficult undertaking. Closed systems commonly have been used (e.g., McGarity and Hauck 1969, Stefanson 1972), but they are of limited applicability because they require maintenance of a normal atmosphere in a small volume.

Many denitrification investigations have involved measurement of the rate at which nitrate disappears. This can lead to large overestimates, however, because nitrate may be reduced to ammonia and organic nitrogen as well as be denitrified (Brezonik and Lee 1968, Keeney 1973, Stanford et al. 1975). Investigators often have used unrealistic conditions such as completely anaerobic chambers, addition of massive amounts of organic carbon, or large additions of nitrate to anoxic samples. Effects of soil pretreatment on rates of denitrification also can be serious. In laboratory studies, McKenzie and Kurtz (1976) found that oven-dryed and crushed-screened soil samples lost much more (90 percent) fertilizer nitrate by denitrification than did field-moist, intact soil cores (34 percent losses).

The most feasible quantitative approach to estimating the extent of denitrification in the field is to determine the transformations of ^{15}N-labeled nitrate. Even this approach is complicated by leaching of nitrate. Nitrate leaching, however, can be evaluated by assessing the rate of movement of a companion tracer such as chloride (Saffigna et al. 1977).

Measurement of N_2O in closed chambers inserted in the soil (Dowdell and Smith 1974) or on the soil surface (Focht et al. 1975) can provide qualitative estimates of denitrification. However, unless the N_2O/N_2 ratio in the product gas is known accurately, these procedures cannot provide quantitative estimates of the total rate of denitrification. The possibility of N_2O formation during nitrification (Ritchie and Nicholas 1972, Yoshida and Alexander 1970) also might preclude the use of N_2O evolution to estimate denitrification. Further, N_2O and N_2 are subject to leaching with the soil water. Leaching of N_2O might explain, at least in part, its occurrence in the subsoil, where denitrification would not be expected to occur because of low organic matter levels (Dowdell and Smith 1974).

The recent finding that acetylene effectively inhibits the reduction of N_2O to N_2 in denitrification (Balderstone et al. 1976, Yoshinari and Knowles 1976) may aid materially in measuring denitrification rates under incubation conditions approaching those of the _in situ_ environment. Sensitive gas chromatographic methods exist for the measurement of background levels of N_2O in the atmosphere, which are very small (250-300 ppb; see above in this chapter).

The measurement of denitrification rates in aquatic systems and in flooded soils, sediments, and marshes also poses problems. The use of ^{15}N for denitrification assessments in anoxic lake waters is relatively uncomplicated (Brezonik and Lee 1968, Brezonik 1977), but simulation of _in situ_ turbulence and of mass transport rates for dissolved oxygen and nitrate is difficult in partially oxygenated systems such as shallow lake and marsh sediments.

Mass-balance calculations can be used to estimate denitrification rates in aquatic systems (Vollenweider 1968). The amount of nitrogen lost annually from a lake, including its sediments, is determined by the difference between the total input and total outflow of nitrogen, taking the amount of sedimented nitrogen and change in nitrogen storage in the lake into account. This method has the advantage of not requiring any short-term incubations, and is a holistic or ecosystem-level approach. On the other hand, the accuracy of the method depends on the accuracy of the nutrient balances, which are themselves complicated and difficult to measure. Chapter 5 and Appendix A describe calculations of denitrification in Lake Okeechobee, Florida, using the mass-balance approach.

Prediction of Residual Nitrogen and the Potential for Mineralization of Nitrogen in Soils

Most crops take up a varying but significant portion of their nitrogen from the soil nitrogen pool, which consists of mineral nitrogen remaining in the rooting zone from the previous season plus that nitrogen made available to the crop during the growing season by mineralization of soil organic nitrogen. Maximum efficiency in the use of fertilizer nitrogen requires that the size of this pool be considered.

Tests for the availability of soil nitrogen have many inherent problems, especially the difficulty in obtaining a representative soil sample (Kurtz and Smith 1966). Because crop yields are influenced by many factors besides the amount of fertilizer applied, (see Chapter 8), most fertilizer recommendations are based on past fertilization, cropping history, and the current crop and management level. This approach can lead to inaccurate recommendations, particularly when considerable nitrate remains in the profile, as often occurs in semi-arid regions (e.g., Carter et al. 1976). In humid regions, residual nitrate concentrations are of little importance, since spring and summer rains may lead to leaching and denitrification.

Various procedures for estimating the relative rate of mineralization of nitrogen in different soils have been proposed (Bremner 1965d). Usually these involve measurement of the amount of inorganic nitrogen formed on incubation of a small sample (10 to 100 g) of soil at a constant temperature under aerobic or anaerobic conditions for several weeks, or measurement of the amount of nitrogen released from soil by treatment with acids, alkalies, or heat. The poor results of these measures have discouraged their use. However, Stanford and Smith (1972) have proposed a mineralization test that involves estimation of potentially mineralizable soil nitrogen through sequential determination of the amount mineralized over a 32-week period. The mineralization potential is calculated graphically, assuming first-order kinetics. Later work by these researchers indicated that the amount of ammonia released on heat treatment of the soil correlated closely to the mineralization potential (Stanford and Smith 1976). Stanford (1977) suggested that estimates of the amount of soil nitrogen mineralized could be modified by taking into account variations in soil temperature and soil water content. This approach successfully explained about 64 percent of the variability in response to nitrogen of sugar beets in Idaho (Stanford et al. 1977), but it has not been evaluated for other crops and other regions of the United States.

Nitrification

Measurement of rates of nitrification in natural systems or laboratory samples is difficult, because the products (nitrite and nitrate) are subject to rapid denitrification or assimilation by plants and to reconversion to ammonia and organic nitrogen. Rate measurements based on accumulation of nitrate therefore indicate only net nitrification. Except in conditions where nitrification is the dominant nitrogen cycle reaction, such as in streams receiving ammonified sewage effluents, net rates are likely to be considerable underestimates of gross rates.

In unpolluted surface waters, assimilation of nitrate is likely to be more rapid than nitrification; in soils, both assimilation and denitrification within microanoxic zones can cause nitrate losses. Use of ^{15}N as a tracer can circumvent these problems if periods of incubation are short, but this technique is cumbersome and has other disadvantages. In this technique, ^{15}N-enriched ammonia is added to a sample and the amount of ^{15}N in the nitrate fraction is measured after incubation by mass spectrometry. Such tracer measurements are subject to great uncertainties, because the interchange of ammonia with organic nitrogen is rapid compared to rates of nitrification and it is likely that the ^{15}N content of the reactant ammonia pool will vary during incubation. In natural aquatic systems, tracer experiments on nitrification also are complicated by the usually low concentrations of ammonia and nitrate in these systems. As a result, only a few in situ ^{15}N measurements of nitrification have been made in unpolluted aquatic systems (Goering 1972, Brezonik 1972).

Billen (1976) recently reported a novel method of estimating the rate of autotrophic nitrification in surface sediments. He measured the amount of ^{14}C-bicarbonate assimilated by the samples both in the presence and absence of the nitrification inhibitor nitrapyrin. Autotrophic nitrifiers use carbon dioxide as their carbon source; the difference in ^{14}C uptake between treated and untreated samples was assumed to measure the activity of these organisms.

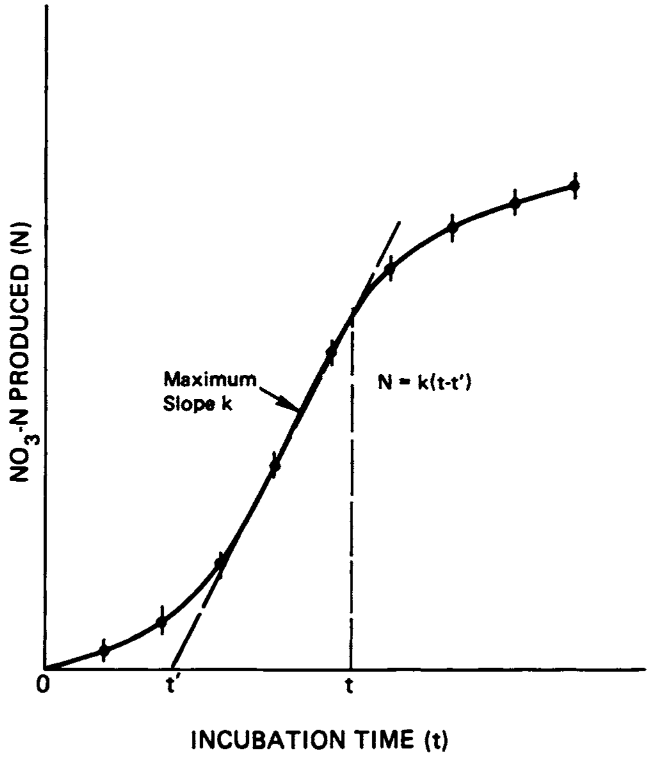
Measurement of nitrification in soils also is quite difficult. Two contrasting situations are of major interest in considering the rate and extent of nitrification in aerobic soils: the nitrification of ammonia mineralized from soil organic nitrogen, and the nitrification of added fertilizer nitrogen. In the first case, the rate of nitrification generally is limited by the amount of substrate (ammonium ion) available, but in the second situation, soil and environmental factors usually limit nitrification.

Under ideal conditions, the production of nitrate from ammonia over time follows a course like that shown in Figure 4.2 (Frederick and Broadbent 1966). Under conditions where ammonium is not limiting, the rate of nitrification (maximum slope, k) at 25 to 30°C can vary from near zero for acid soils to as high as 350 mg NO_3^--N formed per kg of soil per week.

Two main problems are associated with laboratory incubation procedures for assessing nitrification rates: (1) Air-dried soil is usually used. Air-drying profoundly affects, and usually increases, the rate of initial mineralization of soil organic nitrogen (see, for instance, Keeney and Bremner [1966]); and (2) The constant temperature and moisture conditions do not duplicate the continually fluctuating conditions found in the field.

Control of water is critical in any experiment that attempts to measure in situ nitrification rates. For example, Miller and Johnson (1964) found that nitrification increased with increasing soil moisture, reaching a maximum at a matric potential of about 0.5 bar. In the moist range (0 to 0.5 bar), nitrate accumulation decreased, probably because of denitrification in microanoxic zones. At high potentials (dry conditions), nitrification apparently was limited by the volume of water (and thus the volume of medium available for microbial activity).

As an alternative to laboratory incubations, small plastic bags can be filled with soil and then buried. Bremner and Douglas (1971) indicated that this approach could lead to erroneous findings because of excessive build-up of carbon dioxide in the bags. Campbell et al. (1974) used highly permeable plastic bags (0.012 mil thick) to overcome this problem, but found that the bags were permeable to water also, and that denitrification resulted when heavy rains entered them. The same investigators also simulated in the laboratory the diurnal temperature



SOURCE: Adapted from Frederick and Broadbent (1966), in Anhydrous Ammonia: Technology and Use, page 206. Reprinted with permission of the American Society of Agronomy and Soil Science Society of America.

FIGURE 4.2 General nitrification curve showing an increasing rate phase with a delay period, O-t, a maximum rate phase with a slope k, and a retarded rate phase.

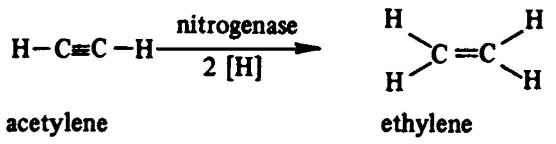
fluctuations recorded in the field, and found this approach matched field conditions to some extent. Their field results showed that marked increases in temperature led to a flush of mineralization. Alternate wetting and drying of the surface layer of soil markedly increased the rate of nitrate produced over that found when soils were incubated at a constant water content; this phenomenon has been found by other workers as well.

Valid estimates of nitrification rates are of increasing importance, particularly with increased emphasis on nitrification inhibitors as a potential pollution control strategy. Because handling of soil inevitably leads to the death of some of the nitrifiers (Alexander 1965), care must be taken to ensure a representative nitrifier population in experiments that test nitrification inhibitors.

In summary, laboratory incubation techniques to assess the rate of nitrification are not sufficiently able to simulate field conditions to produce a true measure of the nitrification rate. If careful attention is paid to soil pretreatment and water content, however, laboratory incubations can provide information on the relative extent of nitrification under the influence of the variables being examined.

Nitrogen Fixation

Biological nitrogen fixation is most reliably measured by ^{15}N tracer methods, which measure the incorporation of ^{15}N into cellular material by mass spectrometry following incubation of a sample with ^{15}N-enriched nitrogen gas. A simpler, less expensive, and more sensitive method was developed by Stewart et al. (1967), based on the fact that acetylene is reduced to ethylene by the nitrogen-fixing enzyme nitrogenase. Acetylene and molecular nitrogen (N_2) are isoelectronic and similar in size and shape:



$$N\equiv N \xrightarrow[6\ [H]]{\text{nitrogenase}} 2NH_3$$

The amount of ethylene produced in a sample spiked with acetylene can be quantified by simple gas chromatographic methods, and serves as a measure of nitrogenase activity, and hence of nitrogen fixation, in the sample. The acetylene reduction method (Burris 1972) has gained widespread use in the past decade because of its simplicity and low cost, and it has led to important advances in understanding the process of nitrogen fixation. The technique is indirect, however, and acetylene reduction results should be checked against $^{15}N_2$ fixation rates for proper validation (Burris 1974). A theoretical conversion factor (moles of acetylene reduced/mole of ammonia fixed) of 1.5, based on the number of electrons involved in the respective reductions (two per ethylene produced and three per ammonia produced), is commonly used to convert acetylene reduction results to equivalent nitrogen fixed. The reliability of this factor has been questioned unless it is validated by $^{15}N_2$ under identical conditions (Burris 1974). Recent literature reviews (Hardy et al. 1973, Hauck and Bremner 1976, Criswell et al. 1976) indicate that the conversion factor can range from 1 to 12. This variability could be caused by lack of proper controls to ensure that ethylene is not produced by other mechanisms or that ethylene produced from acetylene reduction is not degraded or absorbed in the system (Hauck and Bremner 1976). The principal reason for the variations, however, appears to be related to the production of hydrogen gas by nitrogen-fixing organisms (Schubert and Evans 1976, Peterson and Burris 1976). When nitrogen gas is the substrate, ATP-dependent production of gaseous hydrogen from hydrogen ions occurs, diverting electron flow from nitrogen reduction. Acetylene inhibits the evolution of hydrogen and raises the conversion factor above 1.5. According to Peterson and Burris, the ratio commonly is closer to 2.0-2.2.

The great sensitivity of the acetylene reduction method and its requirement for short-term (minutes to hours) incubations, while advantageous for many detailed studies, are serious disadvantages for field studies seeking to determine total annual rates of nitrogen fixation. The typically large, short-term variabilities of fixation rates in natural systems require large numbers of measurements to integrate instantaneous rates of fixation accurately over long time scales. Furthermore, evaluation of nitrogen fixation in soils by symbiotic and associative fixers, such as legumes and alder trees, requires an assay of the entire root system of the plant. Rates of fixation in legumes depend strongly on the integrity of the root nodule-plant system; studies with excised small samples of soil and nodules may yield results that are not representative of undisturbed plants. If only portions of the root system are used for an assay, measurements must be made to determine the percent of the total nodule mass of the plant actually used for the assay.

Legg and Sloger (1975) tried to avoid these problems by using an integrative, indirect ^{15}N isotope-dilution method. They labeled soil organic nitrogen uniformly by applying glucose and ^{15}N-enriched ammonium sulfate to the soil and allowing microbial action to incorporate the ^{15}N into the organic nitrogen pool. They then measured nitrogen fixation by growing soybean plants and comparing the ^{15}N content of plants grown with nodules (which obtained some of their N from unlabeled atmospheric nitrogen) with the ^{15}N content of non-fixing strains of the same plant (which received all their nitrogen from the pool of labeled soil organic nitrogen). Results obtained by the isotope dilution method and by direct $^{15}N_2$ uptake measurements were comparable, but total fixation estimated by acetylene reduction assays was much lower.

D.H. Kohl (Center for the Biology of Natural Systems, Washington University, St. Louis, Mo., personal communication, 1977) has proposed a natural-isotope abundance method to determine integrated fixation rates in field studies. The process of nitrogen fixation does not involve isotopic discrimination (Hoering and Ford 1960). Since atmospheric nitrogen has a $\delta^{15}N$ of 0.0 by definition, and soil organic nitrogen typically has positive $\delta^{15}N$ values in the range of +2 to +13 (see Table 4.5), plants that fix atmospheric nitrogen will have lower $\delta^{15}N$ levels in their tissues than those that obtain all their nitrogen from soil. On the other hand, fertilizer nitrogen typically has negative $\delta^{15}N$ values. The natural isotope abundance method cannot, therefore, readily distinguish between fertilizer nitrogen that may be present and atmospheric nitrogen as sources of plant nitrogen. The accuracy and reliability of this technique remain to be tested, but the approach may provide an estimate of the amount of nitrogen fixed over meaningful time periods (e.g. a growing season) and under natural conditions. However, the method is subject to many of the uncertainties discussed earlier in relation to the use of natural abundance values.

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CHAPTER 5

THE MASS-BALANCE APPROACH AND MASS-BALANCE STUDIES FOR NITROGEN

INTRODUCTION

A variety of case studies described in Chapter 6 of this report demonstrate that human activities have modified the natural cycle of nitrogen; this also has occurred with numerous other elements. These activities have changed the temporal and spatial distributions of nitrogen in its various chemical forms, resulting in both real and potential deleterious effects in certain ecosystems. This chapter examines the application of the materials balance approach to evaluating the impact of human activities on flows and storages of nitrogen in the environment.

In the United States and most other western industrial nations, control of and accounting for material flows is based primarily on the economic value of materials. Input-output analysis of economies is based on monetary values of materials and goods (Leontief 1966). Wastes and discarded materials, which have little or no economic value, are not fully considered in economic studies unless the damage they inflict on the environment can be assigned economic value. Traditional economic controls on material flows generally fail to prevent environmental damages because the effects are often removed spatially or temporally from the source activity, and damages that are difficult to relate to causal activity become "externalities". In essence, this problem is the result of inadequacies of the normal economic system in material accountability (Kneese et al. 1970).

A comprehensive materials management system must ultimately be based on the fundamental physical law of conservation of mass. A materials or mass-balance approach defines all of the inputs, outputs, and storages of a material or element in a defined, bounded region (e.g., factory, lake, globe) in order to study the behavior of the substance in the system. This approach contrasts with common pollution monitoring methods by emphasizing the interactions between components in the system, thus providing a basis for predicting future concentrations of the element in a particular reservoir. Focusing on material flows at sources and transfer points in a system may provide a more effective basis for pollution control than does monitoring ambient concentrations of a chemical once it has been dispersed into the environment. Monitoring programs initiated without consideration of material balances may overlook significant inputs or outflows. The difficulties and expenses of designing and implementing comprehensive monitoring systems, particularly at regional and global scales, often allow for serious impacts before pollution problems are detected by routine monitoring programs.

The mass-balance concept has been important to the development of science in general, and it has played an especially significant role in the environmental sciences. Mass-balance methods have been applied to problems in geochemistry (Bertine and Goldberg 1971, Garrels and Mackenzie 1967, Garrels et al. 1975), water quality (O'Connor and Mueller 1970, Whipple 1970), waste treatment, oceanography (Goldberg 1963), limnology (Vollenweider 1969, Middlebrooks et al. 1973), ecosystem modeling (Odum 1970, Patten 1968), and economics (Kneese et al. 1970).

This chapter reviews the principles and techniques of mass-balance analysis, and discusses the kinds of information obtainable from mass balances and the limitations of the approach. As part of the present study on nitrate in the environment, the panel has constructed or examined existing mass balances for nitrogen at several levels of system size, complexity and aggregation, ranging from small ecosystems (lakes and terrestrial ecosystems) to larger regions (river basins and political states) and ultimately to the global scale; details of the mass balances are given in Appendix A. This chapter summarizes those studies and discusses the methodological issues that apply to such studies on each scale. An important aspect of the mass balances summaries is an examination of their accuracy and of the availability of information (data) for their construction. At each level, the relationships between critical issues, analysis of potential pollution by nitrate, and management or control options are discussed.

ADVANTAGES OF THE MASS-BALANCE APPROACH

Construction of mass balances is useful for several reasons. In a sense, a mass balance is a conceptual model of a real system and therefore serves as a useful organizational tool. Even crude mass balances enable one to evaluate information needs and data gaps, therefore allowing one to design a better (more efficient) monitoring or data gathering program.

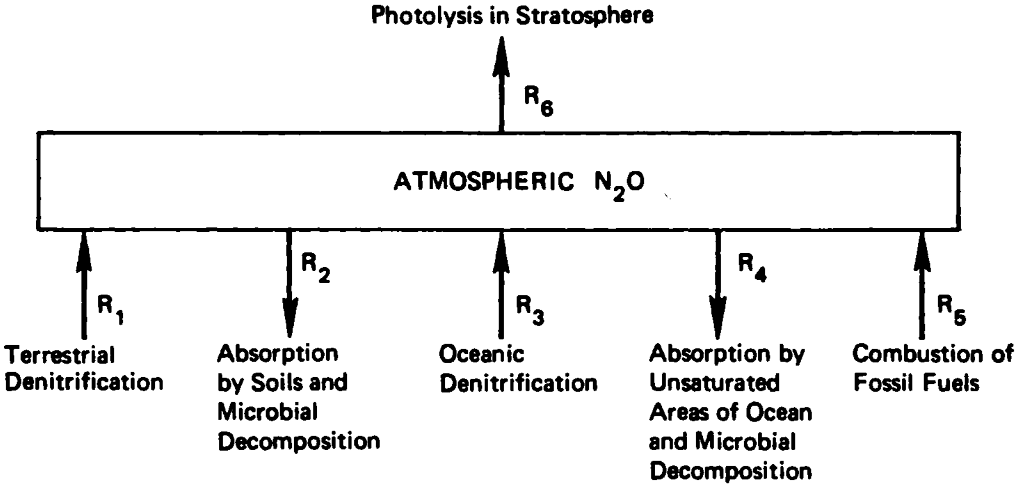
In a complex system, a mass-balance model can provide important insight into interactions between components (reservoirs or flows) that may at first seem unrelated or only loosely related. Sensitivity analysis of mass-balance data provides information on the importance of various mechanisms and processes in controlling reservoir sizes and flows from one part of the system to another. From a practical viewpoint, mass-balance models can be used to evaluate the importance of anthropogenic versus natural sources or flows of a substance in a given system. Examination of a sequence of mass balances over time can reveal a buildup or decay in various reservoirs, and human (cultural) actions that produce changes in any input, outflow, or reservoir size can be detected by such studies. Information of this sort is prerequisite to sound planning and to development of efficient management strategies.

Components of Mass-Balance Models

The initial step in any mass-balance analysis is definition of the boundaries of the system of interest. Measurement points must be identified where the flow and inventory of the material of interest (in this case nitrogen) can be quantified.

The components of a simple mass balance include all the sources and sinks for a given element or substance with respect to a particular reservoir or pool (Figure 5.1). The magnitudes of the source and sink flows and of the reservoir pool size are also required for a quantitative analysis. The concept of the mass balance can be generalized to larger, more complicated systems involving a number of different reservoirs for an element or substance. The components of mass balances in such cases include the sizes for all reservoirs (or pools) and source/sink rate information for each pool. Figure 5.2, and Figures A.2, A.4, A.9, and A.10 in Appendix A, illustrate the components and flows involved in several more complicated mass-balance models for nitrogen in environmental systems.

After identification of system boundaries, reservoirs and flows, the next step is to define the time increment of interest. The type of mathematical formulation used to describe the mass transfers between reservoirs depends on whether the system is in a steady or pseudo-steady state or in an unsteady or transient state. In the former case, the flows have constant rates and the mass balance can be written as a series of simultaneous algebraic equations. In a true steady state, the mass of the element or substance in each reservoir is constant over time. True steady states are rare in nature, but if appropriate time intervals are chosen, some transient (oscillating) systems can be treated as steady-state systems. Steady-state formulations have certain practical advantages, including simpler data requirements and mathematical formulations. The steady-



$dN_2O/dt = R_1 + R_3 + R_5 - R_2 - R_4 - R_6 = \Sigma R_i - \Sigma R_j$

where R_i = rate of the ith source of N_2O, and

R_j = rate of the jth sink for N_2O.

At steady state, $dN_2O/dt = 0$, and

$R_1 + R_3 + R_5 = R_2 + R_4 + R_6$, or $\Sigma R_i = \Sigma R_j$.

In general, for j outflows: $R_j = k_j[N_2O]$,

where k_j = loss rate constant for the jth mechanism,

and $[N_2O]$ = pool size for atmospheric N_2O.

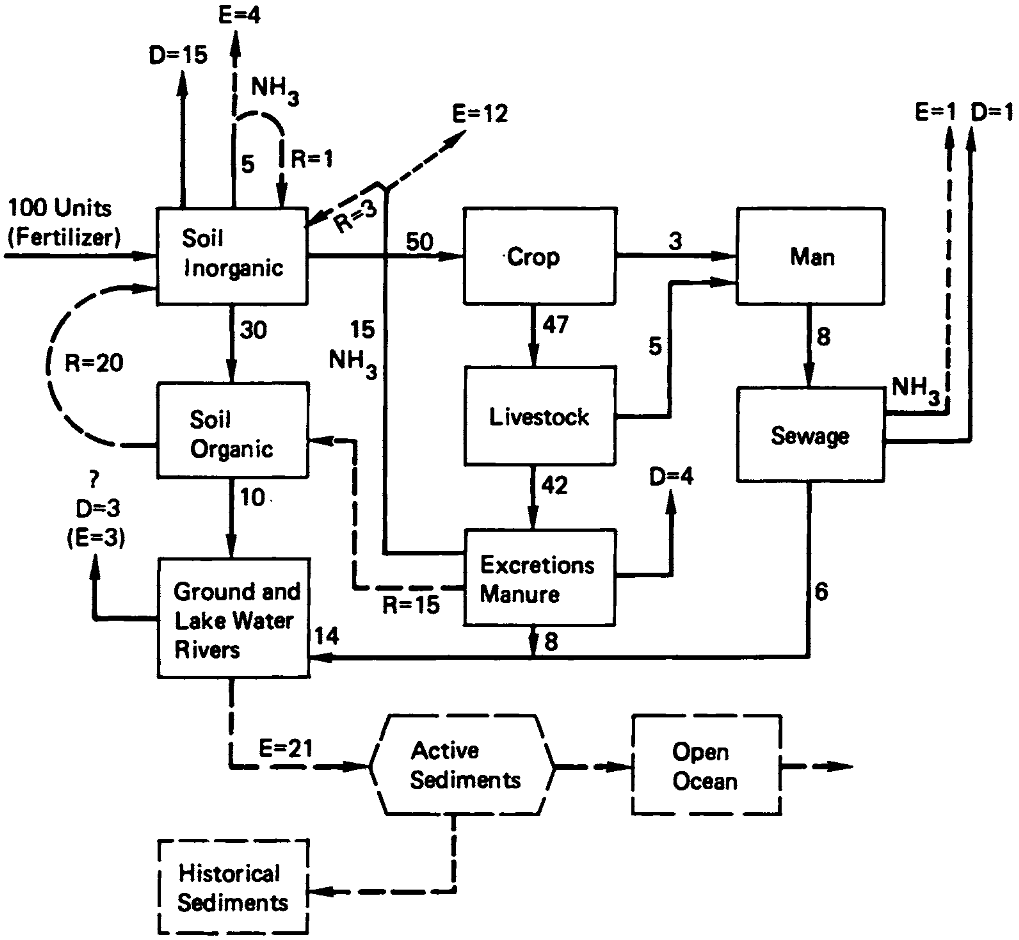
Furthermore, $\Sigma R_j = R_{out(total)} = [N_2O]\Sigma k_j$, and

$\Sigma k_j = 1/\tau_{N_2O}$,

where τ_{N_2O} = atmospheric residence time for N_2O.

Hence, $\tau_{N_2O} = [N_2O]/R_{out(total)}$.

FIGURE 5.1 Simple (one-compartment) mass-balance model: nitrous oxide in the atmosphere. Numerical values for the R_i and R_j are poorly known.



SOURCE: Crutzen (1976).

FIGURE 5.2 Tentative estimates of the partitioning of 100 arbitrary units of fixed nitrogen (fertilizer) in modern agriculture. E = escape to pools with very long time scales or with no formation of N_2O measured; $E_{total} = 38$. R = recycling; $R_{total} = 39$. D = denitrification; $D_{total} = 23$.

state assumption allows one to compute values for some flows by difference, i.e., by balancing the unknown flow with the known flows, so that inputs equal outflows for each reservoir.

Natural systems are characterized by diurnal, seasonal and longer-term variations, but if climatic conditions, soil structure, and nutrient supply rates do not change significantly, a steady state can be assumed on an annual basis. However, climatic conditions that control plant growth and mineral cycling, such as rainfall patterns, length of growing season, and daily and mean monthly temperatures, often vary dramatically from one year to another, even if annual climatic conditions (e.g., mean annual temperature and total annual rainfall) show only small variations. Because of these variations in weather patterns, natural systems usually oscillate randomly about some mean state. A practical implication of this variability is the fact that measurements made on a system over only one year may not be representative of the true mean "steady-state" conditions. Furthermore, if the steady-state model for a natural system is based on data for some parameters from one year (e.g., a wet year) while other data are from another (e.g., a dry year), the calculated rate values for various transfer processes can be seriously in error. Chapra and Tarapchak (1976) recently discussed some implications of nonsteady-state conditions in the application of simple steady-state models of nutrient loading and trophic response in lakes.

Nonsteady-state systems can be treated at several levels of detail. In the simplest case, flow rates are assumed constant, but net changes may occur in reservoir pool sizes over the time period of interest (e.g., from the beginning to the end of an annual cycle). In such cases, the transfer relationships and hence the mass balance can still be written as a series of algebraic equations. Many of the nutrient balances performed on lake systems are of this type, and the local and regional mass balances described in Appendix A generally fit into this category.

At a greater level of sophistication, mass-balance concepts form the basis for complex simulation models that treat the dynamic aspects of flows, using differential equations to describe the flows and interrelationships between reservoirs. Relatively simple simulation models assume that the flow rate of a substance out of its reservoir is proportional to the size of the reservoir. This approach results in a series of simultaneous first-order differential equations (one for each reservoir). The equations can be solved readily using analog or digital computers. In nature, many transfer relationships between reservoirs are more complicated than the first-order model, and more sophisticated dynamic simulation models use non-linear differential equations to describe these functional relationships. Dynamic simulation models have been used widely in ecosystem and water pollution studies over the past decade (e.g., Thomann 1972, Patten 1971-1974). A few simulation models involving some nitrogen cycle processes in natural and culturally perturbed ecosystems also have been developed recently (e.g., Beek and Frissel 1973; Dutt et al. 1972; Endelman et al. 1972, 1973; McLaren 1970; Mehran and Tanji 1974; Tanji et al. 1975, 1977).

Dynamic mass-balance models have several major problems. The mathematical nature of the transfer relationships for many natural processes is unknown or poorly understood. Furthermore, as the differential equations used to describe the behavior of a system become more complicated, the data requirements and coefficients needed to solve the model also become impractically large, and validation of the model becomes impossible.

Although dynamic simulation models are based on the principle of conservation of mass, their purposes and the techniques used in their solution are considerably different from the simpler models described earlier. In fact, the term "mass-balance model" generally is reserved for models of steady-state systems or of nonsteady-state systems in which flows are described by algebraic rather than differential equations. Although simulation models are useful in the analysis of ecosystem functioning, they have had only limited application to management problems involving nitrogen cycle processes.

Residence Times

The concept of residence (or turnover) time is useful in characterizing the dynamic behavior of substances in steady-state systems. Residence time is determined by dividing the mass of a substance in a system reservoir by its rate of addition to or removal from the reservoir. (At steady state, input and outflow are equal). For example, the residence time of water in a well-mixed lake of constant volume is:

$$\tau_w = V/Q_{in} = V/Q_{out} \tag{5-1}$$

where V = total lake volume (e.g., in m^3) and Q = total inflow or outflow (e.g., in m^3/yr). The derivation of the residence time of nitrous oxide in the atmosphere is illustrated in Figure 5.1. In order to compute the residence time of N_2O in the atmosphere, quantitative rates of all the source or sink processes shown in Figure 5.1 must be determined on a global basis. At present these rates are poorly known, and the residence times for N_2O reported in recent studies range from a few (1-10) years to about 160 years (see Chapters 3 and 7). Best estimates of τ_{N_2O} appear to be in the range of 5-40 years.

Similarly, the turnover times of nitrogen in other pools ranging from sub-ecosystem to global scales can be determined from the steady-state value of the pool size and the sum of the source or sink rates. Turnover times for inorganic nitrogen pools in many productive lakes are on the order of a few days during the summer; on the other hand, the turnover time of nitrogen in the humic fraction of soil organic matter may be several centuries.

If we assume that a reservoir is well mixed and at steady state, and if the loss of the substance from the reservoir follows a first-order reaction rate process, it can be shown that 1-1/e (where e = 2.718, the base of natural logarithms), or 63.2 percent of the material in the reservoir, is exchanged ("turned over") in one residence time. For systems not at steady state, the concept of residence time, strictly speaking, is not valid, although it often is assumed.

Residence times can be used to estimate response times for various pools of nitrogen in relation to perturbations imposed by man, and thus they are an aid in designing effective environmental monitoring programs. From the relationship between residence time, reservoir size, and input rate, it is obvious that a long residence time implies a slow input rate (relative to pool size). Thus a given perturbation in the absolute input rate of a substance will have a greater effect on the steady-state reservoir size if the substance has a long residence time (hence low natural input rate compared to pool size) than if it has a short residence time (rapid turnover being synonomous with high input and high removal rates).

Implications of these relationships in the current example of potential depletion of stratospheric ozone by N_2O produced from fertilizer are obvious (also see Chapter 7). If the residence time of N_2O in the atmosphere were short, the natural production and decomposition rates would be relatively high compared to the size of the N_2O reservoir in the atmosphere. A given increase in N_2O production from fertilizer nitrogen consequently would exert a relatively small influence on the content of N_2O in the atmosphere, and hence a small influence on the stratospheric ozone level; however, the effect would occur rapidly. On the other hand, if the residence time of N_2O were long, the natural production and decomposition rates would be small relative to the atmsopheric reservoir size, and a given increase in N_2O production from fertilizer nitrogen would have a large effect on the atmospheric N_2O content and hence on stratospheric ozone. Fortunately, in this case the full impact of the perturbation would not occur for a long time, thus giving society sufficient opportunity to implement solutions.

A major assumption of the above example and of the application of the residence time concept in general is that residence time for a compartment remains constant even when the system is perturbed to a new steady state. Intuitively this seems to be the case for simple systems, but for complicated environmental systems with many controlling variables and feedback loops, this may not always be true. There does not appear to be adequate information on any environmental system to check the constancy of residence times for nitrogen under a range of conditions.

LIMITATIONS OF MASS-BALANCE MODELS

The degree to which any model represents a real system depends on the ability of its developers to conceptualize the physical system and express its essential qualities in abstract terms. In this regard, the most fundamental decisions to be made in developing mass-balance models concern the establishment of system boundaries, the time period of interest, and the division of the system into a series of compartments or reservoirs. The most important consideration in setting up compartments is that their size and the transfer rates of substances into and out of the compartment must be measurable with some degree of accuracy and ease. Indeed, judicious selection of reservoir boundaries is probably the most important decision variable determining whether or not a mass-balance model can be solved.

Determination of compartment size often is difficult because of the heterogeneity of the material of interest in a given compartment. For example, concentrations of various nitrogen forms such as ammonium ion and nitrate in soil are highly variable even within a small field. Determination of transfer rates frequently is even more difficult than determination of reservoir sizes. In some cases, analytical methods do not exist to measure transfer rates; in other cases measurements are theoretically possible but are not practical because of money or manpower limitations.

Transfer processes for mass balances of nitrogen can be divided into physical transport (e.g., sources and sinks for nitrogen into a lake or soil system) and chemical and biological transformations that convert nitrogen from one chemical form to another. Chapter 4 describes procedures for measuring rates of nitrogen cycle transformations in aquatic and terrestrial systems; in particular, ^{15}N tracer techniques are described in detail. Limitations of these techniques are discussed in Chapter 4 and will not be repeated here.

Kohl et al. (1978) recently listed 14 types of transfer and transformation processes for which data are often needed in mass balances for nitrogen, and they ranked the quality of data available or potentially available for each process in categories ranging from poor to good (Table 5.1). Even though the rankings are subjective and general, it is obvious that mass-balance models for nitrogen in natural systems are subject to large uncertainties. Not only are the errors for some types of data likely to be large, but the uncertainties in assigning values to the errors are also great. Furthermore, the above statement often applies to several input-output terms in a mass balance for a given reservoir, thus compounding the uncertainties in the analysis. Obviously, the conclusions drawn from mass-balance models must be measured against the quality of the data.

In the previous section it was noted that the steady-state assumption allows calculation of one flow (input or outflow) by difference, if all others are known. The validity of this approach depends not only on the accuracy of all the measured flows but also on the accuracy of the assumption that the system is at steady state. In systems with reservoir sizes that are very much larger than the annual fluxes, the assumption that reservoir size is indeed constant becomes impossible to validate experimentally. For example, it is not possible to validate the assumption that the rates of nitrogen fixation and denitrification are balanced globally on an annual basis from the apparent constancy of the atmosphereic reservoir of N_2, because each of these processes involves only about 6 x 10^{-6} percent of the total atmospheric reservoir on an annual basis (Kohl et al. 1978). Thus, even if one of the processes ceased altogether, the other still would either add or remove an unmeasurable quantity of N_2 from the atmosphere over the time scale of human life. Of course, direct measurement methods may be used to determine whether global rates of denitrification and nitrogen fixation are in balance, but accurate direct measurement is extremely costly and time-consuming. Examples of limitations on uses of other difference calculations and steady-state assumptions are given in several of the mass balances of Appendix A and are mentioned in the summaries of those balances later in this chapter.

The level of detail or specificity necessary for a particular mass-balance analysis depends on the questions that the mass balance is supposed to answer. In general, however, as the size of the system increases, the level of aggregation in mass-balance analysis also increases.

TABLE 5.1 Data Requirements on Transfer and Transformation Processes for Mass-Balance Studies for Nitrogen

Parameter	Potential Quality of Data
1. Precipitation	good
2. Ammonia absorption	poor (but small)
3. N fixation	poor to fair
4. Industrial wastes	good
5. Municipal wastes	good
6. Animal wastes	fair to good
7. Fertilizer nitrogen	good
8. Net Mineralization	poor
9. Stream inflow	good
10. Volatile loss of NH_3	poor
11. Denitrification	poor
12. Leaching to substrata	poor
13. Plant uptake	good
14. Stream outflow	good

SOURCE: Kohl et al. (1978).

Physically different reservoirs and flows become grouped together, either for convenience, or out of the necessity to perform the analysis, given certain data limitations. For example, in balances at the ecosystem level, scientists may separate a lake into several physical compartments (e.g., epilimnion and hypolimnion; littoral and pelagic zones), but in balances at the global level, the oceans usually are lumped together as one reservoir, because information is insufficient to construct compartment models. Ironically, more complicated real systems tend to be described by simpler mass-balance models, at least partially because less detailed information is available about the behavior of large systems and the interactions among their components. Aggregation thus is a necessary consequence of ignorance, and as a result, only limited inferences can be made concerning the behavior of substances in large systems.

According to Levins (1966), all models represent compromises among three qualities: generality, precision, and reality. No model can be optimized for all three features, and one of these usually is sacrificed for the sake of the other two. Mass-balance models are highly simplified descriptions of real systems. The models lack functional relationships for flows between compartments, which often are highly aggregated reservoirs. On the other hand, the basic constructs of mass balances are quite general; for example, the flow diagram for the Florida mass balance (Figure A.9) can readily be applied to any other state, although the names of some of the reservoirs might be modified. Similarly, the mass balance shown in Figure 5.2 is a very general one; and the mass-balance structure used for the lakes in Appendix A is easily applied to other lakes, or for that matter to mass balances for other elements. Thus mass-balance models sacrifice realism for generality. The precision of a mass balance is directly related to the adequacy of the data base. Compared to complicated simulation models, mass-balance models are probably rather precise (as far as they go), in that most reservoir sizes and flows are actually measured rather than computed by the model. The precision of mass balances probably decreases as larger systems are considered, because of the aggregation and simplification that must occur.

Global nitrogen balances that were developed to study the impact of increased nitrogen fixation on stratospheric ozone depletion (CAST 1976 and Chapter 7 of this report) illustrate some of the problems that result from aggregation. As Kohl et al. (1978) point out, these global mass balances lump all nitrogen fixation processes together; but industrially-fixed nitrogen used for fertilizer may have a higher probability of being denitrified rapidly than would biologically-fixed nitrogen. Furthermore, the fixed nitrogen from these two sources may undergo denitrification in quite different circumstances, resulting in different fractions of nitrous oxide produced per unit nitrogen denitrified.

Despite these problems and limitations, the concept of mass continuity is too important to neglect. Many pollution problems developed because the fate of wastes in the environment was ignored or because it was assumed that an almost infinite sink exists for wastes. The development of a mass balance can reveal whether there are leakages from the system of interest with subsequent impacts on adjacent systems. The mass balance thus offers a warning mechanism to identify processes or actions that should be monitored for potential leakages and impacts on levels of existing pools of nitrogen.

Other examples of the values and limitations of mass-balance models in nitrogen cycle studies are best given by describing specific case studies. The following sections summarize the mass-balance analyses for nitrogen that the panel developed <u>de novo</u> or by analysis of available literature.

SUMMARY AND ANALYSIS OF CASE STUDIES

The case studies developed for the nitrate study can be classified by media and the geographic scales of concern. The time units used in each of the mass balances were years; much of the shorter-term dynamics of nitrogen cycling processes in the study areas is lost by integration to produce annual rates of input and outflow. The lake studies focus on a single medium (water) enclosed within the natural boundaries of the lakes and their sediments, providing a relatively well-defined material balance problem. All other studies are multimedia attempts to relate water, air, and land pools confined by either natural or political boundaries. The natural boundaries used are watersheds and the globe, and the political boundaries used are states and the United States. In each case study, the utility and difficulties of developing a mass balance on annual basis are discussed. Because the various forms of nitrogen are so interrelated, mass balances that focus on one form (e.g., nitrate) are neither feasible nor very useful. Consequently, the mass balances discussed below involve all active forms of nitrogen; in some cases, N_2 is not considered, because it is comparatively inert and independent of "fixed" nitrogen forms.

Lakes

As early as 1887, the ecologist S.A. Forbes noted that lakes represented a convenient laboratory in which to study the functioning of ecological systems (Forbes 1887). Lake boundaries are well defined, compared to many other natural systems; the medium is homogeneous compared to soil, and thus it is easily sampled; and the size is manageable, at least for small lakes. The pressures of urbanization and intensified agriculture have resulted in the cultural eutrophication of many lakes over the past several decades, leading to a decline in their water quality. Consequently, knowledge of the transport and cycling of algal nutrients such as nitrogen and phosphorus has become an important aspect of water quality management, and mass-balance models for these nutrients have played an increasing role in lake management in recent years. The use of such models to develop critical nutrient loading rate standards for lakes is discussed briefly in Chapter 8. Nitrogen mass balances obtained from various reports for three culturally eutrophic lakes--Lakes Mendota and Wingra, Wisconsin, and Lake Okeechobee, Florida--are presented in detail in Appendix A, and some important conclusions developed from these balances are presented below.

Mass Balances: Summary and Methodological Problems

Most lake mass balances set the system boundaries at the lake surface, at the bottom of the sediments, and at the inlets and outlets of influent and effluent streams. This reduces the required data to influent and effluent flows and concentrations, seepage flows and concentrations, flows from atmospheric sources (mainly bulk precipitation and biological nitrogen fixation), and internal sinks (mainly denitrification and sedimentation). The choice of the bottom boundary depends on the information required from the model. Setting the boundary at the bottom of the sediment column simplifies the model by incorporating the opposing processes of sedimentation and internal loading (release of nutrients from the sediments to the overlying water) as part of a single term, the change in storage. Conversely, if other inputs and outflows are well quantified, internal loading or sedimentation information can be obtained by setting the lower system boundary at the sediment surface and treating the sediment as an external source/sink.

Percent contributions of nitrogen from atmospheric, surface water, and groundwater sources for the three lakes are summarized in Table 5.2. While surface inflows are the major nitrogen sources for all of the lakes, atmospheric and groundwater sources contribute between one-third and one-half of the nitrogen loadings. Both of the latter sources are probably underestimated in the balances, since the atmospheric sources do not include gaseous deposition, and undetected springs could deliver considerable amounts of nitrogen to a lake. Mass balances for conservative ions, together with $^{16}O:^{18}O$ data, led Brooks (1974) to conclude that there is considerable groundwater seepage into Lake

TABLE 5.2 Percentage of Nitrogen Contributed by Different Sources and Annual Areal Loading in Lake Okeechobee, Florida and Lake Medota and Lake Wingra, Wisconsin

Nitrogen Source	Lake Okeechobee	Lake Mendota	Lake Wingra
		Percent	
Atmosphere	30	24	18
Surface Runoff	70	51	47
Groundwater	--	25	35
Areal Loading (g/m^2)	3.72	14.6	9.2

Okeechobee, but a quantitative estimate was not possible. Unestimated groundwater inputs would lower the percentage contributions of atmospheric and surface sources in Table 5.2. The implication of these data is simple: the nitrogen sources that are easiest to monitor and control may represent only a fraction of the annual nitrogen input to a lake.

Relatively little information has been distilled from the nitrogen balance data concerning the importance of nitrate to the total nitrogen loading. In Lake Wingra, nitrate was 47 percent of the total input of nitrogen. Inspection of nutrient input data for Lake Okeechobee suggests that nitrate contributions are comparatively low (about 20 percent of total inputs). Nitrate inputs exceeded outputs and storage changes by a factor of about 6.5 in 1973-1974, indicating that the lake acts as a nitrate sink.

Residence times of nitrogen in the three lakes are relatively short, on the order of a year or less, suggesting that the lakes should respond rapidly to changes in nitrogen input. Water residence times (τ_W) are comparable to or slightly higher than the τ_N values in Lake Okeechobee, but are larger in the two Wisconsin lakes.

Information on system sinks and changes in storage is necessary for a complete mass balance. Most of the nitrogen is lost from the three lakes by diffuse processes which are not well measured and are subject to great temporal and areal variability. Surface outflows accounted for only 16 percent of the calculated nitrogen losses from Lake Mendota. In shallow Lake Okeechobee, surface outflows account for 28 to 66 percent of the nitrogen losses; the highest percentage occurred in an abnormally wet year.

Annual changes in storage of nitrogen in the water of Lake Okeechobee ranged from -26 (i.e., storage decreased) to +11 percent of the annual inputs. Concentrations of nitrogen forms can vary considerably in different parts of this large lake, and errors in measuring storage changes could contribute significantly to errors in the mass balance. Such problems are less pronounced in smaller lakes, although the vertical differences in stratified lakes also may produce errors. The potential for sampling error can be placed in some perspective when one considers that 50 samples of perhaps one liter each would represent an extensive one-day sampling effort. The total volume analyzed for nitrogen would thus represent only one part in 10^8 of the water volume in tiny Lake Wingra, and only one part in 10^{11} of the volume in Lake Okeechobee.

The four mass balances on Lake Okeechobee were used with other information to calculate losses of nitrogen by sediment denitrification. These losses ranged from 26 to 34 percent of the annual nitrogen inputs in the three most complete budgets, but a negligible loss was calculated from a less thorough budget for 1969. Uncertainties in the mass-balance estimates and in the validity of certain assumptions involved in calculating denitrification from mass balances prevent us from evaluating the extent to which the above range represents real year-to-year differences.

Denitrification is likely to occur in the sediments of Lakes Mendota and Wingra, but it cannot be quantified at present. Denitrification in the hypolimnion of Lake Mendota accounted for 11 percent of the calculated loading to the lake in 1966. Most of the remaining unaccounted-for nitrogen in the lakes is probably deposited in the sediments. About two-thirds of the annual input to Lake Mendota was assumed to enter this storage, but relatively smaller losses to sediment (14 to 46 percent of the annual inputs) occur in shallow Lake Okeechobee. Only minor amounts of nitrogen are lost from the lakes by fish and weed harvesting.

Accuracy of Nutrient Budgets

The existence of several budgets for Lakes Mendota and Okeechobee permits some qualitative conclusions about the reliability of the analyses, but the likelihood of real differences in inputs from one year to another precludes quantitative statements on this subject. Nitrogen inputs to Lake Mendota (Table A.5 in Appendix A) have increased in each succeeding analysis over the period 1949-1974, from 2.3 to 14.6 g/m^2-yr. Although some increases in loading have undoubtedly occurred over the past 30 years as a result of urban development in the lake's watershed, such large increases seem unlikely. Most of the increases can be attributed to differences in methods of loading rate analysis. The two earliest budgets measured only surface stream inputs, and these differed by nearly a factor of two, even though they were done for succeeding years. The two more recent budgets (1966 and 1974) considered diffuse sources and synthesized budgets from information in the literature, using similar methodologies but different data bases. Inputs in the 1974 budget were 2.5 times those of the 1966 estimate. Presumably the 1974 estimate is more accurate, but even it required many assumptions about diffuse sources. Information on nutrient export rates from various land uses (e.g., urban, forest, cropland) is accumulating at a rapid rate, but the ability to calculate loading rates from diffuse sources accurately is still several years away.

The four budgets for Lake Okeechobee (Appendix A, Table A.1) involved similar measurement techniques, and two of the budgets were done by the same organization for succeeding years (1973-1974 and 1974-1975). Thus the differences in these budgets probably reflect real differences in loading, even if neither budget is absolutely correct. Total nitrogen loadings were 3.2 and 4.3 g/m^2-yr for the two years. On the other hand, independent budget analyses were done on the lake by the South Florida Water Management District and the U.S. EPA for overlapping periods from January of 1973 to spring of 1974. The two agencies used somewhat different methodologies, and measured loadings in those studies were 3.2 and 3.8 g/m^2-yr.

In summary, measurement of nitrogen balances in lakes is still an inexact science. Differences of ± 25 percent in loading rate estimates are common, even when major sampling programs are undertaken. In many cases, estimates of inputs are accurate probably within only a factor of two. Except for losses through surface outflow, nitrogen sinks are even more difficult to quantify.

Watershed Models

River basin or watershed models are more complex than lake models, since several media are involved. The heterogeneity of terrestrial systems is far greater than that of lakes, and a high degree of aggregation is required for the mass balance of the land reservoirs. The many microenvironments provided by different soil types and plant cover complicate the estimation of atmospheric fluxes. The introduction of cultural activities adds even more complexity to this analysis. Furthermore, system boundaries are more difficult to define accurately in these systems than in lakes. Groundwater flows and reservoir sizes are difficult to measure. In situations in which deep seepage can be ruled out or quantified, however, the watershed mass balance can offer considerable information on the accumulation and movement of nitrate in shallow groundwater.

Elevated concentrations (above recommended drinking water standards) of nitrate in water supplies provided impetus for the construction of nitrogen mass balances for two predominantly agricultural watersheds in California: the upper Santa Ana River Basin (Ayers and Branson 1973) and the southern San Joaquin Valley (Miller and Smith 1976). Details of the mass balances on these agricultural watersheds are given in Appendix A, Section 4.

Both of the California river basin studies involved extensive groundwater and soil sampling programs which provided unusually reliable data on aquatic fluxes of nitrogen. The primary purpose of the two California studies was to examine simple mass-balance models for crop nitrogen use and human and animal wastes, in order to suggest management practices and research guidelines. These models were used to produce equations relating groundwater nitrate concentrations to fertilizer application and irrigation water rates. The agricultural mass balances indicated that although the efficiency of nitrogen use by some crop varieties increased slightly between 1961 and 1971, the percentage of nitrogen removed by crops decreased during this period because increases in rates of fertilizer application far outstripped that increased efficiency.

In addition to the mini-models, overall mass balances for the watersheds were constructed. While the basin-wide mass-balance models provide useful information on the relative magnitude of the various sources and sinks for nitrogen, they contain some flaws that can easily occur in mass-balance models. Because the present state of the art is exploratory and tentative, a brief examination of the shortcomings in the California models may help to avoid some conceptual problems in future models.

Although calculations of sources, sinks, and reservoir sizes are displayed in either the body or the footnotes of tables in the two papers, no basis or reference is provided for many of the assumptions. Because of the common tendency for admitted "ballpark" estimates in original reports to become accepted concrete figures in later publications, it is important that assumptions and caveats be explicit. Mass-balance models are subject to constant revision as new information becomes available, and the heuristic value of their construction exceeds the present value of their estimates of fluxes and storages. Without detailed information regarding their construction, the usefulness of the final balances becomes tenuous.

The mass-balance diagrams for the California watersheds in Appendix A (Figure A.2) appear to have inappropriate system boundaries. Specifically, fertilizer is not included as an input to the system in the diagrams, although it is listed as contributing 46 percent of the annual nitrogen flux from the land surface pool to the soil nitrogen pool. The San Joaquin balance, relying heavily on the Santa Ana study, included a similar mass-balance diagram with the same omission. The only way of not including fertilizer as a system source is to fix it industrially within the watershed, but then it should be included in the atmospheric inputs, and calculations indicate it is not. The land surface pool is not clearly described in either study, and there appear to be other inconsistencies in transferring nitrogen into and out of this compartment. Imports and exports of livestock and crop nitrogen from this pool are not explicitly considered in either model, although such fluxes would appear to be important in regions of intensive agriculture. Further discussion of methodological problems concerning this compartment appears in Appendix A.

Table A.10 in Appendix A-4 lists volatilization, denitrification, and crop uptake as sinks for nitrogen in the soil of the two basins. Ayers and Branson (1973) suggest that when these are subtracted from the sources of soil nitrogen, the remainder is available for leaching, increased storage, or future removal by plants. However, the first two of the sinks were estimated arbitrarily as simple percentages of the various inputs, and apparently no calculations from direct measurements were involved in these estimates. Forcing all of the remaining nitrogen into the leaching flux or into change in storage appears inadvisable.

Finally, failure to separate nitrogen pools into subcompartments according to chemical form, at least during initial phases of model construction, may result in a lack of important information in the final mass balance. The relatively labile pools (nitrate, nitrite, and ammonia), which are also the most important as pollutants, are dwarfed by the large pools of atmospheric N_2, soil organic nitrogen, and nitrate in deep groundwater. These refractory pools have long average residence times. In constrast, however, the atmospheric NO_x and ammonia pools, and those for plant biomass and soil inorganic dissolved nitrogen, cycle rapidly. If compartment sizes, average residence times, and similar concepts are to be useful, the model compartments must be chosen judiciously.

Statewide Models

Although the selection of political rather than hydrogeological boundaries for a mass-balance model may rest on tenuous logic, this situation is often imposed on the scientist-planner, and its ramifications deserve some attention. State mass-balance models present two problems in addition to those encountered in watershed mass balances. The first is the need for a higher level of aggregation within a medium. For example, composites of several watersheds must be used; all surface waters are combined; and many cultural activities are lumped. The second problem is the use of artificial rather than natural boundaries for the system. As a result, a statewide model may contain several partial water- and airsheds. Because flows and storages are often reported for natural units (such as whole watersheds), it may be difficult to disaggregate data to apply to the partial watershed.

Mass balances were constructed for this report for Wisconsin and Peninsular Florida (Appendix A, Sections 5 and 6), using statistics available from various state reporting services and data from the scientific literature. The two studies in total required approximately one worker-year of effort; much of this time was spent in ascertaining the types of information available and in gaining access to the data. Clearly, considerable guidance for further research and data gathering can be obtained in this manner at relatively little cost. Verification of such statewide models is, of course, very difficult.

Wisconsin

Because land use in Wisconsin is largely dominated by agriculture, the nitrogen mass balance for the state focused on crop and livestock fluxes of nitrogen. However, Wisconsin differs from the Corn Belt states discussed in Chapter 6 in that the major nitrogen input is from leguminous nitrogen fixation associated with livestock (primarily dairy) industries. Of the 5.85×10^8 kg of nitrogen estimated to be cycled in Wisconsin agriculture yearly, fertilizer supplied 22 percent, nitrogen fixation 61 percent, and bulk precipitation only 7 percent. Crops remove about 65 percent of the total nitrogen cycled, and a major portion of the nitrogen removed by crops (about 68 percent) reappears as animal wastes.

The model centers around an "available soil nitrogen" pool, with inputs to this pool from fertilizer, atmospheric nitrogen, and mineralization of soil organic nitrogen. Outputs from the pool are crop removal, largely by nonlegumes, and losses by leaching and denitrification. The introduction of an available soil nitrogen pool requires estimating a value for net mineralization of soil organic nitrogen, including manure and crop residues. A value of 1 percent per year was arbitrarily used in the Wisconsin model; typical values for net mineralization reported in the literature range from 1 to 3 percent. Use of larger or smaller estimates of mineralization rates would directly change the estimated losses by leaching and denitrification, since those losses were estimated by difference. Of the total nitrogen inputs to the system, nearly one-third is unaccounted for, and is assumed to be lost by these two routes. The largest uncertainties in the model are the mineralization rates of manures, legume residues and soil organic nitrogen, and extent of nitrogen loss by leaching and denitrification. Further, the model covers an area that is heterogeneous with respect to soils, climate, and cultural practices; as a result it gives little information on actual localized problems.

Despite the large uncertainties, several interesting points emerge from this mass balance. For example, in good crop years with favorable weather, corn production mined nitrogen from the soil (i.e., it required more nitrogen than was added in fertilizer), while in poor (dry) years, corn failed to remove all of the applied fertilizer nitrogen. The model does point out that about twice as much nitrogen is imported into the state as is exported in food and feed products; improved use of manures and legume residues might help bring exports and imports more into balance.

From the large size of the soil nitrogen pool, one might expect that a relatively small increase in nitrogen added to the system would cause only a small perturbation in outputs or system storage. Actually, however, much of the soil organic matter exists in a rather refractory reservoir, which is largely unavailable to the soil micro- or macroflora. The portion that actually participates in short-term changes is small, perhaps a few percent, and the effects of increasing fertilizer additions may therefore be felt rather readily in receiving streams or in increased rates of denitrification. The concept of an available soil nitrogen pool as used here accounts for the relatively greater responsiveness of the system to fertilizer nitrogen than the proportional contribution of fertilizer to nitrogen inputs to agriculture would otherwise indicate. For instance, doubling fertilizer use would more than double losses of nitrogen from the system. However, the model also suggests that fertilizer nitrogen does not now cause large-scale (statewide) pollution problems.

Peninsular Florida

Peninsular Florida offers an attractive opportunity for a mass-balance model, since it is hydrologically isolated from the remainder of the continent. This fact allows rather accurate measurements of hydrologic flows. Because of concern about transport of agricultural pests into the state, good records are kept on fluxes of various agricultural commodities into and out of the peninsula. Agriculture in Florida is dominated by citrus and vegetable crops and the production of feeder calves. Legumes are not major agricultural crops, and fertilizer input is far more important than symbiotic nitrogen fixation.

Submodels were constructed to quantify hydrologic, agricultural, and atmospheric flows, and to understand the operation of the system as a whole. Inputs of nitrogen by precipitation exceed outputs by streamflow by a factor of slightly more than two. Unless major unaccounted groundwater flows exist, this finding implies that either the storage of nitrogen in the system is increasing rather rapidly, or that gaseous losses exceed gaseous inputs. A separate atmospheric submodel for fixed nitrogen indicated that the production of NO_x and NH_3 exceeded the return of these gases to the system through atmospheric deposition processes, but the NO_x cannot be considered a true loss from the land/water system, since it is produced from atmospheric N_2 in combustion processes.

An incomplete agricultural submodel indicated that leaching or volatilization losses must be high in Florida's agricultural lands in order to balance nitrogen inputs. Since export in surface runoff is low, this could indicate a potential problem for Florida's deep limestone aquifer, which serves much of the state as the source of drinking water. A citrus submodel indicated that only 31 percent of the fertilizer input was removed in the fruit. In mature groves, where increases in soil organic nitrogen and in tree trunk nitrogen may be very slow, the excess could be nitrified to nitrate and could cause groundwater pollution problems, since groves often occupy aquifer recharge areas.

Examination of the peninsular macromodel indicates an excess of inputs over outputs. Major sources of nitrogen and their percentage contributions to the total input are: precipitation (32), fertilizer (28), nitrogen fixation (10), and the deposition of gases, NH_3 and NO_2 (24). Surface runoff removes only 20 percent of the inputs, and an additional 6 percent is exported in agricultural products. Calculations based on literature values for volatilization and denitrification yield a total loss of only 33 percent of the incoming nitrogen; the remaining 41 percent of the input nitrogen is unaccounted for. If the accuracy of the input data is accepted (the estimates are, if anything, conservative), either denitrification and volatilization are higher in Florida than literature-based calculations suggest, or a slow change in system storage (or seepage to groundwater) is occurring. The average nitrogen content of Florida's extensively leached soils is 0.04 percent, and the total soil pool (top 30 cm) in the system contains about 2×10^{13} g of nitrogen. The unaccounted-for nitrogen would thus cause an increase of 0.7 percent per year in the soil nitrogen pool; such an increase could go undetected for several years. It seems likely, however, that the unaccounted-for nitrogen is partially a reflection of inaccuracies in the data base and underestimates of gaseous losses.

Limitations of Statewide Mass Balances

The main problems encountered in statewide mass balances involve the heterogeneity of the environment, and the difficulties in applying process rates measured in one type of system to the conditions occurring in another. For example, southwestern Wisconsin has different soil types than the eastern portion of the state. Similarly, the Florida peninsula ranges from well-drained, acid sands along the central ridge, to low marshland and pine flatwoods along the coast. The extrapolation of nitrogen fixation or denitrification rates measured in temperate soils to Florida, where no measurements are available, is highly risky. As the level of aggregation in a mass-balance model increases, the data base rapidly becomes more tenuous. In the Wisconsin balance, nearly one-third of the nitrogen input is unaccounted for; the Florida study indicates that 40 percent of nitrogen input is unaccounted for. In both studies, the lack of information on denitrification and volatilization are critical analytical problems. These mass balances suggest that the lack of better knowledge of rates for these processes limits the possibility for determining how and where to monitor for nitrate accumulation and how to take corrective actions, if necessary. On the other hand, statewide balances often can be done at relatively low cost, since a statistical data base exists, and the balances may be useful for broad-scale planning and decision making.

National Level Nitrogen Balance

The principal effects of anthropogenic additions of nitrogen on the environment occur at local and regional scales (e.g., eutrophication, groundwater pollution) and at the global level (e.g., effects of a change in the atmospheric N_2O pool on stratospheric ozone). With the possible exception of the contributions of nitric acid to the acidity of rain, there do not appear to be any significant nitrogen pollution issues that a national-scale nitrogen mass balance could address. Even acid rainfall is not yet a national problem; for the most part it is confined to the eastern part of the United States. The role of nitrate and nitrite in formation of nitrosamines, with the associated risk of cancer, is an issue of national concern, but this problem does not seem amenable to analysis by mass balance. For these reasons, we saw little point in deriving a national-scale mass balance for nitrogen. There are no further conceptual difficulties in deriving a national balance beyond those already described in the watershed and statewide balances; but, of course, the large size and heterogeneity of the United States would exacerbate the problems of aggregation and data availability encountered in the smaller-scale models.

A previous study by the National Research Council (NRC 1972) developed a highly simplified nitrogen mass balance for the United States (see Table 5.3). That report concluded that large data gaps existed in 1972, and except for fertilizer additions, values in the table were considered to be gross estimates. Most probably, large data gaps still exist. In Chapter 6 of this report, we have revised some of the estimates of fluxes used in the NRC (1972) report, especially the inputs from biological fixation (see Table 6.1). However, since we did not attempt a complete balance, the comments here are based on the earlier study and Table 5.3.

TABLE 5.3 Estimates of Nitrogen Inputs and Returns to the Total Land Area of the United States, 1970 (millions of metric tons of N)[a]

Annual Inputs to Soil Compartment	
Nonsymbiotic N_2 fixation	1.2
Symbiotic N_2 fixation	3.6
Rainfall	5.6
Chemical fixation	7.5
Mineralization of soil organic nitrogen	3.1
Total input	21.0
Utilization in Plant-Animal-Human Food and Fiber Chains	
Production of fiber	0.2
Production of sugar	0.6
Production of plant protein	0.9
Production of animal protein	15.1
Total	16.8
Total input	21.0
Not utilized in food chains	4.2
Fate of Nitrogen in Food and Fiber Chains	
Excreted by humans	1.2
Excreted by animals	4.2
Other nitrogenous wastes[b]	15.6
Total	21.0
Annual Returns to Atmospheric Compartment	
As ammonia or oxides to atmosphere moisture	5.6
By denitrification after loss to waterways	5.0
By denitrification from soil	8.9
Total	19.5
Total input	21.0
Net Retention in Soil and Water per Annum	1.5

[a] The values are only estimates.

[b] Total input minus that excreted by humans and animals.

SOURCE: National Research Council (1972).

A few interesting conclusions can be reached by examining the national mass balance. Rainfall contributes more nitrogen (5.6 Mt/yr) to the soil compartment than does symbiotic and nonsymbiotic nitrogen fixation combined (4.8 Mt/yr), although those estimates of biological fixation are likely to be low. Chemical fertilizer is a somewhat more important input (7.5 Mt/yr in 1971), and this source is still increasing in importance (see Chapter 6). Nitrogen excreted by animals (mainly cattle) was nearly four times the amount excreted by humans in the United States in 1970. The portion of animal excretion that occurs in confined areas (feedlots) rather than open pastureland has increased sharply in the past two decades, and animal waste disposal problems were cited as a major concern by the NRC study. Finally, the national balance reveals that most of the nitrogen flows in the agricultural sector, and thus most of the related adverse environmental impacts, were asociated with the production of animal protein (16.8 Mt out of a total of 21.0 Mt/yr in the plant-animal-human food and fiber chains). The NRC (1972) panel concluded that if a shift occurred toward consumption of vegetable protein (away from meat), one result would be an effective reduction of nitrate pollution. They noted, however, that such a change would involve very complex social trends of which environmental concerns were but a small part (see Chapter 12 of this report).

Global Mass Balances for Nitrogen

Mass balances for nitrogen at the global scale have several methodological advantages. The system boundaries are the most natural, and the degree of aggregation is the highest, of nitrogen models on all scales. Furthermore, most of the globe is covered by oceans, which are considerably more homogeneous than terrestrial environments, and fewer observations are required to define the mass balance of the oceans. Also, small-to-middle-scale atmospheric transport processes (e.g., between industrial and rural areas) can be ignored, and attention can be focused at the scale of transport processes between maritime and continental air masses. Balancing these advantages, however, is the reality that basic data on nitrogen fluxes and reservoir sizes are lacking for most of the Southern Hemisphere, for most developing and communist-bloc countries of the Northern Hemisphere, and for much of the world ocean.

Lack of data has not discouraged the development of several global nitrogen mass balances during the past quarter century, however, and useful insights haves been gained from such efforts. Most of the global balances actually have been refinments of pre-existing balances, rather than radically new attempts. Clarke's (1924) geochemical data was used by Hutchinson (1954) to produce the first sophisticated global nitrogen balance, and Delwiche (1965, 1970) modified Hutchinson's budget somewhat. Robinson and Robbins (1971) emphasized atmospheric fluxes in a model that is controversial because of the differences in its estimates of major fluxes compared to other analyses. Burns and Hardy (1975) extended the global mass balance of nitrogen to include recent data on nitrogen fixation. Söderland and Svensson's (1976) balance is probably the most ambitious analysis to date, and it forms the basis for a revised model in Appendix A, Section 7, which includes additional data.

Like the models done on intermediate scales, the global mass balances indicate that if soil nitrogen is at steady state, denitrification must be an important sink for fixed nitrogen. Because of the difficulties in measuring denitrification directly, few data are available (see Chapter 2). Consequently, most mass balances calculate denitrification by difference (see Table A.25). As discussed earlier in this chapter, such calculations are less desirable than direct measurements, because they require assumptions that are difficult or impossible to verify. In the present case, uncertainties in each of the directly estimated flows compound the uncertainty of the final estimate for denitrification. Furthermore, assumptions of steady state for various large pools (e.g., for soil and sediment nitrogen) cannot be verified in the short term. As we have discussed earlier in this chapter and in Chapter 2, rates of denitrification and of the sum of all processes of N_2 fixation need to balance only over time scales of thousands of years in order to prevent large changes in the sizes of major reservoirs. The present uncertainties suggest that none of the calculated denitrification rates in the global mass balances can be regarded as accurate. Unfortunately, the estimates based on direct measurements (see Table A.25) have such a limited data base that they cannot be regarded as more reliable than the estimates based on difference calculations.

In the Söderlund and Svennson balance, N_2O evolution from land surfaces was estimated as 16 to 69 Mt N/yr, based on two experiments reported in the literature. In comparison, CAST (1976) estimated this flux to be 7 Mt N/yr, based on a single experiment. The paucity of data upon which the estimated global N_2O flux is based is apparent. According to the Söderlund-Svensson model, 10 Mt N_2O-N/yr is lost to the stratosphere, where it participates in ozone-consuming photochemical processes. This amounts to only 3 to 8 percent of the estimated nitrogen that undergoes denitrification annually. Clearly a small change in the global denitrification rate, or in the $N_2O:N_2$ ratio of the denitrification products, could lead to a large changes in the delivery of N_2O to the stratosphere.

The NO_x and NH_3 reservoirs and fluxes in the troposphere now (i.e., in the Söderlund and Svensson [1976] model) appear to be much smaller than those given in the Robinson and Robbins (1971) model. Because the differences between the Robinson-Robbins results and the Söderlund-Svensson results are so great, and because the two sets of results have significantly different implications regarding the relative importance of natural versus anthropogenic sources of these gases, a brief discussion of the reasons for the differences is presented below. Table 5.4 compares reservoir sizes, sources, sinks, and residence times for ammonia (NH_3 and particulate NH_4^+) and NO_x given in the two models. The large differences in reservoir sizes are explained simply by recent acquisitions of more reliable data on concentrations of these gases in remote areas, such as the tropics and marine environment, and by the fact that Söderlund and Svensson considered vertical variations in ammonia concentration within the troposphere.

Differences in fluxes are more complicated to explain and relate to differences both in data bases and in the way the fluxes were calculated. Robinson and Robbins (1971) calculated the flux of ammonia-N to the atmosphere to be 870 Mt/yr, by difference, to balance estimated scavenging mechanisms (gaseous deposition, rainfall, and dry fallout of particulate NH_4^+). The large estimate for gaseous deposition (680 Mt/yr) is a direct consequence of the high global average concentration of NH_3 (6 ppb, or 27 Mt in the entire atmosphere) assumed by these authors. Gaseous deposition was calculated as the product of the global average concentration and a deposition velocity of 1 cm/sec (the concept of deposition velocity is discussed in the atmospheric section of Chapter 6). Söderlund and Svensson (1976) calculated deposition of NH_3 to be much smaller, although they used the same approach and a similar deposition velocity (0.8 cm/sec). However, they used much lower concentrations for NH_3, which varied according to geographical region (see the atmospheric section of Chapter 6). Robinson and Robbins estimated dry fallout of NH_4^+ aerosol to be 25 percent of rainfall deposition; Söderlund and Svensson calculated this flux from average concentrations of particulate NH_4^+ over different geographical regions and a deposition velocity of 0.3 cm/sec, which they obtained from the literature. Both sets of authors relied heavily on compilations of precipitation chemistry by Eriksson (1952), and both sets of authors accounted for latitudinal variations in deposition. However, Söderlund and Svensson made separate calculations for rainfall deposition over terrestrial and oceanic areas, whereas Robinson and Robbins did not differentiate between these areas. In spite of the much larger surface area of the oceans compared to land, Söderlund and Svensson computed a lower ammonia flux over the oceans (8 to 25 Mt/yr) than over land (30 to 60 Mt/yr). Intuitively, this trend makes

TABLE 5.4 Comparison of Two Global Nitrogen Balances In Regard to Ammonia and Nitrogen Oxides

	Ammonia		NO_x	
	Robinson and Robbins (1971)	Söderlund and Svensson (1976)	Robinson and Robbins (1971)	Söderlund and Svensson (1976)
Reservoir size (Mt)[a]				
Gas	27	0.9	14	1-4
Aerosol	3.7	1.8	--[b]	0.5
Residence time (days)				
Gas	∼7	1-4	4	2-8
Aerosol	--	7-19	--	4-20
Sinks (Mt/yr)				
Gaseous deposition	680	67-134	132	25-67
Rainfall	150	38-85	75	18-46
Particulate dry fallout	40	5-17	20	0.3-2.9
Atmospheric conversion of NH_3 to NO_x	--	3-8	NA[c]	NA
Total	870	113-244	227	43-116
Sources (Mt/yr)				
Direct estimates				
Combustion	--	4-12	15	19
Other direct estimates	--	22-41	--	4-22
Calculated sources (by difference)	870	87-191	212	20-75

[a] Gases: NH_3 and NO_x (= NO plus NO_2)
Aerosols: particulate NH_4^+ and NO_3^-

[b] Not considered or not reported

[c] NA = not applicable

sense in view of the large terrestrial sources of ammonia. Söderlund and Svensson accounted for 26 to 53 Mt/yr of ammonia sources from combustion and volatilization, leaving 87 to 191 Mt/yr of unknown sources required to balance the estimated sinks.

Differences in fluxes of NO_x between the two models are similarly explained. The much larger reservoir sizes in the Robinson and Robbins model "forced" much larger fluxes of gaseous and particulate deposition than those calculated by Söderlund and Svensson. Separate calculations of NO_2 absorption and nitrate deposition in rainfall and dry fallout over oceanic and terrestrial areas again led to lower fluxes in the Söderlund and Svensson model. The smaller value for total sinks of NO_x in the latter model thus required a smaller value for total sources to balance the flows, as indicated in Table 5.4.

Estimates of the global rate of biological nitrogen fixation have greatly increased in recent balances, mainly because of the greatly expanded data basis that has resulted from the widespread use of the acetylene reduction bioassay (see Chapter 4). Burns and Hardy (1975) increased Delwiche's (1970) estimate of 54 Mt/yr to 139 Mt/yr, and Söderlund and Svensson (1976) further increased the estimate to 169 to 269 Mt/yr, with the range representing uncertainties in oceanic fixation.

The best present estimate is that anthropogenic nitrogen fixation (ammonia fixation plus NO_x emissions) accounts for about 20 to 35 percent of the global nitrogen fixation (see Chapter 2 and Appendix A, Section 7). If fixation by legumes is considered to be negligible in the absence of human activities, natural biological fixation may be only 50 to 60 percent of the total fixation rate. The uncertainties in the data are large, but anthropogenic processes are clearly an important factor in global nitrogen fixation.

The most striking characteristic of global mass balances is the enormous size of the relatively inert reservoirs of nitrogen (e.g., deep sediments, atmospheric N_2) relative to the species that participate in the biogeochemical cycle. Primary rocks contain slightly less than 98 percent of the total global nitrogen in tightly bound forms, and about 2 percent occurs in the atmosphere and ocean as N_2, which has low biological availability. Less than 100 out of 10^6 nitrogen atoms exist as labile, fixed forms. It is clear that small changes in the large, relatively inert pools, caused by changing tectonic or climatic conditions, could alter significantly the sources or sinks for the global system. Furthermore, the small reservoirs of fixed nitrogen forms in the atmosphere have the shortest turnover times. This suggests potential instability and variability in these compartments. This variability implies that intensive monitoring is required for accurate modeling of the flows through these compartments.

CONCLUSIONS

Authors and students of mass balance models should heed Beadle's (1974:3) "Declaration of faith...in the supreme value of imaginative guesswork, provided only that the guess is based on a background of knowledge and is not accepted without supporting evidence as a certain step toward the truth." With this philosophy in mind, mass balances can be an effective tool for studying complex biogeochemical cycles such as that of nitrogen. The potential impacts of anthropogenic nitrogen fixation on denitrification or pollution of groundwater by nitrate can emerge from even cursory examination of such models, and clues to the heretofore unexpected importance of specific nitrogen transformations or fluxes in a given system can result from the models. Some verification for experimentally determined biogeochemical transformation rates may be achieved, at least on small-scale models. The usefulness and accuracy of mass-balance models will undoubtedly improve as they become more widely used as aids for both planning and analysis. Specifically, the fact that crude models indicate major data gaps and thus guide in assigning research priorities and in designing monitoring programs inevitably leads to more accurate "second-generation" models.

It is difficult, if not impossible, to choose a most useful or reasonable size for a nitrogen mass balance. Rather, the suitable level of aggregation reflects the purposes of the model. Detailed information on nitrate accumulation or net soil mineralization rates may be restricted to lake or watershed models. Conversely, atmospheric processes may be best studied on a global or regional scale, despite or perhaps because of the increased aggregation. Regional models may provide useful tools to organize data generated by a many different agencies and scientific disciplines. It is important, above all, to consider the nitrogen mass balance as a process, rather than as a final product.

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CHAPTER 6

NITRATE POLLUTION: SOURCES AND ENVIRONMENTAL PROCESSES LINKED TO EXCESSIVE NITRATE IN THE ENVIRONMENT

For centuries, human activities have had important influences on the nitrogen cycle in local ecosystems. Although modern industrial societies often look back on earlier agrarian ages in idyllic terms, such societies were in their own way as disruptive of ecosystems as are many modern practices. Preindustrial societies, however, could perturb the nitrogen cycle only on a relatively limited geographic scale, while the activities of today's human populations can affect large sections of the biosphere.

Human impacts on the nitrogen cycle begin either with a source of input of fixed nitrogen into the environment or with a major perturbation of the nitrogen cycle. The net result is a change in either the sizes of or the transfer rates to or from one or more pools of fixed nitrogen in the environment. The pollution problems most pertinent to this report ensue when an excessive amount of nitrate or an associated nitrogen compound accumulates in one or more compartments of the environment. Examples include potentially toxic amounts of nitrate in drinking water, food, or forage; excessive nutrient enrichment of lakes, rivers, or coastal waters; nitric acid in precipitation; or increased nitrous oxide content of the atmosphere. The possible health and environmental consequences of such accumulations are described in Chapters 8 and 9. Prevention of adverse impacts requires an understanding of the sources of fixed nitrogen, and of the the processes of environmental transport and transformation that link sources to observed perturbations of nitrogen balances.

SOURCES OF FIXED NITROGEN

On a global scale, biological processes (principally nitrogen fixation and the mineralization of organic nitrogen to ammonia and nitrate) are the largest sources of inorganic nitrogen compounds in the environment. On a local and regional scale, however, inputs resulting from industrial and agricultural activities often exceed those from natural sources. In general, the most important anthropogenic sources of fixed nitrogen are fixation by cultivated legumes, combustion, and the industrial synthesis of ammonia. Industrially fixed nitrogen may enter the environment either as fertilizer (the major use of ammonia), or in waste streams from certain industrial processes. Some of the nitrogen fixed by combustion is returned to the land in precipitation. Animal manures and human wastes, two additional important sources, represent recycled transfers of nitrogen that are also anthropogenic in origin.

Table 6.1 presents quantitative estimates of the inputs of fixed nitrogen to the United States for 1975. The estimate of 12 million metric tons (Mt) for biological nitrogen fixation is considerably larger than the 4.8 Mt attributed to this source in an earlier (1972) study by the National Research Council. Our revised estimate is based on fixation rates reported by Burns and Hardy (1975), and on other information in this report; for discussion, see Chapters 2 and 4, and section 7 of Appendix A. The table does not include nitrogen fixed by combustion as a specific input; about 6.5 to 7.0 Mt N/yr are fixed by combustion in the United States, but only a portion of that nitrogen is removed from the atmosphere within the national boundaries (see the section on atmospheric sources later in this chapter).

It is important to avoid double-counting when compiling such source inventories. If a list of sources does not consider the actual routes of transfer of nitrogen within the agricultural-industrial system, the total may well overestimate actual nitrogen inputs. For example, human wastes and animal manures may be locally important sources of pollution; but on the national scale, they represent major internal transfers of nitrogen that is accounted for elsewhere in the list of sources (e.g., as leguminous fixation or fertilizer). Many earlier summaries of national sources of nitrogen, however, have treated such wastes and crop residues as additional sources of input, rather than as transfers within the system (e.g., Stanford et al. 1970, Viets and Hageman 1971, Parr 1973, Frere 1976).

While it is not a complete national-scale mass balance for nitrogen, Table 6.1 attempts to avoid such double-counting by distinguishing between sources and internal transfers. No net transfer by mineralization from the soil organic nitrogen pool is included here, on the assumption that an equivalent amount of organic nitrogen is returned to the soil each year in crop residues and wastes.

As Table 6.1 shows, 19.5 Mt, or 65 percent of the total of 29.9 Mt/yr of fixed nitrogen inputs, originates from human activities. Sixty-four percent of that anthropogenic

TABLE 6.1 Inputs and Major Transfers of Fixed Nitrogen for the United States in 1975.[a]

Source or Transfer	Amount of Nitrogen	Amount Due to Human Activities
	(Mt N/yr)	
Biological Nitrogen Fixation[b]		
Tilled Land		
Nonleguminous fixation	0.7	
Leguminous fixation	4.4	
Pasture and Range	2.9	
Forest and Federal Lands	3.8	
Other Land	0.2	
Total	12.0	4.3[c]
Other Inputs of Fixed Nitrogen		
Fertilizers	9.4	9.4
Other Industrial Fixation	3.1	3.1
Precipitation[d]	5.4	2.7
Total	17.9	15.2
TOTAL INPUTS	29.9	19.5
Major Internal Transfers of Nitrogen		
Uptake by Crops[e]	16.8	16.8
Human Wastes[f]	1.3	1.3
Animal Wastes[f]	5.3	5.3

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[a] Excluding Alaska and Hawaii.
[b] Estimates are calculated by multiplying fixation rates for different land use categories (Burns and Hardy 1975) by land area in the United States in each category (U.S. Department of Agriculture 1971).
[c] Calculated by assuming an average rate of fixation in the absence of human activity of 10 kg N/ha-yr for all land of the United States and subtracting calculated background fixation (7.7 Mt N/yr) from the total of background plus anthropogenic contributions.
[d] Inputs from precipitation calculated using an average value of 7 kg N/ha-yr for the total land area of the United States (7.7 x 10^8 ha). Anthropogenic fraction was arbitrarily assumed to be 50 percent.
[e] Based on estimates in National Research Council (1972).
[f] Estimates from Frere (1976).

total is industrially fixed nitrogen, principally fertilizer. The estimates of human contributions via precipitation and biological nitrogen fixation are significantly more uncertain than the estimates for other sources. The anthropogenic component of biological fixation was computed by assuming that in the absence of human activity the average rate of fixation for all land types would be 10 kg N/ha-yr (Burns and Hardy 1975), over the 7.7 x 10^8 ha of land in the United States. The resulting estimate of 7.7 Mt/yr of "background" nitrogen fixation was then subtracted from the estimated total to give the human contribution. Less information was available to determine the extent to which, on the average, human activities contribute to the nitrogen content of precipitation. However, since significant inputs to the atmosphere are known to occur as nitrogen oxides from combustion and as ammonia from animal wastes and fertilizers, we chose 50 percent as an arbitrary but reasonable estimate of the anthropogenic share of this flux. Because a significant part of the nitrogen in precipitation is derived from other inputs listed in the table, inclusion of this item as a source represents some double-counting. We cannot, however, determine the fraction of the atmospheric input that should more properly be considered an internal transfer.

Characteristics of Major Sources

Most nitrate-related environmental impacts occur on local or regional scales, rather than on the national scale. The nature of those impacts is usually quite closely related to the nature and spatial distribution of the sources. For example, some point sources of nitrogenous wastewater streams (such as sewage outfalls or industrial effluents) can cause localized but intense pollution. Other inputs, such as emissions of nitrogen oxides from combustion, may originate with "point" sources but can contribute to nitrate problems over large areas, because of the transport and transformation processes typically associated with such emissions. On the other hand, dispersed (nonpoint) sources, such as agricultural operations, are often responsible for pollution of groundwater or surface waters and for the release of nitrous oxide.

Point Sources

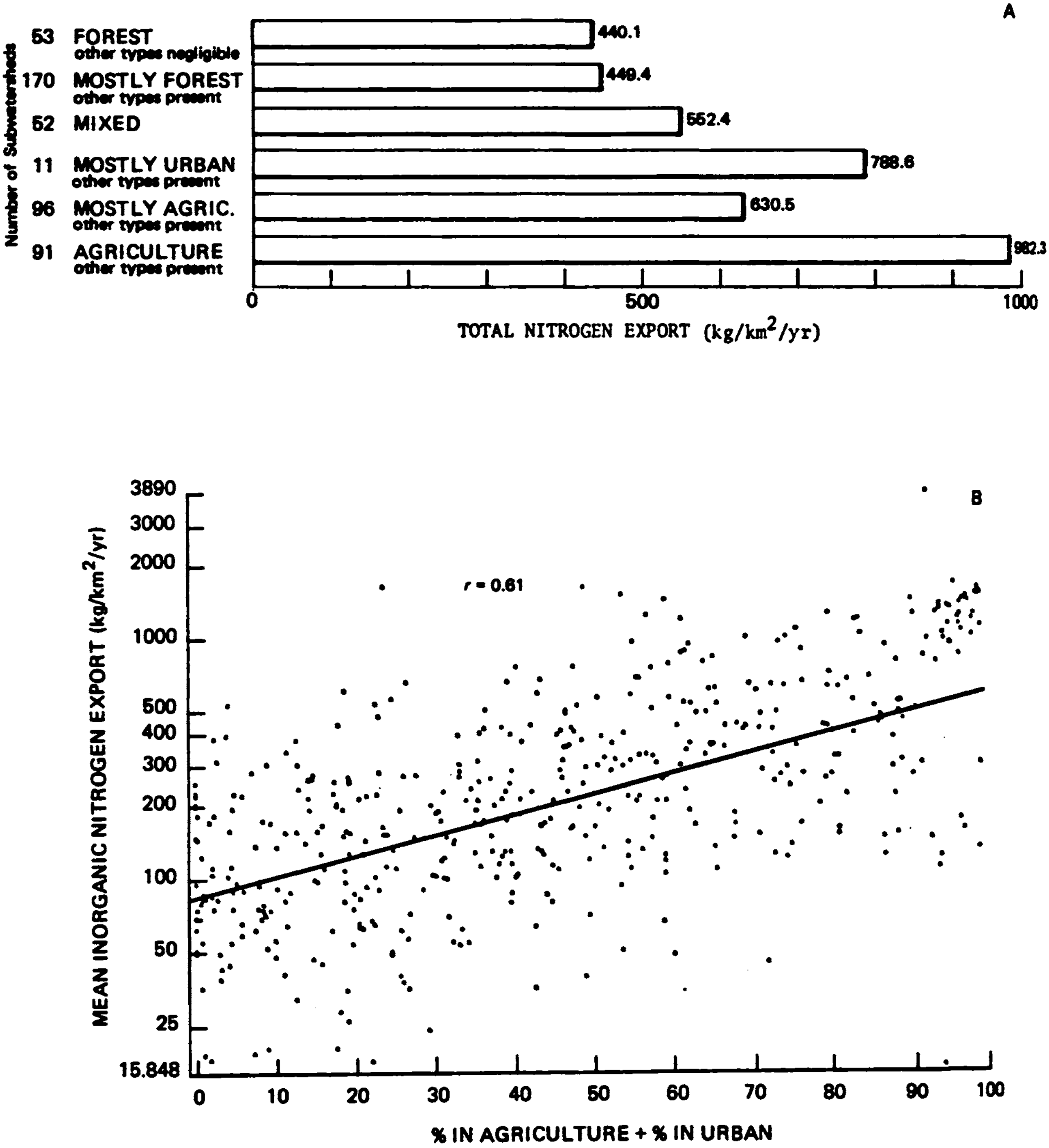
Most of the nitrate pollution problems that are traceable to point sources have been thoroughly reviewed elsewhere (see, for example, National Commission on Water Quality [1975]). The U.S. Environmental Protection Agency has already established effluent limitations or other regulations that apply to many point sources. Because point sources of nitrogenous wastes represent a relatively small fraction of nitrogen inputs to surface and groundwaters on a national scale, and because the problems related to such sources are well-defined and largely regulated, only a brief summary of pollution by nitrogen in sewage and industrial wastes is presented in this chapter.

Nonpoint Sources

In contrast, so-called "nonpoint" contributions to water pollution, including urban stormwater runoff, leaching and surface runoff from croplands, and similar dispersed sources, have generally been more difficult to define quantitatively, and control techniques for such sources have been less readily proposed. In terms of nitrogen inputs to surface and groundwaters, nonpoint sources make by far the largest contributions (Loehr 1974). The National Commission on Water Quality (1975) estimated that of 5.1 Mt of nitrogen entering navigable streams by 1977, 93 percent would come from nonpoint sources, and that 82 percent of the nonpoint pollution would be from agricultural activities (including livestock operations). One major emphasis of this chapter is therefore on such sources.

Knowledge of the routes and rates of transport and of the temporal patterns of discharge is essential to an understanding of nitrate pollution from nonpoint sources. Pisano (1976) equated nonpoint pollution with surface runoff, but others (e.g., Lin 1972, Uttormark et al. 1974, Stewart et al. 1975) have included surface runoff, subsurface leaching, and transport through groundwater as the important routes. While it is more reasonable to consider all three vectors as components of nonpoint pollution, to do so further complicates the identification and quantification of sources. A general discussion of these transport processes was presented in Chapter 3; case studies in this chapter attempt quantitative assessments for some specific sets of environmental conditions and sources of nitrogen.

The heterogeneity of soils and of hydrologic characteristics from site to site make general quantitative relationships for nonpoint pollution difficult to define. Several studies, however, have shown a clear correlation between land use and nitrogen levels in surface waters. An analysis by Omernik (1976) of inorganic and total nitrogen data from 473 nonpoint drainage areas in the eastern United States indicated that, on the average, streams draining agricultural lands had about five-fold higher total nitrogen concentrations than those from forested watersheds (Figure 6.1, Table 6.2). Inorganic nitrogen comprised a larger fraction of the total in streams with larger percentages of land in agriculture. However, because of the variability of watershed characteristics and stream flows, comparisons of



SOURCE: Omernik (1976).

FIGURE 6.1 Relationships between land use and exports of nitrogen in streams. (A) indicates relative total nitrogen exports for six classes of land use, and (B) relates the percent of watersheds in the two largest-contributing land uses to average inorganic nitrogen exports.

TABLE 6.2 Relation Between Annual Loadings of Nitrogen to Streams and Land Use, as Determined by Two Studies

Land Use Category	Nitrogen Loadings, kg N/ha-yr			
	Inorganic N		Total N	
	Omernik (1976)	Uttormark et al. (1974)	Omernik (1976)	Uttormark et al. (1976)
Forest	1.3	1.6 (0.5-3.0)[a]	4.4	2.5 (1.0-5.0)
Mostly forest	1.8	--	4.5	--
Mixed	2.9	--	5.5	--
Mostly urban	5.4	2.0 (1.0-5.0)	7.9	5.0 (2.5-10)
Mostly agriculture	3.7	--	6.3	--
Agriculture	7.4	5.0 (1.0-10)	9.8	5.0 (2.0-10)

[a] Numbers in parentheses are high and low values, available only from the study by Uttormark et al.(1974).

areally weighted export rates (e.g., in kg/km^2-yr) are probably a more reliable index of the relative pollution potential of lands subject to different uses than are comparisons of nitrogen concentrations per se. The average total nitrogen export from agricultural watersheds reported by Omernik (1976) was only 2.2 times greater than from forested watersheds. Loadings from urban watersheds were about four times greater than those from forests. Uttormark et al. (1974) reported similar but somewhat lower nitrogen levels related to land uses on the basis of an extensive literature survey (see Table 6.2).

The case studies presented below are concerned chiefly with fertilized croplands, and with attempts to determine the contributions of specific sources of nitrogen to pollution problems. Viets (1975) reviewed the extensive published literature on nitrogen pollution from fertilized lands; he concluded that the data base is still inadequate to support general statements, particularly about the environmental hazards of fertilizers, because of the diversity of soils, climate, and agricultural practices. This same diversity of problems also prevents this report from examining all, or even many, of the cases in which nitrate pollution may occur. Instead, we have chosen some specific examples on which there has been sufficient recent research to permit scientific assessment of the contributions of specific sources to particular environmental impacts. Three rather different cases are presented: nonirrigated production of corn in the Midwest; irrigated agriculture in California; and production of potatoes, an irrigated, heavily fertilized specialty crop. The chapter also briefly examines pollution by animal wastes, the impacts of land disposal of nitrogenous wastes, nitrogen contributions from urban stormwater runoff, and pollution from septic tanks.

Atmospheric Sources

The third major class of sources examined here is atmospheric inputs. The flux of fixed nitrogen entering terrestrial and aquatic systems in precipitation over the contiguous United States is estimated (Table 6.1) at 5.4 Mt N/yr; this flux is comparable to the 5.3 Mt of nitrogen in animal wastes, or to the estimated 5.1 Mt of nitrogen entering navigable streams each year. Nevertheless, relatively little information is available to support specific quantitative assessments of the nature and significance of specific sources of the nitrogen in precipitation, or of the influence of atmospheric transport and chemical transformations on the forms and amounts of nitrogen deposited in various locations. The final section of this chapter examines sources of ammonia and nitrogen oxides, and factors that affect the spatial and temporal patterns of distribution of nitrogen compounds in precipitation. A major emphasis of the section is an assessment of the contribution of nitrates (nitric acid) to the acidity of rainfall.

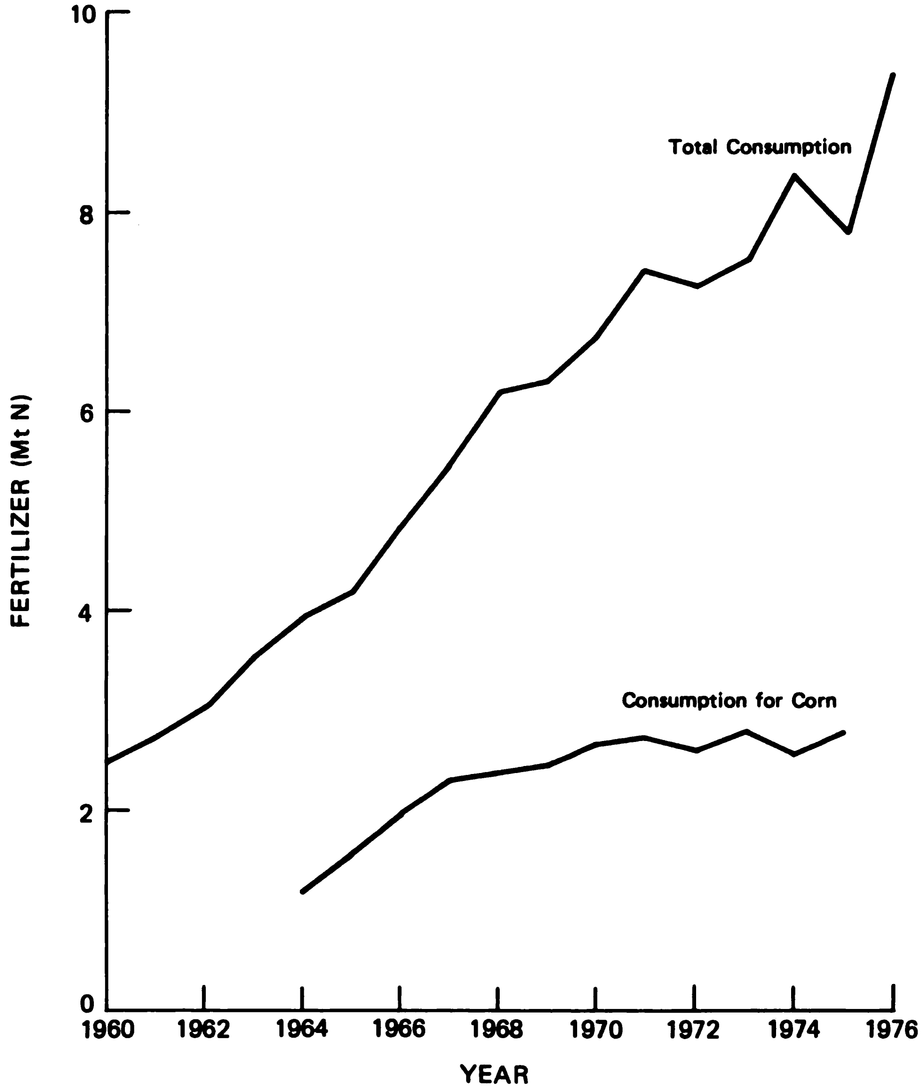
NITRATE POLLUTION FROM FERTILIZED CROPLANDS

The largest single anthropogenic input of nitrogen in Table 6.1 is fertilizer. Use of chemical fertilizers in the United States has grown rapidly since World War II; Figure 6.2 shows the growth in nitrogen fertilizer sales for the period 1960-1975. The figure also presents data for fertilizer use on corn (maize), a crop that accounted for 2.8 Mt of nitrogen fertilizer, or 30 percent of the national total, in 1975. No other single crop receives a comparably large share of fertilizer applications; in 1975, wheat received 0.85 Mt and cotton, 0.3 Mt of nitrogen, respectively. Figure 6.3 illustrates the geographical distribution of fertilizer applications in the United States in 1970. As the figure indicates, two areas of the heaviest use are the so-called "corn belt" of the Midwest, and the central valley of California. The corn belt is characterized by largely nonirrigated cultivation of a few crops (chiefly corn) in extensive monocultures; California agriculture, in contrast, is highly diversified, and the semi-arid climate of the region requires irrigation for economically successful production of most crops. The contrasting character of cropping practices, climate, and soils of these two regions have produced some marked differences in the nature of nitrate-related pollution problems encountered in each area; the specifics of these problems make up the substance of the two case studies that follow.

Case I: The Corn Belt

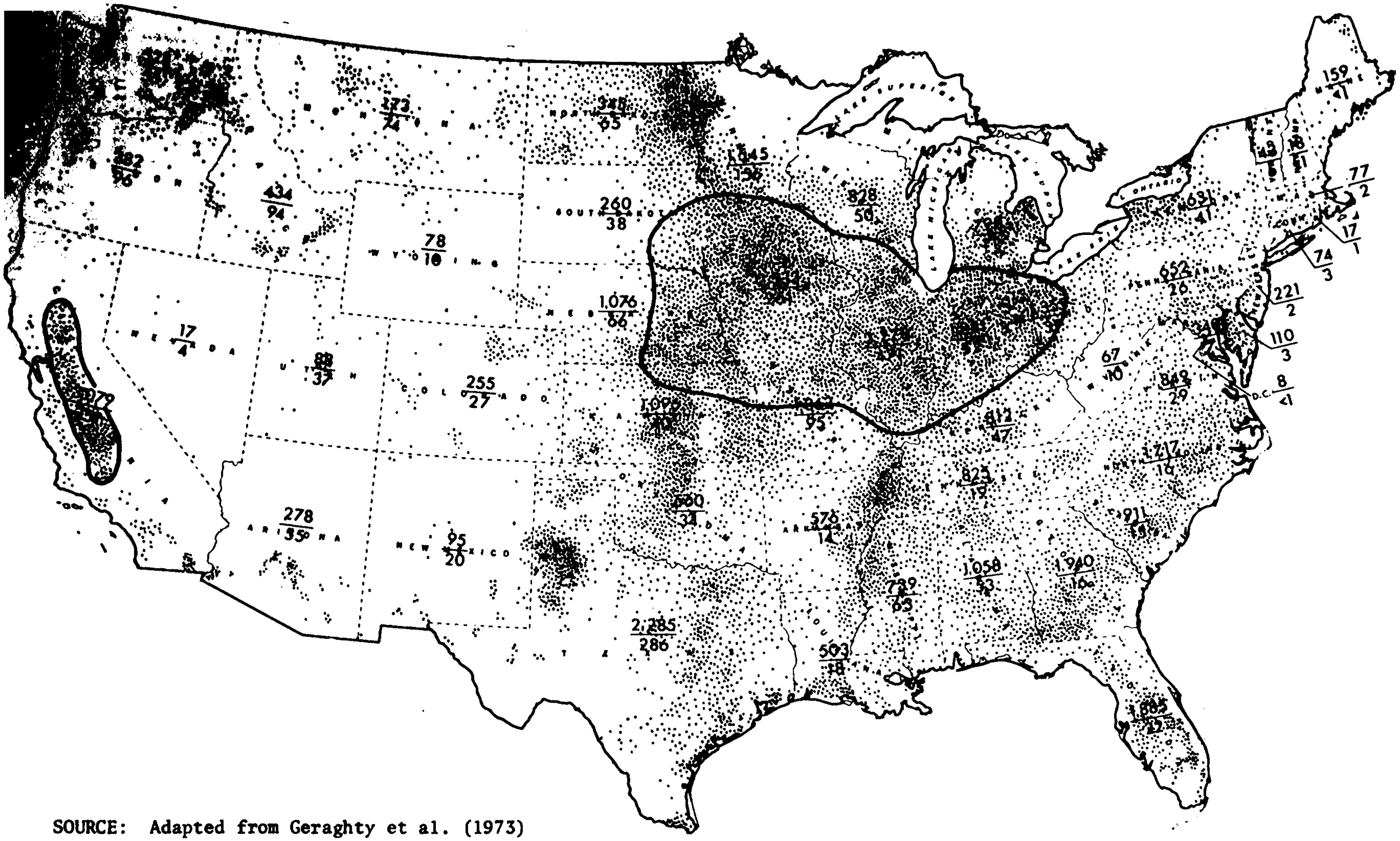
Figure 6.4 depicts nitrogen fertilizer application rates for corn (maize) production in the five major corn-producing states for the period 1964-1975. Nearly 60 percent of the total harvested corn area (13.7 million hectares in 1973) and 53 percent of the nitrogen fertilizer use on corn (1.7 Mt) was in Iowa, Illinois, Indiana, Minnesota, and Ohio. For the United States as a whole, fertilizer use on corn increased from 1.24 Mt of nitrogen in 1964 (56 kg/ha) to 2.78 Mt (111 kg/ha) in 1973. In general, rates of fertilizer use were maximum between 1968 and 1972 and fell off slightly by 1975; an exception was in the irrigated portion of the corn belt, in western Nebraska and Kansas.

Prior to the period shown in Figure 6.4, fertilizer application rates had increased steadily for two decades, in parallel with an increasing trend in corn yields per



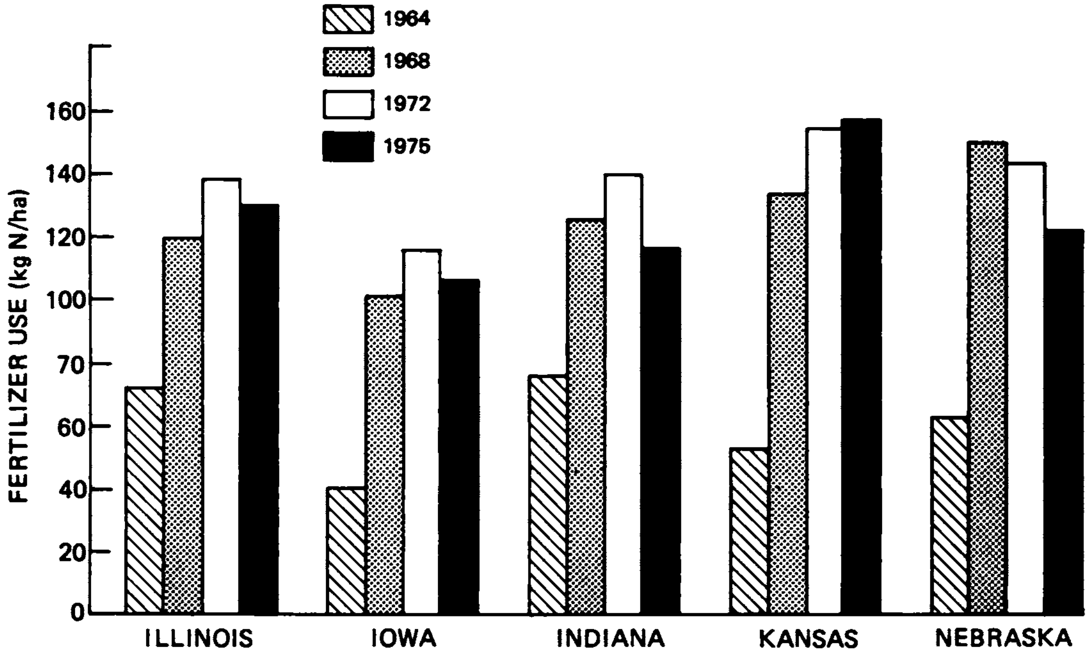
SOURCE: Data obtained from USDA (1976).

FIGURE 6.2 Consumption of nitrogen fertilizer in the United States, 1960-1976.



SOURCE: Adapted from Geraghty et al. (1973)

FIGURE 6.3 Geographic distribution of fertilizer use in the United states, 1969-70. Each dot represents 4,000 fertilized hectares. Enclosed areas indicate the approximate regions discussed in case studies in the text: the midwestern corn belt, and the central valley of California. Numbers within states indicate total fertilizer use (upper number) and phosphate use (lower number), in thousands of tons.



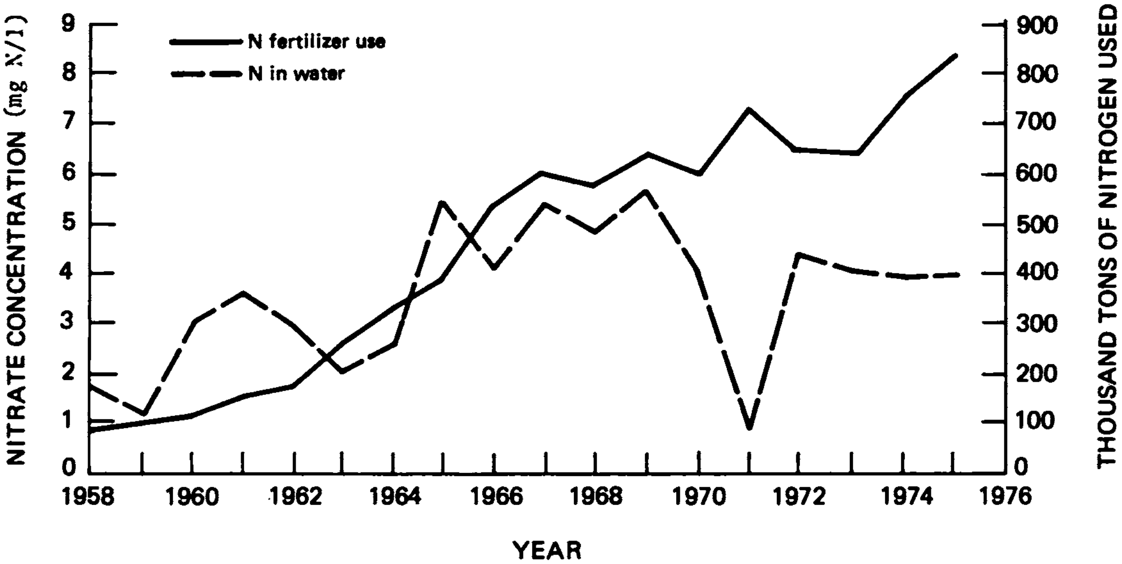
SOURCE: Data obtained from USDA (1976).

FIGURE 6.4 Rates of application of nitrogen fertilizer to corn in five corn belt states, 1964-1975.

hectare. During the same period, the concentrations of nitrate-nitrogen in many streams in the Midwest exhibited a similar upward trend. However, as Figure 6.5 shows, the rate of fertilizer use in Illinois continued to increase throughout the interval shown, while the upward trend in nitrate in the Kaskaskia river peaked in 1969, but has remained relatively steady at a somewhat lower level since then. In portions of the corn belt, especially areas with clay-pan soils and shallow water tables, nitrate pollution of well waters also has been an important problem (see Chapter 3 for data and discussion).

The correlation between growing use of fertilizer nitrogen and increasing nitrate concentrations in surface waters sparked a heated debate over the magnitude of impacts of fertilizer nitrogen on water quality in the corn belt. In a paper presented at the 1968 meeting of the American Association for the Advancement of Science, Commoner (1970) concluded that about half of the nitrogen in surface waters came from fertilizers, and suggested that the use of fertilizer might need to be restricted in order to preserve water quality. This presentation focused national attention on the issue, and prompted responses from agricultural scientists who disagreed with Commoner's point of view. The debate continued in scientific journals (e.g., Kohl et al. 1971, Hauck et al. 1972, Kohl et al. 1972), in scientific meetings, and in hearings before administrative agencies, such as the Illinois Pollution Control Board (e.g., Commoner 1971, Kohl 1971, Aldrich 1972). The controversy has significant implications for public policy. If fertilizer is responsible for an important part of the increase in nitrate concentrations in surface waters of the Midwest, and if those concentrations are judged to be a health or environmental hazard that requires abatement, the implementation of possible control measures might have substantial economic and social impacts (see Chapter 10).

Only a limited number of scientific approaches can be used to evaluate estimates of fertilizer nitrogen contributions to nitrate contamination of water in a given watershed. Controlled studies of paired watersheds, of sufficient size and duration to provide meaningful results, are far too costly, and the data they provide are largely site-specific. Smaller-scale field experiments face serious limitations in extrapolating results to the larger area. Use of tracer materials, such as ^{15}N-enriched fertilizers, on a watershed scale is not feasible because of high cost and limited availability; ^{15}N-depleted compounds are also limited in availability, and cannot give sufficiently accurate results on a watershed basis because of isotopic dilution. Approaches based on the natural isotopic abundance of source materials also are insufficiently sensitive to provide more than qualitative estimates (see Chapter 4). Statistical evaluation of fertilizer use and



SOURCE: Data from S. R. Aldrich, Department of Agronomy, University of Illinois, Champaign-Urbana, personal communication, 1976.

FIGURE 6.5 Trends in the use of nitrogen fertilizer in Illinois and in the average nitrate concentration in the Kaskaskia River at Shelbyville, Illinois.

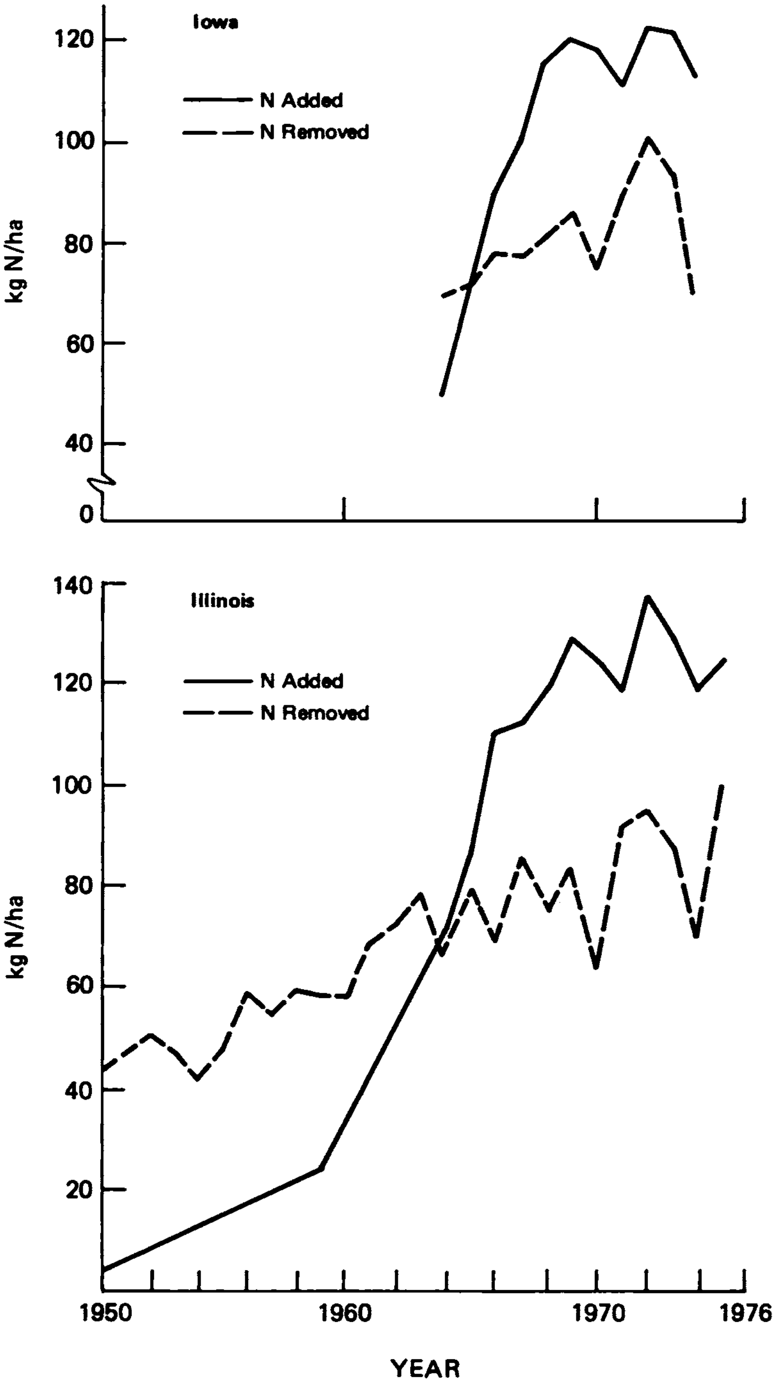
water quality data in the regions of interest may produce results that lack credibility because even strong correlations do not prove cause/effect relationships. While no single approach is sufficient to resolve the complex issues involved, however, a coherent picture eventually can emerge through multifaceted study of a region, if each of these approaches is used in coordination with others.

Fertilizer and Nitrogen Balances in the Corn Belt

Welch (1972) and Boone and Welch (1972) reported that since about 1965, more fertilizer nitrogen has been added to Illinois harvested cropland than has been removed in harvested crops; the same situation exists in Iowa (R. Voss, Department of Agronomy, Iowa State University, Ames, personal communication, 1976) (see Figure 6.6). Illinois and Iowa each consumed about 0.5 Mt of nitrogen on corn in 1975, for a combined total of 11 percent of U.S. nitrogen fertilizer use. As the figure shows, prior to the mid-1960s corn production removed more nitrogen from the soil pool of organic nitrogen than was added as fertilizer.

The most widely used form of nitrogen fertilizer in the corn belt is anhydrous ammonia; this form accounted for nearly 55 percent of the fertilizer nitrogen used in Illinois in 1971, and most of the remainder consisted of ammonia-forming materials such as urea (Illinois Pollution Control Board 1975). Fall application of these fertilizers in preparation for the following year's crop is a common practice; up to 10 percent of the fertilizer nitrogen in Illinois and 25 to 28 percent of the nitrogen used in Iowa is applied in the fall. This practice often leads to loss of nitrogen by nitrification and by subsequent leaching or denitrification (see Chapter 10). Similarly, excess nitrogen applied during spring or summer, but not taken up by the crop, is usually lost by leaching, denitrification, or immobilization. Westerman et al. (1972) and Westerman and Kurtz (1972) added ^{15}N-labeled urea to test plots in Iowa during spring of 1966, and measured crop uptake in 1966 and 1967. They found that little residual fertilizer nitrogen was available to the second year's crop. From 22 to 25 percent of the fertilizer nitrogen was unaccounted for, and probably was lost by denitrification (Westerman et al. 1972).

During the winter, cooler temperatures limit the extent of nitrification. Feigin et al. (1974) noted no change in the distribution of nitrate in the soil to a depth of 150 cm from October 1971 to May 1972 in two central Illinois tile-drained cornfields. During the cropping season, the amount of nitrate decreased, but a balance could not be estimated because the complex hydrology prevented accurate estimation of leaching losses. Gast et al. (1974) found that nitrate



SOURCE: Data from R. D. Voss, Department of Agronomy, Iowa State University, Ames, and L. F. Welch, Department of Agronomy, University of Illinois, Champaign-Urbana, personal communications, 1976.

FIGURE 6.6 Annual average rates of addition in fertilizer nitrogen and removal of crop nitrogen for corn production in Iowa and Illinois.

accumulated under cropland planted to corn each year in Minnesota only when excess fertilizer nitrogen (195 or 336 kg/ha) was added. Leaching rates were estimated by the use of a companion anion (Cl^-), and a mass balance indicated that considerable nitrogen was lost by denitrification.

The Role of Fertilizer Nitrogen in Nitrate Pollution of Water Supplies

The Illinois Pollution Control Board in 1971 began a series of ten public hearings on water pollution by nutrients, primarily nitrate. The hearings reviewed available data and stimulated some subsequent research. Ultimately, the Board concluded that the violations of water quality standards for nitrate in certain streams, particularly in East Central Illinois, were due in a significant part to fertilizer nitrogen. However, the board determined that the efficiency of fertilizer use by corn depended more heavily on the management of crop production than on fertilizer application rates per se (see Chapters 8 and 10 for detailed discussion). Farms that use the most fertilizer and achieve the highest yields may be using nutrients more efficiently, and may contribute less leachable nitrate than farms that produce average yields. The Board also noted that prices of nitrogen fertilizers increased by a factor of 3.4 from 1971 to 1975, while corn prices increased only 2.2 times, and concluded that farmers were likely to monitor more carefully their nitrogen fertilizer applications as a result.

The nitrate in ground or surface waters in Illinois could have several origins: fertilizer, mineralized organic soil nitrogen, animal manures, human sewage, and atmospheric inputs. In the watersheds that have been most thoroughly studied, sewage is a localized problem, and animal manures are not present in significant quantities. There are, however, notable cases of groundwater pollution by nitrate that accumulated in soils beneath sites of former barnyards, feedlots, or septic tanks (Dickey et al. 1972). Atmospheric fluxes have not been extensively measured, but are probably a small (<10 percent) component of inputs to the region. The chief sources of the nitrate in surface waters, therefore, are fertilizer nitrogen and other soil nitrogen, released from humus, manures, or crop residues by gradual mineralization. Aldrich (1972) has noted that, in addition to increased use of fertilizer, other parameters, related to the amount of land in cultivation, may also be in part responsible for the water quality trend. In particular, Aldrich points out, the area planted in soybeans has increased at the expense of land planted to oats, wheat, and hay. Results of this shift in cropping patterns include increased tillage, and an associated increase in the rate of mineralization of organic nitrogen; a period in spring when soils are bare, rather than in crops such as hay or oats; and a reduction in scavenging of residual nitrogen, since soybeans remove less nitrogen from soils than do early season small grain crops.

Several investigations have attempted to quantify the relationships between specific factors, especially fertilizer use, and nitrate in surface waters through statistical correlation studies (Taylor 1973, Abrams and Barr 1974, Parker et al. 1974, Klepper 1978). Each of the studies indicated a strong positive correlation between fertilizer use and nitrate levels in streams; however, because of the interrelationships of many critical variables, the effects of any single factor could not be accurately isolated. Furthermore, the data base for both fertilizer application rates and water quality trends is seriously deficient. Klepper (1978) used extensive on-farm interviews to obtain better data on fertilizer use and management practices for 16 small watersheds, but was unable to resolve the ambiguities of the correlation approach.

Kohl et al. (1971) attempted to quantify the contribution of fertilizer to nitrate in surface waters by correlating the isotopic composition ($\delta^{15}N$) of the nitrate in streams and in tile drain effluents with the $\delta^{15}N$ of various source materials. They concluded that about half of the nitrogen in water was of fertilizer origin. This report stimulated a vigorous debate on the scientific reliability of the approach used by Kohl and his coworkers (see discussion in Chapter 4 of this report). The consensus is that the approach, based on variations in the abundance of the natural isotopes of nitrogen, does not provide a good quantitative measure of sources of nitrogen. Precise or general conclusions about the percentage of nitrogen in streams that is attributable to fertilizer still are not possible for several reasons, including the complexities of water movement in tile-drained fields, and the rapid loss of isotopic identity of input nitrogen pools through the transformations of the soil nitrogen cycle.

Case II: Irrigated Agriculture in California

The past 30 years have seen a marked increase in the yield and quality of agricultural crops in the United States, largely because of improved cultural practices. Soil water is frequently the limiting plant growth factor, even in humid climates, and the practice of irrigation has expanded rapidly, especially in arid western regions. In 1890, about 1.6 million hectares were irrigated in the United States. Today, the total is about 22 million hectares (Law and Witherow 1971, Irrigation Journal 1975). More than 87 percent of the irrigated land is in the western states. California has the greatest area under irrigation

(3.54 million hectares, 16.1 percent of the total). At present, about 24 percent of irrigation in this country is by overhead sprinklers; most of the remainder is by gravity methods. About 60 percent of all irrigation water comes from surface water storage, and the remainder is pumped from the ground. Irrigated agriculture is the largest single consumptive use of water; in 1965, more than 4.2×10^5 m^3/day were diverted for irrigation. Irrigated lands account for only 10 percent of the cultivated area of the United States, but they produce 25 percent of the cash value of crops (National Water Commission 1968). About 60 percent of the irrigation water is consumed or transpired by crops, and the remainder goes to surface runoff (commonly termed tailwater) and to deep percolation.

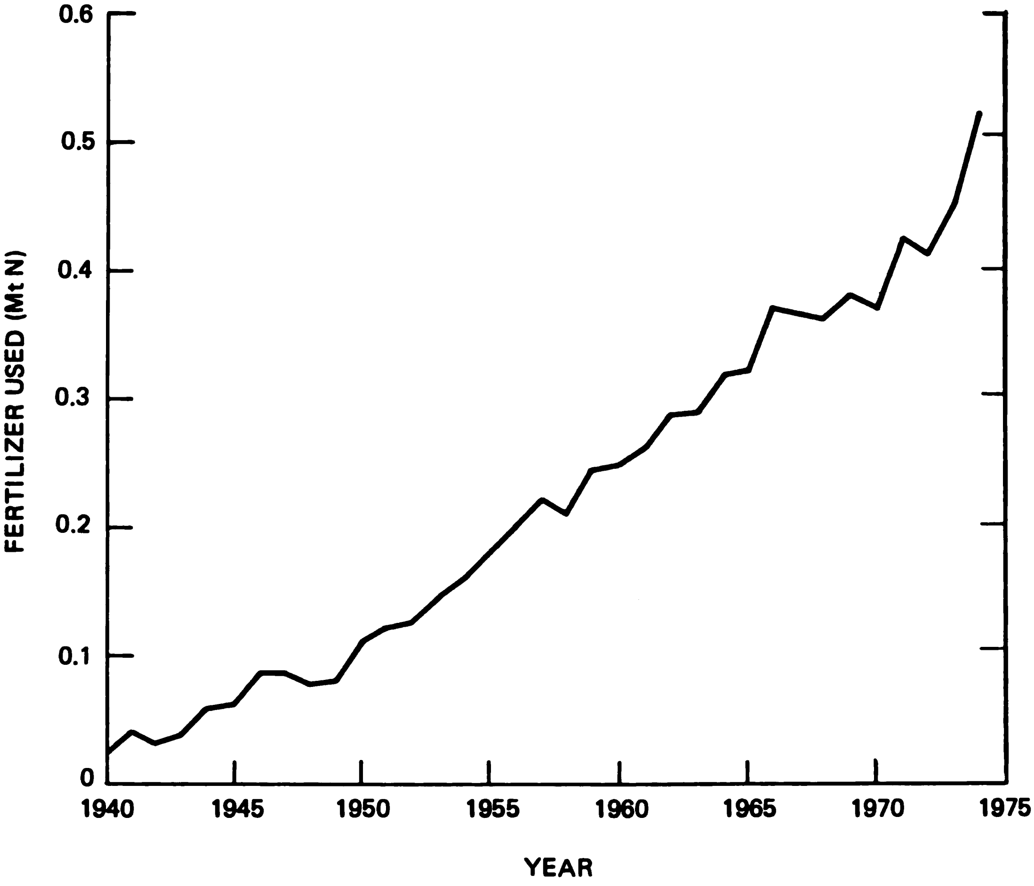
Residual nitrate in the soil profile is leached with the movement of irrigation water (see Chapter 3 for discussion). High leaching rates, high nitrification rates in the permeable soils that are commonly irrigated, and relatively high fertilizer application rates (related to high economic returns for most irrigated crops) combine to make nitrate leaching a serious problem for many irrigated soils (Branson et al. 1975).

The impacts of irrigated agriculture on nitrate levels in surface and ground waters have been evaluated most extensively in California. The groundwater in a number of southern and central California watersheds now exceeds the 10 ppm NO_3^--N drinking water standard recommended by the U.S. Public Health Service.

Nitrogen fertilizer use in California has increased markedly in recent decades, in keeping with the national trend (see Figure 6.7). In 1974, California agriculture consumed slightly more than 5 percent of the fertilizer nitrogen used in the United States (an estimated 0.5 Mt of N). In contrast to the monocultures of the corn belt, however, fertilizer in California is applied at widely variable rates to a great diversity of grain, vegetable, and fruit crops. Table 6.3 presents information on the use of nitrogen fertilizer on some important crops in California, and Table 6.4 shows trends since 1950 in both the percents of land fertilized and the rates of fertilizer application for major crop categories.

Nitrogen Balances and Impacts of Fertilizer Nitrogen on Groundwater

Several approaches have been employed in efforts to determine the importance of different sources of nitrogen, such as fertilizer, and of different cropping practices, especially irrigation rates, in the contamination of groundwater by nitrate in California. Mass balances have



SOURCE: Data from Hargett (1975) and from D.R. Nielsen, University of California at Davis, personal communication, 1975.

FIGURE 6.7 Use of nitrogen fertilizer in California, 1940-1974.

TABLE 6.3 Average Rates of Application of Nitrogen Fertilizer, and Percent of Surveyed Cropland, Land Fertilized, and Total Fertilizer Use for Selected Crops in California in 1973

Crop	Percent of Cropland[a]	Percent of Land Fertilized with Nitrogen	Common Rate of Application, kg N/ha	Percent of Total N Fertilizer Use
Barley (irrigated)	8	78	89	6
Corn	3	91	191	7
Cotton	10	93	122	11
Rice	4	97	96	5
Wheat (irrigated)	4	85	117	4
Alfalfa	9	17	22	--[b]
Pasture (irrigated)	12	55	71	5
Almonds	2	83	142	4
Walnuts	2	76	135	2
Peaches	1	95	145	1
Prunes	1	73	107	1
Wine Grapes	2	71	59	1
Oranges	2	92	138	2
Olives	--	69	92	--
Avocados	1	100	140	--
Asparagus	1	86	159	1
Carrots	--	95	135	--
Lettuce	2	96	178	3
Melons (cantaloupe)	1	92	106	1
Tomatoes	3	99	159	3
Turf	2	77	224	8

[a] Rangelands not included in total.

[b] Less than one percent.

SOURCE: D.R. Nielsen, University of California, Davis, personal communication (1975).

TABLE 6.4 Changes in Harvested Area, Area Fertilized with Nitrogen, and Rate of Application of Nitrogen for California Crop Categories Since 1950

Crop Category	Surveyed Area x 1,000 Hectares	Percent of Area Fertilized	Rate of Fertilization, kg N/ha
		1950	
Agronomic Crops[a]	2662	29	61
Fruits and Nuts	573	58	133
Vegetables	272	81	103
Total	3507	38	86
		1960	
Field Crops	1810	70	108
Forage Crops	1039	22	52
Fruits and Nuts	597	77	121
Vegetables	290	90	157
Total	3736	61	105
		1973	
Field Crops	1587	84	139
Forage Crops	958	50	74
Fruits and Nuts	575	82	126
Vegetables	330	89	202
Total	3450[b]	74	131

[a] Forage and field crops were combined into one category in 1950.

[b] For comparative purposes, range and turf are not included in these totals.

SOURCE: D.R. Nielsen, University of California, Davis, personal communication (1975).

been constructed for nitrogen in two of the state's river basins (Ayers and Branson 1973, Miller and Smith 1976); those mass-balance studies are discussed in Chapter 5, and presented in some detail in Section 4 of Appendix A of this report. In summary, while they presented much information about major fluxes of nitrogen at the regional level, neither study was able to resolve uncertainties about the actual magnitude of major transfers (e.g., leaching), or to partition such estimates according to possible nitrogen sources.

Most of the research data now available are site-specific, and the great diversity of crops, soils, and management practices in California makes the drawing of general conclusions difficult, and perhaps inappropriate. Many findings do indicate, however, that groundwater under heavily fertilized, irrigated croplands can contain extremely high concentrations of nitrogen. For example, Branson et al. (1975) reported nitrate concentrations in the shallow soil water (3-6 m depth) in the Santa Ana Basin of 405, 326, and 290 mg N/l for corral, pasture and crop land, respectively. At the top of the water table, the respective concentrations were 251, 326 and 198 mg/l.

In a related study, Adriano et al. (1972b) found nitrate concentrations of 36 to 122 mg N/l in the saturation extract at depths of 3 to 15 m beneath nine row crop sites in the same basin. Estimated losses by denitrification at these sites ranged from zero to as much as 52 percent of the total nitrogen input. Although the high nitrate concentrations below the root zone suggested that leaching losses are considerable, nitrate was shown to move through the soil very slowly. The investigators estimated that from 10 to 50 years would be required for drainage water to move 30 m through the unsaturated zone in such soils (see Chapter 3). The time required for the fertilizer nitrogen currently being applied to reach the groundwater reservoir would thus depend on the depth of the water table, but could be many decades in some sites. Current fertilization rates in the basin supply about 135 kg N/ha-yr more than is removed by the vegetable crops. Well waters pumped from deeper aquifers at these sites average only about 5.8 mg N/l currently, but some wells in the basin exceed 20 mg N/l. The nitrate concentration of the Santa Ana River increased from about 2 mg N/l in 1930-1950 to about 6 mg N/l in 1969 (Ayers and Branson 1973).

The effects of overfertilization and subsequent nitrate leaching have been determined quite accurately in a small (388 ha) watershed of sandy loam soils planted largely to oranges (Davis and Grass 1966, Bingham et al. 1971). The watershed is underlain by impervious granite, and water leaves the watershed as surface flow at only one point. The only inputs of water are precipitation and irrigation;

hence, the area functions as a macrolysimeter. From 1967 to 1970, about 45 percent of the water added percolated through the soil. This percolate contained from 37 to 81 mg N/l, and removed 51, 62 and 78 kg of NO_3^--N/ha in 1967, 1968 and 1969, respectively. The authors concluded that essentially all of this nitrogen was from fertilizer; from 20 to 30 kg/ha of the average application rate of 130 kg N/ha-yr was then still unaccounted for. In similar studies on the same (Santa Ana) river basin, Pratt et al. (1972) estimated leaching rates of up to 100 kg N/ha, and leachate nitrate concentrations of up to 80 mg N/l for citrus groves.

In related studies, Adriano et al. (1972a) and Pratt and Adriano (1973) found nitrate levels of 21 to 123 mg N/l in the soil water under various irrigated vegetables. The latter investigators estimated rates of leaching beyond the root zone to be from 25 to 912 kg N/ha-yr. From zero to 960 kg N/ha-yr was unaccounted for in the sites studied, and this nitrogen was assumed to be denitrified.

Field data in California (Adriano et al. 1972b, Pratt et al. 1972, Lund et al. 1974) indicate that denitrification losses can be considerable in flood-irrigated soils that are free-drained (i.e., not tile-drained). Considerably less nitrate was present in the unsaturated zone under citrus groves where the soil profiles had high clay horizons overlain by sands than where no textural discontinuities existed. Focht et al. (1975) found little denitrification in the unsaturated zone of a well drained, irrigated soil.

Several studies of irrigation drainage have indicated little or no increase in the nitrate content of tailwater. Such findings have been reported in the Imperial Valley (Meek et al. 1969) and Coachella Valley (Bower et al. 1969) in California, and in the upper Rio Grande River system of New Mexico and Texas (Bower and Wilcox 1969). Ideal conditions for denitrification at those sites are probably responsible for the low nitrate in the drainage water; however, some samples of tile drainage from the same areas do have high nitrate contents, indicating that the capacity for denitrification is quite variable even within a relatively small region.

Monitoring data from tile drains in Southern California (Letey et al. 1975, Devitt et al. 1975) indicated losses of from zero to 350 kg N/ha in tile drainage from irrigated lands. In general, the nitrate content of the tile effluent was correlated positively with rates of application of nitrogen fertilizer. As in free-drained fields, lower levels of nitrate in tile drainage generally were associated with the presence of a clay layer.

Most data from California indicate that the nitrate levels in groundwater under irrigated croplands are typically about 25 to 30 mg/l, and that excessive nitrogen is leached only when application rates exceed those which are efficiently utilized by the crops. It appears, however, that for many crops, good agronomic practices and profitable production will inevitably result in nitrate levels of at least 20 mg N/l in drainage effluents and groundwater (P.F. Pratt, University of California, Riverside, personal communication, 1976).

More efficient use of water by decreasing irrigation rates is one method to reduce the rate of nitrate leaching and the loss of fertilizer nitrogen. The result of reduced irrigation would be a smaller volume of drainage water, which would probably have an elevated nitrate content. Inadequate information is available to estimate the quantitative effects of such changes in irrigation practices on nitrogen fluxes under field conditions. In tests using lysimeters, however, careful management of irrigation has been shown to reduce the nitrate content of the leachate and the total amount of fertilizer lost (See Chapter 10 for discussion).

Reduced rates of irrigation probably would decrease both the leaching of nitrate into groundwater and the loss of fertilizer by denitrification, but this practice could cause other problems, particularly a buildup of salts in irrigation return flows. Such increasing salinity is already a major concern in the western states. Salts from irrigation water, animal wastes, and fertilizers are concentrated by evaporation and transpiration, and additional dissolved salts enter the return flow from percolation through the soil. As a result, the salinity of many western streams increases with each irrigation diversion. The resulting accumulation of soluble salts in the root zone can markedly decrease crop yields. Furthermore, as irrigation water quality declines, more water must be used to leach salts below the root zone in order to prevent adverse effects on crops. Irrigation practices can be modified to minimize salt loads by lowering the fraction of water that is leached below the root zone. This causes salts to form insoluble precipitates, minimizes the use of irrigation water, and reduces the amount of return flow (Law and Skogerboe 1972, Branson et al. 1975). Other innovative irrigation practices to minimize leaching are discussed in Chapter 10.

Case III: Potatoes

Certain vegetable and root crops that require high levels of nitrogen fertilizer can be difficult to manage efficiently in terms of fertilizer use. An example is commercially grown potatoes. Potatoes are grown on coarse-textured soils that are susceptible to leaching. Potato plants are shallow-rooted (Lesczynski and Tanner 1976), which lessens the effective soil volume and hence the amount of nitrogen and water available to the plant, compared to a deep-rooted crop such as corn. Potatoes require heavy fertilization (3 to 4 kg N/ha-day), and must be irrigated to avoid water stress (Saffigna and Keeney 1977b).

In the central Wisconsin sand plain, about 20 percent of the area is under sprinkler irrigation, and about one quarter of the irrigated cropland is in potatoes. Saffigna and Keeney (1977a) monitored the nitrate and chloride content of groundwater in this region and found nitrate levels of from 4 to 23 mg N/l, which were significantly above background. The chloride-nitrate ratio was relatively constant, suggesting that much of the nitrogen and chloride was of fertilizer origin.

Meisinger (1976) examined potato production in Long Island, New York, and estimated a mass balance for nitrogen. The water from many wells in this area is high in nitrate (10 to 15 mg N/l), presumably from agricultural fertilization. Meisinger's analysis indicated that a loss of more than 55 kg N/ha-yr by leaching would result in groundwater nitrate concentrations above 10 mg N/l. Through a number of simplifying assumptions, he estimated leaching losses as the difference between nitrogen fertilizer applications and nitrogen removals in harvested crops. According to this model, current average fertilization rates (224 kg N/ha-yr) and average yields (104-142 kg N/ha-yr) would lead to excessive leaching of nitrate into the groundwater recharge flow. Meisinger's model predicted that an average application rate of 170 kg N/ha would be environmentally sound and would not lead to significantly lower potato yields. In years with poor weather conditions and below-average crop yields, leaching of nitrate might still be excessive, even at 170 kg N/ha-yr; but in average and better-than-average crop years, Meisinger predicted that leaching losses would be less than the estimated 55 kg/ha maximum. This theoretical analysis, however, has not yet been supported by on-site monitoring data.

NITRATE POLLUTION FROM LIVESTOCK OPERATIONS

In the past, wastes from domestic animals were carefully husbanded as fertilizers; as food demands have changed and agriculture has become mechanized, however, chemical fertilizers have been increasingly used to meet crop nutrient needs. As technology improved, the price of fertilizers declined to less than the costs of handling and spreading manure on the land. Major shifts in the American diet have occurred concurrently with the changes in production methods. Per capita consumption of eggs, poultry and meat increased from 79 to 114 kg/yr from 1910 to 1970, while yearly consumption of flour, cereals and potatoes declined from 218 kg to 113 kg per capita in the same period (Stout 1972).

Pimentel et al. (1975) analyzed protein consumption patterns and showed that while many agronomic and vegetable crops have high protein yields, the protein in many of these crops is unavailable to man without further processing, at additional energy and labor costs. As Table 6.5 shows, much of this processing is accomplished in the United States by feeding crops to animals. An estimated 91 percent (24.6 Mt) of the cereal, legume, and vegetable protein produced is fed to livestock to produce 5.3 Mt of animal protein. Dairy cattle convert vegetable protein to animal protein most efficiently, and poultry are also quite efficient converters. Meat animals are less efficient protein converters; however, rangeland production of beef and sheep and pasture feeding of dairy animals convert otherwise unusable protein to a consumable form at relatively low costs in terms of fossil fuel energy (Pimentel et al. 1975).

Production and Fate of Nitrogen in Animal Wastes

Part of the protein consumed by animals is undigested or only partly digested, and is excreted in the feces. Part of the feed protein that is digested is metabolized, and the nitrogen not converted to animal protein is excreted in urine, primarily as urea, or for poultry, as uric acid (Nye 1973). From 70 to 75 percent of the nitrogen in feeds normally appears in the wastes; some also is lost from the animal to the atmosphere. The partitioning of nitrogen between urine and feces varies considerably; for example, 72 percent of the nitrogen excreted by swine is in urine; corresponding values for sheep are 62 percent, for horses, 37 percent and for cattle, 48 percent (Azevedo and Stout 1974).

The National Research Council (1972) estimated that animal wastes containing 6 Mt of nitrogen are produced annually in the United States. Of that total, 2.9 Mt are from beef cattle, 1.1 Mt from dairy cattle, and the remainder from swine, poultry, and sheep. Frere (1976) revised the estimated total to 5.3 Mt; Frere's estimate is incorporated in Table 6.1. According to Webber et al. (1968), the per-animal annual production of waste nitrogen of 1 dairy cow (65 to 75 kg N) is equivalent to that of two beef cattle, 10 hogs, 100 laying hens, or 1000 broilers. Much of the nitrogen excreted by farm animals falls on pasture or holding areas where it is not collectible, but nearly all of the nitrogen in operations such as caged poultry production or beef feedlots is collectible. Frere (1976) estimated that about half of the nitrogen in

TABLE 6.5 Estimated Vegetable and Animal Protein Produced, Fed to Livestock, and Available to Man in the United States

	Total Protein Produced	Protein Fed to Livestock	Protein Available to Human
		(Millions of Metric Tons)	
Cereals	17.0	15.5	1.5
Legumes	9.3	9.0	0.3
Other Vegetables	0.8	0.1	0.7
Livestock	6.0	0.7	5.3
Fish	1.0	0.8	0.2
Total	34.1	26.1	8.0

SOURCE: Adapted from Pimentel et al. (1975).

collected manure is lost during storage, handling and spreading, and that only about 1.1 Mt of the 2.2 Mt of manure nitrogen collected in the United States is ultimately made available for crop growth by incorporation into croplands. About 40 to 50 percent of the organic nitrogen in manure is mineralized during the first cropping year (Frere 1976); the remainder is released subsequently, but not necessarily at the time when needed by the plants.

The waste disposal problems of the livestock industry are related in large part to the intensity of operations. Animals dispersed on rangelands present no obvious problem, but the trend to increasing efficiency of production has led to high-density confinement of poultry, hogs and cattle, and to concentrated accumulation of wastes. Egg producers may have up to one million birds in confined housing, and pork operations with confinement from birth to finishing are becoming common (Nye 1973).

The trend to confined feeding is most noticeable in the beef industry, in which the number of very large feedlots has increased dramatically since 1960 (Viets 1971). High-density beef cattle feeding operations currently account for close to 70 percent of the beef produced in the United States. These operations are concentrated in four areas of the country: southern California and Arizona; the Texas/Oklahoma panhandles; the central Corn Belt; and from eastern Colorado through Nebraska to the North Dakota line. More than 90 percent of the animals are kept on unsurfaced feedlots, at densities that range from 5 to 37 m^2 per animal. The highest density operations are in the California-Arizona area. At a density of 30 m^2 per animal, about 8.5 metric tons of nitrogen will be deposited per hectare in the 150-day feeding period (0.17 kg N/animal-day) (Viets 1971).

Some of the nitrogen in wastes is removed during cleaning operations, and some is carried from the land in storm runoff. There are four possible fates for the remaining nitrogen: it may accumulate in the soil; percolate to the subsoil as ammonium, nitrate and soluble organic nitrogen compounds; be denitrified; or be lost to the atmosphere as ammonia and volatile bases. Under warm, moist conditions, urea hydrolyzes rapidly to NH_3 and CO_2. The pH in the feedlot surface layer rapidly rises to between 8.5 and 9.9 (Stewart 1970, Adriano et al. 1974), and NH_3 is evolved. The amount of NH_3 and volatile bases lost from feedlots depends on evaporation, stocking rates and cleaning operations. Stewart (1970) reported that from 25 to 90 percent of the nitrogen in urine alone was volatilized as NH_3, while Adriano et al. (1974) found that losses from a mixture of urine and feces approached 50 percent. Elliot et al. (1971) measured ammonia losses of 148 kg N/ha and losses of volatile organic nitrogen of 21 kg N/ha from a feedlot.

The NH_3 volatilized from wastes is transported by wind away from the immediate vicinity of a feedlot, and can cause odor nuisances. The nitrogen transferred by this process can represent a significant loading to nearby areas, especially lakes (Hutchinson and Viets 1969, Luebs et al. 1974; see the section on atmospheric pathways, later in this chapter). Table 6.6 presents data from Hutchinson and Viets (1969), who measured the transport of ammonia from feedlots to surrounding areas.

The high ammonia concentrations and high pH at the surface of a feedlot initially retard nitrification (Stewart 1970). These conditions especially inhibit nitrite-oxidizing microorganisms, and considerable amounts of nitrite may be formed at the onset of nitrification; Stewart (1970) found nitrite levels of 10 to 92 ppm in soil columns four weeks after treatment with cattle urine. Volatile amines have been identified in acid traps adjacent to a cattle feedlot (Mosier et al. 1973); the presence of amines and nitrite suggests that nitrosamines such as dimethylnitrosamine (DMN) could be formed (Ayanaba et al. 1973a). Nitrosamine formation has been noted in sewage (Ayanaba et al. 1973b), but Mosier and Torbit (1976) suggest that the high pH that normally occurs in feedlot soils makes formation of DMN unlikely.

Although a mass balance would be helpful in understanding the transfers of nitrogen in a feedlot operation, such balances are difficult to obtain for actual operating conditions. In most feedlots, rainfall and snowmelt runoff carries some manure into surface or ground water; the extent of losses by this route depends on climate, the intensity and spacing of precipitation, and the steepness and length of slope. Gilbertson et al. (1971) kept a close accounting of nitrogen fluxes over a period of six months in a series of unpaved feedlots at varying slope of land and density of animals (see Table 6.7). From 18 to 42 percent of the nitrogen added to feedlots was not accounted for in the cases they examined; undoubtedly some was lost by volatilization, and some was converted to nitrate and subsequently leached through the soil profile.

The amount of nitrate in deep percolation beneath a feedlot depends on the amount of nitrate formed, the rate of infiltration of water, and the extent of denitrification, which in turn depend on temperature and soil characteristics. Active feedlots often have low infiltration rates because of the puddled condition of the soil, but when a lot is taken out of use the soil surface dries, nitrification is rapid, and significant amounts of nitrate may be leached. Significant nitrate leaching may also occur when feedlots are established on coarse-textured soil, or when stocking rates are low or manure is removed frequently (McCalla and Viets 1970). Organic compounds and

TABLE 6.6 Amounts of Ammonia Absorbed in 0.01 N H_2SO_4 in the Vicinity of Animal Feedlots in Colorado, and Estimated Annual Loading to Lakes in the Area

Site	Absorption Rate kg N/ha-week	Estimated Annual Loading, kg N/ha-yr[a]
Control - no feedlots or irrigated fields nearby	0.15	3.9
Small feedlots within 0.8 to 4 km	0.34	9.1
0.2 km east of 800-unit feedlot and 0.6 km west of 800-unit feedlot	0.57	15.0
0.5 km southwest of 9,000-unit feedlot	0.62	17.0
2 km northwest of 90,000-unit feedlot	1.3	34.0
2 km east of 90,000-unit feedlot	1.3	34.0
0.4 km west of 90,000-unit feedlot	2.8	73.0

[a] Estimated by assuming that an open water surface will absorb ammonia at one half the rate of absorption by dilute acid.

SOURCE: Hutchinson and Viets (1969).

TABLE 6.7 Nitrogen Balance for Unpaved Feedlots, January to June 1969

	Animal density (m^2/animal)					
	9			18		
	Slope			Slope		
Nitrogen Flux	3%	6%	9%	3%	6%	9%
N added (kg)	494	494	494	259	259	258
N removed (kg)						
Cleaning	291	230	264	192	145	189
Winter runoff	60	51	64	15	21	13
Rainfall runoff	4	4	5	4	7	6
Runoff, percent of added	13	11	14	7	11	7
N not accounted for (kg)	138	208	159	48	86	49
Percent of added	28	42	32	18	33	19

SOURCE: Gilbertson et al. (1971).

ammonium also can leach through the profile under feedlots. Conditions that promote denitrification and limit leaching of nitrate have been found under a number of active feedlots (Elliot et al. 1972, Mielke et al. 1974). Gilbertson et al. (1971) found little nitrate in the soil profile under feedlots except in the border areas. They suggested that the latter may have been the result of deposition of volatilized ammonia in areas immediately adjacent to the feedlot. Stewart et al. (1968) compared the ammonium and nitrate concentrations in groundwater beneath four Colorado feedlots and beneath adjacent irrigated fields, and concluded that the feedlots were a significant source of nitrate and ammonium in groundwaters (see Table 6.8).

Land disposal of livestock wastes can also cause contamination of surface waters (Miner and Willrich 1970). Application of animal wastes to snow-covered or frozen land, in particular, results in high concentrations of nitrogen in spring runoff (Hensler and Attoe 1970, Frere 1976). When manure is applied in the spring and incorporated into the soil, the loss of nitrogen in runoff is minimized. Wastes can be stored in pits or lagoons until soil and climate conditions are suitable for application (see chapter 10 for discussion).

Land disposal of manures can also result in considerable volatilization of ammonia. Adriano et al. (1974) reported losses of 40 to 45 percent of the total nitrogen in such wastes, and Lauer et al. (1976) reported volatilization of 99 percent of the NH_3 in land-applied manures. As would be expected, higher losses occurred during warm, dry periods than during cold or wet conditions, and less NH_3 was lost when the manure was incorporated into the soil soon after it was applied. The significance of such losses in terms of atmospheric inputs to other systems is discussed in more detail later in this chapter.

For a typical feedlot, cleaning operations remove much of the waste nitrogen and, ideally, return it to the soil at environmentally compatible rates, i.e., about equivalent to the nitrogen needs of the crop. The concentration of nitrogen in manure is highly variable (Peterson et al. 1971). Numerous agronomic studies, some dating back to the early 1900s, have shown relatively little difference in increases in crop yields when nitrogen is added as properly handled and applied manure or as chemical fertilizers, although manure nitrogen is less immediately available than fertilizer nitrogen (Peterson et al. 1971). The use of manure in place of commercial fertilizers to enrich croplands seldom if ever shows a profit; instead, this practice still must be regarded as an expense associated with the waste generating enterprise (Clawson 1971).

TABLE 6.8 Concentration of Ammonium-Nitrogen and Nitrate-Nitrogen in the Surface of the Groundwater Beneath Feedlots and Adjacent Irrigated Fields in Colorado

Location	Depth to watertable, m	NO_3-N mg/l	NH_4-N mg/l
Feedlot 1	10	8.6	5.1
Field	10	0.1	0
Feedlot 2	5	18.0	5.7
Field	3	31.0	0
Feedlot 3	4	21.0	5.8
Field	3	8.5	0
Feedlot 4	11	1.1	38.0
Field	11	18.0	0.4

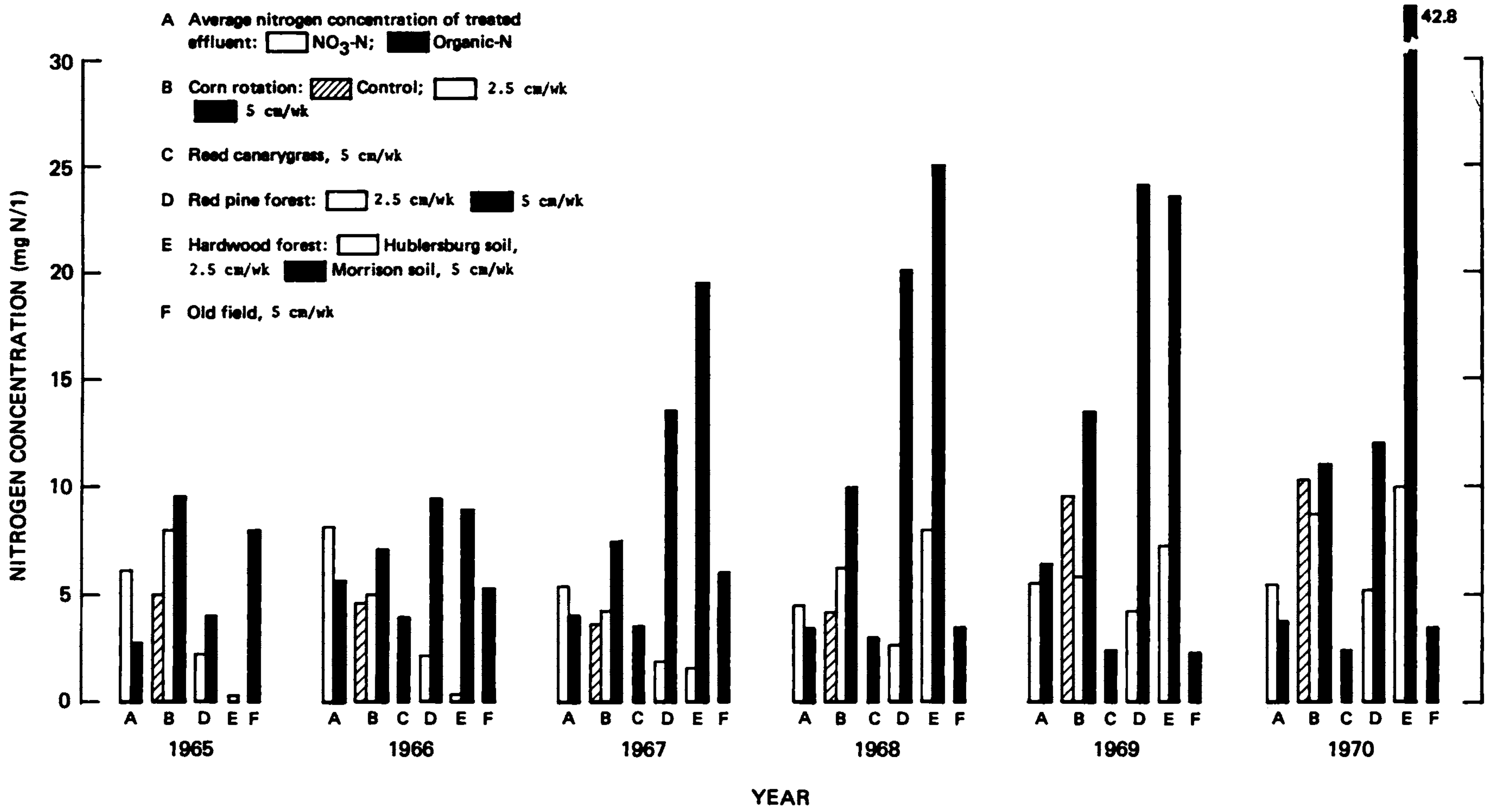
SOURCE: Stewart et al. (1968).

NITRATE POLLUTION FROM LAND DISPOSAL OF MUNICIPAL AND INDUSTRIAL WASTES

Land disposal of liquid sewage effluents, sewage sludge and other organic wastes is attractive as both a relatively non-polluting disposal option and a means of recycling wastes to the landscape. The number of communities that use land disposal methods for municipal effluents is increasing; in 1972, 571 communities with a total population of 6.6 million were served by land disposal systems (Thomas 1973). The majority were crop irrigation systems and were located in the 13 western states. In addition to municipal wastes, many food processing industries, especially fruit and vegetable producers with rural locations, have made effective use of land disposal (U.S. EPA 1971b). With the restriction or elimination of discharges of many wastes to surface waters that are mandated by current laws and EPA regulations, land disposal seems likely to be practiced on an increasing scale. Some studies on the capacities of different soils to absorb nitrogenous wastes are discussed in Chapter 10, in relation to the usefulness of this control option. The possible impacts of land disposal as a nonpoint source of pollution, particularly of groundwater, are examined here.

Some risk of nitrate pollution is present whenever the amounts and rates of application of wastes exceed the capacity of the soil to assimilate nitrogenous compounds. The nitrogen in land-applied wastes may ultimately be retained in the soil or vegetation, or may be removed through a variety of mechanisms described earlier in this chapter. Long-term studies at Pennsylvania State University have examined the consequences of land disposal in a humid environment (Kardos and Sopper 1974). Secondary sewage effluents that contained annual average concentrations of 4.5 to 14.4 mg N/l as nitrate and 2.7 to 7.3 mg N/l as organic nitrogen and ammonia were applied over eight years to diverse soil types in different ecosystems. The same effluents were applied to land planted in corn or reed canary-grass, and to red pine, old field, and hardwood forest ecosystems. Figure 6.8 illustrates the nitrate content of percolating water beneath fields to which effluents were applied at two rates. The different soil systems clearly have different capacities to assimilate nitrogenous wastes, depending on soil properties, hydraulic loading and vegetation type.

The use of wastewaters for irrigation is also practiced in many arid regions, where land disposal of liquid wastes is attractive both as an economic waste treatment and as a way to recharge groundwater supplies that are being depleted by increasing urban, industrial and agricultural use. Data from the Salt River Water Reclamation Project in central Arizona illustrate both the value of such a practice and its



SOURCE: Modified from Kardos and Sopper (1974).

FIGURE 6.8 Mean annual nitrate-nitrogen concentrations in lysimeter leachates at a depth of 120 cm beneath a variety of ecosystems receiving treated wastewater effluents at rates of 2.5 or 5 cm per week over a six-year period.

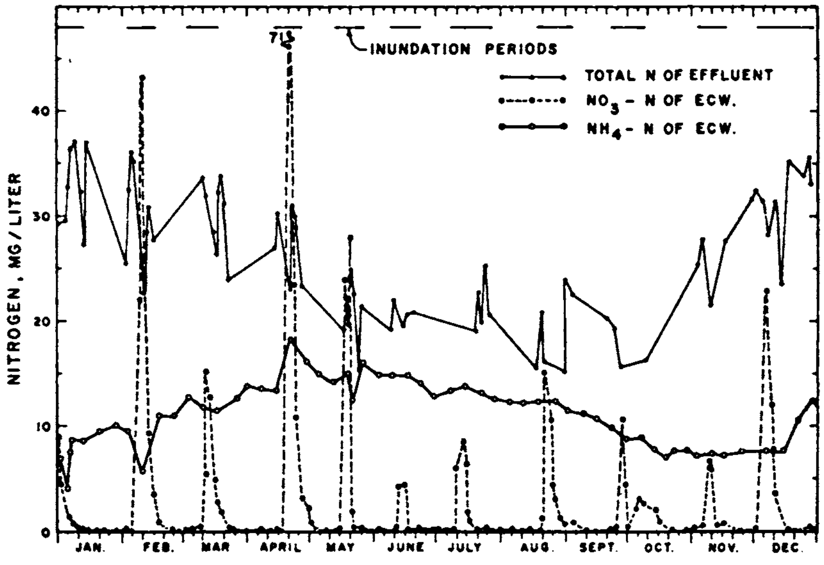
limitations (Bouwer 1974). The system uses infiltration basins in the river bed, which are periodically inundated with effluent. The soil beneath the basins consists of about 1 meter of fine loamy sand underlain by coarse sand and gravel layers, with a static water table at a depth of about 3 meters. During the study period, the effluent contained on the average from 2 to 6 mg/l of organic nitrogen; 0 to 1 mg N/l of nitrite; 0 to 3 mg N/l of nitrate; 20 to 40 mg N/l of ammonia; and 25 to 35 mg/l of total nitrogen.

Nitrate levels in the renovated water were measured at well points in the center of the river bed. As Figure 6.9 shows, the nitrate content of the ground water had peaks well in excess of the nitrogen concentrations of the effluent input. During drying periods, aerobic conditions in the upper soil layers promote nitrification, and nitrate accumulates in capillary water; flooding displaces the nitrate-rich water, causing the observed peaks. Continued use of the system gradually led to elevated ammonium levels at the monitoring points, presumably because the input rate exceeded the capacity for nitrification; the limiting factor appeared to be the amount of oxygen entering the soil during drying (Lance and Whisler 1972). The trend toward increased ammonium concentrations could be reversed by adjusting the sequence of flooding and drying. With high-rate land disposal systems (hundreds of acre-feet per year), nitrogen loading is so high (thousands of kg/ha) that the role of assimilation by vegetation is insignificant.

Operation of a high-rate land disposal system requires that the aquifer receiving the renovated effluent be isolated from adjacent aquifers, and that some subsequent uses of the aquifer be restricted. In the Salt River study, modeling of hydrologic conditions suggested that an operational system following the basic design described above would yield water suitable for unrestricted irrigation, for primary contact recreation, and for certain industrial applications.

Research is also under way on the use of wetlands as disposal sites for sewage effluents. Wetlands have generally high rates of biological productivity, and frequently are located close to large population centers where sewage accumulates. Odum et al. (1975) reported high nitrogen removal rates in cypress swamps. However, the ultimate fate of the removed nitrogen is not known; it may reside in sediments, or be assimilated in tree growth.

Coastal marshes also have been studied as potential disposal sites for sewage effluents and sludges (Odum and Chestnut 1970, Chalmers 1976). Because coastal marshes are adapted to the nutrient loads and flux patterns of the natural waters that flow through them, their efficiency for



SOURCE: Bouwer (1974).

FIGURE 6.9 Nitrogen concentrations in secondary effluent and in renovated water from the Salt River project, 1970.

removing nutrients from municipal wastes, which differ in chemical and physical properties from natural waters, may be low. Sewage nutrients thus may be exported to adjacent coastal waters. For example, Chalmers (1976) demonstrated that salt marsh plants do not respond proportionally to increased nitrogen loading applied as sewage sludge; less than 10 percent of the added nitrogen was converted to plant growth in a year.

In summary, land disposal of nitrogenous liquid wastes can perturb the nitrogen cycle of the ecosystem receiving the wastes. If the capacity of the system to assimilate nitrogenous inputs is exceeded, the nitrogen content of some outputs will be elevated. With proper understanding and consideration of biotic and hydraulic properties of the soil, successful land disposal systems have been placed in operation. However, monitoring data cover insufficient periods of operation to allow assessment of the long-term efficacy of this practice.

Sludge from municipal sewage treatment is a secondary waste that frequently requires land disposal. In 1976, about half of the sewage sludge produced in the United States was disposed of in landfills (25 percent) or by application to croplands (20 percent) or other lands. A considerable amount of sludge was also simply stored in lagoons, with no identified further disposal method (Bastian 1977). The potential for nitrate pollution by land application of sludge appears to be small. Most sludges contain only about 3 percent (range: 1.5 to 6 percent) nitrogen on a dry-weight basis, and most of that nitrogen is in organic forms that are slowly mineralized in soils. The low nitrogen content of sludge makes its use as fertilizer uneconomical; the primary value of sludge is as a soil conditioner. The chief environmental problems associated with land application of sludges are likely to be related to heavy metals and other toxic contaminants, rather than nitrogen (NRC 1978).

NITRATE POLLUTION FROM SEPTIC TANKS

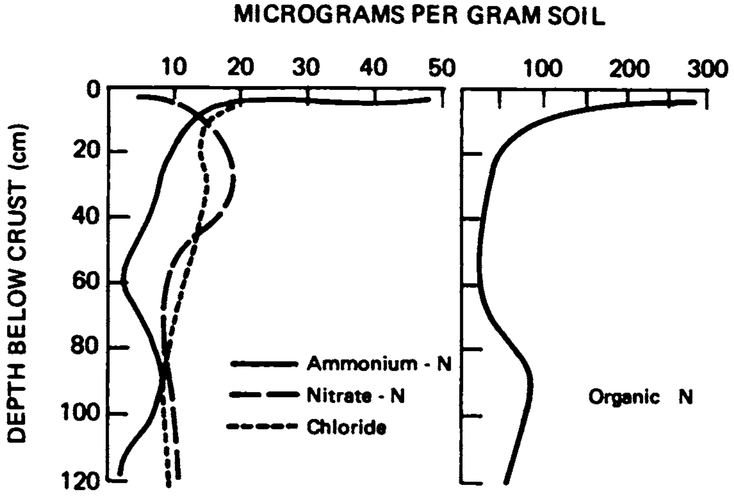
About 25 percent of the population of the United States lives in rural areas without sewer systems, where septic tanks are the principal means of disposal of household wastes. Wolf (1973) estimated the nitrogen content of wastes delivered to septic tanks to be about 0.3 Mt N/yr, or about 6 percent of the total nonpoint nitrogen pollution load estimated by the National Commission on Water Quality (1975). The raw effluent to a septic tank disposal field typically contains 50 to 70 mg N/l, primarily as ammonia (75 percent) and organic nitrogen (25 percent). As the effluent percolates through the soil, the nitrogen is nitrified, and moves with the effluent flow to the groundwater. For practical purposes, all of the nitrogen entering a septic tank system is eventually delivered to the groundwater (Walker et al. 1973a).

Figure 6.10 illustrates the movement of nitrate and chloride through soil profiles beneath a septic tank disposal field; nitrate concentration increased, and ammonia concentration decreased with depth. Walker et al. (1973b) reported nitrate concentrations of from 2 to 42 mg N/l in groundwater around several nonsewered households in a sandy soil area of central Wisconsin; the highest concentrations were just down the flow gradient from the disposal field. As distance from the septic tank field increased, nitrate concentrations declined rapidly because of dilution with low nitrate groundwater. The authors estimated that nitrate input from a typical four-family system would double the natural background nitrate inputs from four hectares of land in this area.

Contamination of groundwater by nitrate from septic tanks is of little significance in sparsely population rural areas; however, increased population density can produce high nitrate levels in groundwater supplies. Such impacts have been identified in Long Island, New York (U.S. EPA 1974) and in Wisconsin (Dudley and Stephenson 1973). Current trends toward subdivisions with rural atmospheres, located too far from cities to make sewer connections feasible, and toward development of second homes around lakes that are recreation sites seem likely to aggravate this problem.

NITRATE POLLUTION FROM RUNOFF OF URBAN STORMWATER

Nitrogen is one of a large number of contaminants transported from urban lands to receiving waters in stormwater runoff. The sources of nitrogen in urban runoff include atmospheric fallout of soil particles and ammonium or nitrate aerosols; leaves, litter, and other organic materials; fertilizers from lawns and gardens; excreta from pets; and soil erosion from construction sites. Nitrogen loadings delivered to receiving waters in urban runoff can be substantial; Omernik (1976) reported mean total nitrogen exports of from about 5.3 to 10.2 kg/ha-yr from lands classified as mostly urban (see Figure 6.1). Comparable loadings for agricultural lands ranged from about 6.5 to 26.6 kg N/ha-yr. Predicting the loading function for a given urban area is complex and difficult, because of the spatial heterogeneity of surfaces, differences in rainfall events, and many other factors. Similarly, it is very difficult to apportion the total nitrogen load to the different contributing sources. Some loading functions for nitrogen in urban runoff have been developed by McElroy et al. (1976) and Heaney et al. (1977).



SOURCE: Adapted from Walker et al. (1973a), J. Environ. Qual. 2:475-480, by permission of the American Society of Agronomy.

FIGURE 6.10 Concentrations of nitrogen forms and chloride in unsaturated soil beneath the crust in a septic tank soil disposal field system.

The rate of delivery of nitrogen to surface waters in a given storm event depends on such factors as the amount of time since the preceding rainfall, the intensity and duration of the storm, and the nature of the surface area involved. In general, nitrogen accumulates during dry periods and is washed off during rain events. For impervious areas, the accumulated pollutants are removed in a first flush; that is, initial concentrations are relatively high, and pollutant levels gradually taper off. A standard assumption in urban runoff models is that runoff of one-half inch (1.3 cm) in one hour will wash away 90 percent of the accumulated pollution during that time period. The actual pollutant washoff process is far more complex, and involves the transport of a heterogeneous mixture of suspended, colloidal, and dissolved materials at highly variable runoff rates. However, simple pollutant buildup/washoff models have been widely used because the data base needed to support a more refined characterization is lacking.

For pervious areas, the pollutants are assumed to wash off as a linear function of sediment washoff, which is typically estimated using the Universal Soil Loss Equation (McElroy et al. 1976). This equation assumes that sediment transport is an increasing function of runoff rates, i.e., disproportionately higher washoff rates occur from larger storms.

A critical consideration is how much of the nitrogen estimated to leave a given area actually reaches the receiving waters. For impervious areas, all of the pollutants are assumed to be washed off. For pervious areas, however, some portion of the pollutant load will be removed in transit. The delivery ratio is usually a function of the size of the drainage area and of the volume of water exported per unit of surface area (Heaney et al. 1977). Increases in the latter variable may have a more significant impact on loads to receiving waters than increases in nitrogen loading per se. Drainage (or stream) density, which is defined as the length of streams and ditches per unit land area, is inversely related to the average distance that runoff water must travel by overland sheet flow or subsurface seepage before it reaches a surface stream. Drainage density also has been shown to be an important factor in the nutrient loadings delivered to streams from various rural and suburban lands (e.g., Huber et al. 1976).

Pollution from urban and suburban nonpoint sources may involve transport of nitrogen through groundwater and in subsurface flow, as well as in surface runoff. For example, studies on lakes Wingra and Mendota, near Madison, Wisconsin (an area of mixed urban, suburban, and rural land uses), indicated that groundwater flow is an important source of nitrogen input to both lakes, especially Lake Wingra. A detailed discussion of this particular case is presented in Appendix A of this report.

NITRATE POLLUTION FROM DOMESTIC SEWAGE

The National Research Council (1972) estimated that Americans consume 16 g of nitrogen in protein per capita per day; it is reasonable to assume that daily excretion of nitrogen in wastes is also about 16 g per capita. The Hazardous Materials Advisory Committee of the U.S. EPA (1973b) used data on the nitrogen content of human wastes to calculate the same estimated rate of excretion, 16 g N/day. The current population of 218 million therefore produces about 1.3 Mt of nitrogen in wastes per year. According to a study by the engineering firm of Metcalf and Eddy (1976), three-quarters of the population of the United States is served by sewage systems; the remainder lives in rural areas where septic tanks are the primary disposal method (see the earlier section of this chapter). Metcalf and Eddy estimated that, in 1974, 113 million Americans used separated sewers; in the other sewage systems, domestic wastes were combined with stormwater runoff.

The nitrogen in domestic sewage originates as human excreta and as food wastes. The concentrations of nitrate, ammonia, urea, and organic nitrogen in sewage are determined largely by the amount of carriage water that is mixed with the wastes; furthermore, nitrogen forms will undergo some transformations, depending on the amount of time spent in sewers and on the conditions there. Total nitrogen concentrations in domestic sewage may range from less than 20 to about 85 mg/l (Metcalf and Eddy 1972), but concentrations in the range 30 to 50 mg N/l are most common. The ammonia fraction is usually one-half to three-fourths of the total nitrogen present; nitrate levels in raw domestic sewage are generally negligible (U.S. EPA 1973b, 1975; Reeves 1972).

Most of the domestic sewage produced in the United States receives sewage treatment. The survey by Metcalf and Eddy (1976) indicated that, of the population of 155 million served by sewers in 1974, wastes from 30 million people received only primary treatment, and sewage from an additional 90 million received primary and secondary treatment. Primary treatment removes approximately 20 percent of the nitrogen in raw sewage, and combined primary-secondary treatments can remove a total of 30 to 40 percent (see Chapter 10). In the process from initial input through treatment, much of the organic nitrogen in wastes is converted to inorganic forms, and some nitrification of ammonia may occur. The nitrogen that is removed by primary treatment (settling, filtration) or secondary treatment (biological digestion) is accumulated in sludges, chiefly in organic form.

A crude accounting for the nitrogen in sewage can be derived as follows: of the 1.3 Mt N/yr produced in human wastes, about 1.0 Mt is collected by sewers. Primary and secondary treatments remove about 0.25 Mt of that nitrogen; most of the removed fraction is trapped in sludges, which also require disposal (see Chapter 10). At least half (0.5 Mt) of the nitrogen that enters sewage treatment facilities is not removed, and is discharged to the environment, largely as ammonia or nitrate. As noted in the earlier section on land disposal, only a small but increasing fraction of sewage effluents (treated or untreated) is disposed of on land. Virtually all of the sewage nitrogen not removed in waste treatment is discharged into surface waters.

On a national basis, domestic sewage is not a large fraction of potential nitrogen inputs to surface waters (see Table 6.1), but in many local situations, domestic wastes can be a major source of nitrogenous pollutants. For example, in the San Francisco Bay drainage basin, which has a population of about 5 million and a moderate amount of agriculture, domestic sewage accounts for about half of the nitrogen loading to the bay and its tributaries (see Table 6.9).

The transformations and transport of nitrogen in natural waters were reviewed in Chapters 2 and 3 of this report, and the effects of nitrogen as a water pollutant, primarily as a stimulant to biotic productivity, are examined in Chapter 8. Congress, in enacting the Federal Water Pollution Control Act Amendments of 1972, set as a national goal the elimination and prevention of adverse impacts of pollution on fish, shellfish, wildlife, and recreation values, to be attained by 1983. To meet this goal, extensive construction of municipal waste treatment facilities will be required, to control a large number of constituents of domestic wastes. Specific treatment methods for removing nitrogen are examined in Chapter 10.

NITRATE POLLUTION FROM INDUSTRIAL WASTES

Industrial nitrogen fixation in the United States amounted to about 12.5 Mt of nitrogen in 1975 (see Table 6.1). The primary industrial process is the synthesis of ammonia from atmospheric nitrogen and a hydrogen source, usually natural gas, using the Haber-Bosch process. Ammonia in turn is used to produce many other materials, such as fertilizers (predominantly ammonium nitrate and ammonium sulfate), nitric acid, and urea. Table 6.10 presents data on the production capacities for major nitrogenous products

TABLE 6.9 Estimated Nitrogen Loadings for the San Francisco Bay Basin

Identified Nitrogen Source[a]	Nitrogen mass emission (metric tons/yr)	Percent of total
Municipal wastewater, before treatment	26,000	49
Industrial wastewater, before treatment	16,000	30
Vessel wastes, before treatment	60	0.1
Dustfall directly on Bay	590	1.1
Rainfall directly on Bay	390	0.8
Urban runoff	1,400	2.7
Non-urban runoff	1,900	3.6
Nitrogen applied to irrigated agricultural land[b]	900	1.7
Nitrogen from dairies and feedlots[b]	6,000	11
Total	53,000	100

[a] A major source not included is biological fixation.

[b] An estimated 50 percent percolates to groundwater.

SOURCE: Modified from U.S. EPA (1975).

in the United States, and Figure 6.11 illustrates the rapid growth of the ammonia industry in this country over the last 25 years. About 75 to 80 percent of the ammonia produced annually is used in fertilizers; the principal uses of urea and nitric acid are also in fertilizer production. Other important uses of ammonia are in the pulp industry and in production of hydrocyanic acid. Nitric acid has a wide range of industrial uses, and urea is a feedstock for the plastics industry. Many organic nitrogen compounds are important industrial intermediates or products; however, these represent a very small fraction of the nitrogen flux through industrial process, and will not be considered further here.

As Figure 6.12 shows, major ammonia production facilities tend to be clustered near sources of natural gas (i.e., along the Gulf Coast), and in the midwestern states, where the greatest markets for fertilizer exist. Fertilizer, urea, and nitric acid manufacturing facilities often are integrated with ammonia production, and multi-plant complexes are commonplace within the industry. Figure 6.12 therefore illustrates the approximate geographic pattern of most major nitrogen-using industries (U.S. EPA 1971a).

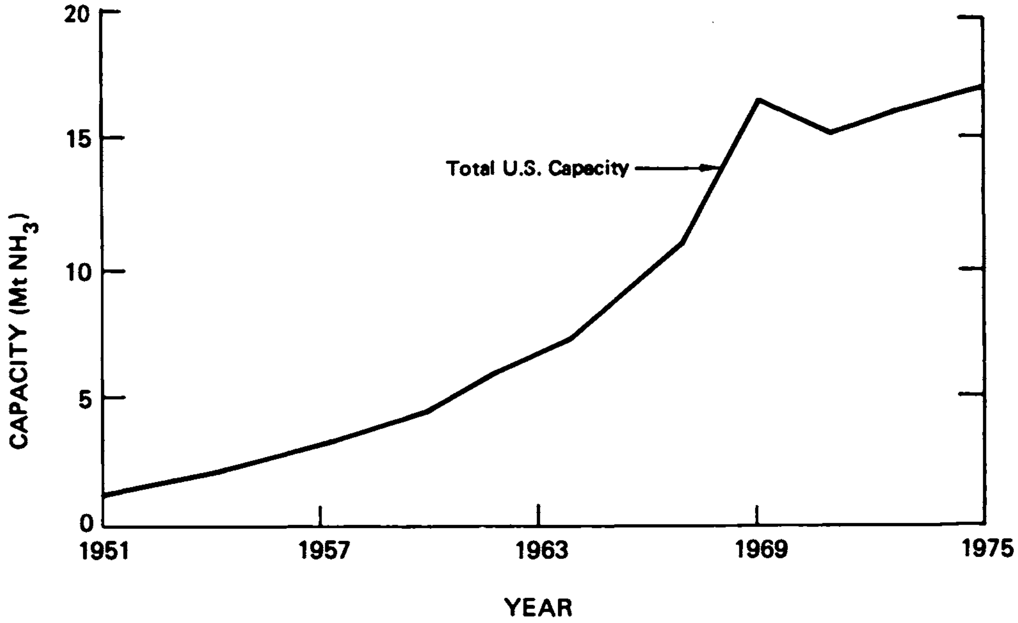
Ammonia production requires large quantities of process water and cooling water; 75 to 80 percent of the cooling water may be recycled process water. Typical nitrogen concentrations in waste streams from various processes within a nitrogen industry complex are shown in Table 6.11. If the upper limits of such concentrations are multiplied by wastewater volumes and production rates for each category of product, the approximate upper limit of the total nitrogen discharged in industrial wastewaters can be calculated to be about 0.1 Mt N/yr (U.S. EPA 1971a, Davis 1973, Development Planning and Research Associates, Inc. [DPRA] 1975). The fraction of nitrogenous products that is lost in wastewaters amounts to less than 0.1 percent of total production. Nitrogen industries also may pollute the air with ammonia emissions and with nitrogen-rich dusts from production processes or spills. Stormwater runoff can transport this nitrogen into surface waters, producing more diffuse pollution than direct discharge of process wastes.

Although the significance of industrial wastes in the national inventory of environmental sources of nitrogen is minimal, the local impacts of such discharges can be severe. For example, it is estimated that a sulfite pulping plant discharges 50 pounds of ammonia (18.7 kg N) as waste for each ton of pulp produced (U.S. EPA 1970). A pulp mill with a capacity of 100 tons/day therefore could discharge about two metric tons of ammonia-nitrogen in its wastes each day; such a discharge is equivalent to the nitrogen load in the sewage of a city of more than 100,000 people. Similarly, if

TABLE 6.10 Industrial Production Capacity in the United States for Major Nitrogenous Materials[a]

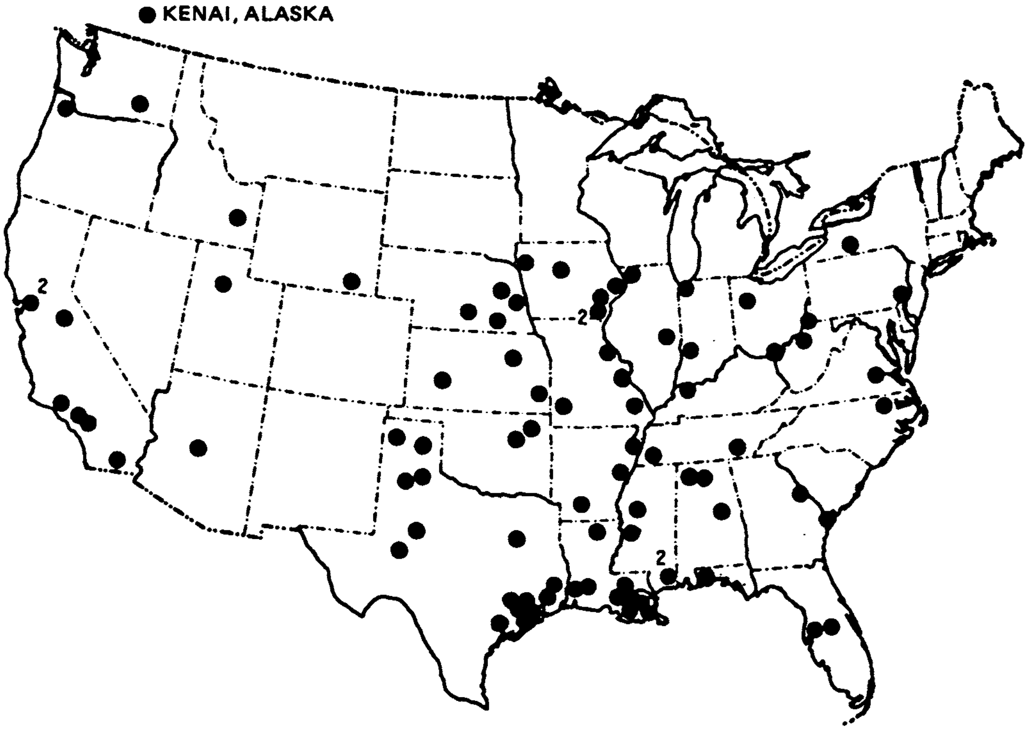
Product	Number of Plants	Capacity Mt/yr, as Product	Capacity Mt/yr, as N
Ammonia	87	15.8	13.0
Ammonium nitrate	63	6.9	2.4
Urea	40	3.9	1.8
Nitric acid	72	6.7	1.5
Ammonium sulfate	64	2.5	0.5

[a] Data from Davis (1973) and DPRA (1975).



SOURCE: Modified from Paul et al. (1977).

FIGURE 6.11 Production capacity for the anhydrous ammonia industry in the United States, 1951-1975.



SOURCE: U.S. EPA (1971a).

FIGURE 6.12 Location of major ammonia-producing facilities in the United States.

TABLE 6.11 Typical Concentrations of Nitrogenous Contaminants in Wastewaters from Major Nitrogen-Using Industries[a]

Industry	Volume of wastewater (gal/ton of product)[b]	Contaminant levels			
		NH_3	NO_3^-	Urea	BOD
		mg/liter (mg N/l)			mg/l
Ammonia Plant	100-1,000	20-100 (16-82)	--	--	50-150
Ammonium Nitrate Plant	50-1,200	200-2000 (164-1640)	50-1000 (12-230)	--	<20
Ammonium Sulfate Plant[c]	100-10,000	10-1000 (8-820)	--	--	<20
Urea Plant	50-2000	200-4000 (164-3280)	--	50-1000 (24-470)	30-300

[a] Data from U.S. EPA (1971a).

[b] 1 gal/ton = 4.16 l/metric ton.

[c] Wide range of values because of possible recycling of aqueous scrubber solutions.

we apply the upper limit of the waste-nitrogen to product-nitrogen ratio of 0.1 percent to a large ammonia and fertilizer complex with a capacity of 1,000 tons/day, the nitrogen wastes would be the equivalent of sewage nitrogen from about 600,000 people. Wastes from industries such as fertilizer plants generally contain high levels of ammonia, but very little organic material; they therefore do not create the high BOD characteristic of sewage. It is clear, however, that in areas where several industrial nitrogen sources are clustered or where the volume of receiving waters is small, industrial discharges can contribute substantially to nitrogen pollution loads.

Until very recently, most nitrogen-discharging industries used no control measures other than dilution to treat their waste streams; a survey by the firm of Development Planning and Research Associates, Inc., undertaken for the National Commission on Water Quality (DPRA 1975), found that only 4 percent of the facilities in the nitrogen fertilizer industries met "best practical treatment" standards at that time. Furthermore, most control measures were directed at solids, oils, toxic metals, or BOD; such treatments generally have little effect on the nitrogen content of wastewaters. To meet national water quality goals and to prevent local impacts of the sort described in Chapter 8, many industrial plants may need to provide waste treatment facilities to remove nitrogen from their effluents. Chapter 10 reviews some of the techniques available to accomplish such controls.

ATMOSPHERIC SOURCES, TRANSPORT, AND LOADINGS OF NITRATE

There are two important environmental issues regarding the presence of anthropogenic nitrate in the lower atmosphere: (1) the significance of anthropogenic nitrogen in rainfall and dry fallout as a potential nutrient for aquatic and terrestrial ecosystems; and (2) the contribution of nitric acid formed from nitrogen oxides (NO_x) of combustion origin to the acidity of rainfall. To a great extent these effects are offsetting, the first tending to increase the productivity of some ecosystems, and the second to decrease it.

This section reviews the sources of nitrate and other nitrogen compounds in atmospheric precipitation (including rain, snow, and dry fallout), with emphasis on human contributions. Historical and geographic trends in the levels of nitrate and other nitrogen forms in precipitation and in rainfall acidity are described, and factors that affect the distribution of nitrogen compounds in the atmosphere and in rainfall are discussed here. Closely related topics are presented in other sections of this report. The atmospheric reactions that produce nitrate aerosols and nitric acid from oxides of nitrogen are discussed in Chapter 2, and air quality data for NO_x and nitrates are presented in Chapter 3. The significance of rainfall as a nitrogenous nutrient source for terrestrial and aquatic ecosystems and the effects of acid rainfall on ecosystems are discussed in Chapter 8, and effects of atmospheric nitrates on human health are reviewed in Chapter 9. Methods for the control of nitrogen emissions to the atmosphere are reviewed in Chapter 10.

Sources of Atmospheric Fixed Nitrogen

Sources of fixed nitrogen in the atmosphere are listed in Table 6.12. The major forms of nitrogen emitted to the atmosphere are ammonia (NH_3) and two oxides of nitrogen, nitric oxide (NO), and nitrogen dioxide (NO_2). The latter compounds are readily interconvertible and are measured collectively as NO_x (see Chapter 4). Organic nitrogen compounds in dust and soil particles may also be a major local source, but since the transport and atmospheric residence times of such particles are quite limited, this source will not be reviewed here.

Nitrogen Oxides (NO_x)

Nationwide Sources and Trends. The largest anthropogenic source of nitrogen oxides is the combustion of fossil fuels, which results in the fixation of atmospheric N_2. National emission inventories for NO_x have been reported by the National Research Council (1975); see Figure 6.13 and Table 6.13. Total production of NO_x in the United States (7.5 Mt N in 1972) is about 40 percent of the global rate of anthropogenic NO_x emissions discussed below. Stationary fuel combustion accounts for nearly half of the total emissions in the United States, and emissions from generation of electricity account for nearly half of the stationary combustion emissions. Transportation accounts for about 35 percent of the NO_x emissions, and industrial process losses are the other major source, accounting for about 12 percent of emissions.

Figure 6.14 shows trends in nationwide emissions of NO_x by major categories of sources during the period 1940-1972, and projected emissions to the year 1990, assuming that the present statutory control program continues (NRC 1975). Between 1940 and 1970, nationwide emissions approximately quadrupled from 6.5×10^6 tons of NO_x as NO_2 (1.8 Mt N) to 22.7×10^6 tons of NO_x (6.3 Mt N).

Estimates of nationwide emissions of nitrogen oxides for the period 1970 to 1975 were recently recalculated by EPA, based on their current emission factors (U.S. EPA

TABLE 6.12 Sources of Atmospheric Fixed Nitrogen[a]

Source	Major Species
Natural	
Soil: decomposition and volatilization of organic matter and animal wastes under alkaline conditions	NH_3
Chemodenitrification in acidic swamps and soils	NO
Forest fires	NH_3, NO_x
Volcanoes	NH_3, NO_x?
Lightning	NO_x
Inflow from the Stratosphere (from photolysis of N_2O)	NO_x
Anthropogenic	
Volatilization of fertilizer (especially anhydrous NH_3)	NH_3
Animal wastes (feedlots and pastures)	NH_3
Combustion (1) Fuels--coal, petroleum wood, natural gas, refuse. (2) Processes--power generation, industry, domestic heating, refinery production, transportation, controlled burning, (forest, sugar cane), incineration.	NH_3[b], NO_x

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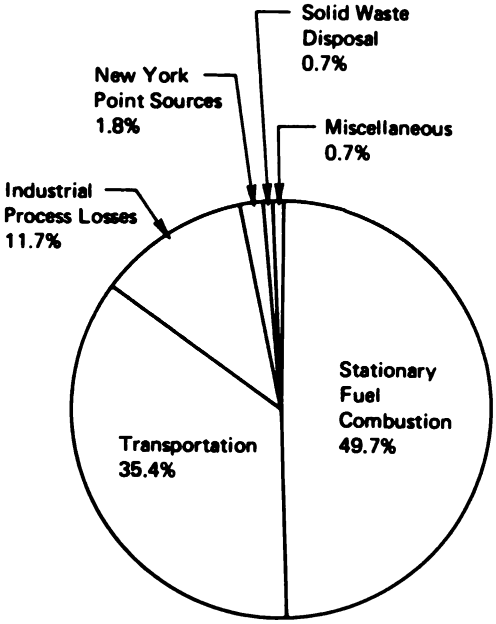
[a] Sources of N_2O are not considered since this gas is apparently unreactive in the troposphere.

[b] Some combustion sources (e.g. natural gas) are not significant emitters of NH_3.



SOURCE: NRC (1975).

FIGURE 6.13 Proportional contributions of source categories to nationwide NO_x emissions in 1972.

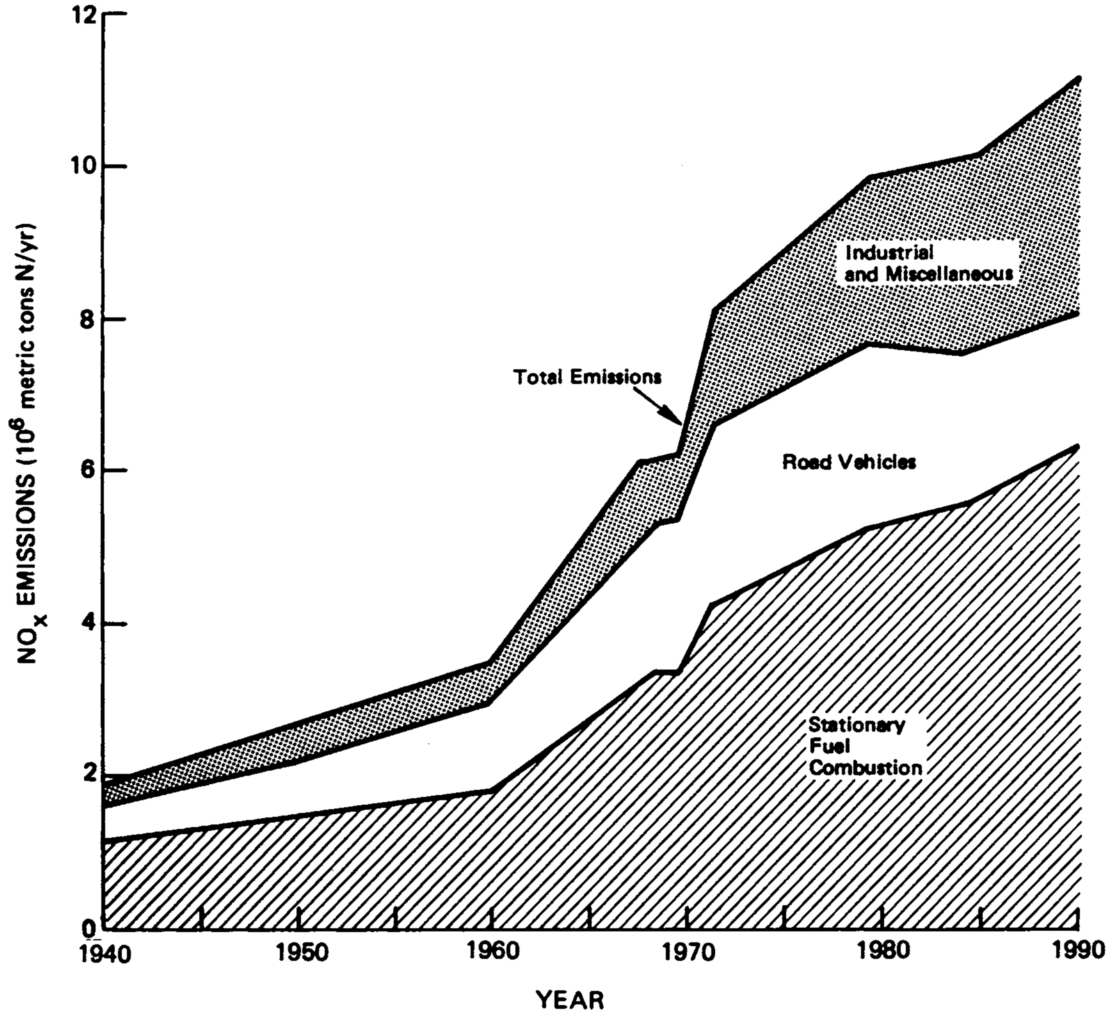
TABLE 6.13 Summary of Emissions of Oxides of Nitrogen by Source Type and Fuel Use for the United States in 1972

Source Type	Emissions Million U.S. tons NO_x (as NO_2)/year[a]	Emissions, Mt NO_x-N[a]	Percent of Total Emissions
Stationary Fuel Combustion	12.27	3.39	49.7
Electric Generation	5.94		24.1
Coal	3.95		16.0
Oil	0.85		3.4
Natural Gas	1.14		4.7
Industrial Fuel Combustion	5.39		21.8
Coal	0.76		3.0
Oil	0.41		1.6
Process Gas	2.58		10.5
Natural Gas	1.64		6.7
Commercial-Institutional	0.65		2.6
Residential	0.29		1.2
Transportation	8.72	2.41	35.4
Gasoline	6.62		26.9
Diesel	1.90		7.7
Other	0.20		0.8
Industrial Process Losses	2.88	0.80	11.7
Solid Waste Disposal	0.18	0.05	0.7
Miscellaneous	0.17	0.05	0.7
New York Point Sources[b]	0.42	0.12	1.8
Total	24.64	6.82	100.0

[a] Conversion from U.S. tons x 10^6 of NO_x to Mt N: NO_x assumed to be all NO_2; 1 U.S. ton NO_x = 0.273 metric ton N.

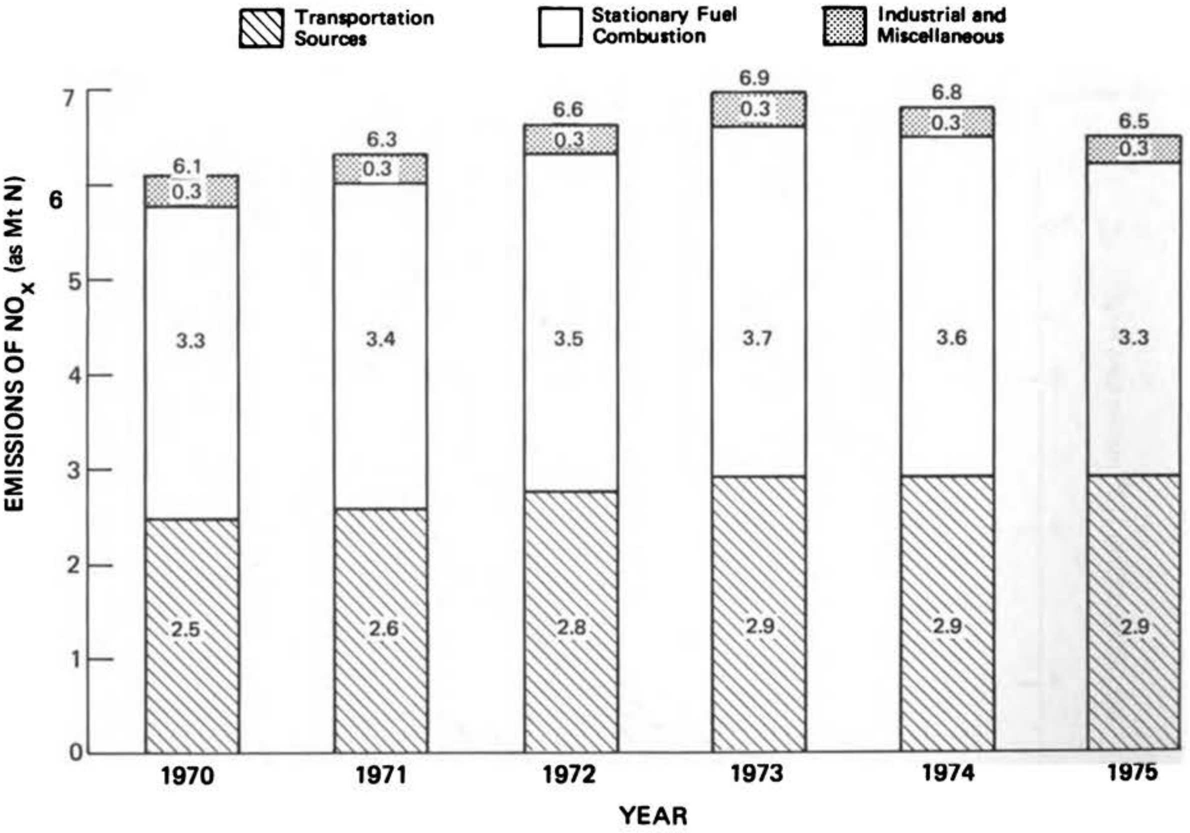
[b] Computed separately because of the nature of the data base.

SOURCE: Adapted from NRC (1975).



SOURCE: Modified from NRC (1975).

FIGURE 6.14 Actual and projected trends in emissions of NO_x in the United States, by source categories.



SOURCE: Data from U.S. EPA (1976).

FIGURE 6.15 Estimated emissions of nitrogen oxides by source category for the United States, 1970-1975.

1976); the results of these calculations are shown in Figure 6.15. · The effects of the 1973 energy crisis are clearly reflected in the emission trends. From 1970 to 1973, total NO_x emissions (as NO_2) increased from 22.7 to 25.7 million tons (6.2 to 7.1 Mt N), but in both 1974 and 1975 emissions decreased (to 24.2 million tons as NO_2 [6.7 Mt N] in the latter year), primarily because of decreases in stationary fuel combustion sources. Figure 6.15 indicates that the large increases in nationwide emissions of NO_x projected in Figure 6.14 by the National Research Council (1975) for the early 1970s did not occur. COnsequently, it does not seem prudent to base long-term projections of future emissions on this figure. The data in Figure 6.15 are also inadequate to define long-term trends; however, a reasonable estimate of nationwide emissions of NO_x for 1978 apears to be around 7.0 Mt N.

Estimates of Global Fluxes. The significance of noncombustion sources of NO_x has rarely been evaluated quantitatively. Some insights may be gained from studies of the global nitrogen budget, but it should be noted that global emission rates from both natural and human sources are poorly quantified. Robinson and Robbins (1971) estimated global urban emissions of NO_x to be 16 Mt N for 1965. Most of this represented NO_x from the burning of fossil fuels. These authors estimated the total global emission of NO_x to be 228 Mt N, on the basis of mass-balance calculations (see Chapter 5), but the large implied natural source was not identified. More recently, Söderlund and Svensson (1976) updated Robinson and Robbins' estimate for global urban emissions of NO_x to 19 Mt N for 1970, and based on mass balance calcuations they estimated total global NO_x emissions to be from 43 to 116 Mt N/yr. For reasons noted in Chapter 5, this estimate appears to be more credible than the estimate by Robinson and Robbins. The Council for Agricultural Science and Technology (CAST 1976) estimated worldwide emissions from combustion to be 20 Mt N/yr in 1974. Except for an estimate of nitrogen fixed by lightning (discussed below), CAST concluded that evidence pertaining to other natural sources of NO_x was too insubstantial to support a quantitative estimate of total global emissions.

Lightning. The significance of lightning as a source of atmospheric NO_x has been controversial for many years. Lightning was long thought to be the major source of nitrate in rainfall; this hypothesis originated with Liebig in 1827 (see Hutchinson 1954). Because of the lack of correlation between the intensity of lightning and nitrate concentrations in rainfall, however, Hutchinson (1954) concluded that lightning produced less than half of the nitrate in rain; on similar grounds, Junge (1958) concluded that lightning contributes only 10 to 20 percent of the nitrate found in rain. Viemeister (1960) and Visser (1961) also found poor correlations between lightning events and levels of nitrate in rain. Citing these results, Söderlund and Svensson (1976) dismissed lightning as a negligible source of fixed nitrogen. However, Delwiche (1970) and CAST (1976) estimated global production of NO_x by lightning at 10 Mt N/yr, and Holland (1973) estimated that the process fixes 10 to 20 Mt N/yr.

Griffing (1977) presented a theoretical model for production of ozone (O_3), nitrous oxide (N_2O), and NO during thunderstorms. Because certain parameters in his model could not be evaluated, Griffing did not derive quantitative estimates of global production rates for these substances. He concluded, however, that lightning is probably an important local source of ozone and nitrogen oxides, and that it could be an important global source of N_2O (if certain suggested reactions are verified). Chameides et al. (1977) also examined the production of NO_x in lightning. They noted that previous attempts to correlate the intensity of lightning with the nitrate content of rainfall were based on a misconception. Because the lifetime of a thunderstorm is short and the conversion of NO_x to nitric acid and nitrate aerosols is relatively slow (12 to 20 hours; Chameides 1975; see Chapter 2), the absence of strong correlations does not necessarily imply that lightning is unimportant as a source of NO_x. Chameides et al. (1977) developed theoretical calculations for the production of nitric oxide (NO) in lightning by analogy to high temperature shock waves (see Uman 1969), and obtained corroborative data for these calculations from laboratory observations of NO_x production in electrical discharges. They estimated that global production of nitrogen oxides by lightning is 30 to 40 Mt N/yr, and concluded that lightning could account for as much as 50 percent of the global production of NO_x.

Burning of wood. Previous global mass balances for nitrogen have considered wood burning to be a negligible source of NO_x (see Appendix A, Section 7). However, recent studies of the global carbon cycle suggest that the combustion of biomass, largely in land-clearing for agriculture in tropical regions, makes an important contribution to global atmospheric inputs of CO_2. As much as 3 percent of the forested area in some large states of Brazil has been burned each year recently, and the global rate of loss of wood carbon may be from 0.1 to 1.0 tons per capita per year (Adams et al. 1977). The global input of carbon to the atmosphere from the combustion of biomass is currently estimated at from 400 to 8000 Mt C/yr (Adams et al. 1977, Woodwell et al. 1978, Stuiver 1978).

Because biomass (chiefly wood) contains nitrogen, these recent calculations also have important implications for the global nitrogen cycle. The exact contribution of NO_x from combustion of biomass is not accurately known; however, if it is assumed that wood has an average carbon/nitrogen ratio of 40:1, and that all the nitrogen in biomass is released in fixed forms by burning, the annual global contribution by combustion of biomass to atmospheric fixed nitrogen implied by the carbon cycle studies would be 10 to 200 Mt N. Clearly, this would be a significant input in comparison to other sources of atmospheric fixed nitrogen. However, the actual amounts of the nitrogen in wood that are released as NO_x, NH_3, N_2O, and N_2 under conditions of open burning are not accurately known, and further investigations seem warranted to quantify this potentially important flux.

Ammonia

On a global basis, volatilization of ammonia from natural sources on land (and possibly the sea) dominates over anthropogenic sources (combustion and volatilization related to agricultural use of nitrogen). Robinson and Robbins (1971) calculated that the ammonia emitted annually from urban sources worldwide was only 3.5 Mt out of the total estimated global emission of 870 Mt N. The fraction of total global emissions from agricultural activities was not estimated. Söderlund and Svensson (1976) calculated much lower global emissions of ammonia: a total of 113 to 244 Mt N/yr, of which burning of coal accounted for 4 to 12 Mt, and volatilization from animal and human wastes accounted for 20 to 35 Mt. Chapter 5 discusses the reasons for the large differences in the two estimates of global emissions of ammonia.

No complete national inventory of ammonia emissions to the atmosphere is available. A recent National Research Council study estimated total emissions of NH_3 in the United States to be 0.32 Mt N/yr (NRC 1977a), but this figure seems low. Emissions from the production and use of ammonia in fertilizer and industrial chemicals were estimated at 0.30 Mt N/yr, and more than half of this loss (0.17 Mt N/yr) was from direct application of ammonia fertilizer to soil. On the other hand, CAST (1976) estimated a global loss of 7 Mt N/yr from inefficiencies in handling and applying ammonia fertilizers. Since the United States accounts for about 25 percent of the global use of ammonia fertilizer, these two estimates clearly are not concordant. Total mass emissions of ammonia in the United States from combustion of coal, petroleum, and solid wastes were not calculated by the NRC, but emission factors for these combustion processes were listed in terms of kg NH_3 emitted per unit fuel burned. Compared to emissions of ammonia from natural sources, emissions from all combustion processes are thought to make only a small contribution to the ammonia loading of the atmosphere.

Emissions from feedlots represent a significant local and regional source of ammonia (as discussed earlier in this chapter). According to studies reviewed in the recent report of the National Research Council (1977a), 50 to 100 percent of the urea-nitrogen in urine generated in feedlots may volatilize as ammonia. There are 10.2 million cattle in feedlots in the United States, and the average waste generation is 0.17 kg N/day (62 kg N/yr) per animal. Since half the nitrogen excreted by cattle is in the form of urea, which is rapidly hydrolyzed to NH_3 and CO_2, the total atmospheric input from feedlot-generated urine in the United States could range from 0.16 to 0.32 Mt N/yr, a negligible amount on a national scale, but possibly significant on a local scale. If it is assumed that 50 to 100 percent of the urea nitrogen excreted by all cattle in the United States (132 million head) is volatilized, 2 to 4 Mt N/yr could be emitted from cattle wastes. This amount is roughly one-fourth to one-half of the rate of anthropogenic emissions of nitrogen as NO_x in the United States.

Recent studies indicate that substantial amounts of ammonia are volatilized in heavily grazed pastures. Denmead et al. (1974) found much smaller losses in ungrazed areas than in grazed pastures, implicating animal urea as the major source of ammonia. Denmead et al. (1976) also found, however, that most of the volatilized nitrogen was reabsorbed by the plant canopy. Luebs et al. (1973) reported that the presence of 143,000 head of cattle in the 150 km^2 Chino-Corona dairy area of southern California resulted in ammonia and volatile amine concentrations in the air over a 560 km^2 area that were 20 to 30 times higher than control values. Simpson (1968) found ammonia losses of 1.35 g N/m^2-day in heavily grazed sheep pastures under arid conditions, while Kim (1973) measured ammonia volatilization rates of 0.03, 0.05, and 0.04 g N/m^2-day respectively from grassland, pine, and oak forests in Korea.

The role of aquatic environments as a source or sink for ammonia has not been well studied. At pH values above about 8.3, such as occur during algal "blooms," ammonium tends to be deprotonated to ammonia (pK = 9.3 for $NH_4^+ <===> NH_3$), and the water acts as a source of ammonia for the atmosphere. Stratton (1969) reported ammonia volatilization rates of 0.035 and 0.098 g N/m^2-day from two eutrophic lakes with pH values greater than 9. At lower pH levels, absorption of ammonia from the atmosphere will occur; the balance point depends on the partial pressure of NH_3 in the atmosphere. The oceans are generally regarded as net sinks for ammonia, but some areas such as estuaries and upwelling zones may be sources on a seasonal basis.

Factors Affecting Levels of Nitrogen in Rainfall

Factors affecting the nutrient content in rainfall have been discussed by Chapin and Uttormark (1973) and Brezonik (1976). Table 6.14, adapted from those two sources, lists the major factors and gives the direction of their effects on atmospheric nutrient fluxes. Many of these factors are also important in controlling rainfall acidity. From a practical viewpoint, the number of factors that must be considered makes generalizations about atmospheric inputs of nutrients and acidity difficult, and accurate measurement of these inputs for specific sites requires detailed and intensive sampling programs.

The factors listed in Table 6.14 are understood qualitatively, but in most cases quantitative assessments are not possible. Many of the factors can be explained simply in relation to the sources of atmospheric nutrients described earlier. For example, agricultural activity, automobile emissions and solid waste disposal sites are all direct sources of ammonia, nitrogen oxides or nitrate aerosols. Increased soil acidity can decrease the amount of volatilization of ammonia from animal wastes and fertilizer, and high soil exchange capacity tends to tie up soil ammonia as the ammonium ion (NH_4^+). Hutchinson and Viets (1969) found ammonia levels were two to three times higher in rain and snow near large cattle feedlots in Colorado than in control areas, and Hoeft et al. (1972) found four to five times as much ammonia in rainfall collected near barnyards than at other rural sites in Wisconsin. Total organic nitrogen levels in precipitation near barnyards were twice those of rural control areas, but nitrate levels were relatively constant (Table 6.15). Snow is considered less effective than rainfall in scavenging contaminants from the air, and consequently has generally lower concentrations. Snowfall nutrient concentrations have been reviewed by Feth (1964) and Brezonik (1976).

A major factor affecting the concentration of nitrate in rain is the length of time since previous rain. The buildup of atmospheric contaminants such as nitric acid and nitrate aerosols depends in a complex fashion on the emission rates of precursor NO_x; on rates of transformation of NO_x to nitrate in the atmosphere; and on rates of dissipation by advection, diffusion, and gravitational settling. The net effect of these processes in a given locality probably is an asymptotic increase in contaminant concentrations toward some maximum level between each cleansing of the atmosphere by rainfall. Atmospheric transport processes can move air masses several hundreds of kilometers per day, and the residence times of ammonia and nitrogen oxides in the atmosphere are on the order of several days. Emissions therefore can result in regional rather than strictly local effects (see later discussion on acid rain).

TABLE 6.14 Factors that Affect the Nutrient Content of Rainfall

Increases the Nutrient Content		Decreases the Nutrient Content
	CLIMATIC FACTORS	
Length of time since antecedent rainfall		Amount of rain (duration of storm)
Heavy precipitation in given year relative to previous years		Inshore ocean winds
Frequent presence of fog and dew		Predominance of snow as form of precipitation
Wind prior to rain (stirs up dust)		Polar conditions
Tropical conditions		High altitude
	EDAPHIC FACTORS	
Saturated, poorly aerated soil		Arid conditions, dry soil
Alkaline soil		Acid Soil
Weathered soil with high humic content		High exchange capacity of soil
	OTHER NATURAL FACTORS	
Forest fires		
Heavy bird populations		
	ANTHROPOGENIC FACTORS	
Agricultural activity		
Feedlots		
Urbanization		
Unpaved roads		
Industrial activity (especially fertilizer/explosive plants, power plants)		
Automobiles		
Solid waste disposal sites		

SOURCE: Adapted from Brezonik (1976) and Chapin and Uttormark (1973).

TABLE 6.15 Fluxes of Nitrogen in Rainfall in Wisconsin

	Locations		
Form of N	Rural (Near Barnyards)	Rural (Removed from Barnyards)	Urban
		(kg N/ha-yr)	
Ammonia	12.2	2.9	3.6
Nitrate	3.5	2.7	3.6
Organic N	14.4	7.5	6.2
Total N	30.1	13.1	13.4

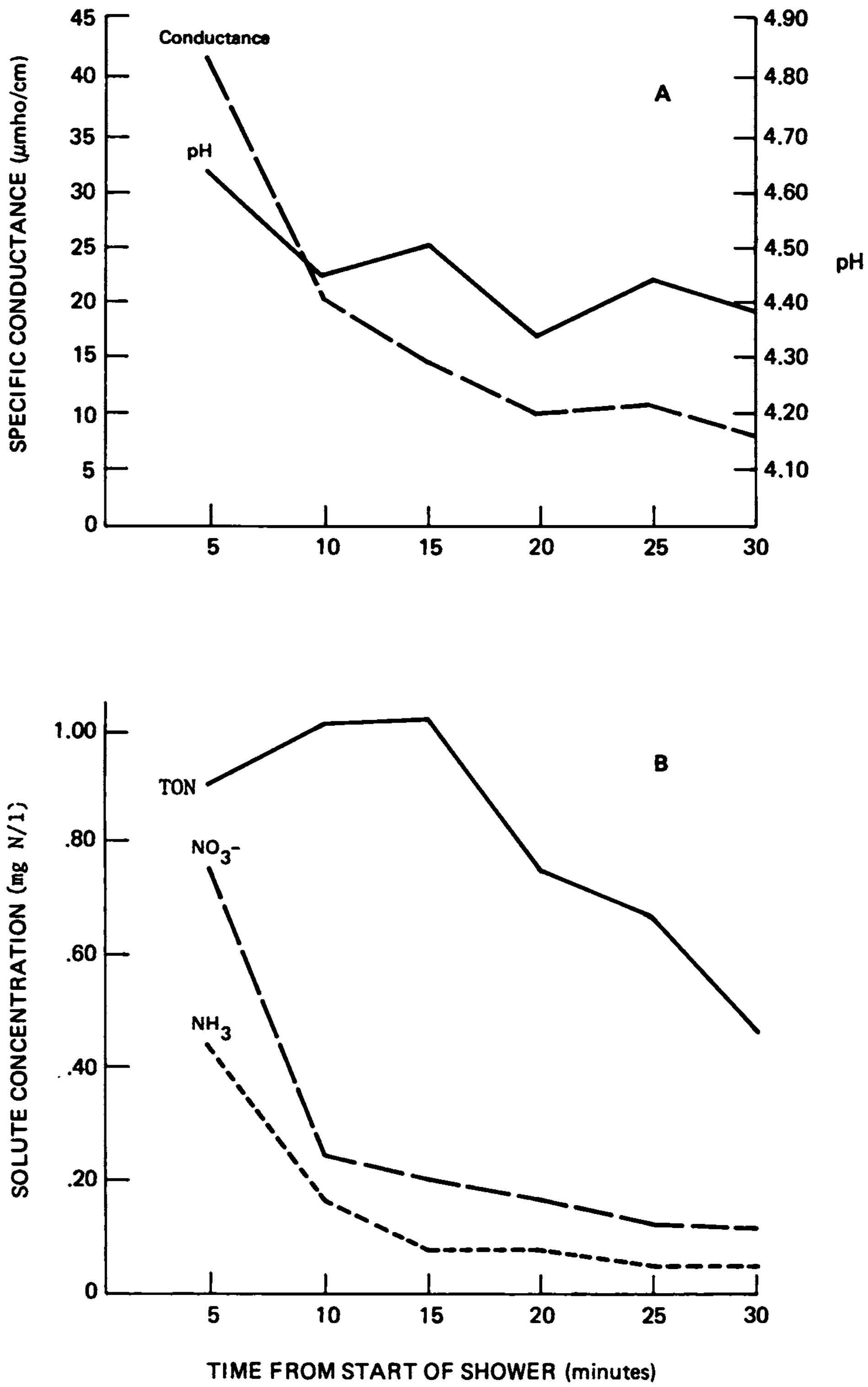
SOURCE: Adapted from Hoeft et al. (1972).

Scavenging by rainfall produces large changes in atmospheric contaminant concentrations during a given rainfall event. Figure 6.16 shows an example of the phenomenon for a rain shower in Gainesville, Florida (Hendry 1977). The decline in nutrient levels is usually rapid, at least in localized convective showers, and low, steady-state concentrations are usually reached within the first half hour of a rain event.

The temporal trends in solute concentrations during a rain event can be explained as the result of two deposition processes: rainout and washout (Junge 1963). In the former process, substances enter rain drops within a cloud by mechanisms such as the buildup of droplets on condensation nuclei and the absorption of gases and scavenging of aerosols by growing drops within the cloud. Rainout processes are relatively constant during a rain event. Washout involves the scavenging of particles and gases by rain drops as they fall through the atmosphere; the importance of this process decreases as a rain continues. The efficiency of scavenging depends on particle size in a complicated manner (Fuchs 1964, Hidy and Brock 1970).

Nitrogen aerosols are produced either by terrestrial erosion (primary aerosols) or by synthesis of ammonium sulfate and ammonium nitrate particles from the gaseous forms, NH_3 and NO_x, in the atmosphere (secondary aerosols; see Chapter 2). Primary aerosols are large particles that are susceptible to washout, but secondary aerosols are small and possibly in a range that is not effectively washed out. Nitrogen aerosols, however, are highly hygroscopic, and as they grow by absorbing water, they may be important as condensation nuclei for the formation of rain drops (i.e., the process of rainout).

No general conclusions about the relative abundance of these two types of nitrogen aerosols can be drawn from available information, although some data has been published on specific locations (e.g., Junge 1963; Lundgren 1970, 1971; Grosjean et al. 1976). Lundgren (1970) found a mass mean diameter of 0.8 μm for nitrate aerosols at Riverside, California, and reported that high concentrations of ammonium nitrate aerosols, mainly in the 0.5 to 2 μm diameter size range, were associated with days of heavy smog. Grosjean et al. (1976) measured particle size distributions of nitrate aerosols at the same location and reported that submicron (<0.6 μm) particles of nitrate aerosols were produced at rates exceeding 10 $\mu g/m^3$-hr during photochemical episodes. Kadowaki (1977) recently reported a bimodal distribution of nitrate aerosols in the atmosphere over Nagoya, Japan. A submicron fraction with a modal diameter of 0.4 to 0.6 μm was found to be composed of NH_4NO_3, whereas a coarser fraction with a modal diameter of 3 to 5 μm was found to be $NaNO_3$. Kadowaki hypothesized that



SOURCE: Modified from Hendry (1977).

FIGURE 6.16 Time trends of specific conductance and pH (A) and of solute concentrations (B) in rainfall from a single shower at Gainesville, Florida, October 16, 1976.

the latter particles are formed from the reaction of gaseous HNO_3 with NaCl aerosols from ocean spray. The amount of nitrate occurring in the larger particles was found to increase during periods with southerly winds that brought maritime air to the study site.

The literature is equivocal on the relative importance of rainout and washout in scavenging nutrients from the atmosphere. Results for convective rain showers in Gainesville, Florida, indicated that washout was the predominant mechanism (Brezonik 1972). Wolaver and Lieth (1973) developed an exponential die-off model for rainfall constituents based on the two scavenging processes. They used the model to analyze monthly data on rainfall quantity and concentrations of seven inorganic constituents in samples from 33 stations in the National Precipitation Sampling Network that was operated in the 1960s by the National Center for Atmospheric Research. Results suggested that both processes removed chloride but that only rainout was important for nitrate and ammonia. However, the data upon which this analysis was based may have been invalid because of changes in nitrogen forms during the long period of sample collection and storage (Brezonik 1976). Hendry (1977) found that washout predominates for both ammonia and nitrate (Figure 6.16). On the other hand, organic nitrogen levels in rainfall declined more slowly, and pH showed only small variations as showers progressed, implying that rainout (nucleation) processes are more important in scavenging organic nitrogen and H^+. Results for several rains in central Illinois indicate large and rapid decreases in both nitrate and total Kjeldahl nitrogen (organic nitrogen plus ammonia) (D.H. Kohl, Washington University, St. Louis, Mo., personal communication, 1977).

The rapid decline of solute concentrations with time during a rainstorm has important implications for the design of precipitation sample collectors. Total solute fluxes will be underestimated unless the entire event is sampled, especially the first few minutes of rain when scavenging is greatest. In order to avoid measuring nutrient fluxes from dry fallout, samplers must be covered betwen rains. For convenience, automated samplers triggered by moisture detectors can be used, but these devices must be designed to open rapidly so as not to miss the initial rainfall. Galloway (1976) compared the performances of several "wet-only" precipitation collectors.

If samplers are left open to the atmosphere between rain events, the resulting samples are called "bulk precipitation". Unfortunately, the funnel/bottle samplers usually used to collect bulk precipitation are not totally efficient collectors of dry fallout; hence it is difficult to relate bulk precipitation measurements to either total atmospheric (wet plus dry) fluxes or to rainfall fluxes.

Levels and Variations of Nitrogen in Rainfall

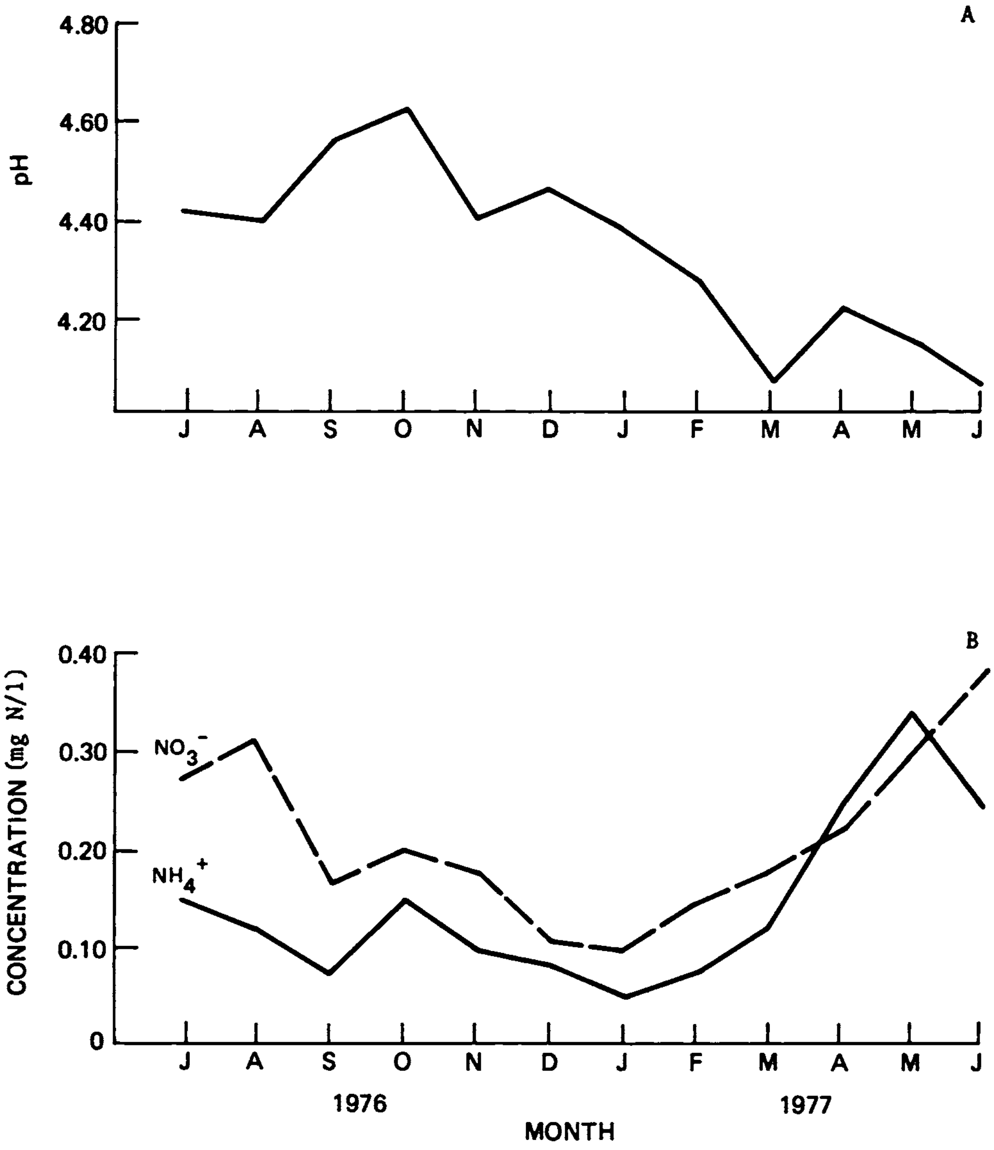
Although the availability of nitrogen compounds in precipitation as a source of plant nutrients has been studied for more than a century, research on this topic has been sporadic and not geographically widespread.

The variability of rainfall volume within small geographic areas over short periods of time and on a year-to-year basis for larger geographic regions is well known. Variations of up to 50 percent of the long-term average amount of precipitation are relatively common for any given year. Large annual differences in rainfall amounts can also occur within small geographic regions of 10 to 50 km^2, but this variability is probably more pronounced in areas where convective rain showers predominate. Unfortunately, for reasons described in the previous section, rainfall nutrient fluxes are not linearly proportional to the total amount of precipitation. As a result, calculated nutrient fluxes cannot be adjusted for an unusually wet or dry year by applying simple rainfall volume corrections to the mean flux.

Seasonal Variations

Seasonal variations of nitrogen compounds and of pH in precipitation have been reported by several workers, but no simple trends are apparent. Hoeft et al. (1972) found relatively constant levels of nitrate in rain and snow collected in Wisconsin throughout the year, but deposition of ammonia and organic nitrogen was lowest in winter and highest in spring, perhaps because of the thawing of frozen animal wastes. Brezonik et al. (1969) reported large but apparently random variations for nutrient concentrations in a one-year study of bulk precipitation at a rural north Florida site. Haines (1976) reported large random variations, but relatively small seasonal variations, for nitrogen forms in wet-only precipitation at Sapelo Island, Georgia; nutrient concentrations were lowest during the rainy summer months. Hendry (1977) found relatively smooth seasonal trends in ammonia and nitrate concentrations in both wet-only and bulk precipitation at Gainesville, Florida, with lowest concentrations in winter (Figure 6.17). The relatively high concentrations of nitrate in rain in summer storms suggest that lightning discharges are indeed an important source of nitrate, at least in Florida rain. Summer showers in this area typically are intense thunderstorms with much electrical activity, whereas winter rains seldom are associated with lightning.

Likens (1972) found significant seasonal fluctuations in ammonia and nitrate in rainfall at three sites in central New York, and Likens and Bormann (1972) found the same



SOURCE: Modified from Hendry (1977).

FIGURE 6.17 Seasonal variations in pH (A) and ammonium and nitrate concentrations (B) in wet-only precipitation at Gainesville, Florida. Values are monthly volume-weighted averages of levels in rain from individual storms.

trends for rainfall in rural New Hampshire. Fluctuations were synchronous and similar for the two forms, with the lowest concentrations occurring during the mid-winter snow cover and during late summer.

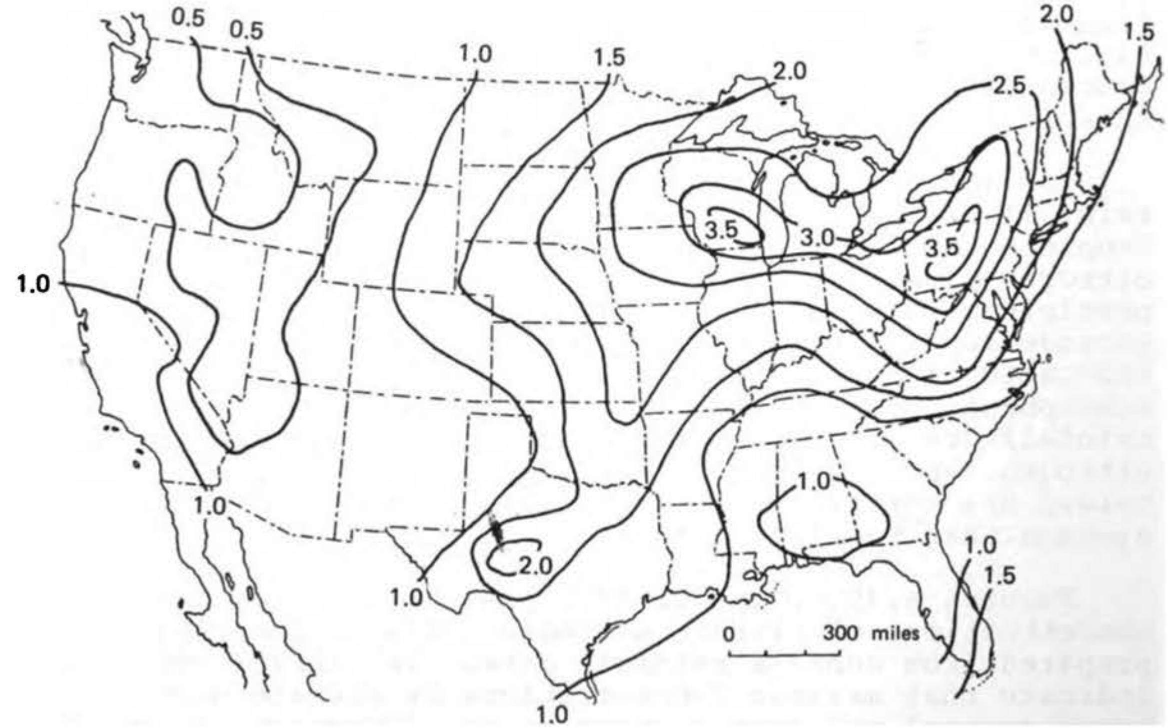
Geographic Variations

Only limited data are available on the variations of nutrient levels in rainfall over large geographic areas (e.g., the coterminous United States). Because nitrogen concentrations in rainfall are so variable, as discussed above, short-term concentration data are probably not meaningful for assessing differences over large geographic areas. Recent reviews have recommended reporting of annual fluxes of nutrients in precipitation (e.g., kg/ha-yr), to facilitate comparisons. Of course, numerous measurements of concentration and accumulation must be made to estimate these fluxes.

The most extensive synoptic data on nitrogen levels in rainfall is the often-cited work of Junge (1958). An isopleth map (Figure 6.18) of Junge's data for ammonia-nitrogen plus nitrate-nitrogen fluxes from wet-only precipitation was prepared by Chapin and Uttormark (1973). Because Junge's results were for wet precipitation and inorganic nitrogen only, they may seriously underestimate atmospheric nitrogen fluxes. Organic nitrogen levels in rainfall are often comparable to levels of inorganic nitrogen, and dry fallout and gaseous absorption, discussed below, may contribute greater loads of nitrogen to receiving systems than rainfall itself.

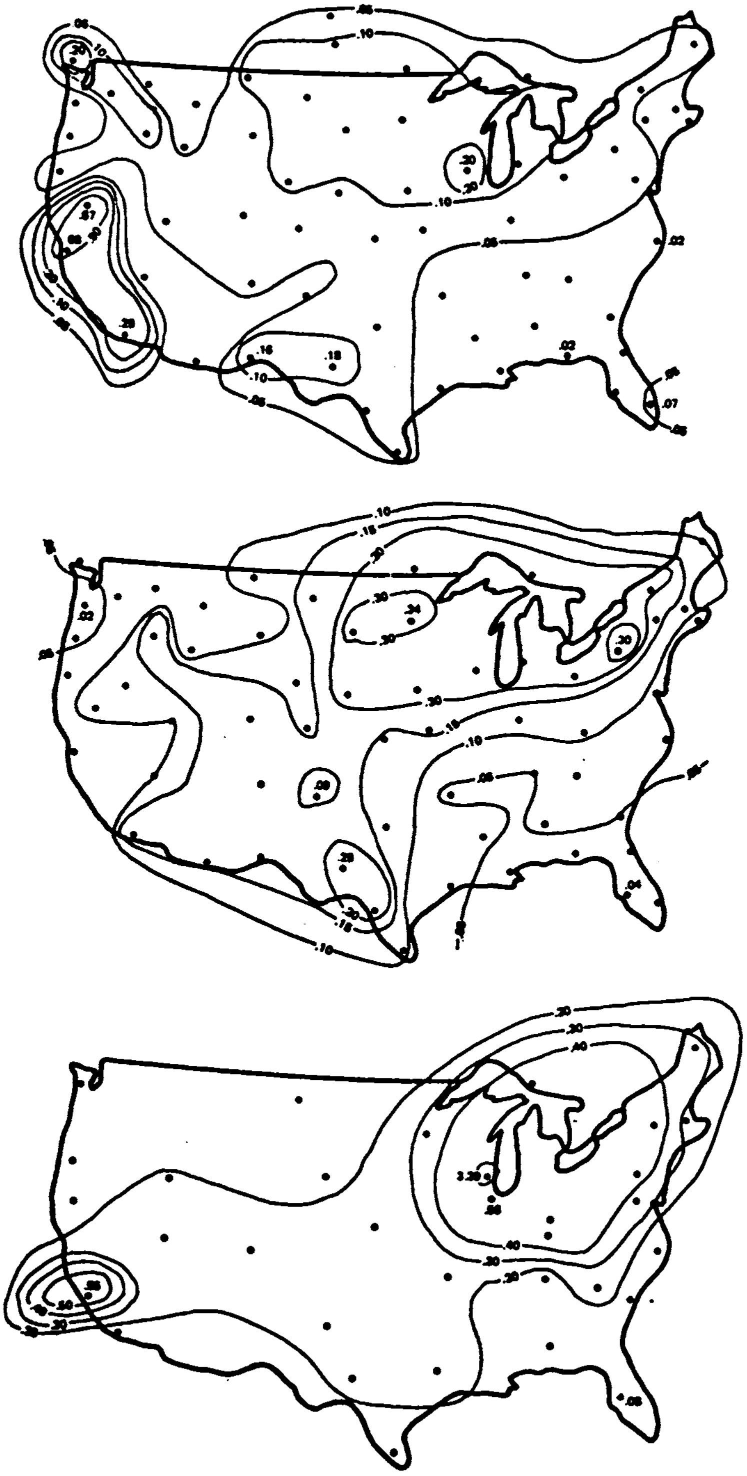
Figures 6.19(a) and 6.19(b) present maps for mean annual concentrations of nitrate-nitrogen and ammonium-nitrogen, prepared from Junge's rainfall data. In general the maps indicate that maximum concentrations of nitrate occur in the north central and northeastern states (Wisconsin to New York and Pennsylvania), while maximum ammonia levels occur in California.

Lodge et al. (1968) reported chemical data on rainfall over the United States for the period 1960 to 1966, but gave values only for total inorganic nitrogen; their results are summarized in Figure 6.19(c). Pearson and Fisher (1971) measured nitrate and other solutes in rainfall at 18 sites in New York and New England for the period 1965-1966, but reported only summary data. Gambell and Fisher (1966) and Fisher (1968) reported average nitrate concentrations over the period 1962 to 1964 for 12 stations in eastern North Carolina and Virginia. Their results indicate that the ocean is not a major source of nitrate in rainfall; the lowest concentrations of nitrate (50 to 55 μg N/l) were



SOURCE: Chapin and Uttormark (1973).

FIGURE 6.18 Geographic pattern of annual fluxes (kg N/ha-yr) of inorganic nitrogen (ammonia plus nitrate) in rainfall over the United States in 1955-56, as reported by Junge (1958).



A. Ammonium (1955-56)

B. Nitrate (1955-56)

C. Total Inorganic Nitrogen (1960-68)

SOURCE: Adapted from Chapin and Uttormark (1974).

FIGURE 6.19 Geographic patterns of mean annual concentrations of inorganic nitrogen forms in rainfall in the United States. (A), Ammonia, and (B) Nitrate, for 1955-56, based on data in Junge (1958). (C), Total Inorganic Nitrogen, average of seasonal summaries for 1960-1968, reported by Lodge et al. (1968). Points represent sample locations.

found at coastal stations, similar to the results of Junge (1958).

In contrast to findings for the United States, data for rural inland and rural coastal stations in northern Europe do not indicate lower nitrogen levels in coastal rain (Feth 1964, Odén 1976). However, both coastal and inland sites in northern Europe are probably influenced by the large-scale regional transport of nitrogen contaminants from elsewhere in Europe and from Great Britain, and data from the coastal stations probably are not valid indications of marine derived-nitrogen.

Only a few measurements of nitrogen in rainfall over the open ocean have been reported. Junge (1958) reported an average of 15 μg NH_3-N/l and 32 μg NO_3^--N/l at Bermuda. Menzel and Spaeth (1962) found an average of 70 μg NH_3-N/l in rain collected at Bermuda, but gave no data on nitrate. Tsunogai (1971) reported that atmospheric ammonia concentrations decrease rapidly in the marine atmosphere away from land.

Table 6.16 lists average ammonia and nitrate concentrations in rainfall from a wide variety of locations. Ratios of nitrate to ammonia in rainfall depend on the nature of local sources and are highly variable, especially on an individual storm basis; consequently, trends are difficult to discern. Likens (1972) found, however, that ammonia was the predominant form of nitrogen in precipitation at Ithaca before 1945, but that nitrate is now.

Historical Trends

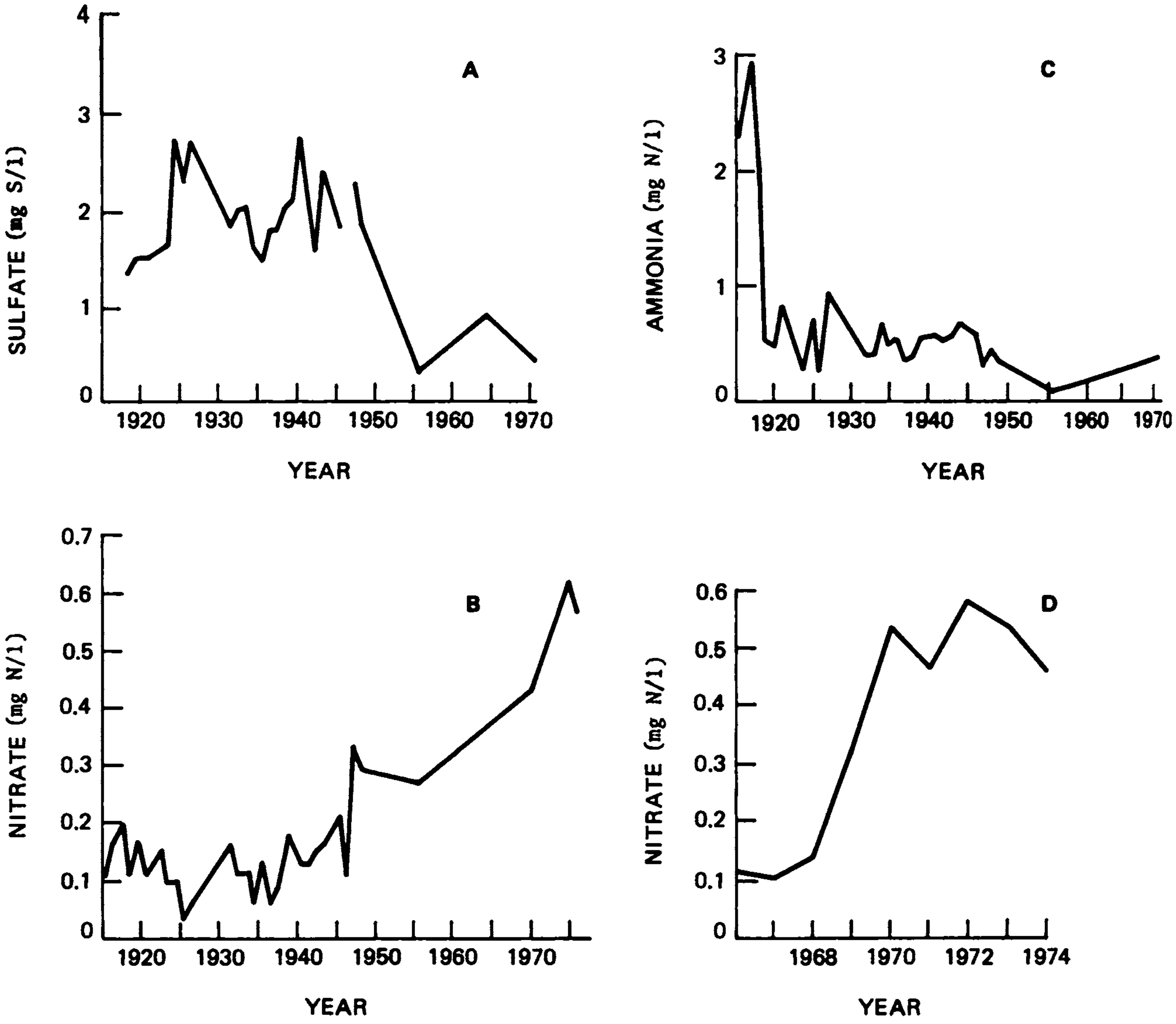
Long-term measurements of nitrogen concentrations in rainfall are available for very few sites. According to Likens (1972), data for nitrate, ammonia and sulfate in rain at Ithaca and Geneva, New York, constitute the longest record of precipitation chemistry in the United States. Data are available from 1915 to the present, but long gaps exist in the measurements, especially at the Geneva site. Figures 6.20(a) to (c) show that marked changes in composition have occurred at Ithaca: a gradual decline in ammonia, an increase in nitrate beginning around 1945, and a marked decrease in sulfate starting between 1945 and 1950. Early data for Ithaca showed higher concentrations of sulfate in winter than in summer, presumably because of greater local burning of coal in winter. Data for 1971 showed the reverse trend, however, with nearly half the annual sulfate input occurring during the months of June to August. Likens (1972) concluded that, despite deficiencies in the historical data and questions concerning their reliability, the trends are real and can be explained by

TABLE 6.16 Nitrate and Ammonium Concentrations in Wet Precipitation[a]

Location	Ammonium Mg N/1	Nitrate mg N/1	Ratio, $\frac{NO_3^--N}{NH_4^+-N}$	Reference
temperate zone	0.64	0.20	0.31	Hutchinson (1957)
tropical zone	0.31	0.27	0.87	Hutchinson (1957)
(provisional estimates of "typical" levels)	0.5	0.2	0.4	Hutchinson (1957)
Harpenden, England (average over 28 years)	0.41	0.20	0.5	Lyon et al. (1952)
Continental United States (seasonal averages for 60 stations)	0.01-2.18	0.01-2.47	variable	Junge (1958)
Central New York (average of 12 sites)	0.39	0.62	1.59	Likens (1972)
Ithaca, New York (average over 11 years)	0.55	0.10	0.19	Lyon et al. (1952)
Western United States (snow)	0.2	0.1	0.5	Feth (1964)
Ottawa, Canada				
(rain)	0.84	0.41	0.49	Lyon et al. (1952)
(rain)	1.9	0.29	0.15	Feth (1964)
(snow)	0.8	0.05	0.05	Feth (1964)
Northern Florida	0.21	0.21	1.00	Brezonik et al. (1969)
Gainesville, Florida	0.10	0.15	1.5	Hendry (1977)
Tallahassee, Florida	0.15	0.14	0.94	Turner (unpublished)[b]
Sapelo Island, Georgia	0.088	0.111	1.26	Haines (1976)
Eastern Tennessee (forest site)	0.13	0.25	1.9	Swank and Henderson (1976)
Western North Carolina (forest site)	0.02	0.12	6.0	Swank and Henderson (1976)
Nebraska (average and [maximum] values)	1.3 [3.3]	0.7 [2.0]	0.5	Olson et al. (1973)

[a] Not an exhaustive compilation. In some cases the references are secondary sources. Values usually are annual means.

[b] R. R. Turner, Oak Ridge National Laboratory, Oak Ridge, Tenn., personal communication, (1978).



SOURCE: (A), (B), and (C) modified from Likens (1972); (D) modified from Likens (1976).

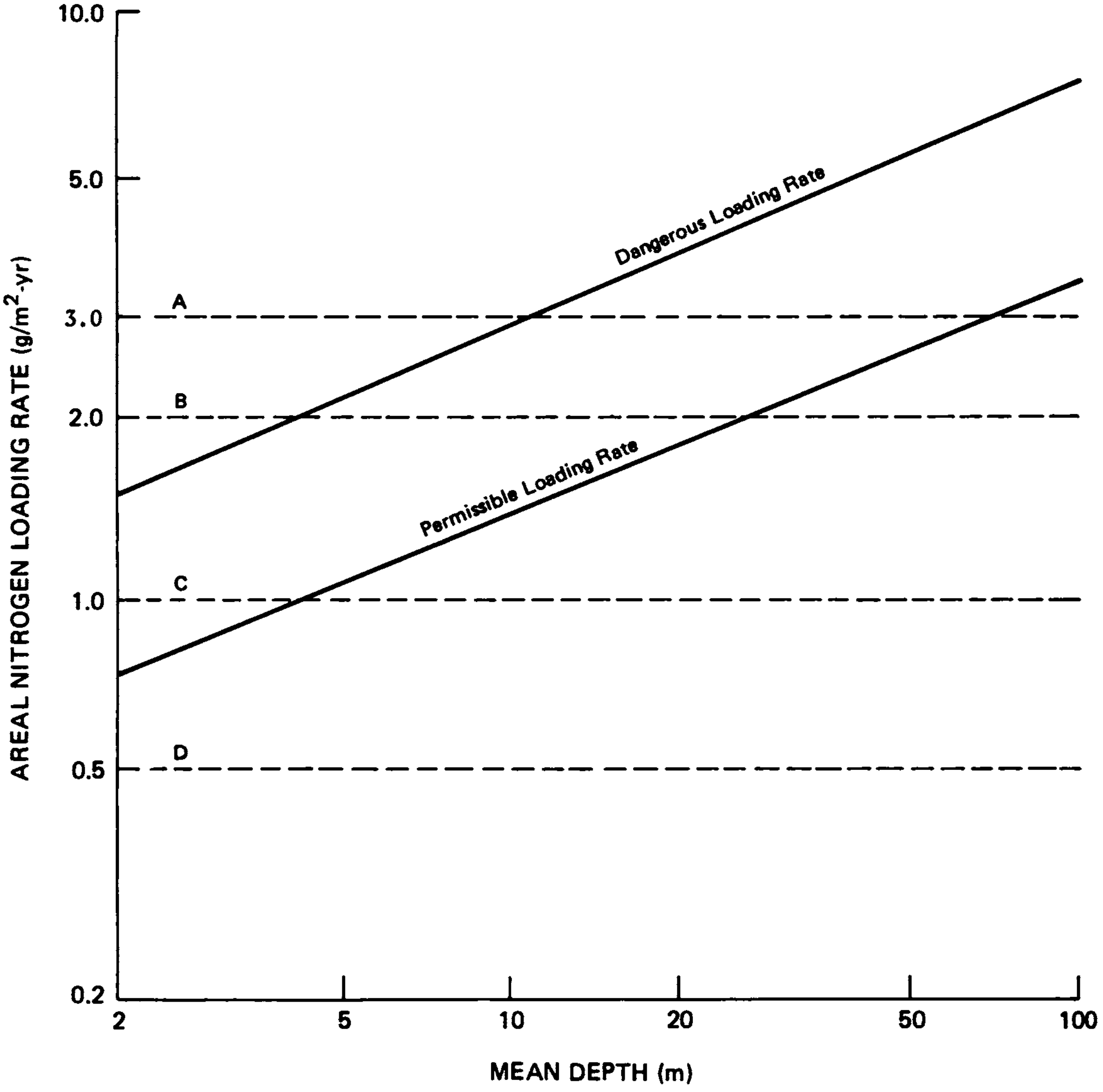
FIGURE 6.20 Trends in mean annual concentrations of sulfate, ammonia, and nitrate in precipitation. (A), (B), and (C) present long-term data for Ithaca, New York; (D) presents data for eight years averaged over eight sites in New York and one in Pennsylvania. One point in (A), for 1946-47, is believed to be an anomaly (see Likens [1972] for discussion).

changes in fuel consumption patterns; i.e., natural gas began to replace coal for home heating near the time of the shifts in precipitation chemistry. Likens (1976) reported a fourfold increase in nitrate concentrations in New York state during the past decade (Figure 6.20 [d]), on the basis of U.S. Geological Survey data for nine stations.

Rainfall Nitrogen as a Nutrient Source

The magnitude of atmospheric fluxes of fixed nitrogen to the surface of the earth depends on the many factors described earlier in this chapter and in Chapter 2. The relative importance of atmospheric fixed nitrogen to aquatic and terrestrial ecosystems depends in turn on the contributions from other sources, such as surface runoff and groundwater. In general, atmospheric sources are most important for lakes with low watershed area to lake surface area ratios and small nitrogen loadings from human activities, and for forest ecosystems in nutrient-poor regions. Brezonik (1976) reviewed the contributions of atmospheric loadings to the nitrogen and phosphorus budgets of lakes. In culturally eutrophic lakes, the percentage of total nutrient loading contributed from the atmosphere is generally small, especially for phosphorus, but 10 to 40 percent of the nitrogen loading may come from the atmosphere. Mass balance information given in Appendix A for Lakes Wingra and Mendota, Wisconsin, and Lake Okeechobee, Florida, indicates atmospheric nitrogen loadings of 29, 17 and 25 percent of the respective nitrogen budgets. Nitrate probably represents less than half the total nitrogen input of rainfall.

Brezonik (1976) concluded that bulk precipitation deposits from 1 to 2 g/m^2-yr (10 to 20 kg/ha-yr) of total nitrogen over large areas of the United States, and that deposition rates outside the range of 0.5 to 3 g/m^2-yr are likely to occur only under unusual circumstances. Figure 6.21 compares these fluxes with the loading rates that may produce eutrophication in nitrogen-limited lakes, as proposed by Vollenweider (1968). For lakes with mean depths of five meters or less, the critical loadings are in the range of 1 to 2 g/m^2-yr. The smaller value corresponds to an average total nitrogen concentration of 0.8 mg N/l for an area receiving 50 inches of rain per year, or an average of 1.3 mg N/l for areas receiving 30 inches of rain per year. Annual amounts of rainfall over most of the eastern United States are in the above range, and nitrogen levels in rainfall (Table 6.16) are also in the general range given above. Thus, it seems likely that atmospheric loadings of nitrogen are sufficient to support moderate biotic production in many lakes (see Chapter 8). Furthermore, because atmospheric sources are relatively difficult to control, (see Chapter 10), it may not be possible to reduce



SOURCE: Brezonik (1976); based on Vollenweider (1968).

FIGURE 6.21 Critical areal loading rates for nitrogen input to lakes, plotted against mean lake depth. Dashed lines show the range of loadings expected from atmospheric deposition (rainfall plus dry fall-out): (A), upper limit except near intense local sources; (B) and (C) delimit the range of loadings typical over large areas of the United States; (D), probable lower limit of atmospheric loading except for unusual climates (e.g., polar or desert areas).

total nitrogen loadings below the critical loading values for lakes.

In forested or undisturbed watersheds, concentrations of total nitrogen in rainfall are often higher than levels in stream runoff (e.g., Bouldin et al. 1975). On geological time scales, atmospheric inputs may provide nearly all the nutrients for some ecosystems developed on granitic bedrock, such as the Canadian Shield (Schindler et al. 1976).

Dry Fallout and Gaseous Deposition of Nitrogen Forms

Typical concentrations of ammonia, nitrogen oxides, and nitrogen aerosols in the atmosphere have been described in Chapter 3. Rates of dry deposition of nitrogen species are poorly known compared to rates of deposition in rainfall, but the limited evidence described below indicates that dry fallout may be even more important than rainfall as a nitrogen source.

Quantitative sampling of dry fallout is difficult because of the great spatial variability in aerosol concentrations, because two mechanisms (gaseous absorption and particle deposition) are involved, and because deposition rates depend strongly on the nature of the solid or liquid surface upon which deposition occurs. Sampling devices usually do not simulate the natural surfaces that aerosols encounter, and design of reliable samplers is a major problem.

Chapin and Uttormark (1973) and Brezonik (1976) have discussed the relative importance of dry fallout and rainfall as nitrogen sources. A wide range of ratios between the two inputs is found in the literature. Eriksson (1952) estimated that fallout in Scandinavia contributed three times as much nutrient loading as rainfall, and Kluesener (1972) estimated that dry fallout contributed twice the nitrogen and three times the phosphorous of rainfall in Madison, Wisconsin. Bulk precipitation often contains 5 to 10 times the mineral content of rainfall alone, even though bulk precipitation samplers may not be efficient in trapping dry fallout. On the other hand, samplers placed near roads, plowed fields, or close to the ground can seriously overestimate dry fallout by trapping large particles that are transported only very short distances in the atmosphere.

Deposition of gaseous forms of fixed nitrogen is known to be important locally (e.g. downwind from cattle feedlots), and some data suggest that the phenomenon is also important on a regional and even global scale. In a widely quoted study, Hutchinson and Viets (1969) collected ammonia volatilized from cattle feedlots by absorption in dilute acid, and concluded that atmospheric ammonia could add significant amounts of nitrogen to lakes near feedlots. Absorption rates as high as 7.3 g N/m^2-yr were found in the vicinity of feedlots, whereas absorption in control areas was about 0.4 g N/m^2-yr (see Table 6.6, in the section on animal wastes, above). Hutchinson and Viets calculated that ammonia absorption added about 0.6 mg N/l per year to a small lake near a feedlot.

Foliar absorption of atmospheric ammonia may account for uptake of as much as 1 g/m^2-yr in pastures (Denmead et al. 1976). Hutchinson et al. (1972) reported ammonia absorption rates of 0.35 to 0.56 mg/m^2 of leaf surface per hour for four common crops under conditions of bright light and atmospheric ammonia concentrations of 24 to 44 μg/m^3.

Where direct measurements of gaseous deposition are not available, the flux of a gas from the atmosphere into terrestrial or aquatic systems can be calculated by using deposition velocity coefficients obtained from the literature. Deposition velocities (typically expressed in m/sec) characterize the mass transport of a substance from the gas phase to a solid or liquid surface that acts as a sink. The flux of a gas to a liquid is given by the product of the deposition velocity coefficient and the difference between the concentration of the gas in the atmosphere and its concentration at the gas/liquid interface. Often the interface concentration can be ignored, and the flux is given simply as the product of the deposition velocity for the gas and its average concentration in the atmosphere. Unfortunately, only a few deposition velocity measurements have been made for gases of interest in the atmospheric nitrogen cycle; and for a given gas, the deposition velocity depends strongly on the nature of the absorbing phase (ground, water, type of plant canopy and the physiological state of the plants), as well as on physical conditions such as temperature and wind. Additional field measurements of deposition velocities are needed for nitrogenous gases under varying conditions of ground cover and for varying water phase conditions.

Robinson and Robbins (1971) calculated a global deposition rate for gaseous ammonia of 680 Mt N/yr by assuming an average concentration of 6 ppb for ammonia in the atmosphere and a deposition velocity of 1 cm/sec. The latter figure was derived from data for sulfur dioxide, because no measured deposition velocities for ammonia were available. These authors also calculated that global dry deposition of particulate ammonium was 40 Mt N/yr. Their total deposition rate for NH_3 and NH_4^+ is large compared to other known atmospheric fluxes in the nitrogen cycle; for example, their value for the global deposition of ammonium and nitrate in rainfall (225 Mt N/yr) is less than one-third the rate of dry deposition of ammonia alone. Söderlund and

Svensson (1976) estimated global dry deposition of gaseous ammonia to range from 67 to 134 Mt N/yr. These authors used a deposition velocity of 0.8 cm/sec, again by analogy to SO_2. Concentrations of ammonia in the atmosphere varied geographically, from 0.4 ppb over ocean areas to 6 to 12 ppb over tropical land areas. Particulate ammonia deposition, calculated in a similar manner, was estimated to be 5 to 17 Mt N/yr. The total dry deposition of ammonia calculated by Söderlund and Svensson is only 10 to 21 percent of the estimate by Robinson and Robbins (1971). Although both the above estimates are crude, and a large degree of uncertainty is inherent in all extrapolations to the global scale, Söderlund and Svensson's estimate is more reliable, since it is based on more recent and better values for atmospheric ammonia levels (see Chapter 5 for further discussion). On the other hand, the absence of direct measurements for the deposition velocity of ammonia renders both estimates little more than educated guesses.

Absorption of nitrogen oxide gases by terrestrial and aquatic systems has received limited research attention, and the extent to which plants absorb NO_x is poorly known. Robinson and Robbins (1971) considered gaseous deposition of nitric oxide to be negligible, because NO is relatively insoluble in water and it reacts slowly with surfaces. According to Hill (1971), alfalfa plants absorbed NO_2 at a rate of 1.2 $\mu l/m^2$-min per ppb NO_2 in the atmosphere of an experimental chamber, and NO was absorbed at a rate of 0.06 $\mu l/m^2$-min per ppb NO under similar conditions. These rates convert to deposition velocities of 1.9 and 0.09 cm/sec for NO_2 and NO, respectively. Measurements of uptake rates for other types of vegetation unfortunately have not been made. Ghiorse and Alexander (1976) studied the absorption of NO_2 by sterile and nonsterile soil. Their data showed rapid removal of NO_2 from air, but do not permit determination of deposition velocities.

The transfer of NO_x from air to surface waters is another flux of interest, since dissolved NO_2 reacts rapidly to form nitrite. Kabel (1976) used a detailed theoretical model of the absorption of gases by water to estimate the flux of NO_2 into water. At an assumed atmospheric concentration of 20 $\mu g\ NO_2/m^3$ (about 10 times the natural background concentration, but low compared to typical urban concentrations), his model predicted a flux of 87 ng NO_2/m^2-sec across the air/water interface. This estimate is equivalent to an annual loading of 0.8 g N/m^2, which is a significant value for the nutrient enrichment of lakes (see Figure 6.21 and Chapter 8). The calculation requires experimental validation, but it suggests that absorption of NO_x from the atmosphere can be an important source of nitrogen to lakes.

In summary, limited data indicate that dry fallout of nitrogenous aerosols and the direct absorption of gaseous ammonia or nitrogen oxides can be important mechanisms for input of nitrogen to terrestrial and aquatic ecosystems, overshadowing inputs from wet precipitation in some cases. While data exist for only a few local situations, plausible calculations suggest that these processes may be significant on the regional and global scales as well. A more definitive assessment of their importance, however, must await the gathering of more extensive data.

Acid Rainfall and the Role of Nitric Acid

The occurrence of highly acidic rainfall over large areas of the eastern United States and northern Europe has received much attention in recent years (Cogbill and Likens 1974; Cogbill 1976; Likens 1972, 1976; Dochinger and Seliga 1976; Matheson and Elder 1976). Studies to date have demonstrated trends toward decreasing pH of rainfall in the northeastern United States and expansion of the area receiving acidic rains (Figure 6.22). Acid rain is defined here as having a pH less than 5.6, the minimum pH expected from atmospheric carbon dioxide. Currently the average annual pH of precipitation in the northeastern United States is between 4.0 and 4.2, and average pH values around 4.5 have been reported as far south as northern Florida. The pH of rainfall throughout southern Scandinavia is less than 4.5, and the hydrogen ion content of precipitation in some parts of Scandinavia has increased 200-fold (2.3 pH units) in the past two decades (Likens 1976, Odén 1976, Braekke 1976).

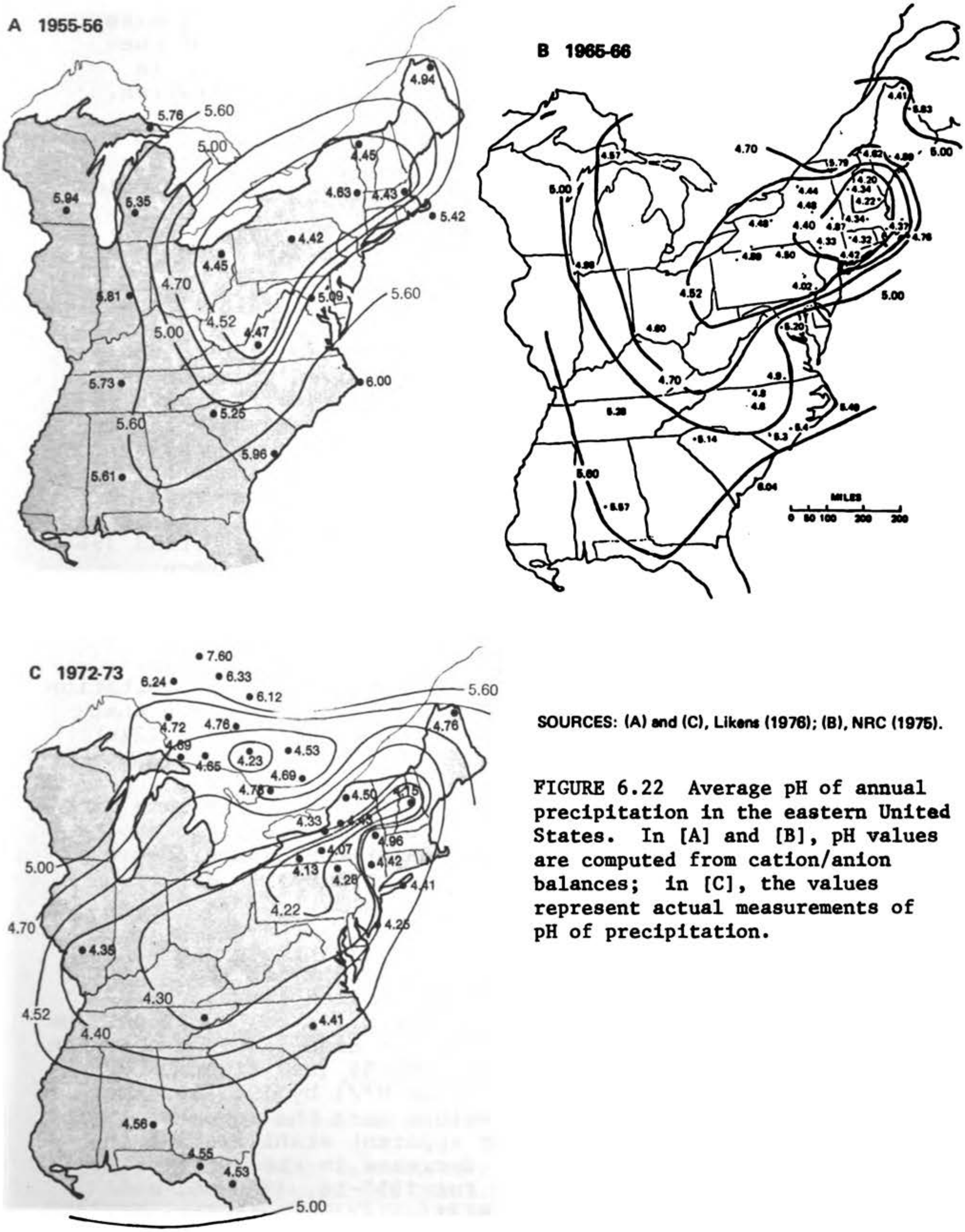
While it is clear from recent studies that acidic rainfall is a manmade problem with potentially serious ecological impacts over widespread geographic areas (see Chapter 8), several aspects of the problem remain controversial, because existing data are ambiguous or inadequate. Important unresolved issues include:

1. the rate at which rainfall is becoming more acidic and the rate at which the problem is becoming geographically more widespread;

2. the quantitative contributions of various acids to the overall acidity of rainfall;

3. the cause(s) of the widespread acidification of rain in the eastern United States over the past 20 years;

4. the relative extent to which the acidity of rainfall in a region depends on local emissions of sulfur and nitrogen oxides versus emissions transported from distant sources; and



SOURCES: (A) and (C), Likens (1976); (B), NRC (1975).

FIGURE 6.22 Average pH of annual precipitation in the eastern United States. In [A] and [B], pH values are computed from cation/anion balances; in [C], the values represent actual measurements of pH of precipitation.

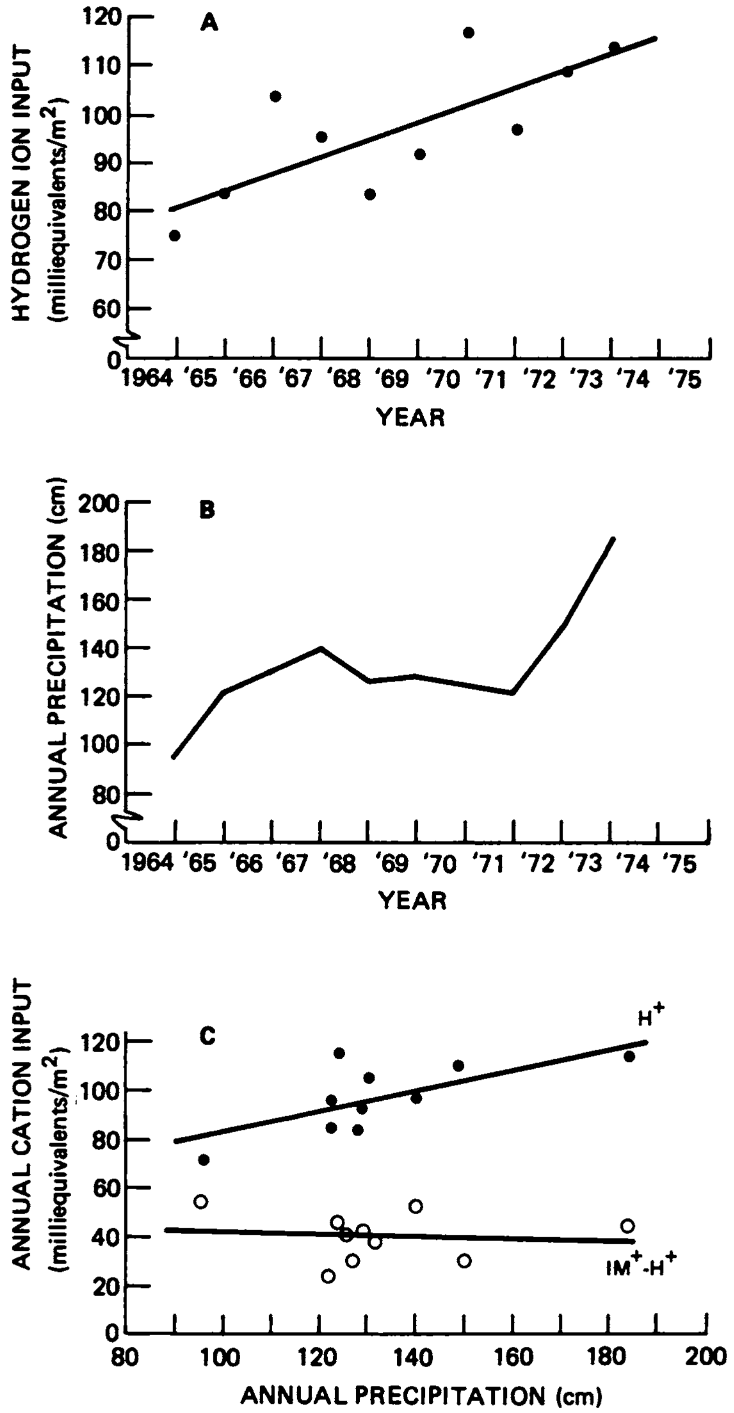
5. the relative importance of changes in total mass emission rates compared to changes in the nature of the emission patterns (ground level versus tall stacks) in contributing to regional acidification of precipitation.

The following sections discuss evidence related to these five issues, and in particular assess the contributions of NO_x emissions and the resulting nitric acid to the problem.

Temporal and Spatial Trends in Rainfall Acidity

Long-Term Trends. The isopleth maps of rainfall pH presented in Figure 6.22 show that the acidity of rainfall over the eastern United States has increased during the past 20 years, but the rate of change at a given location is difficult to quantify, largely because historical data on the pH of rainfall are extremely rare. Even where fairly long-term records are available (e.g., measurements have been made since 1964 at Hubbard Brook, New Hampshire), values are scattered over a wide range. Likens et al. (1976a) reported that the mean annual pH of rainfall at Hubbard Brook varied from 4.03 to 4.21 over the period 1964-1973, with no statistically significant trend. When concentrations were multiplied by the amount of precipitation to give areal deposition rates (equivalents of H^+/ha-yr), a trend of increasing H^+ deposition (a 36 percent increase over the decade) was noted (Figure 6.23 [a]). Increases in the annual amount or frequency of precipitation will increase the rate of deposition in the same way that increases in acidic emissions will; and as Figure 6.23(b) shows, the annual amount of rainfall at Hubbard Brook increased significantly over the decade. However, deposition rates for cations other than H^+ at the same site were not related to the annual amount of precipitation (Figure 6.23 [c]); thus, the increase in H^+ deposition over time cannot be explained solely by increases in annual rainfall amounts.

Cogbill (1976) reviewed the temporal trends and the geographic distribution of rainfall acidity in the northeastern United States, and summarized the sparse information on rainfall pH available prior to the 1960s. He found that the acidity of rainfall at nine stations near the periphery of the acid center in 1955-56 (see Figure 6.22) showed an average increase of 12 $\mu g\ H^+/l$ by 1965-66. More recent data for two of the stations near the northern limit of the acidic region showed an apparent stabilization in rainfall pH after the initial decrease in the 1960's. At Caribou, Maine, the pH values for 1955-56, 1965-66, and 1972-73 were 4.94, 4.63, and 4.76; and at Sault Ste. Marie, Michigan, the pH values for the same years were 5.76, 4.76, and 4.69. Other reviews of available data suggest that the average pH is decreasing in the most affected areas, from



SOURCE: Modified from Likens et al. (1976a).

FIGURE 6.23 Cation inputs in precipitation at Hubbard Brook, New Hampshire. (A) Annual input of hydrogen ion, 1964-73; (B) Annual precipitation, 1964-1973; (C) Comparison of annual input of hydrogen ion and annual input of total cations less hydrogen ion plotted against amount of annual precipitation.

about 4.4 in the 1950s to 4.0 to 4.1 in the 1970s (Likens 1976, Nisbet 1975), but quantitative inferences should be made cautiously.

Seasonal Variations. The pH of individual rain events may be as low as 2.2 to 3.0. Seasonal variations in pH measured at several sites in New York during 1970-71 (Likens 1972) were erratic and site-specific, but pH values tended to be lower in summer than in winter. Hornbeck et al. (1976) also reported that precipitation was most acidic at nine stations in the northeastern United States during the growing season (May to September) and least acid during winter (December to February). At Hubbard Brook, New Hampshire, the mean H^+ content of precipitation was 46 µg/l (pH = 4.34) in winter, and 102 µg/l (pH = 3.99) in summer. The seasonal trends in pH were mirrored by seasonal trends in sulfate content of precipitation, and the trends in both components could be explained by the lower efficiency of snow (compared to rain) in scavenging substances from the atmosphere. No significant seasonal trends were noted in pH of bulk precipitation rainfall at Gainesville, Florida, during 1976-77 (Hendry 1977), but wet-only precipitation showed a trend of highest pH in fall and winter months and lowest pH in spring months (see Figure 6.17).

Geographic Extent of Acid Rain. The isopleth maps in Figure 6.22 indicate that the area affected by acid rainfall has grown significantly over the past 20 years, and that it now covers nearly all of the United States east of the Mississippi River. However, this apparent trend must be accepted with caution for two reasons: (1) the pH values in the 1955-56 and 1965-66 maps are computed rather than measured values, and (2) the number of sampling stations is too small for accurate placement of the isopleths in all of the maps. In the absence of measured pH values, it is possible to calculate the pH of a rain sample by taking the difference between the sums of the anions and cations (expressed in equivalents/l) measured in chemical analysis of the rain (see Granat 1972). This method is based on the fact that the total positive and negative charges must balance in any sample, and on the assumption that the chemical analyses account for all major ions except H^+. Cogbill and Likens (1974) stated that pH can be computed by this method to within 0.1 units of the measured pH, but this may overestimate the accuracy of data from most routine monitoring programs.

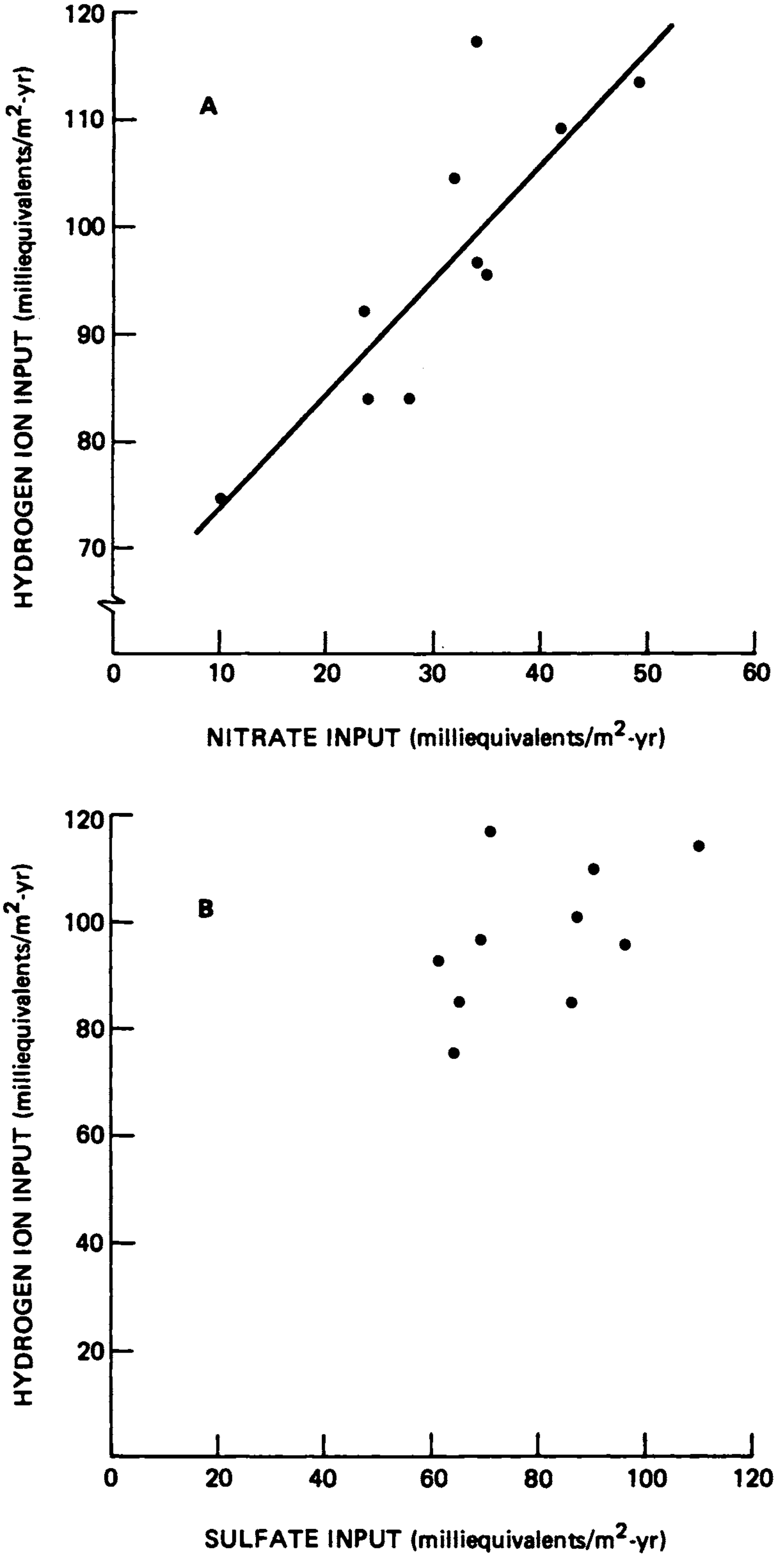
The second reason for caution about the rate of expansion of the area receiving acid rainfall is the small number of data points used to draw the isopleths. The pH 5.60 isopleth was drawn through mid- or southern Georgia in the first two maps in Figure 6.22, but in Likens' (1976) map for the early 1970s, the pH 5.00 line was moved to central Florida. This change was based on recent acquisition of data for two Florida cities, Tallahassee and Gainesville, in a region where pH measurements had not previously been made, and it does not necessarily imply a rapid expansion of the acid rainfall area.

Contributions of Nitric Acid to Total Acidity

There is general agreement that the acidity of rainfall in the United States results primarily from two mineral acids, sulfuric acid (H_2SO_4) and nitric acid (HNO_3), with minor contributions from hydrochloric acid (HCl). Recent contentions that the acidity of rainfall is controlled by weak unidentified acids (Frohliger and Kane 1975) have been shown to be erroneous. Careful titrations under conditions in which atmospheric CO_2 was excluded from the precipitation sample have shown that the pH of the rain can be accounted for by strong mineral acids and that weak organic acids are quantitatively unimportant (Galloway et al. 1976, Likens et al. 1976b, Hendry 1977). While a variety of acids, weak and strong, contribute to total rainfall acidity (defined as the amount of strong base required to titrate a sample to a given pH, e.g., 7.0), the weak acids do not affect the ambient pH of the rainwater, nor do they exert significant pH buffering effects below pH 7.

The relative importance of sulfuric and nitric acid contributions to rainfall acidity has changed with time. Following the reasoning of Granat (1972), Likens et al. (1976a) found that the contribution of sulfate declined from 83 to 66 percent of the total acidity between 1964 and 1974 at Hubbard Brook, and the contribution of nitrate increased from 15 to 30 percent of the total during the same period. Furthermore, increased annual input of H^+ was closely correlated with increased input of nitrate, but there was little correlation between H^+ input and sulfate input (Figure 6.24). Hendry (1977) found that sulfate contributed 69 percent, nitrate 22 percent and chloride 6 percent of the free acidity in rainfall at Gainesville, Florida, during 1976. On the other hand, Gorham (1955, 1958) reported that hydrochloric acid was the dominant acid in urban precipitation in Great Britain. Coal used in Great Britain is high in chloride, but low in sulfur.

Available data indicate a roughly three-fold increase in nitrate in rainfall since 1955, whereas sulfate in rain has roughly doubled in this period. According to Nisbet (NRC 1975), sulfate/nitrate ratios in rainfall averaged about 4 in the eastern United States in 1955-56, but the ratios had fallen to about 3 in 1972-73. Nisbet calculated that the fraction of H^+ deposition attributable to nitric acid rose from 19 percent in 1955-56 to 24 percent in 1972-73 (see Table 6.17). He also projected trends in acid deposition from 1970 to 1980 for a number of scenarios assuming



SOURCE: Modified from Likens et al. (1976a).

FIGURE 6.24 Hydrogen ion deposition in precipitation plotted against (A) nitrate deposition and (B) sulfate deposition. Data from Hubbard Brook, New Hampshire, 1964-1973.

TABLE 6.17 Deposition[a] of Sulfuric and Nitric Acids in Precipitation in Eastern North America

	1955-56	1972-73	Percent change 1956-73
Total deposition of acid (as H+)	4.0	10.8	+170
Estimated deposition as sulfuric acid (percent of total)	3.2 (80)[b]	7.9 (73)[b]	+150
Estimated deposition as nitric acid (percent of total)	0.76 (19)[b]	2.60 (24)[b]	+240
Total deposition of sulfates	16.4	31.8	+94
Sulfuric acid as % of sulfates	19.7	24.8	+27

[a] Deposition rates are expressed as multiples of the chemical equivalent weight, so that rates for different chemical species can be compared directly. 1 ton H^+ is equivalent to 49 tons sulfuric acid or to 63 tons nitric acid.

[b] A small but increasing fraction of the acid in precipitation is attributable to hydrochloric acid.

SOURCE: Modified from Nisbet (1975).

continued control of SO_2 emissions, but no controls on projected NO_x emissions. Even if SO_2 emissions were held constant by source controls on new power plants, a small increase in acidity would be likely because of increases in NO_x emissions.

Nearly all of the nitrate in rainfall is formed in the atmosphere from NO_x (Chapter 2), and little is derived from wind erosion of nitrate salts in soils. Similarly, nearly all of the sulfate in rainfall is formed in the atmosphere from SO_2. The reactions that produce nitrate and sulfate from NO_x and SO_2 are well-known and result in the production of equivalent amounts of hydrogen ion, regardless of the reaction mechanism:

$$OH + NO_2 \longrightarrow HNO_3, \text{ or}$$
$$N_2O_5 + H_2O \longrightarrow 2HNO_3, \text{ and}$$
$$SO_2 + 1/2\ O_2 \longrightarrow SO_3;\ SO_3 + H_2O \longrightarrow H_2SO_4.$$

Thus, all atmospherically derived nitrate and sulfate contributes to the acidification of rainfall, since H^+ is associated stoichiometrically with the formation of each. A second stoichiometric process that affects the acidity of rain is the reaction of nitric and sulfuric acids with ammonia or other alkaline substances (e.g., dust particles) in the atmosphere to form neutral nitrate and sulfate aerosols. To the extent that such neutralization occurs, the free acidity of rainfall will be reduced. Reuss (1975) noted, however, that even ammonia in rain can contribute to the acidification of soil, since ammonia that enters the soil may be nitrified, resulting in the formation of nitric acid.

Causes of the Acid Rainfall Problem

Several lines of evidence suggest that the widespread acidification of rain began no earlier than 1950-1955, but although this shift has been linked to changes in the amounts of SO_2 and NO_x emissions, the precise causes are still unclear. Likens and Bormann (1974) suggested that acidification was partially a consequence of the decrease in emissions of alkaline fly ash from coal-burning power plants, coupled with increasing emissions of SO_2 and NO_x. Nisbet (1975) related the increased acidification to increases in tall-stack emissions of both SO_2 and NO_x (from power plants, smelters, and industrial processes), and Likens (1976) noted that the trend toward higher smokestacks to disperse pollutants may be responsible in part for the widening geographic extent of the acid deposition problem.

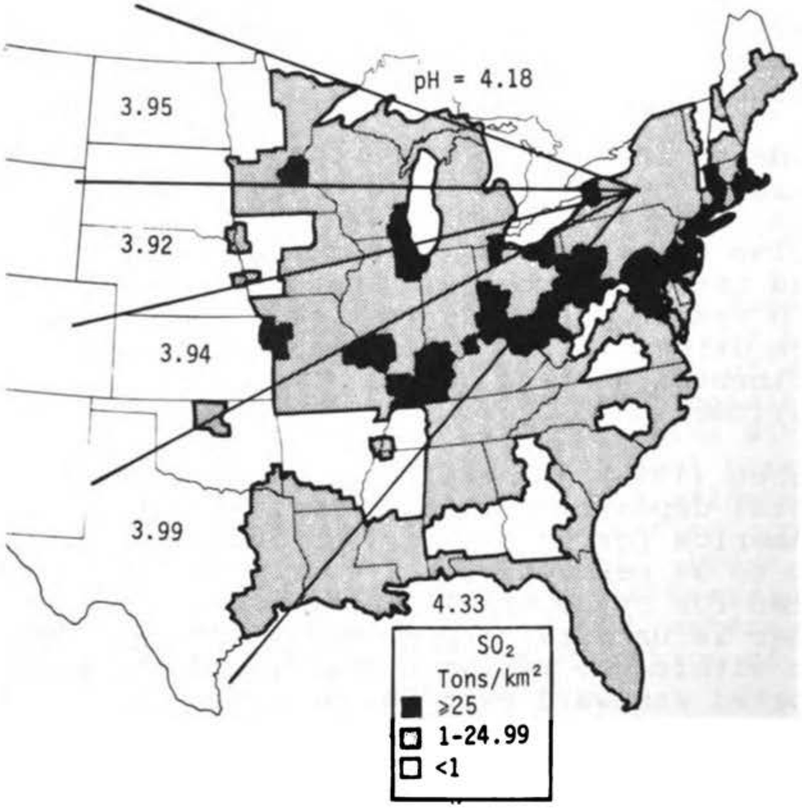
Cogbill and Likens (1974) associated acid rainfall in New York with high altitude air masses transported into the region from the Midwest, implying that the SO_2 and NO_x that cause acid rain may be transported distances of perhaps 300-1500 km. Gatz (1976) criticized the procedure used by Cogbill and Likens to track air masses, and recommended that trajectories of lower altitude air masses be used to trace the source of acids in rainfall. He suggested that the major source of rainfall acidity in the Northeast is the Ohio Valley region of Ohio, Pennsylvania, West Virginia, and Maryland, an area of large SO_2 emissions (Figure 6.25). The high-altitude trajectories used by Cogbill and Likens showed little variation in pH of rainfall borne in by air masses from different directions, even though the sources of SO_2 are concentrated to the south and southwest of the rainfall collection area at Ithaca, New York.

Evidence from northern Europe also supports the idea that acid rainfall is a large-scale regional problem involving long distances between emission sources and deposition of acid rain. The acidic rains that have received intensive study in southern Scandinavia have been shown to result primarily from emissions of sulfur and nitrogen oxides in Great Britain and the industrial regions of continental Western Europe (e.g., Holland, Belgium, West Germany) (Odén 1976).

Nisbet (1975) compared estimated total SO_2 emissions with total deposition of sulfate in precipitation in eastern North America for the years 1955-56, 1965-66, and 1972-73. Only 30 to 38 percent of the emitted sulfur could be accounted for by rainfall deposition. The fate of the remainder is uncertain; presumably some was deposited as dry fallout within the region studied, and the rest was transported eastward over the Atlantic Ocean. A similar calculation is not available for the fraction of NO_x-N deposited as nitrate in rainfall, but such an exercise would be interesting.

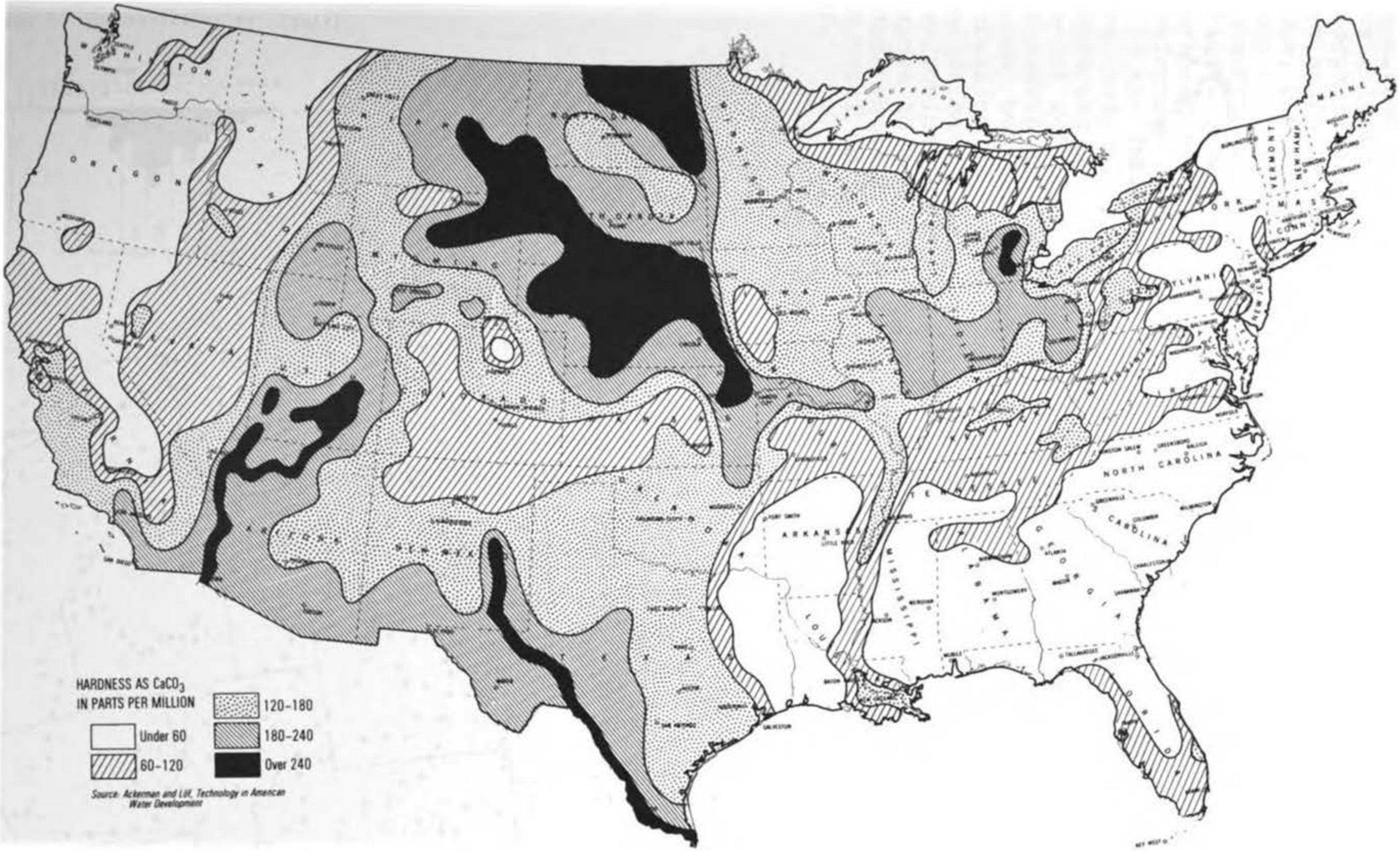
The ecological effects of acid rainfall are discussed in Chapter 8, but the potential for such effects can be placed into some perspective by examining patterns of the buffer capacity of soils and waters in the United States. Figure 6.26(a) shows the distribution of hardness in surface waters of the United States, and Figure 6.26(b) shows the distribution of calcium, which can be taken as an approximate index of cation exchange capacity, in soils of the United States. Hardness is closely correlated with alkalinity, and hence with buffer capacity, and cation exchange capacity is related to the buffer capacity of soil. The figures show that the regions in which rainfall acidity is highest include large areas with soft water (hence low buffer capacity) and low soil exchange capacity.

In summary, the causes of widespread acidification of rainfall in the eastern United States are still controversial. The principal agents of acidity, sulfuric



SOURCE: Gatz (1976), Water Resources Research 12:569, copyrighted by and used with permission of the American Geophysical Union.

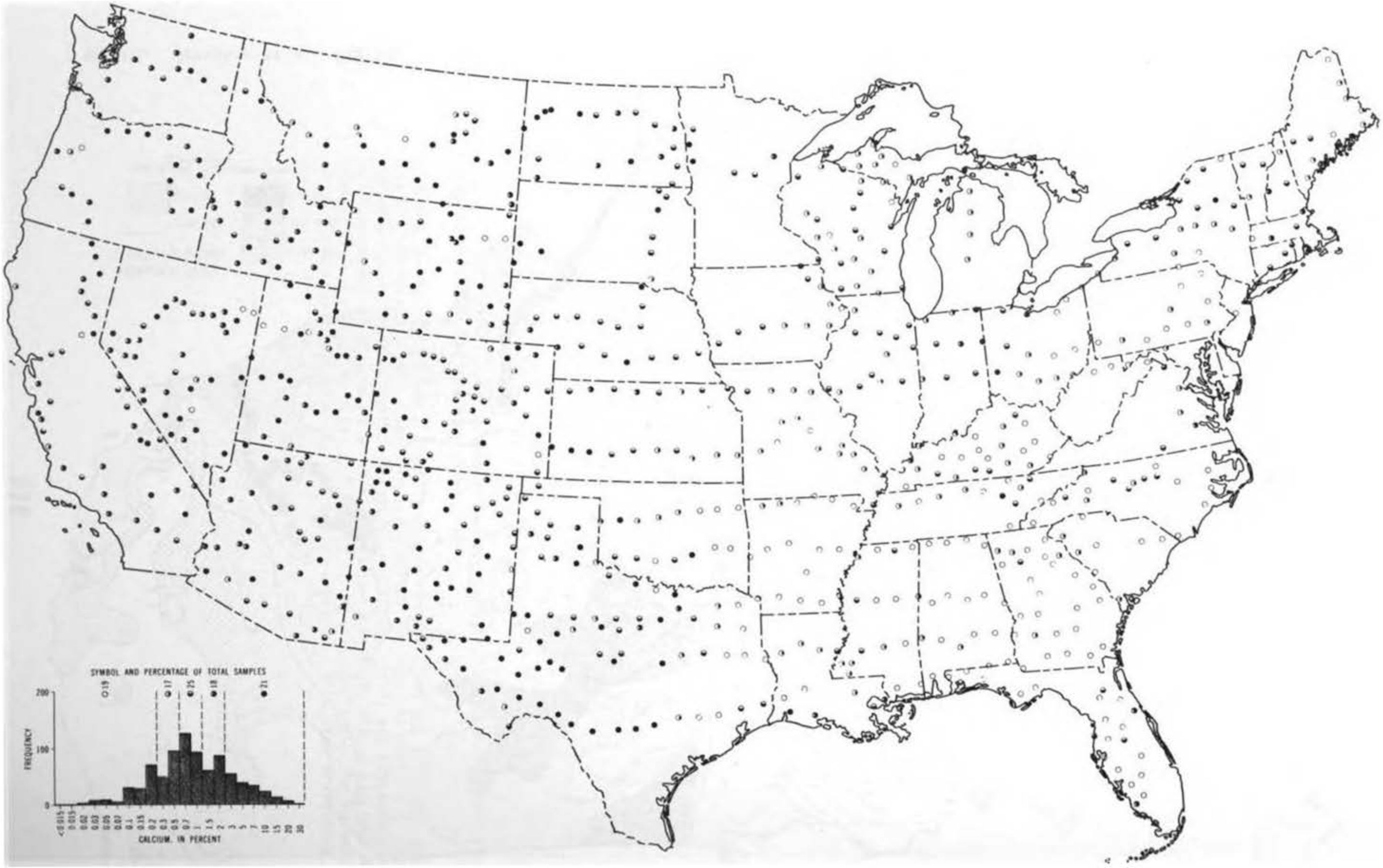
FIGURE 6.25 Trajectory map indicating source strengths for SO_2 emissions affecting the eastern United States. Emission rates of SO_2 are shown by shading of the map. 500-mbar trajectory corridors from Cogbill and Likens (1974) are superimposed on the map to indicate directions of movement of air masses at ca. 5500 m altitude for several days preceding specific rain events at Ithaca, New York. The numbers between the lines are mean pH values for rain events associated with each trajectory corridor.



Source: Ackerman and Löf, *Technology in American Water Development*

SOURCE: Geraghty et al. (1973).

FIGURE 6.26(A) Hardness of surface waters in the United States.



SOURCE: Shacklette et al. (1971).

FIGURE 6.26(B) Calcium content of surface soils in the United States.

and nitric acids, are derived primarily from combustion of fossil fuels and consequent emissions of SO_2 and NO_x. The atmospheric reactions involved in transforming these gases into acids are reasonably well understood on a qualitative basis, but rates of transformation, atmospheric residence times for the acids, and the scale of transport prior to deposition are not known with precision. The lack of more definite quantitative estimates of linkages among sources, transport processes and deposition patterns hinders the development of appropriate control measures. Furthermore, while the intensity and geographic extent of the problem have obviously increased over the past few decades, recent trends and the exact geographic extent of the problem still are not well known. Nitric acid accounts for only about one-fourth of the acidity of rainfall in the eastern United States, but its proportional contribution has been increasing as controls on stationary emissions of sulfur dioxide have taken effect. The current legislative restrictions on emissions of nitrogen oxides from stationary sources do not apply to many large existing operations, even though these sources account for an important fraction of the total emissions of NO_x in the United States (see Chapter 10).

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CHAPTER 7

NITROGEN FIXATION BY HUMAN ACTIVITIES AND PERTURBATIONS OF THE STRATOSPHERIC OZONE LAYER

INTRODUCTION

In recent years, increasing attention has been given to the potential effects on the stratospheric ozone layer from human-induced increases in microbial production of nitrous oxide (N_2O). The major concern is that enhancement of the global rate of nitrogen fixation, chiefly in the manufacture of fertilizers and cultivation of legumes, may lead to increased global rates of denitrification and of N_2O production, thus posing a risk of depleting the ozone layer.

The only known atmospheric sink for N_2O is photolytic decomposition to N_2 and O• radicals and reaction with electronically excited atomic oxygen to produce N_2, O_2, and NO in the stratosphere. This production of nitric oxide is the principal source of NO_x in the stratosphere (NO_x = NO and NO_2). The NO_x thus formed reacts with ozone in a catalytic cycle that serves as a principal agent in the natural ozone balance (see Chapter 2, Figure 2.8). The natural rate of ozone formation is determined by the amount of solar radiation and the oxygen content of the stratosphere, and is not affected by human activities; any increase in the amount of N_2O reaching the stratosphere, therefore, is likely to lead to some depletion of the ozone layer.

There are substantial gaps and uncertainties in current scientific understanding of the sources and processes that determine the amount of atmospheric N_2O. These severely limit the ability to predict the possible impacts on the stratospheric ozone layer of increases in nitrogen fixation resulting from human activities. Several of the critical variables that determine the size of the global atmospheric N_2O pool, however, can be analyzed independently and related to each other and to ozone depletion in simplified mathematical terms. Although the exact values of these critical variables are unknown, a range of reasonable values for each variable can be identified from what is known of the natural nitrogen cycle. Specific values can then be chosen from within the ranges and used as working assumptions to support further analysis.

The above procedure is used here to calculate a "most probable" impact on the ozone layer, given stated assumptions. The analysis projects a decrease of from 1.5 to 3.5 percent in stratospheric ozone by the year 2100. It must be emphasized that the values chosen for the variables in this analysis have not been scientifically established; other values might also be reasonably assumed. Even with a fairly restricted set of assumptions, the magnitude of expected reduction in ozone can vary from 0.15 to 13 percent. New scientific data also could easily necessitate adjustment of the value for a critical variable and, consequently, for the projected reduction of stratospheric ozone.

Despite the many simplifying assumptions of the analysis presented here, the results are comparable to those of more complex modeling efforts. The framework developed in this chapter can easily be used with any set of assumed values for the critical variables to test the implications of new discoveries.

HISTORICAL BACKGROUND

The role of N_2O produced by denitrification in the formation of stratospheric NO_x was suggested in the work of Bates and Hays (1967), but Crutzen (1971) was the first to articulate effectively this role and its implications. The subject was further examined by a number of atmospheric scientists, including McElroy and McConnell (1971), Nicolet and Vergison (1971), and Johnston (1972). Other studies were made by soil scientists who had become increasingly concerned about the impacts of human activities on the global nitrogen cycle. Delwiche (1970) noted that the rate of fixation of nitrogen as chemical fertilizer and by cultivated legumes was equal to about one half of the natural global rate of fixation. He pointed out that continued rapid growth in the manufacture of nitrogen fertilizer could make industrial and agricultural fixation of nitrogen exceed natural fixation of nitrogen within a few decades, and he expressed concern about such a situation in general terms. Crutzen (1970) and Johnston (1971) showed that the abundance of stratospheric ozone is limited by a catalytic destruction process involving natural nitrogen oxides in the stratosphere.

The potential for increased concentrations of atmospheric nitrous oxide and decreased stratospheric ozone levels resulting from nitrogen fertilizers was discussed by scientists in 1971-1972, but there apparently were no publications specifically on the subject. So little was known then about stratospheric nitrogen oxides and about the sensitivity of stratospheric ozone to added nitrogen oxides that quantitative treatment of the nitrogen fertilizer problem was not feasible.

During 1972-1975, the Climatic Impact Assessment Program (CIAP) administered by the U.S. Department of Transportation carried out extensive measurement of stratospheric nitrogen oxides and other species and supported many approaches to numerical modeling of the effect of increased nitrogen oxides on stratospheric ozone. The CIAP study also considered health effects and other biological consequences of reduced ozone and enhanced uv radiation and considered possible climatic effects of perturbation of the stratosphere. This work was published in 1975 as 5000 pages of technical monographs and as a Report of Findings (Grobecker et al. 1975). The primary data were examined independently by the Climatic Impact Committee of the National Academy of Sciences-National Research Council (NRC 1975).

The CIAP confirmed that an increase in stratospheric NO_x would decrease the stratospheric ozone layer and, within a fairly large range of uncertainty, it estimated the sensitivity of ozone to changes in NO_x. It concluded that nitrous oxide from soils and possibly from oceans is the principal source of stratospheric NO_x. These findings provided a basis for renewed, quantitative consideration of the possible impact of fertilizer nitrogen on ozone.

Crutzen (1974) estimated the magnitude of stratospheric ozone reduction by a man-induced increase in N_2O and followed this report with more detailed consideration of nitrogen fertilizers (Crutzen 1975a, 1976). McElroy and co-workers (Bishop 1975, McElroy 1976, McElroy et al. 1976) reviewed the biological aspects of the nitrogen cycle in soils, oceans, sediments, and the lithosphere in the context of the fertilizer-ozone issue, and the Council for Agricultural Science and Technology (CAST) reviewed the subject from the perspective of agricultural scientists (CAST 1976). The American Geophysical Union sponsored a special symposium on the subject in April 1976; papers presented there included those by Craig et al. (1976), Crutzen (1976), Johnston (1977), Liu et al. (1976), McElroy et al. (1976), and Sze and Rice (1976). More recently, Hahn and Junge (1977) have reviewed current knowledge and assessments of factors and processes affecting the global atmospheric N_2O balance.

SENSITIVITY OF STRATOSPHERIC OZONE TO CHANGES IN NITROUS OXIDE

The findings of the CIAP (Grobecker et al. 1975, NRC 1975) that are pertinent to this study are used as a starting point. These are:

(1) The natural abundance of stratospheric ozone is determined largely by the balance between formation from solar radiation and destruction by the oxides of nitrogen (NO and NO_2, or NO_x). (See Chapter 2 of this report.)

(2) Doubling stratospheric NO_x would reduce ozone by about 20 percent.

(3) Stratospheric NO_x is produced primarily from the oxidation of nitrous oxide (N_2O) in the stratosphere.

(4) Atmospheric nitrous oxide is produced primarily from bacterial action (denitrification) in the soil and in the oceans.

The second conclusion, illustrated by Figure 7.1, is simply stated by the expression:

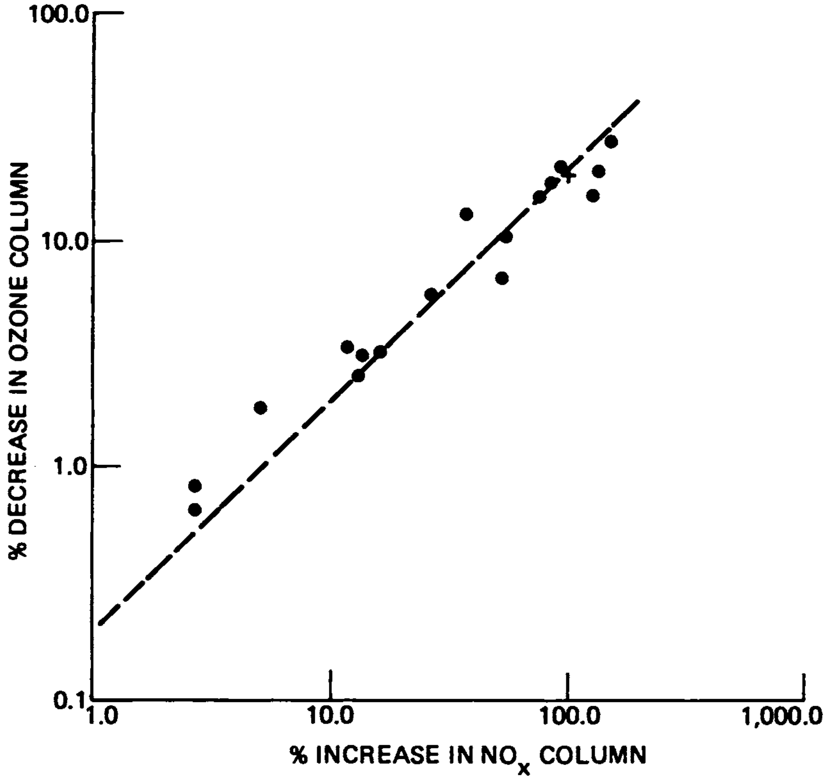
$$-\frac{\Delta[O_3]}{[O_3]} = \frac{1}{5}\frac{\Delta[NO_x]}{[NO_x]} \qquad (7\text{-}1)$$

In this equation $[NO_x]$ represents the global inventory of natural nitrogen oxides in the stratosphere, $\Delta[NO_x]$ represents a change in that global inventory sustained over a period of at least 10 years (about two stratospheric residence times for NO_x), $[O_3]$ represents the global inventory of natural ozone in the stratosphere, and $-\Delta[O_3]/[O_3]$ is the fractional change in the steady-state ozone inventory in response to the NO_x perturbation.

Since the termination of the CIAP in 1975, some of the CIAP conclusions cited above have been modified as a result of further study:

(1) It has been shown that combustion produces a significant amount of nitrous oxide (Pierotti and Rasmussen 1976, Craig et al. 1976), but soils and oceans are still considered the primary source of N_2O.

(2) Recent measurements (Anderson 1976, Anderson et al. 1977) of ClO in the stratosphere indicate that chlorine may play an important role in the natural ozone balance, reducing somewhat the role of NO_x.



The line represents the equation: $\Delta[O_3]/[O_3] = (1/5)\,\Delta[NO_x]/[NO_x]$. The point (+) represents the ozone depletion following an explicitly assumed doubling of $[N_2O]$. All calculations are based on injection of NO_x at 20 km altitude.

SOURCE: Adapted from Grobecker et al. (1975).

FIGURE 7.1 The percentage decrease of ozone as a function of the percentage increase in stratospheric nitrogen oxides, as determined by the CIAP study.

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(3) Recent measurements of rate constants involving the free radicals HO• and HOO• indicate stronger coupling between HO_x and NO_x chemistry than appeared to be the case during the CIAP study. Specifically, recent measurements (Howard and Evenson 1977) yield much higher values than were previously known for the rate constant of the reaction, $HOO\bullet + NO \text{ -----> } HO\bullet = NO_2$. This reaction is the limiting step in a null cycle involving NO_x and O_3. The net effect of this new information is to decrease the effectiveness of NO_x as a sink for ozone (see Chapter 2).

(4) The CIAP model that considered three dimensions of atmospheric motion (Cunnold et al. 1974) found a greater sensitivity (1/3 instead of 1/5) of stratospheric ozone response to increased stratospheric NO_x than the one- and two-dimensional models used earlier; however, the recent findings with regard to the roles of chlorine and HO_x radicals from water tend to decrease the sensitivity factor at least to 1/10.

Although uncertainties remain that cannot be resolved with present knowledge, a value of 1/10 appears to be the maximum reasonable estimate for the sensitivity factor (P.J. Crutzen, National Center for Atmospheric Research, Boulder, Colorado, personal communication, 1977). Equation 7-1, modified to include 1/10 instead of 1/5, is thus accepted as the best current expression of the relationship between stratospheric NO_x and ozone, and is used here.

For this analysis, the simple general equation for global ozone reduction can be expressed in terms of nitrous oxide:

$$-\frac{\Delta[O_3]}{[O_3]} = \frac{1}{10}\frac{\Delta[N_2O]}{[N_2O]} \qquad (7\text{-}2)$$

This substitution is based on the fact that N_2O is the chief source of NO_x in the stratosphere, and on the finding of Vupputuri (1974), who calculated the reduction in ozone caused by an explicitly assumed doubling of the concentration of N_2O in the atmosphere. Vupputuri's results, represented by the point marked (+) in Figure 7.1, indicated that doubling the N_2O concentration would lead to a 19 percent reduction of ozone. (With the more recent information on rate constants for HO_x-NO_x reactions, Vupputuri's estimate would have been about half as large.)

The present fraction of the atmosphere that is nitrous oxide is about 330 ppb by volume in the troposphere (see Chapter 3), and the fraction decreases in the stratosphere. The global inventory of nitrogen as atmospheric N_2O has been calculated to be 1.5×10^{15} grams, or 1500 million metric tons (Mt) (Schütz et al. 1970, Craig et al. 1976, Crutzen and Ehhalt 1977).

THE NITROGEN CYCLE AND GLOBAL PRODUCTION OF NITROUS OXIDE

In order to assess the impact of nitrogen fixation by human activities upon the global atmospheric inventory of N_2O, it is necessary to determine or estimate the values of the following critical variables: (1) the anthropogenic increase in the rate of nitrogen fixation over the natural global rate; (2) the fraction of fixed nitrogen that is denitrified within a few decades; (3) the fraction of the gaseous products of denitrification that is N_2O; and (4) the atmospheric residence time of N_2O. In this analysis, these variables are represented as follows:

ΔN_F = The increase in global nitrogen fixation due to human activities (Mt N/yr)
α = Fraction of denitrified nitrogen that is N_2O
β = Fraction of fixed nitrogen that is denitrified within a few decades
τ = Atmospheric residence time of N_2O

The following discussion is intended chiefly to support the assignment of values to the critical variables, none of which can at present be precisely quantified. Other portions of this report should be consulted for more complete assessments of specific points about the processes themselves. (See particularly Chapter 2 and Appendix A, Section 7.)

Nitrogen Fixation

The global aspect of nitrogen fixation was reviewed recently by Burns and Hardy (1975), CAST (1976), and Söderlund and Svensson (1976), and others. Summation of recognized sources and extrapolation to the global scale produce an estimate of about 200 to 350 Mt (as N) per year as the current global rate of nitrogen fixation. Of that amount, an estimated 79 Mt results from the synthesis of nitrogen fertilizer and the cultivation of legumes, and another 21 Mt is fixed as NO_x by combustion. (For recently updated estimates of global rates of nitrogen fixation, see Appendix A, Section 7. In this analysis, the rate of 79 Mt/yr estimated by CAST [1976] is used; substitution of other recent estimates for ΔN_F would have only small impacts on the projected effects on ozone.)

Both the fertilizer and the combustion components of anthropogenic nitrogen fixation have increased dramatically over the last three decades, to the point that between one quarter and one half of the estimated current total global rate of nitrogen fixation is due to human activities. If projected increases occur in the combustion of fuels and in the agricultural use of chemical nitrogen fertilizers and cultivated legumes, the anthropogenic fraction of nitrogen fixation will become still greater.

It is possible that not all natural sources of fixed nitrogen have been accounted for. The thermodynamics of nitrogen fixation was reviewed by Safrany (1974), who emphasized that thermodynamic work must be performed to reduce N_2 to lower oxidation states (e.g. to ammonia). On the other hand, air and water are thermodynamically unstable with respect to becoming dilute aqueous nitric acid (Lewis and Randall 1923):

$$H_2O(l) + N_2(g) + 5/2\ O_2(g) = 2\ H^+(aq) + 2\ NO_3^-(aq) \quad (7\text{-}3)$$

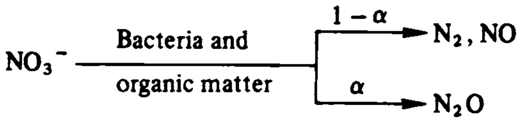
If the water in the oceans and the nitrogen and oxygen in the atmosphere underwent this reaction to chemical equilibrium at 298°K, the pressure of oxygen at sea level would be reduced to about 0.02 atmosphere, and the pH of the oceans would be about 1.5. Fortunately, the atmosphere and ocean are not in equilibrium with respect to this process! As Lewis and Randall (1923:568) remarked: "It is to be hoped that nature will not discover a catalyst for this reaction, which would permit all of the oxygen and part of the nitrogen of the air to turn the oceans into dilute nitric acid."

On the other hand, since chemical equilibrium favors this process, it is possible that unknown inorganic or biological mechanisms bring about this reaction to some degree. If some process in the ocean catalyzed the reaction to only a small degree, a significant amount of nitrogen could be fixed relative to identified terrestrial sources.

Denitrification

Denitrification by certain bacteria in the soil and in the ocean under appropriate conditions reduces nitrate to gaseous nitrogen, nitrous oxide, and in some cases nitric oxide, NO (see Chapter 2). Nitric oxide has a short residence time in the troposphere, eventually forming nitric acid and nitrate aerosols which are removed from the atmosphere by wet and dry precipitation. Since there is a net flux of NO from the stratosphere to the troposphere rather than vice versa, the NO formed as a result of denitrification has no bearing on the problem of stratospheric ozone depletion.

On the other hand, nitrous oxide is thought to be inert in the troposphere, and there is a net flux upward to the stratosphere where some N_2O reacts to form NO_x, which catalytically destroys ozone. Consequently, the fraction of the gaseous products of denitrification that is N_2O, herein called α [$= N_2O/(N_2 + N_2O + 1/2\ NO)$], is of fundamental concern in the present analysis. The fate of a given sample of denitrified nitrate can be expressed in terms of the fraction α, as follows:



(7-4)

In soils, α varies widely with temperature, pH, moisture, and the availability of oxygen (see Chapter 2). CAST (1976) estimated α to be about 1/16, but some measurements indicate only half of that value. Environmental conditions that favor a large value of α are low temperature, low pH, and marginally anaerobic conditions; however, these same factors also lead to a low rate of denitrification. The fraction of N_2O produced by denitrification in the ocean is unknown (CAST 1976). These considerations suggest the following ranges for the fraction α:

$$\begin{aligned} &\text{Land}: && 0.025 < \alpha < 0.1 \\ &\text{Ocean}: && 0 < \alpha < 1 \\ &\text{Global}: && 0.025 < \alpha < 0.4 \end{aligned} \qquad (7\text{-}5)$$

The global limits are selected from a list where each higher or lower possibility differs from the previous limit by a factor of two; they are not rigorous upper and lower bounds. Because it seems unlikely that α could be as great as 0.8 or as small as 0.012, the numbers in Equation 7-5 are taken as a plausible range.

A second critical variable in the process of denitrification is the fraction (herein designated β) of the nitrogen fixed by human activities that is denitrified within a period of time between days and decades, as opposed to the fraction $1-\beta$ that is incorporated into long-lived reservoirs such as soil minerals or the deep ocean. The greatest fraction of anthropogenic fixed nitrogen is applied directly to agricultural soils, where some denitrification may occur. If the nitrogen is added in the form of ammonia fertilizers, manures, or cultivated legumes, nitrification and/or mineralization must precede denitrification (see Chapter 2).

As little as 1 percent or as much as 75 percent of the nitrogen added to agricultural soils may be lost rapidly by denitrification, but the average amount is probably about 10 to 15 percent (CAST 1976). Such denitrification typically occurs within a few weeks after fertilizer is applied.

If the fertilizer nitrogen is incorporated in annual plants, denitrification typically will be delayed a year or more, while the plant is eaten, digested, and in part returned to the soil. If the digested nitrogen is incorporated in the body of animals, denitrification may be delayed several years; and if the original soil nitrogen is incorporated in bushes or trees, there may be several decades between fixation and denitrification. Finally, if the nitrate goes into deep ocean waters, denitrification may not take place for hundreds or thousands of years. Incorporation of fixed nitrogen into soil minerals or sediments also may result in a great delay in denitrification (Liu et al. 1976). Figure 7.2 is a semi-quantitative statement of the idea that the rate of denitrification is expected to be greatly different for fixed nitrogen in different samples and locations.

For a given application of nitrogen fertilizer, the degree of denitrification as a function of time might be something like that illustrated in Figure 7.3. As the figure shows, after some period of time (i.e., at the right-hand axis) the original sample of fixed nitrogen has been divided into the fractions β, which has been denitrified, and $1-\beta$, which has passed into reservoirs of fixed nitrogen with long residence times. The point τ_D on the time axis represents the time required for the fraction $1-1/e$ of the original sample to be denitrified. Unless β is very small (in which case τ_D could be centuries or millennia), the first $1-1/e$ fraction denitrified could be taken as an approximation of β, and τ_D taken as an approximate time for denitrification of the fraction β. The great complexities of the long-lived fraction could thus be deferred for future consideration. This definition is somewhat forced, since (as Figure 7.3 suggests) the course of denitrification is almost surely not a first-order reaction.

The products of a given input ΔN_F of fixed nitrogen can be stated in terms of the two fractions, α and β:

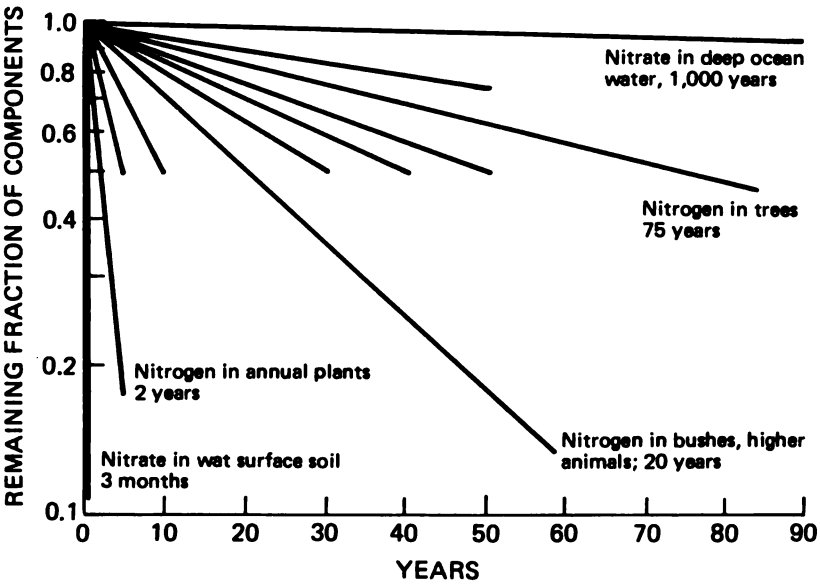
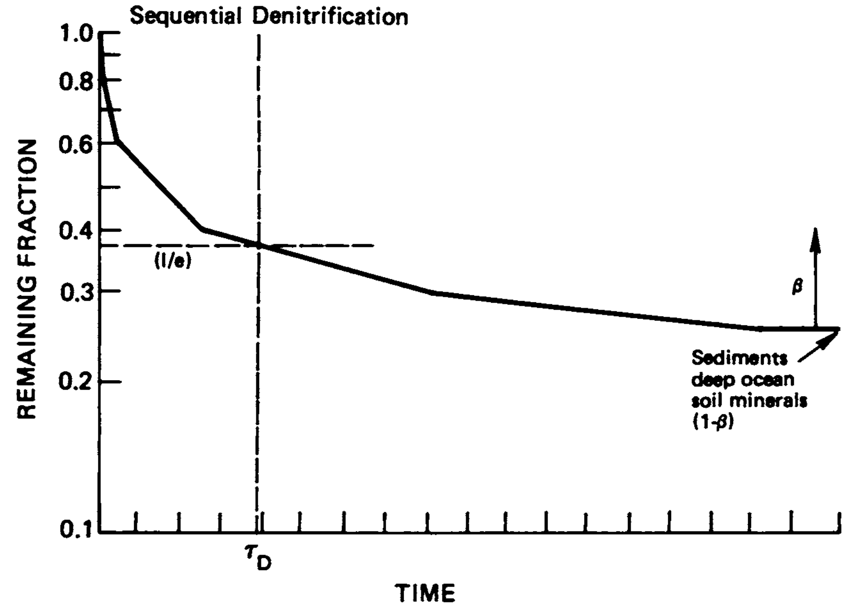


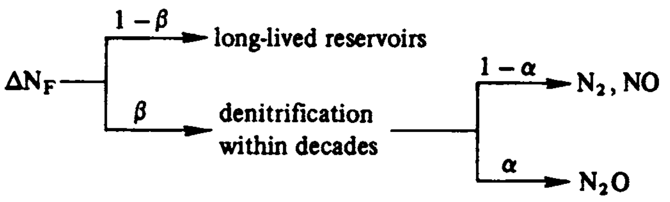
FIGURE 7.2 A semi-quantitative statement that different samples or forms of fixed nitrogen are denitrified at widely different rates.



A portion of the nitrogen is denitrified rapidly in the soil; some is denitrified more slowly in the soil; some is incorporated in plants or animals and denitrified later; and some is transported into soil minerals or the deep ocean, where denitrification is delayed indefinitely. The time scale is deliberately not specified. β (the fraction denitrified within one or two decades) is represented as the distance above the curve at the right-hand axis; $1-\beta$, the distance below the curve, is the fraction incorporated in long-lived reservoirs of fixed nitrogen. The symbol τ_D is the time required for the fraction 1-l/e of the original nitrogen to be denitrified.

SOURCE: Adapted from Johnston (1977), Journal of Geophysical Research 82(12):1767-1772, copyrighted by the American Geophysical Union, and used with their permission.

FIGURE 7.3 A semi-quantitative statement of the denitrification of a particular sample of fixed nitrogen added to agricultural soil.



(7-6)

Thus the production ΔP_{N_2O} of nitrous oxide from the addition of a quantity ΔN_F of fixed nitrogen is:

$$\Delta P_{N_2O} = \alpha\beta\Delta N_F \qquad (7\text{-}7)$$

The values of α and β will vary with different sources and modes of application of nitrogen fertilizer, and with local soil conditions.

Although the emphasis of this analysis is on manufactured and leguminous fertilizer nitrogen, other modes of nitrogen fixation (i.e., that occurring in oceans, forests, grasslands, by combustion, or by lightning) can also be discussed in terms of the fraction β that is denitrified within a few decades, and of the fraction α of denitrified gases that is N_2O.

THE NATURAL ATMOSPHERIC NITROUS OXIDE BALANCE

A differential equation for the global atmospheric nitrous oxide inventory, $[N_2O]$, might be stated in an oversimplified way as:

$$\frac{d[N_2O]}{dt} = P_{N_2O} - \frac{[N_2O]}{\tau} \qquad (7\text{-}8)$$

where τ is the atmospheric residence time of nitrous oxide and P_{N_2O} is the global rate of production of nitrous oxide. If the production rate P_{N_2O} and the destruction rate constant $1/\tau$ remained constant over a long period, the N_2O inventory would reach a steady state:

$$[N_2O] = \tau P_{N_2O} \qquad (7\text{-}9)$$

Presumably the present N_2O inventory is close to a steady state achieved over geological time. The magnitude of the inventory is, as stated before, about 1500 Mt N.

The residence time τ of N_2O can be estimated in various ways. An upper limit can be placed by consideration of the stratospheric photolysis and reactions of N_2O. From the measured distribution of N_2O in the stratosphere (Ehhalt 1974), from measured cross sections for ultraviolet radiation (Johnston and Selwyn 1975), and from measured rate constants for reaction of N_2O with singlet oxygen atoms (Davidson et al. 1976), it can be calculated that the maximum residence time (τ) of N_2O is about 160 years. This value of τ is based only on consideration of stratospheric decomposition processes. From the variability in time and space of N_2O concentrations in the troposphere, Junge (1974) estimated the atmospheric residence time of N_2O as 8 years, with an uncertainty factor of two. (This estimate of a 4- to 16-year residence time is rounded out to 5 to 20 years in this chapter.) These shorter residence times imply a large and probably oceanic source of N_2O, a source that has been proposed by Hahn (1974). The short values for τ also imply a large unknown sink for N_2O, as required by Equation 7-9 (Schütz et al. 1970). These considerations bracket the possible atmospheric residence time of nitrous oxide as follows:

$$5 \text{ years} < \tau < 160 \text{ years} \qquad (7\text{-}10)$$

Recent data and reviews on this subject by various authors within the last two years have suggested atmospheric residence times within this range (see Chapter 3 and discussion below).

RELATION OF CRITICAL VARIABLES TO PERTURBATION OF ATMOSPHERIC NITROUS OXIDE

If the global rate of production of nitrous oxide increased from P_{N_2O} to $(P_{N_2O} + \Delta P_{N_2O})$, and if it held constant at the new value for a time that was long compared to the atmospheric residence time of N_2O, a new steady-state inventory $[N_2O]$ would be attained. For small perturbations, that new inventory would be $(P_{N_2O} + \Delta P_{N_2O})\tau$ (see Equation 7-9). In this case, the ozone equation (7-2) can be extended to give:

$$-\frac{\Delta[O_3]}{[O_3]}=\frac{1}{10}\frac{\Delta P_{N_2O}}{P_{N_2O}} \qquad (7\text{-}11)$$

A strict and detailed account of the relation between a change ΔP_{N_2O} in the production rate of N_2O and a change in the rate of nitrogen fixation would be exceedingly complicated. However, a gross first-order approximation is valuable in identifying the important independent variables. Such a simplified relation can be obtained by extending Equation 7-7 to include global inventories:

$$\Delta P_{N_2O}=\alpha\beta\Delta N_F \qquad (7\text{-}12)$$

where N_F is the natural (background) global rate of fixation of nitrogen, $N_F + \Delta N_F$ is the new rate of nitrogen fixation after some change has occurred, and β and α are the fractions of fixed nitrogen denitrified rapidly and denitrified to N_2O, respectively, as defined above. In order for Equation 7-12 to represent a valid steady state, one must consider times that are long compared to the time for denitrification of β; and for Equation 7-11 to be valid, one must consider times that are long compared to τ, the atmospheric residence time of nitrous oxide.

Equations 7-12 and 7-9 can be substituted into Equation 7-11 to give:

$$-\frac{\Delta[O_3]}{[O_3]}=\frac{1}{10}\frac{\Delta N_F}{[N_2O]}\alpha\beta\tau \qquad (7\text{-}13)$$

The natural global inventory $[N_2O]$ is known to be about 1500 Mt N, and the increased rate of nitrogen fixation can be specified to assess the effect of any assumed rate. The three unknowns, α, β, and τ appear as a single product.

If 100 Mt N/yr is taken as the rate of anthropogenic fixation of nitrogen (i.e., the increase ΔN_F over the natural rate), Equation 7-13 assumes the numerical form:

$$-\frac{\Delta[O_3]}{[O_3]}=6.7\times10^{-3}\alpha\beta\tau \qquad (7\text{-}14)$$

where τ is in years.

Of the three terms, α, β, τ, in Equation 7-14, the real value of β, the fraction denitrified rapidly (within a few decades), is the most complicated to estimate accurately. Independent physical arguments set limits on the other two terms: relationship 7-5 for α, and inequality 7-10 for τ. If both sides of Equation 7-14 are divided by the unknown fraction β, the upper bound for the expected ozone reduction resulting from 100 Mt per year of additional nitrogen fixation can be obtained, subject to assumed values of α and τ:

$$\frac{\Delta[O_3]}{[O_3]} \leq \frac{1}{\beta}\frac{\Delta[O_3]}{[O_3]} = -6.7 \times 10^{-3}\alpha\tau \qquad (7-15)$$

If it is further assumed that all increased nitrogen fixation leads to denitrification within a few decades (i.e., if $\beta = 1$), the ozone reduction would be maximum. If β is less than 1, the reduction of ozone would be less than $6.7 \times 10^{-3}\alpha\tau$ by the factor β.

For an assumed rate of increased nitrogen fixation of 100 Mt N/yr, the maximum ($\beta = 1$) percentage ozone reduction is presented in Table 7.1 for the full range of α (Equation 7.5) and for the full range of τ (Equation 7-10). The indicated ozone reductions vary from less than 0.1 to 21 percent. With such a wide range of possibilities, the subject appears to be hopelessly amorphous. However, the situation is not as indefinite as it appears to be in Table 7.1.

RESTRICTIONS IMPOSED BY THE NATURAL NITROGEN BALANCE

Although various authors and modelers recently have proposed residence times for N_2O as short as 5 years and as long as 160 years, and although the global average value of α could be anywhere between 0.025 and 0.4, there are many pairs of the variables (α,τ) that can be shown to be extremely improbable. Some pairs of α and τ imply impossible values of the natural rate of nitrogen fixation. The present natural rate N_F of nitrogen fixation can be expressed in terms of the same variables (Equations 7-7 and 7-9):

TABLE 7.1 The Maximum Percentage Reduction of Stratospheric Ozone for Various Possible Values of α and τ*

τ (yr) \ α	0.025	0.05	0.1	0.2	0.4
5	0.08	0.17	0.33	0.67	1.3
10	0.17	0.33	0.67	1.3	2.7
20	0.33	0.67	1.3	2.7	5.4
40	0.67	1.3	2.7	5.4	11
80	1.3	2.7	5.4	11	21
160	2.7	5.4	11	21	—

*The percentage reduction in ozone is calculated by the formula: $-\frac{1}{\beta}\frac{\Delta[O_3]}{[O_3]} = 6.7 \times 10^{-3}\alpha\tau$

α is the fraction of N_2O in the products of denitrification, and τ is the atmospheric residence time of N_2O. For this calculation, the factor β, the fraction of fertilizer nitrogen rapidly denitrified, is assumed to be 1, and fertilizer use is assumed to be 100 Mt N per year.

SOURCE: Adapted from Johnston (1977), Journal of Geophysical Research 82(12):1767-1772, copyrighted by the American Geophysical Union, and used with their permission.

$$N_F \geq \beta N_F = \frac{[N_2O]}{\alpha\tau} = \frac{1500}{\alpha\tau}\frac{Mt}{yr} \qquad (7-16)$$

The present situation, which has evolved over geological time, may be presumed to be close to a steady state between nitrogen fixation and denitrification. Thus, the distinction between prompt denitrification (β) and delayed denitrification ($1-\beta$) is not applicable to the natural, unperturbed N_2O balance, and the term β in Equation 7-16 should be taken as unity. Equation 7-16 can then be used to calculate the rates of global nitrogen fixation implied by various assumed values for α and τ. Table 7.2 displays such calculated values for nitrogen fixation (N_F) and has a column giving the rate of global production of N_2O (P_{N_2O}) implied by each value of τ, the atmospheric residence time for N_2O.

As noted above, identified sources of nitrogen fixation add up to 200 to 350 Mt N/yr (also see Appendix A, Section 7). Because of the lack of more comprehensive information on the occurrence of nitrogen fixation in the biosphere and uncertainties in measurements of the process, global nitrogen fixation rates between 150 and 750 Mt/yr may be regarded as within the reasonable range, but values above or below this range seem improbable. The implied nitrogen fixation rates that fall between these limits are enclosed by a solid line in Table 7.2. Values outside the solid line represent improbable combinations of α and τ.

The cases associated with the upper or lower limits of the residence time imply quite different assumptions about the global N_2O balance. If the upper limit on τ (160 years) is assumed, the following conditions for the natural N_2O balance are implied by the plausible rates of nitrogen fixation (see Table 7.2):

(i) N_2O production occurs almost exclusively on land;
N_2O fraction in denitrification (α) about 0.05;
N_2O production rate 10 to 20 Mt N/yr;
N_2O destruction only in stratosphere;
N_2O residence time 100 to 160 years.

Similarly, the lower limit of the N_2O residence time, based on measurements in the atmosphere and in the ocean, is from 5 to 20 years (Schütz et al. 1970, Junge 1974, Hahn 1974). As shown in Table 7.2, several combinations of these residence times for N_2O with plausible rates of nitrogen fixation can imply global average values for α, the fraction of N_2O from denitrification, as high as 0.4. Because the

TABLE 7.2 Natural Global Rates of Nitrogen Fixation Implied by the Values of α and τ* in Table 7.1

α / τ (yr)	α (Including Ocean)					P_{N_2O} (Mt/yr)
		Land (α)				
	0.025	0.05	0.1	0.2	0.4	
5	12,000	6,000	3,000	1,500	750	300
10	6,000	3,000	1,500	750	375	150
20	3,000	1,500	750	375	188	75
40	1,500	750	375	188	94	38
80	750	375	188	94	47	19
160	375	188	94	47	–	9.5

*Natural global rates of nitrogen fixation are calculated by the relationship:

$$N_F = \frac{[N_2O]}{\alpha\tau} = \frac{1{,}500}{\alpha\tau}\,\frac{\mathrm{Mt}}{\mathrm{yr}}.$$

Values are shown for the probable range of α on land and for the possible range of α including oceans and land. The column at the right shows the global rate P_{N_2O} of production of nitrous oxide implied by the residence time τ and equation 7-9. The solid line encloses rates of nitrogen fixation consistent with present knowledge of the natural global rate. The dashed lines enclose rates of fixation associated with upper and lower limits of the atmospheric residence time τ of N_2O.

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probable value for α on land is between 0.05 and 0.1 (CAST 1976), such a global average would seem to indicate that denitrification in the ocean would yield almost 100 percent N_2O, an unlikely prospect. A value of 10 years in Equation 7-9 gives a rate of natural production of N_2O of about 150 Mt N/yr; for a balance to be maintained, there must also be an equal rate of natural destruction of N_2O. Although limited data suggest such an oceanic source of N_2O, they are too sparse and variable to support an accurate estimate of a global production rate. Furthermore, there is no known sink of such magnitude for atmospheric N_2O, although it has recently been suggested by Blackmer and Bremner (1976) that atmospheric N_2O is absorbed or washed back into the soil and then converted to N_2 by bacterial action (see Chapters 2 and 3). The model based on the lower limit of the value of τ has the following implications with respect to the natural N_2O balance:

(ii) N_2O production occurs largely in oceans;
N_2O fraction in denitrification close to 1 in ocean and the expected 0.05 on land;
N_2O production rate about 150 Mt N/yr;
N_2O destruction largely by unknown processes;
N_2O residence time about 10 years.

REVIEW OF VARIOUS MODELS OF OZONE REDUCTION BY NITROGEN FERTILIZER

A number of recent papers and discussions have dealt with the problem of estimating the reduction in stratospheric ozone caused by a change in the global N_2O balance. Although a number of different models and sets of assumptions were used, the points made by different authors in many cases can be simply expressed in terms of Tables 7.1 and 7.2. All of these results were published before the recent findings that lowered the sensitivity factor relating increases in NO_x to decreases in O_3. In effect, the earlier studies used a sensitivity factor of 1/5, rather than the value of 1/10 used above. In comparing our results to those of other models, we have taken into account the impact of this new information by using a sensitivity factor of 1/5, even though it is now known to be too high, in order to give the different calculations a common basis.

Crutzen carried out the calculation for limiting case (i) above in an unpublished 1975 memorandum (Crutzen 1975b). For a steady input of 200 Mt N/yr of fertilizer, he found an upper limit of 8 percent reduction of ozone by the year 2100, and a 14 percent steady-state ozone reduction. Using the same assumptions, (ΔN_F = 200 Mt/yr, α = .04, β = 1, τ = 130 yr), the simple Equation 7-13 (modified, with a sensitivity factor of 1/5 rather than 1/10) also gives a steady-state ozone reduction of 14 percent.

Crutzen (1976) also explored the case in which the lower limit, 10 years, was used as the atmospheric residence time for N_2O. By assuming β to be 1.0, he regarded his calculations as giving the upper limit on stratospheric ozone reduction. He assumed, further, that production of nitrogen fertilizer would grow exponentially from 1975 to 2000 and remain constant at 200 Mt/yr thereafter. He considered three values of α, 0.07, 0.2, and 0.5; he also made one calculation with values for τ of 20 years and for α of 0.2. On the basis of these assumptions, Crutzen projected that steady-state ozone reductions of between 1.5 and 10 percent would occur by the year 2050. By means of the simple formula in Equation 7-13 (again modified to use a sensitivity factor of 1/5), the steady state ozone reduction for these same conditions would be between 1.9 and 13 percent.

A review of the subject by Liu et al. (1976) emphasized the existence of large reservoirs of fixed nitrogen in the deep ocean and in soil minerals, which have slow rates of exchange with biologically available forms of nitrogen. However, the product of the large sizes of the reservoirs and the small rates of exchange gives a turnover rate of available nitrogen that is large compared to industrial sources of fixed nitrogen. Liu et al. emphasized that unless industrial rates of nitrogen fixation are comparable to the natural turnover rate, "the equilibrium between living organic, dead organic, and inorganic nitrogen on land and in the oceans will remain unperturbed." According to their argument, if industrially fixed nitrogen were to have a prompt (in decades) effect on atmospheric nitrous oxide, the fixed nitrogen added by human activities would have to follow some pathway other than the natural equilibrium between free nitrate and other soil nitrogen. In the terminology used here, Liu et al. emphasized the quantity $1-\beta$, the fraction of added fertilizer that enters the long-lived reservoirs.

Sze and Rice (1976) responded to the suggestions of Liu et al. (1976) but emphasized the fraction β of fertilizer that is promptly denitrified. They argued that, to some extent, the nitrogen fertilizer applied to agricultural soils does have a significantly different fate than does nitrogen that is cycling in natural ecosystems. Sze and Rice assumed that the atmospheric residence time for N_2O is 20 years, and that the N_2O fraction of denitrified gases was 0.26 for both land and ocean. They considered three different possible values for the fraction of fertilizer that is promptly denitrified: 0.10, 0.35, and 0.6. In the terms used here, they considered the cases of $\alpha = 0.26$; $\beta = 0.1$, 0.35, and 0.6; $\tau = 20$ yr; and $\Delta N_F = 200$ Mt N/yr. For the year 2025, they calculated ozone reductions from nitrogen fertilizer to be between 1.6 and 9 percent. Using Equation 7-13 and a sensitivity factor of 1/5, calculated ozone reductions range from 1.4 to 8.3 percent for this set of values of α, β, and τ.

McElroy et al. (1976) reviewed this subject with emphasis on the question of the ocean as a source or sink for N_2O. They concluded, in disagreement with Hahn (1974), that the oceans as a whole are a net sink for atmospheric N_2O. McElroy et al. assumed an atmospheric residence time of 20 years for N_2O, a value of 0.23 for α (stated as 0.3 for the ratio of N_2O to N_2 in denitrified gases), a value of 1.0 for β, and 200 Mt N/yr of anthropogenic fixed nitrogen. They concluded that "reductions in ozone on the order of 20 percent during the first half-quarter of the twenty-first century, due to current and future use of fertilizer, are not improbable." For the same values of α, β, and τ, and a sensitivity factor of 1/5, Equation 7-13 gives a 12.3 percent reduction of ozone.

Thus the use of Table 7.1 (subject to restrictions of Table 7.2 and using 1/5 for the NO_x-O_3 sensitivity factor) gives nearly the same results as those derived by other authors from extensive model calculations. The time over which the ozone reduction will be achieved is the sum of the time for the fraction β to be denitrified (one or two decades, by definition), the time for the atmosphere to reach equilibrium with respect to the new source of N_2O (τ represents the time for this process to go to 1-1/e toward completion), and the time for ozone to relax following NO_x production (a short time compared to the residence time of nitrous oxide).

PREFERRED VALUES

The purpose of this analysis has been to identify the relationships among the several independent variables that determine the impact of anthropogenic nitrogen fixation on the stratospheric ozone layer, and not to present any particular solution to this complex problem. The general framework developed here may be used to test the implications of future scientific findings about the values of α, β, and τ. However, we offer here our own best judgments of what the effective average values of α, β, and τ may turn out to be. Given those preferred values, and assumptions about the rate of fixation of nitrogen by future human activities, we can calculate the expected impacts on the ozone layer.

For nitrogen fertilizer, the important values of the fractions α and β concern agricultural soils and nearby land and water areas. Because long-distance transport of fertilizer nitrogen appears limited, the values of α and β for the oceans have only a secondary effect on how much of that nitrogen is converted to atmospheric nitrous oxide. The oceans could, however, be important in determining the global atmospheric inventory $[N_2O]$ and residence time τ of nitrous oxide.

For this analysis, it is assumed that nitrogen fertilizer applied to land produces about 10 percent nitrous oxide upon denitrification ($\alpha = 0.1$) and that about two-thirds of the soil-applied nitrogen is denitrified promptly ($\beta = 2/3$). With these particular values for α and β, the long-term steady-state ozone reduction is expressed in the simple numerical form:

$$-\frac{\Delta[O_3]}{[O_3]} = 4.4 \times 10^{-6} \Delta N_F \tau \qquad (7-17)$$

where τ is the atmospheric residence time of nitrous oxide in years and ΔN_F is the rate of nitrogen fixation by human activities in Mt N/yr. In principle, it takes an infinite amount of time to reach a steady state, but it is convenient to note that 95 percent of the response to a perturbation is attained within three residence times (3τ). The equation for the effect of manufactured and cultivated nitrogen fertilizers on stratospheric ozone when $t = 3\tau$ can then be expressed in the following practical form:

$$-\frac{\Delta[O_3]}{[O_3]} = 4.2 \times 10^{-6} \Delta N_F \tau \qquad (7-18)$$

This relationship may then be used to calculate the projected change in the ozone layer associated with any assumed increase in the amount of anthropogenic nitrogen fixation. Two examples of this relationship seem especially interesting: (1) The present rate of nitrogen fixation for fertilizer, 35 Mt N/yr for legumes plus 44 Mt N/yr for manufactured fertilizer, giving a total of 79 Mt N/yr (CAST 1976); and (2) a possible future situation when cultivated plus manufactured fertilizers total 200 Mt N/yr. These two rates of nitrogen fixation are used as headings in Table 7.3, which gives the percentage ozone reduction and the time to attain this reduction for different assumed values of τ, using the preferred set of values of α and β for fertilizer applied to land.

The atmospheric residence time τ of nitrous oxide has the largest range of uncertainty of the factors considered

TABLE 7.3 Percentage Ozone Reduction for Two Assumed Constant Rates of Manufactured plus Cultivated Fertilizer Application[a]

N_2O Residence Time (τ) in Years	$t_{0.95}$ (3τ years)	ΔN_F, Mt N per Year	
		79 (1976)	200 (future)
5	15	0.2	0.4
10	30	0.4	0.9
20	60	0.7	1.7
40	120	1.5	3.5
80	240	2.5	6.5
160	480	5.5	13

[a] Reduction of ozone would attain 95 percent of the steady state value after 3τ years. Reductions are calculated for $t = 3\tau$, and with assumed values of $\alpha = 0.1$ and $\beta = 2/3$.

here. At present, we believe the value to be between 5 and 160 years; further research in atmospheric, oceanic, and soil sciences will be required to determine the value more exactly. In the meantime, Table 7.3 shows the percentage reductions in the ozone layer that would occur after 3τ years of constant inputs of fixed nitrogen at either 79 or 200 Mt N/yr. The steady-state ozone reduction is only 5 percent greater than the values in Table 7.3, and for all practical purposes the reductions in Table 7.3 represent the total effect.

As Table 7.3 shows, the approximate steady-state ozone reductions to be expected from long-continued use of manufactured and cultivated fertilizer at the 1976 rate, 79 Mt N/yr, are:

(1) Minimum: 0.2 percent ozone reduction after 15 years ($\alpha = 0.1$, $\beta = 2/3$, $\tau = 5$ yr);

(2) Central: 1.5 percent ozone reduction after 120 years ($\alpha = 0.1$, $\beta = 2/3$, $\tau = 40$ yr);

(3) Maximum: 5.5 percent ozone reduction after 480 years ($\alpha = 0.1$, $\beta = 2/3$, $\tau = 160$ yr).

For the possible future case involving 200 Mt N/yr from manufactured and cultivated fertilizer, the corresponding cases are:

(1) Minimum: 0.4 percent ozone reduction after 15 years;

(2) Central: 3.5 percent ozone reduction after 120 years;

(3) Maximum: 13 percent ozone reduction after 480 years.

The various possibilities projected by this analysis can be summarized as follows: the ozone reduction by nitrogen fertilizers could be of <u>small</u> extent and registered over a <u>short</u> period of time, i.e., a few decades; there could be <u>medium</u>-sized ozone reductions building up over <u>moderate</u> periods of time; or there could be a <u>large</u> reduction of ozone brought about only after a <u>long</u> period of time, i.e., several centuries. For nitrogen fertilizers applied to land, a <u>large</u> ozone reduction after a <u>short</u> period of time seems highly improbable.

Finally, we believe that future research probably will fix the value of τ at an intermediate point in the range of possible values, perhaps at about 40 years. Projected reductions in ozone for this preferred set of values ($\alpha = 0.1$, $\beta = 2/3$, $\tau = 40$ years) are enclosed by the dashed lines in Table 7.3. If the current rate of nitrogen fixation by legumes and in manufactured fertilizers is continued indefinitely, a 1.5 percent reduction in ozone would occur after about 120 years, or by the year 2100. On the other hand, if nitrogen fixation for fertilizer increases to 200 Mt N/yr and holds steady at that level thereafter, the expected ozone reduction after 120 years is 3.5 percent. Greater or lesser changes in the rate of nitrogen fixation by human activities would, under the assumptions of this simplified model, have proportional impacts on the ozone layer.

FERTILIZER IN COMPARISON TO OTHER THREATS TO THE OZONE LAYER

At least three classes of human activities could cause a large reduction in stratospheric ozone: (1) direct injection of NO_x into the stratosphere by high-flying aircraft; (2) the breakdown of chlorofluorocarbons in the stratosphere to produce chlorine; and (3) an increase in atmospheric nitrous oxide eventually produced from nitrogen fixed primarily in food production.

The impact of high-flying aircraft on stratospheric ozone was the subject of the CIAP, a major interdisciplinary research program in 1971-1975. Similarly, the effect of chlorine from chlorofluorocarbons has been studied heavily in the period 1974-1977, and a major summarizing report has been issued (NRC 1976). In contrast, the effect of nitrous oxide from nitrogen fertilizers on stratospheric ozone is a much more complex problem than the effects of either SST emissions or chlorofluoromethanes, and yet it has been studied far less. Although it is possible to compare these three threats to stratospheric ozone, the great uncertainty about both the magnitude and the timing of effects of nitrogen fertilizers on ozone must be kept in mind. For each of these three mechanisms, distinctions can be drawn between the amount of ozone reduction expected if present practices were sustained indefinitely, and the reduction resulting from possible future expansion of each activity (Table 7.4).

The CIAP study estimated the size and possible properties of supersonic transport fleets that would be commercially successful, i.e., pay off development costs and return a fair profit. One such fleet, envisioned in 1970 as equivalent to 500 Boeing SSTs, was expected to fly at 20 km and burn 100 Mt of fuel per year. Using NO_x emission properties for 1974 supersonic transports, the CIAP estimated that such a fleet would reduce global ozone by 13 percent, with an uncertainty range of 4 to 20 percent. If this estimate is updated by using 1/10 instead of 1/5 for the sensitivity factor in Equation 7-1, the impact of such a

TABLE 7.4 Comparison of Expected Reductions of Stratospheric Ozone by Three Different Mechanisms

Mechanism	Ozone Response Time	Steady-State Percentage Global Ozone Reduction (range of uncertainty in parentheses): Long-Term Use at Current Level	Long-Term Use at Possible or Proposed Future Level
Stratospheric Aviation[a]	years	<0.1	6.5(1 to 10)
Chlorofluorocarbons[b]	decades	14 (2 to 20)	large
Manufactured and cultivated fertilizer	decades to centuries	1.5 (0.2 to 5.5)	3.5 (0.4 to 13)

[a] Derived from NRC (1975) and Grobecker et al. (1975). The estimate of impact of current level of use is based on 1974 use of military aircraft, six Concorde SSTs, and other civilian aircraft occasionally operating in the lower stratosphere; increased by a factor of two to account for rate constants revised in 1977.

[b] Derived from NRC (1976); reduced by a factor of two to account for rate constants revised in 1977.

fleet might be a reduction in ozone of about 6.5 percent, with a similarly modified uncertainty range. The impact of current stratospheric flight, however, would reduce ozone by less than 0.1 percent (NRC 1975, Grobecker et al. 1975).

For long-term continued use of chlorofluorocarbons at the 1974 level, the National Research Council (1976) estimated an eventual (50 years in the future) global ozone reduction of 7 percent (uncertainty range 2 to 20 percent). Recently acquired information about rate constants for stratospheric reactions (see Chapter 2), however, led the NRC to double its estimate of that impact to about 14 percent (NRC 1977). If chlorofluoromethane production had continued its exponential rate of growth until the year 2000, much larger ozone reductions and major climatic changes would be expected.

It appears, therefore, that anthropogenic nitrogen fixation presents a smaller threat to stratospheric ozone than do chlorofluoromethanes. In both cases the effect is expected to develop slowly over many decades. If stratospheric aircraft with exhaust emissions like those of the present engine design were manufactured in sufficient numbers to be commercially successful, the ozone reduction indicated in Table 7.4 would be about half of that projected for current levels of production of chlorofluoromethanes, and about twice the central value projected for fertilizer nitrogen used at a level of 200 Mt N/yr. The range of uncertainty associated with each of these estimates, however, allows considerable overlap in comparisons of such effects.

If continued research substantiates the hypothesis that increased or continued fixation of nitrogen for use as fertilizer will significantly reduce stratospheric ozone, strategies to decrease human dependence on anthropogenically fixed nitrogen would be indicated. Recycling of nitrogenous wastes (e.g., animal manures and sewage) might be pursued, even if costs exceeded those of manufactured fertilizer or cultivated legumes. Clearly, food production is more vital to society than stratospheric aviation or most uses of chlorofluoromethanes, and limiting the use of nitrogen in food production would not appear to be an acceptable strategy. As this problem develops in the decades ahead, some complex cost/benefit analyses and difficult policy choices will have to be made. (See Chapters 11 and 12.)

SUMMARY

Although the problems are complex and the analysis here is a simple one, Tables 7.1 to 7.3 reflect the broad aspects of current knowledge and uncertainties. The important variables are:

(1) τ, the global atmospheric residence time of N_2O, which is determined by all its natural sources and sinks;

(2) β, the fraction of nitrogen fertilizer denitrified within a few decades;

(3) α, the fraction of nitrogen converted to N_2O during denitrification;

(4) The factor 1/10, connecting ozone decrease and NO_x increase in Equation 7-1 and incorporated in Tables 7.1 to 7.3.

With these four factors, α, β, τ, and 1/10, one can calculate the long-term ozone reduction from any assumed increase in nitrogen fertilizer use, ΔN_F, in Mt N/yr:

$$-\frac{\Delta[O_3]}{O_3} = \frac{1}{10} \times \frac{\Delta N_F}{1500} \alpha\beta\tau \qquad (7\text{-}19)$$

If the rate of application of fertilizer varies with time, this simple equation is, of course, not applicable. It is recognized that the use of loosely-defined average values for α and β is not satisfactory. At present, however, these terms are treated the same way in detailed model calculations and in the method used here. Until experimental data are obtained to give the detailed structure of the functions for these terms, this simple method may be sufficient to respond to many of the questions that may arise.

Using the simple method developed here and assuming preferred values for α, β, and τ, it is calculated that fertilizer use at levels from 79 to 200 Mt N/yr will lead to a reduction of stratospheric ozone of from 1.5 to 3.5 percent by about the year 2100. This effect is, at most, about one-fourth of that projected for current levels of use of chlorofluoromethanes, and is about half the ozone reduction predicted for operation of a fleet of 500 advanced supersonic transport aircraft.

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CHAPTER 8

ECOLOGICAL EFFECTS OF NITRATES, NITRITE, AND NITROSAMINES

INTRODUCTION

Human activities have unquestionably increased the amounts of nitrates and related compounds in some compartments of the environment (see Chapter 6). The effects of such elevated levels of nitrogen compounds may be beneficial or adverse, or both. Effects of both kinds may occur simultaneously, and may be felt in media or in ecological compartments quite removed from those that initially receive anthropogenic nitrogenous inputs. Some of the major pathways linking environmental effects with perturbations of the nitrogen cycle are shown in Figure 8.1.

The relationships suggested by the figure are understood qualitatively; in most cases, however, quantitative cause-and-effect processes have not been well defined. This chapter reviews what is known about the effects of nitrates and some related nitrogenous compounds on plants, animals, and ecosystems. Effects on the stratospheric ozone layer and on the health of humans and livestock are addressed in Chapters 7 and 9, respectively, of this report.

Living organisms are exposed to nitrates and related compounds through air, water, soil, and food webs. The rate of exposure depends on proximity to sources and on a great many environmental processes of transport and transformation (illustrated in Figure 8.1); many of those processes are discussed in Chapters 2, 3, and 6 of this report.

Four kinds of effects of nitrates and related compounds are examined here:

Effects of Nitrate as a Nutrient. Increases in nitrogen inputs to ecosystems can increase biological productivity, either as a deliberate objective of management (e.g., fertilization of agricultural crops), or as an unintended result of other activities (e.g., increased nitrogen loadings to lakes or terrestrial systems, as illustrated in Figure 8.1).

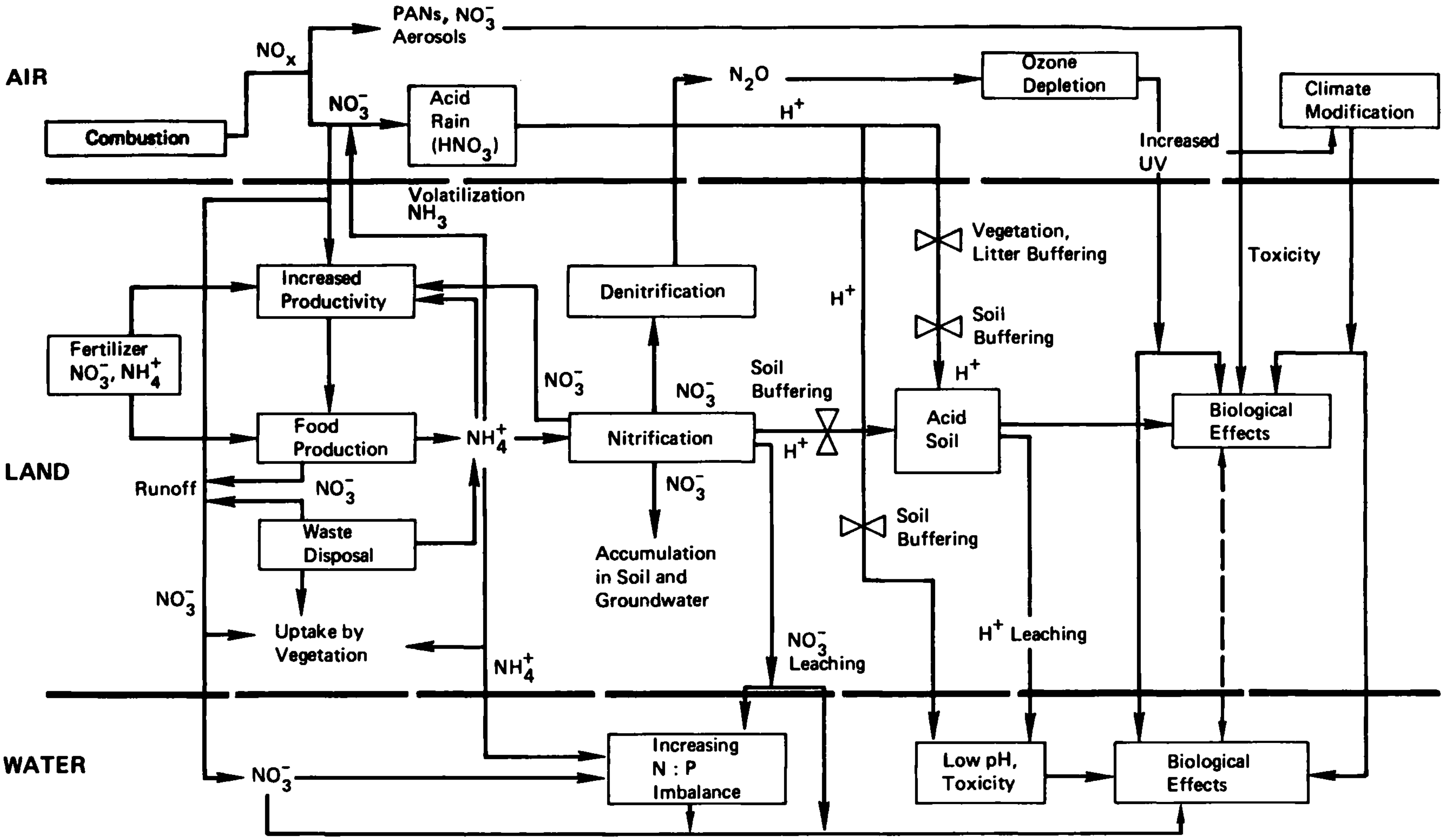


FIGURE 8.1 Schematic presentation of environmental effects of manipulation of the nitrogen cycle. Human-caused perturbations are shown at left, culminating in ecological and climatic effects, at right. Processes that buffer against the effects are indicated with the symbol (⋈) on the arrows representing the appropriate pathways.

Effects of Nitric Acid. Acidic nitrate aerosols and gaseous HNO_3 can be directly toxic to organisms; and, when scavenged from the atmosphere by precipitation, they can contribute to an increase in the acidity of rainfall, soils, and surface waters (see Chapter 6). Such a decline in pH may have adverse impacts on the productivity of ecosystems, and may lead to other potentially hazardous changes in the environment.

Direct Toxic Effects. Nitrite, some organic nitrate aerosols such as the peroxyacyl nitrates (PANs), and N-nitroso compounds are known to have or are suspected of having direct toxic effects on animals, plants, or microorganisms.

Indirect Effects. If anthropogenic increases in nitrogen fixation should lead to depletion of the ozone layer (see Chapter 7), the resulting increase in ultraviolet (uv) irradiation of the earth's surface would have adverse effects on a wide variety of organisms.

These categories of effects are examined here. However, this chapter does not review the ecological effects of several other nitrogenous compounds, specifically ammonia and the oxides of nitrogen. For an assessment of effects of those pollutants, see other recent reports by the National Research Council (1977a, 1977b).

EFFECTS OF NITROGEN SUPPLEMENTS ON CROP PRODUCTION

The most widespread and readily noticed effect of human-induced increases in nitrogen inputs to ecosystems is enhanced primary production, as plants respond to the added nitrogen. The most common and obvious example is the use of fertilizer nitrogen to increase the production of agronomic crops. The nature of crop responses to nitrogen supplements has been thoroughly studied, because of its substantial economic importance; see Viets (1965) for a review. Quantitative knowledge of the response of a particular crop in a particular locale to a given addition of fixed nitrogen would be highly desirable, for several important reasons. First, predictions derived from such knowledge are required for the efficient use of fertilizer. Such information is needed in order both to avoid economically wasteful overfertilization and to minimize the potential environmental impacts of leaching and denitrification of that nitrogen not taken up by crops. Second, crop response curves are needed to estimate the impacts on crop production of pollution control measures that involve limitations on fertilizer application rates (Taylor and Swanson 1973; also see Chapter 10). Third, knowledge of crop responses to fertilizer nitrogen may be used to estimate the effects on crops of other anthropogenic nitrogen inputs to agricultural lands, such as fixation by legumes, land disposal of nitrogenous wastes, and precipitation of nitrates and other atmospheric contaminants. Finally, the responses of agronomic crops to fertilizer may serve as analogies from which the responses of other terrestrial plant communities to a variety of nitrogenous inputs might be projected.

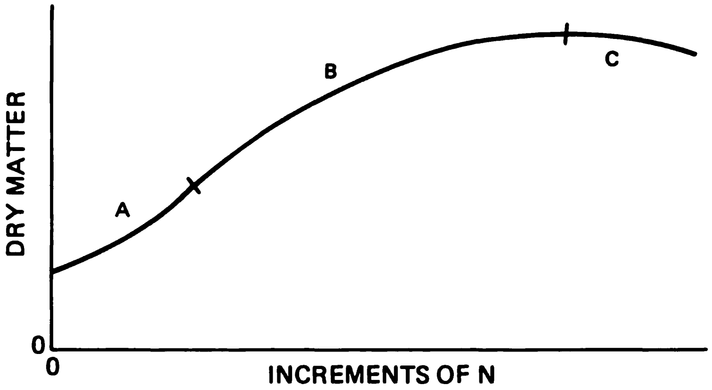
The qualitative relationship between nitrogen fertilizer applications and crop yield is well known (Viets 1965), and is illustrated by the generalized yield-response curve in Figure 8.2. Unfortunately, however, the quantitative prediction of the response of a given crop to fertilization on a site-specific basis remains a complex and uncertain enterprise. In the first place, inputs of fixed nitrogen to a soil system rapidly lose their identity as they move through the various processes of the nitrogen cycle (see Chapter 4); thus it is difficult to determine the relative contribution of any particular source of nitrogen to the crop's needs. Second, the availability of sufficient nitrogen is only one of many factors that interact in a complex manner to influence crop yields. Ultimately, this complexity limits our ability to predict crop response to a given nitrogen input. In the sections that follow, the use of nitrogen by crops and the multiple parameters that influence crop yields are examined.

Uptake and Metabolism of Nitrogen

Nitrogen is a constituent of structural proteins, enzymes and many metabolic intermediates, and it is required by plants in amounts higher than any other nutrient that comes from the soil. Most plants use either ammonium or nitrate with equal efficiency; however, some plants grown solely on ammonium show marked nutrient imbalances and poor growth (Viets 1965). Various explanations of this effect are possible, including differences in the mobility of the two ions in the soil and within the plant; cation/anion imbalances; and plant metabolic needs. The implication, however, is that nitrate is required to sustain yields of some agronomic crops.

Nitrate is absorbed rapidly by plant roots, probably by a combination of active (metabolic) and passive (water flow) mechanisms. Most agronomic plants apparently cannot remove all of the NO_3^- that is in soil solution. According to Kirkham et al. (1974) plants exhibit nitrogen deficiency when soil nitrogen concentrations fall below 10 to 50 mg N/l.

Within the plant, nitrate must be reduced to the metabolically usable ammonium form. This reduction requires the transfer of eight electrons, through nitrate and nitrite



SOURCE: Modified from Viets [1965], Page 507 in Soil Nitrogen, ASA Monograph No. 10. Used with permission of the American Society of Agronomy.

FIGURE 8.2 Idealized response in dry matter production of a nonlegume to increments of nitrogen fertilizer.

reductase enzymes (Viets and Hageman 1971), and constitutes a major use of solar energy. A number of environmental and nutritional factors affect the activity of nitrate reductase, including light, temperature, water stress, molybdenum deficiency, endogenous metabolites and herbicides. Hence, the level of nitrate in plant tissue can vary widely among species and genotypes, as well as seasonally, and even diurnally (Viets and Hageman 1971). Because of these variables, there is little direct correspondence between fertilization rate and the accumulation of nitrate in foods or feeds (Jackson et al. 1967; also see Chapter 3).

The nitrogen requirements of plants vary widely, depending on their dry matter yield and protein content. Crops such as corn have a high nitrogen demand much of the season, assimilating as much as 2 to 4 kg N/ha-day. The total nitrogen removed by most nonleguminous agricultural crops in a growing season ranges from about 75 to 150 kg/ha. There is, however, a wide variation among crops in terms of their requirements for fertilizer. (For instance, see Table 6.3 in Chapter 6 of this report.)

Figure 8.3 and Table 8.1 illustrate the relative efficiency of a typical crop, corn, in removing nitrogen from soil as a function of fertilization rate. At a rate of 224 kg N/ha, crop yield was highest, and the nitrogen removed by corn approached 70 percent of the amount of added nitrogen. Each supplemental addition of nitrogen was used less efficiently, however; at the maximum rate of fertilization (560 kg N/ha), crop uptake was equal to only 35 percent of the added nitrogen. Furthermore, no increases in yield were observed at fertilizer application rates higher than 224 kg N/ha in this study.

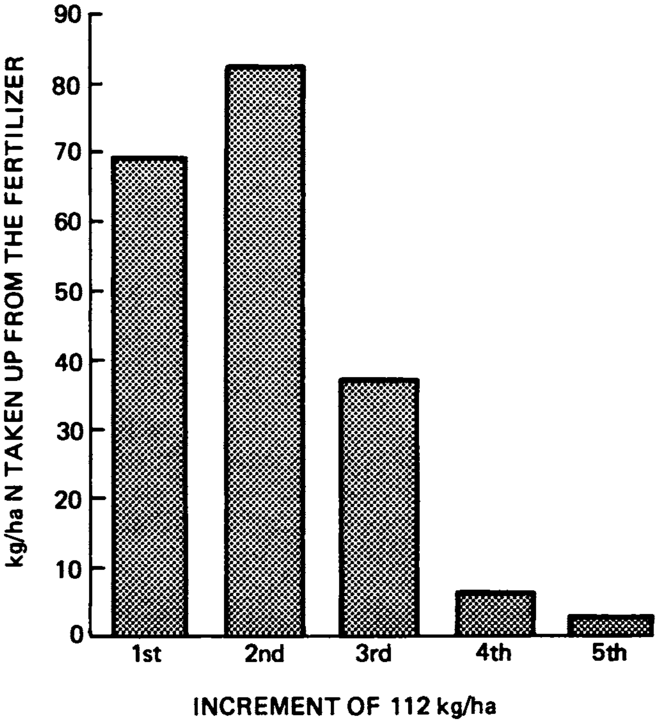
Factors that Affect Crop Yields

Several excellent reviews of the many factors that affect crop yields, including their response to nitrogen fertilizers, are available, e.g., Viets (1965), Pierre et al. (1966), Black (1967), Ingestad (1977), Frissel (1977), and Barber (1976). Table 8.2 summarizes the factors that influence crop yields. These relationships can be quantified only in reference to specific crops and specific regions. To illustrate the complexity of crop response to management, the significance of these factors is examined for corn, as produced in the midwestern United States. (See Chapter 6 for a description of agricultural practices in the corn belt.) Although the specific cases for other major crops might be quite different in many respects, corn is typical in terms of the number of parameters that must be considered and the complexity of their interactions.

TABLE 8.1 Yield Response of Corn to Nitrogen Fertilizer in the Experiment Illustrated in Figure 8.3[a]

Fertilizer (kg N/ha)	Corn Yield (metric tons/ha)
0	1.2
112	9.9
224	13.6
336	13.1
448	12.4
560	12.7

[a] Data from Broadbent (1974).



SOURCE: Modified from Fried et al. (1976), J. Environ. Qual. 5:199. Used with permission of the American Society of Agronomy.

FIGURE 8.3 Nitrogen taken up by corn from successive increments of added fertilizer nitrogen, Kearney Station, California, 1973.

TABLE 8.2 Soil, Climatic and Management Factors That Affect Crop Yields.

Soil Properties	Soil Water Supply in Root Zone	Weather	Short Term Management	Long Term Management
Slope, drainage, texture, structure, permeability, infiltration, presence of restricting layer, depth of topsoil Availability of nutrients (N, P, K, Ca, Mg, S, B, Cu, Fe, Mn, Mo, Zn) Water retention in the root zone Soil aeration (need for artificial drainage) Susceptibility to flooding	Preseason--Precipitation in fall and spring, previous cropping Growing season--Rainfall, evapotranspiration, rooting depth, weeds	Precipitation distribution Temperature Storms (wind, hail) Weather during critical growth periods Date of killing frost	Previous crop Tillage, ground cover Variety of crop Plant density Planting date Timing and rate of application of fertilizers Weed and insect control (pesticides and/or cultivation)	Drainage (tile or surface) Soil conservation practices Irrigation system Land available, land purchases Cropping system Liming Machinery and equipment

Soil factors in most of the corn belt are sufficiently close to ideal, either naturally or through management practices, that other factors limit yield. However, nutrient imbalance often must be dealt with on a yearly basis, and deficiencies in nutrients or in water can limit yield. Soil aeration is an important and dynamic factor, which depends not only on intrinsic soil properties but also on weather and artificial drainage. Water supply in the root zone is especially important in the unirrigated areas of the corn belt. During the growing season, a corn crop uses about 50 to 65 cm of water (Shaw and Burrows 1966). Rainfall during the summer is seldom sufficient to meet this need, and water reserves in the soil make up the deficit. Previous cropping, especially with deep-rooted legumes, can deplete soil water and reduce corn yields, especially in relatively dry locales or during dry years (Shrader and Pierre 1966).

Weather is the least predictable or controllable of the factors listed in Table 8.2. Preseason precipitation, which affects soil water reserves and aeration, is known at planting time, and nitrogen fertilizer rates can be adjusted accordingly. For example, a low water reserve in the spring might be compensated for by lower plant density and reduced application of fertilizer. Rainfall and temperature during spring have critical effects on seedbed preparation, planting date and the fate of residual soil nitrogen and preapplied fertilizer nitrogen. Early planting (late April to early May) is vital for good corn yields (Rossman and Cooke 1966); to prepare for early planting, growers have increasingly relied on fall plowing and fall fertilization.

Low precipitation and high temperatures in summer can lead to wilting, retarded photosynthesis, and reduced yields of corn, especially if such conditions occur during the tasseling-silking period (usually late July to early August). Water stress for only a few days during this critical period has large negative effects on grain yields (Shaw and Burrows 1966). Such effects of weather are largely unpredictable and uncontrollable, although early planting and the use of proper varieties can ameliorate the effects somewhat. Spring and summer hail and wind storms and premature killing frosts can reduce corn yields severely, at least on a local scale; this was the case in much of the corn belt in 1974. Diseases can also be a problem; the corn blight outbreak of 1971 is a prime example.

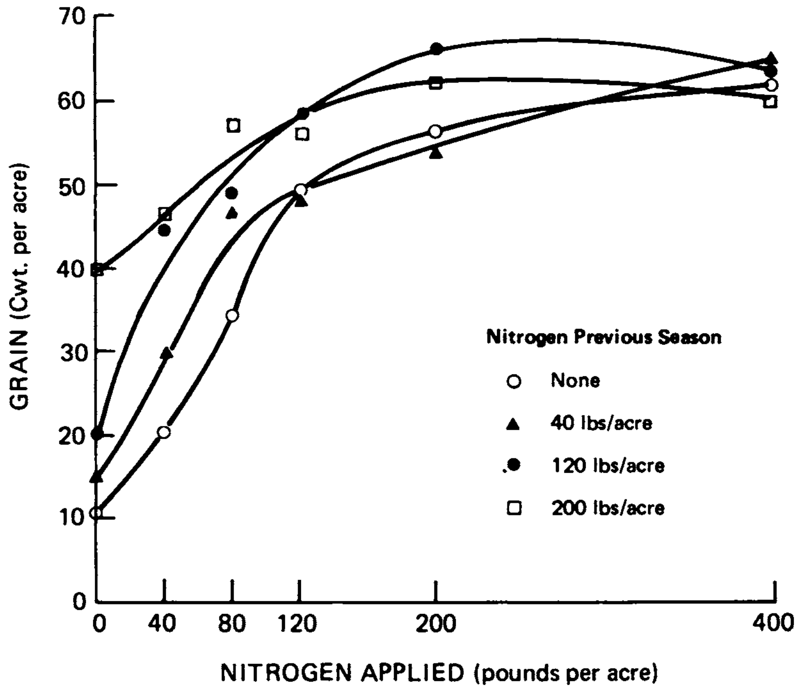
The Role of Fertilizer in Crop Yields

Largely unpredictable weather factors provide the context in which farmers with variable amounts of management skills and available labor and capital must make the short-and long-term management decisions shown in Table 8.2, including decisions about the use of nitrogen fertilizers. In general, corn farmers are aware that fertilizers will give an economic return in all but exceptionally poor weather years. The greatest need, then, is to predict accurately the dose-response relationship for a given crop on a given farm.

An idealized dose-response curve for crop response to added fertilizer is shown in Figure 8.2, and Figure 8.4 gives typical experimentally-derived curves for corn. Segment A of the response curve in Figure 8.2 depicts the seldom-observed region where succeeding increments of nitrogen produce successively larger increments in yield. In segment B, the most commonly observed portion of the response curve, the incremental yield for each additional input of nitrogen declines to a point where no additional response is obtained. In segment C of the curve, yield declines from overfertilization. (This effect rarely occurs with corn, but is common with small grains where excess nitrogen promotes lodging.) In economic terms, at some point on the curve in Figure 8.2, generally below the maximum yield, additional nitrogen fertilizer yields a return in product equal to the cost of fertilizer. In environmental terms, however, since each additional increment of nitrogen fertilizer results in proportionately smaller increments in removal of crop nitrogen, the point of maximum economic return is likely to be at a relatively inefficient level of fertilizer use. In practice, marginal economic benefits are often unknown, and fertilization for maximum yield often is the prevailing philosophy.

Unfortunately, most experimentally-determined nitrogen response curves are of limited value, since they do not apply to actual farming conditions. Table 8.3 summarizes factors involved in the on-farm response of crops to nitrogen fertilizer. As Figures 8.2 and 8.4 show, some yield almost always is obtained with no supplemental nitrogen, because of the nitrogen released from soil organic matter and residual inorganic nitrogen. In lower rainfall areas, considerable residual inorganic nitrogen from the previous crop may be present, and can be used by the next year's crop (e.g., Figure 8.4). As noted in Chapter 4, accurate estimation of the release rate and amount of nitrogen available from the soil pool has proved difficult.

Another important factor in fertilizer-yield response is the rate at which the plant accumulates nitrogen; corn, for example, typically accumulates much of its nitrogen in the period beginning about one month after emergence (Hanway 1960). Loss of nitrogen through leaching or denitrification before this period can result in reduced yields. The use of plant varieties characterized by even more rapid uptake of nitrogen during the early growth period, and timing of



SOURCE: Modified from Viets [1965], Page 508 in Soil Nitrogen, ASA Monograph No. 10. Used with permission of the American Society of Agronomy.

FIGURE 8.4 Shapes of the response curves of corn grain yield to nitrogen fertilizers as affected by the amount of nitrogen applied to the preceding corn crop.

TABLE 8.3 Factors That Affect the Yield Response of Nonleguminous Crops to Nitrogen Fertilizers

Factor	Related Variables
Availability of soil organic nitrogen and of inorganic nitrogen in the root zone	Soil aeration and temperature; amount and type of organic nitrogen in root zone; previous crop, wastes and residues; leaching and/or denitrification; previous nitrogen fertilization
Rate of accumulation of nitrogen by plants	Weather, soil and management factors, genetics
Rooting depth and density	Genetics, weather, soil properties, fertilizer placement
Final yield of nitrogen in crop	Genetics, weather, management (see Table 8.2), availability of other nutrients
Fertilizer formulation	Type and timing of application, slow release or inhibitor characteristics
Availability of fertilizer nitrogen:	
Immobilization	NH_4^+-fixing clay minerals, C/N ratio of residues
Volatilization of NH_3	Application of anhydrous NH_3 to soils which are too dry, moist or sandy, or at too high a rate; application of urea or low pressure solutions to soil surface without incorporation
Denitrification	Soil aeration, temperature, pH, availability of organic C, presence of nitrate
Leaching of nitrate	Rate and amount of soil water movement, plant uptake, denitrification
Competitive plant uptake by weeds, inter-row crops	Weeds, immobilization
Application in the fall	Spring soil temperature, rainfall

fertilizer applications to coincide with that rapid uptake period, can result in more efficient fertilizer use. Similarly, plant breeding and management to encourage deeper and more dense root growth could lead to increased uptake of nitrogen before it is leached from the root zone.

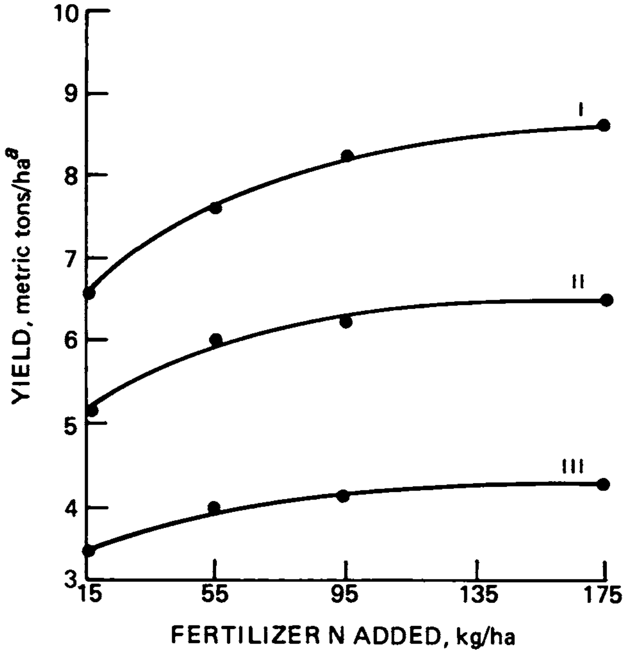
The response function for fertilizer nitrogen is very heavily dependent on crop yield, as determined by other variables (Lathwell et al. 1970). As Figure 8.5 shows, much less response to nitrogen is obtained when other factors limit yield (the low yielding experiments, curves II and III in Figure 8.5) than when high yields are obtained.

In some cases, the type of nitrogen fertilizer used can affect the response curve, though in general it makes little difference whether ammonia, nitrate, or urea fertilizer is chosen (Viets 1965). Other factors that can reduce the efficiency of use of fertilizer nitrogen include immobilization of nitrogen due to addition of carbon-rich residues; poor application practices, such as surface application of NH_3 solutions or urea, poor timing of applications, or fall applications of anhydrous NH_3; and leaching and denitrification of nitrate (see Chapters 2, 3, and 6 of this report for additional discussion).

In short, the number of variables that can affect crop yields is very large, and many of the factors discussed here can have substantial impacts on the efficiency of crop use of nitrogen fertilizer. Because of numerous uncertainties and an inability to separate the influences of the multiple factors acting simultaneously, it is not possible to apply the experimentally derived relationships between fertilizer applications and crop yield response to predict quantitatively the effect of fertilizer use under any set of specific on-farm conditions.

EFFECTS OF ANTHROPOGENIC NITROGEN INPUTS TO ECOSYSTEMS

Predicting the effects of nitrates and other anthropogenic nitrogen inputs on natural ecosystems involves much greater uncertainties than does prediction of the yield response of an agricultural crop. First, it is far more difficult to determine accurately the actual anthropogenic nitrogen inputs to most ecosystems; this is especially true for terrestrial systems, where the major influxes are from atmospheric deposition. Second, far less is known of the responses of nonagricultural plant communities to increased supplies of fixed nitrogen than is known for cultivated crops. It is possible, however, to estimate the approximate magnitude of anthropogenic nitrogen fluxes to ecosystems, using the limited amount of monitoring data available or mass-balance calculations (see Chapter 6 and Appendix A of



[a] Converted from bu/a by the relationship:
1 kg/ha = 0.0159 bu/a (15% water content).

SOURCE: Modified from Parr (1973), J. Environ. Qual. 2:78. Used with permission of the American Society of Agronomy.

FIGURE 8.5 Response of corn (grain) to applications of nitrogen fertilizer for 21 location-years of data in New York: Curve I, mean of high-yield experiments; II, intermediate-yield experiments; and III, low-yield experiments.

this report). Such estimates, and other information about the nitrogen cycle in the specific system under study (see Appendix A, Section 3), make it possible to reach some conclusions about the possible ecological significance of the added nitrogen. In addition, where the data base is more extensive, as it is for a number of lakes in various stages of eutrophication, more quantitative dose-response relationships can be approached.

Terrestrial Ecosystems

Input of nitrate and other nitrogen forms from the atmosphere is an integral component of the terrestrial nitrogen cycle. Higher plants and microorganisms can assimilate the inorganic forms rapidly. The flux of inorganic nitrogen in wet precipitation (rain plus snow) is usually equivalent to only a few percent of the total nitrogen assimilated annually by plants in terrestrial ecosystems; but total nitrogen fluxes, including organic nitrogen, in bulk precipitation (rainfall plus dry fallout) can be significant, especially in unfertilized natural systems.

In absolute terms, atmospheric inputs of nitrate can range from less than 0.1 kg N/ha-yr in the Northwest (e.g., Fredericksen 1972) to 4.9 kg N/ha-yr in the eastern United States (Likens et al. 1970, Henderson and Harris 1975). Inorganic nitrogen (ammonia-N plus nitrate-N) loadings in wet precipitation ranged from less than 0.5 kg/ha-yr to more than 3.5 kg/ha-yr in Junge's (1958) study of rainfall over the United States (see Chapter 6, Figure 6.18). On the other hand, total nitrogen loads in bulk precipitation range from less than 5 kg/ha-yr in desert regions of the West to more than 30 kg/ha-yr near barnyards in the Midwest. Total inputs of nitrogen from the atmosphere commonly range from about 10 to 20 kg N/ha-yr for most of the United States (see Chapter 6).

In comparison, rates of annual uptake by plants that range from 11 to 125 kg N/ha-yr in selected ecosystems from several bioclimatic zones (Appendix A, Section 3). Since the lowest fluxes are generally associated with desert areas, where rates of uptake by plants are low, and the highest fluxes usually occur in moist areas characterized by high plant uptake, the inputs of ammonia and nitrate from rainfall to terrestrial ecosystems are equivalent to about 1 to 10 percent of annual plant uptake. The typical fluxes of total nitrogen in bulk precipitation, on the other hand, represent from about 8 to 25 percent of the annual plant needs in eastern deciduous and western coniferous forest ecosystems. Although these comparisons suggest that plant growth in terrestrial ecosystems depends to a significant extent on atmospheric loadings, it is not yet possible to estimate the importance of these inputs compared to biological nitrogen fixation and mineralization of soil nitrogen. In nutrient-impoverished ecosystems, such as badly eroded abandoned croplands or soils subjected to prolonged leaching by acid precipitation, nitrogen inputs from atmospheric fluxes are certainly important to biological productivity. Such sites, however, are relatively limited in extent. In largely unperturbed forests, recycled nitrogen from the soil organic pool is the chief source of nitrogen for plants, but new nitrogen to support increased production must come either from biological fixation or from atmospheric influxes. It seems possible, therefore, that anthropogenic inputs could play a significant ecological role in a relatively large portion of the forested areas near industrialized regions.

Aquatic Ecosystems: Nitrogen and Eutrophication

Some functions of aquatic ecosystems may also benefit from anthropogenic nitrate inputs. In some oligotrophic lakes, where nitrogen may be the limiting nutrient, the input from runoff or atmospheric fluxes may be essential to maintaining biological productivity. The point at which the effects on productivity of nitrate input to aquatic ecosystems cease to be beneficial is influenced by a number of factors discussed below.

The over-enrichment or eutrophication of surface waters, usually lakes, with nutrients results in an array of water quality changes that are generally considered undesirable. These changes most commonly include the proliferation or "blooms" of algae and aquatic macrophytes, the depletion of dissolved oxygen in the bottom water, a decrease in water clarity, the loss of cold water fisheries, shortened food chains, and takeover by rough fish. Table 8.4 summarizes changes in common trophic state indicators that occur when lakes become eutrophic, and Table 8.5 lists some common water use problems that may result from eutrophication.

Eutrophication in Lakes

Cultural or man-induced eutrophication has been one of the most intensively studied water quality problems in the past ten to fifteen years. Although many lakes become naturally more productive and nutrient-rich as they fill in and age, natural eutrophication is a slow process, and its effects are unlikely to be perceived within a single human lifetime. However, addition of excessive amounts of nutrients from sewage effluents, agricultural runoff, urban runoff and other anthropogenic sources can greatly modify the characteristics of a lake in a matter of a few years; the literature is replete with examples of this phenomenon.

TABLE 8.4 Common Trophic State Indicators and Their Responses to Eutrophication

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<u>Physical Indicators</u>

Transparency (D)[1]
(Secchi disc reading)

<u>Chemical Indicators</u>

Nutrient concentrations (I)[1]
(e.g., annual average and spring maximum)
Conductivity (I)
Dissolved Solids (I)
Hypolimnetic oxygen (D)
(generally goes to zero except in very deep eutrophic lakes)
Epilimnetic oxygen supersaturation (I)

<u>Biological Indicators</u>[2]

Algal bloom frequency (I)
Algal species diversity (D)
Chlorophyll <u>a</u> (I)
Proportion of blue green algae in plankton (I)
Primary production (I)
Littoral vegetation (I)
Zooplankton (I)
Fish (I)
Bottom fauna (I)
Bottom fauna diversity (D)

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[1] (I) after parameter signifies that value increases with eutrophication; (D) signifies that value decreases with eutrophication.

[2] Biological parameters have important qualitative changes, i.e., species changes as well as quantitative (biomass) changes as eutrophication proceeds.

SOURCE: After Brezonik (1969).

TABLE 8.5 Water Use Problems Resulting from Eutrophication

Water Treatment Problems

- Increased color and turbidity in raw water
- Increased taste and odor (necessitating the use of activated carbon)
- Increased chlorine demand
- Shortened filter runs

Recreational Problems

- Loss of desirable fish and increase in rough fish
- Increased costs in boat and dock maintenance resulting from fouling
- Boat access problems from aquatic vegetation
- Economic losses to owners of resorts and fish camps as fewer people swim, fish and boat in lakes with algal blooms
- Public health problems - swimmers' diseases (mainly eye, ear, nose and throat infections)
- General loss in lake's aesthetic appeal

Agricultural Problems

- Transmissibility of water in canals impaired by extensive macrophyte growths
- Toxicity of algal blooms to cattle and wildlife
- Increases in water loss in arid regions caused by evapotranspiration from floating vegetation

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SOURCE: Brezonik (1969).

The definition given above, adopted by the international Organization for Economic and Cooperative Development, states that eutrophication is usually considered undesirable. This somewhat narrow viewpoint, however, ignores the fact that nutrient-rich waters are more productive not only of algae, but also of fish. Lakes are not now a significant source of protein in the United States, but lake fish may be an important food resource in a food-hungry world. Many sports fishermen prefer moderately eutrophic lakes, unless they are seeking coldwater fish, which cannot survive in such lakes because of oxygen depletion in the cold bottom waters. A conflict thus exists between the desires of some fishermen and the preferences of swimmers and other recreational users of lakes, who generally favor the clearest and most oligotrophic situation. On the other hand, continued nutrient enrichment eventually is undesirable to sport fishermen also, since game fish disappear, rough fish predominate, and excessive aquatic weed growths may hinder or prevent boating in highly eutrophic lakes.

Because phosphorus and nitrogen are the nutrients that limit production in most lakes, these two nutrients are most important in stimulating eutrophication (Vollenweider 1968). Oligotrophic lakes (low in nutrients) are commonly thought to be phosphorus-limited (Deevey 1972, Hutchinson 1973), because of the relative paucity of phosphorus in the biosphere compared to nitrogen, and because the phosphorus in minerals and soils is relatively immobile, whereas nitrogen compounds are quite mobile. Lake Tahoe (California, Nevada) is a well-known and important example of a nitrogen-limited oligotrophic lake. In highly eutrophic lakes nitrogen is frequently the limiting nutrient, most often because domestic sewage, the chief nutrient source for many eutrophic lakes, is imbalanced with respect to nitrogen and phosphorus. The total N/P ratio (by weight) in sewage is about 3:1 to 4:1, largely because of the widespread use of phosphate detergents. By comparison, the annual N/P ratio of healthy plants is about 7:1 to 8:1 (by weight).

Miller et al. (1974) conducted algal nutrient bioassays on waters from 49 lakes throughout the United States and found that phosphorus limited growth in 35 lakes; nitrogen was limiting in eight lakes; and some other nutrient was limiting in six. The incidence of phosphorus limitation was lower among lakes that were more productive. The same relationship has been noted in National Eutrophication Survey data on Florida lakes (Brezonik 1977).

Eutrophication in Coastal Waters

Studies of estuarine waters at several locations along the east coast of the United States have indicated that low concentrations of dissolved nitrogen limit primary production (Ryther and Dunstan 1971, Thayer 1971, Goldman et al. 1973, Goldman 1976). Additions of nitrate to such estuarine systems stimulate primary production and can produce changes in the dominant species of plants, leading to cultural eutrophication and ultimately to deterioration of water quality. However, the significance of nitrogen as a limiting nutrient varies in different estuaries and even on a spatial and temporal basis within a single estuarine system (e.g., Thayer 1971, Estabrook 1973, Goldman 1976). Furthermore, not all estuaries are nitrogen-limited; Myers (1977) found that phosphate was the primary limiting nutrient in near-shore waters of the Gulf of Mexico near Appalachicola, Florida. The high degree of heterogeneity in the role of nitrogen as a control on productivity in coastal areas makes it difficult to establish quantitative relationships between nitrate loading and water quality.

The reasons that nitrogen is more important as a limiting nutrient in marine coastal waters than in fresh waters are uncertain. A higher rate of phosphorus exchange between sediment and water in saline waters is one possibility. It has also been suggested that denitrification of the nitrate that diffuses into anoxic sediments limits the amount of available nitrogen in estuarine areas, but this hypothesis needs further study.

Nutrient Mass Balances and Eutrophication

A number of symposia have treated the causes and consequences of eutrophication in considerable detail: see NRC (1969), Likens (1971), Allen and Kramer (1971), Middlebrooks et al. (1973). The problem of cultural eutrophication clearly is not solely a nitrogen-related phenomenon, nor is nitrate the only or often even the main form of nitrogen input. Our focus in this section is on current efforts to quantify the relationships between nutrient loading and trophic states, and on evidence for the extent to which nitrate contributes to eutrophication problems.

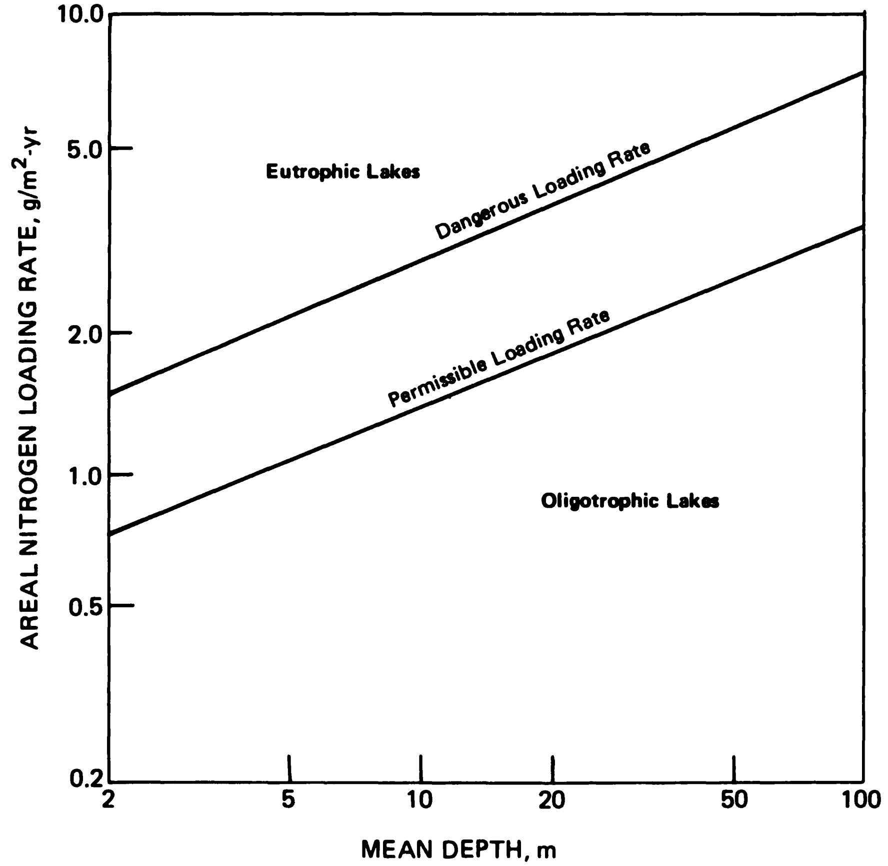
Sawyer (1947) was the first to determine critical nutrient levels associated with water quality degradation in lakes. He concluded from a study of 17 lakes in southeastern Wisconsin that lakes with spring maximum concentrations of more than 300 $\mu g/l$ of inorganic nitrogen and more than 10 to 15 $\mu g/l$ of orthophospate-P could be expected to have algal nuisances in the summer. These numbers have been widely quoted and used as water quality guidelines in many areas of the United States, in spite of the narrow base from which they were developed.

Vollenweider (1968), in a classic study, developed the concept of nutrient loading rates and presented graphs of critical areal nutrient loading (grams of nitrogen or phosphorus per square meter of lake surface per year) versus mean depth, as management guidelines. Figure 8.6 presents Vollenweider's loading graph for nitrogen. Vollenweider (1969) presented a semitheoretical mass-balance nutrient model as the basis for his loading graphs.

The nutrient assimilation capacity of a lake obviously depends on many factors besides mean depth. Hydraulic residence time is a key variable, and Vollenweider (1975, 1976) modified his loading graph for phosphorus (Figure 8.7) to accomodate this variable, plotting loading (L) versus mean depth divided by hydraulic residence time ($\bar{z}/\tau_w$). This term is equivalent to the areal water load (q_s), or the height to which the annual water input would rise if spread over the lake surface area. Because the relationships between nitrogen loading and trophic state have been less clearly defined, Vollenweider did not derive a graph analogous to Figure 8.7 for nitrogen.

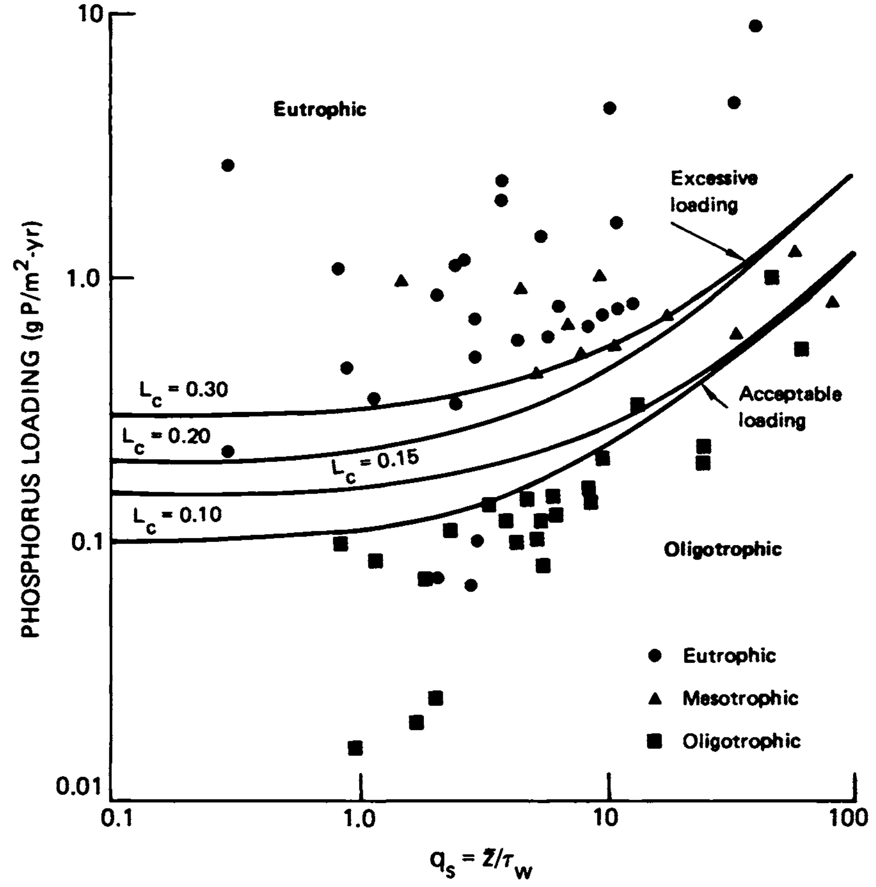
In the past several years, a number of other mass-balance or nutrient input-output models have been developed (e.g., Imboden 1973, Dillon 1975, Vollenweider 1975, Larsen and Mercier 1975). These models characteristically are highly aggregated, treating the lake as a completely mixed system, or in some cases as two well-mixed tanks--an upper box (epilimnion) and a lower box (hypolimnion). Total nutrient (nitrogen or phosphorus) concentration is usually modeled, but a few models (e.g., Snodgrass and O'Melia 1975) separate the nutrients into inorganic and particulate fractions. Nutrient movements and transformations are also highly aggregated into such terms as total nutrient loading, sedimentation (a simple function of the total nutrient level in the lake), and outflow loss (proportional to mean lake concentration and outflow volume).

Table 8.6 presents some basic equations from elementary nutrient mass-balance models. In words, Equation 8-1 states that the change in total nutrient concentration is equal to the sum of the inputs minus loss by sedimentation and minus outlet losses. Equations 8-2 and 8-6 provide the basis for the curvilinear relationship of critical loading rate versus areal water load (q_s) in Figure 8.7. The plot can be divided into two sections: a horizontal line at low q_s (i.e., critical loading rate is independent of q_s), where sedimentation losses control total concentration of the limiting nutrient (and hence, presumably, productivity); and a slanting line approaching a slope of one at high q_s, where



SOURCE: Vollenweider (1968).

FIGURE 8.6 Areal loading rates for nitrogen plotted against mean depth of lakes.



SOURCE: Modified from Vollenweider (1976).

FIGURE 8.7 Critical loading rates (L_C) for phosphorus as a function of mean lake depth ($\bar{z}$) divided by water retention time (τ_w). Data points represent a variety of North American lakes.

TABLE 8.6 Simple Mass Balance Nutrient Models for Lakes

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1. Basic mass balance equation (Vollenweider 1969):

$$\frac{d[S]}{dt} = \frac{\Sigma J}{V} - \sigma[S] - \frac{Q[S]}{V} \qquad (8\text{-}1)$$

$[S]$ = total nutrient (N or P) concentration in well mixed lake, in (g/m^3);
ΣJ = sum of nutrient fluxes into lake (g/yr)
V = lake volume, in m^3;
σ = sedimentation coefficient, in yr^{-1};
Q = outflow volume, m^3/yr.

2. Steady-state solution of mass balance equation:

$$[S] = \frac{\Sigma J}{V(\sigma + 1/\tau_w)} = \frac{\Sigma J}{A(\sigma\bar{z} + \bar{z}/\tau_w)} = \frac{L}{\sigma\bar{z} + q_s} \qquad (8\text{-}2)$$

L = areal loading rate ($\Sigma J/A$), in g/m^2-yr;
τ_w = water residence time in lake (=V/Q), in yr.
q_s = areal water load ($\bar{z}/\tau_w$), in m/yr.

3. Relationship of sedimentation coefficient to nutrient retention coefficient:
According to Dillon (1975):

$$\sigma = \frac{R}{(1 - R)\,\tau_w} \qquad (8\text{-}3)$$

R = retention coefficient or percent of input nutrient (P or N, assuming denitrification is negligible) that remains in the lake, e.g.,

$R = [S_{in} - S_{out}]/S_{in}$

Then from 8-2 and 8-3

$$[S] = \frac{L(1 - R)\tau_w}{\bar{z}} \qquad (8\text{-}4)$$

4. Critical Phosphorus Loading Rate:
From Equation 8-2:

$$L = [S]\,(\bar{z}/\tau_w + \bar{z}\sigma) \qquad (8\text{-}5)$$

For phosphorus, $\bar{z}\sigma \approx 10$ m/yr, and $[S]_{crit} \approx 10$ mg P/m^3 (Vollenweider 1976).

Then

$$L_{crit}\ (\text{mg/m}^2\text{-yr}) \approx 100 + \frac{10\bar{z}}{\tau_w}. \qquad (8\text{-}6)$$

flushing tends to control the limiting nutrient concentration and productivity (Chapra and Tarapchak 1976).

The term $\sigma\bar{z}$ (in units of m/yr) in Equation 8-2 can be considered an apparent settling velocity for the total nutrient mass, (S); Vollenweider (1976) estimated $\sigma\bar{z}$ at approximately 10 for the phosphorus settling rate in relatively small lakes. Because of the difficulty in measuring settling velocities directly, Dillon (1975) and Larsen and Mercier (1975) used Equation 8-1 to derive other mass balance formulations, such as Equation 8-4. These formulations use a measurable parameter, the nutrient retention coefficient (R in Equation 8-3), which is the percent of the input nutrient that remains within the lake. Kirchner and Dillon (1975) and Larsen and Mercier (1975) developed several simple relationships to estimate the phosphorus retention coefficient from lake hydrologic factors (τ_w and q_s). Unfortunately, similar relationships have not been developed for nitrogen retention coefficients.

Simple nutrient input-output models have provided insights into the dynamics of nutrients in lakes, and they offer a rational basis for the development of critical nutrient loading rates and lake management guidelines (e.g., Dillon and Rigler 1975). Such models to date, however, have been oriented primarily toward phosphorus, under the assumption that it is the key limiting nutrient in lakes. Further studies are needed to develop more accurate loading guidelines for nitrogen and to obtain quantitative data to apply the input-output models to nitrogen-limited systems.

Nutrient Uptake by Plants in Eutrophic Systems

Nitrate is used by almost all aquatic plants, but when ammonia and nitrate are both present, the former is assimilated preferentially (Brezonik 1972, McCarthy et al. 1977), since it can be incorporated directly into organic forms without further reduction. As a result, ammonia disappears rapidly after spring ice-out in temperate lakes, while the nitrate in surface waters may not be depleted until later in summer.

Algal species differ in their efficiency of nutrient uptake. Whether ammonia or nitrate is the predominant form of inorganic nitrogen in a water may play a role in determining algal species composition, but this is a complicated subject about which little is known. Using the Michaelis-Menten enzyme kinetic model, Eppley et al. (1969) determined half-saturation constants for nitrate and ammonia uptake by marine phytoplankton, and MacIsaac and Dugdale (1969) determined similar values for natural marine communities. Apparently few measurements have been made with freshwater algae. Table 8.7 summarizes ammonia and

TABLE 8.7 Half-Saturation Constants for Nitrate and Ammonia Uptake by Some Marine and Freshwater Phytoplankton

Organism	Nitrate Ks	Ammonia Ks	Temp. (°C)	Reference
Oceanic species				
Coccolithus huxleyi	0.1	0.1	18	Eppley et al. (1969)
Cyclotella nana	0.3-0.7	0.4		
Neritic diatoms				
Skeletonema costatum	0.4-0.5	0.8-3.6		
Rhizosolenia stolterfothii	1.7	0.5		
Rhizosolenia robusta	2.5-3.5	5.6-9.3		
Asterionella japonicum	0.7-1.3	0.6-1.5		
Neritic or littoral flagellates				
Gonyaulax polyedra	8.6-10.3	5.3-5.7		
Gymnodinium splendens	3.8	1.1		
Dunaliella tertiolecta	1.4	0.1		
Natural marine communities				MacIsaac and Dugdale (1969)
"Oligotrophic"	≤0.2 (6 expts.)	0.1-0.6 (3 expts.)	--	
"Eutrophic"	≥1.0 (3 expts.)	1.3 (1 expt.)	--	
Freshwater phytoplankton				
Diatom *Chlamydomonas reinhardtii*	--	148	--	Wallen and Cartier (1975)
Green algae				Shelef et al. (1971), cited in Goering (1972)
Navicula pelliculosa	--	14.9		
Chlorella pyrenoidosa	--	50	19	
		60	28.5	
Mixed culture (diatoms, greens, flagellates) from San Joaquin delta	--	32.1	25	

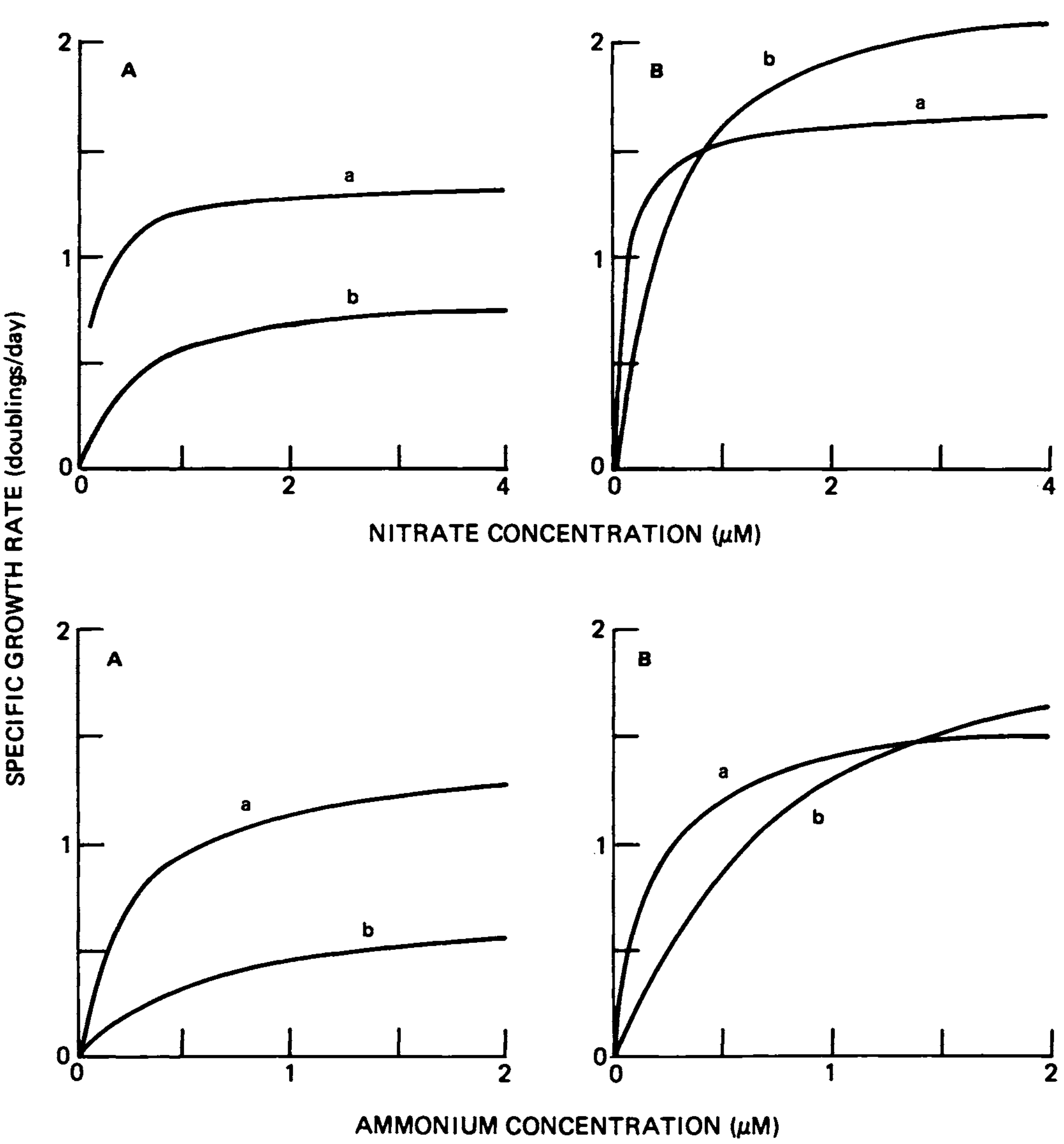
nitrate half-saturation constant measurements from various sources.

Interactions among several growth-limiting variables, such as nutrients, light, and temperature, can lead to changes in species composition, i.e., to phytoplankton succession (Figure 8.8). At low light levels with either nitrate or ammonia as the nitrogen source, the coccolithophore *Coccolithus huxleyi* grows faster than the diatom *Skeletonema costatum*, regardless of nutrient concentrations. At higher light levels, however, the diatom grows fastest at nitrate levels above 0.8 µM, or ammonia levels above 1.5 µM, while *C. huxleyi* outcompetes the diatom at nitrogen levels below these values. Obviously, the situation in nature is considerably more complicated, with many species present and many potential limiting factors varying simultaneously.

The Nitrogen Cycle in Eutrophic Lakes

Eutrophication leads not only to increased rates of nitrogen cycling in lakes; it also provides conditions for some reactions in the nitrogen cycle that normally do not occur in oligotrophic lakes. For example, nitrogen fixation by blue-green algae is essentially limited to eutrophic lakes (Stewart et al. 1971, Horne 1977). Although blue-green algae are cosmopolitan, they are seldom the dominant phylum in oligotrophic lakes, and nitrogen-fixing species (e.g., *Anabaena* spp., *Aphanizomenon flos-aquae*) are rare in non-eutrophic lakes. This fact is ironic in view of the well-known inhibition of fixation by high concentrations of inorganic nitrogen (see Chapter 2). However, fixation in eutrophic lakes is generally associated with nitrogen depauperate periods, such as late summer in temperate surface waters. Maximum bloom development by nitrogen-fixing blue-green algae requires an adequate supply of phosphorus, and dissolved phosphorus is usually growth-limiting in oligotrophic waters. For example, Vanderhoef et al. (1974) studied nitrogen fixation in Green Bay (Lake Michigan) and found that the nonfixing blue-green *Microcystis* predominated in areas where all nutrients were high. Nitrogen-fixing *Aphanizomenon* increased with declining combined nitrogen concentrations and showed increased efficiency of fixation as inorganic nitrogen levels decreased. The standing crop of this species decreased with decreasing phosphate concentrations. Finally, diatoms predominated in the northern reaches of the bay (40 km from the Fox River, the major tributary and source of nutrients for the bay).

The importance of nitrogen fixation in the nitrogen budgets of lakes is controversial. Most reports indicate relatively low contributions (<15 percent) in lakes where



SOURCE: Modified from Eppley et al. (1969).

FIGURE 8.8 Calculated specific growth rates versus nitrate and ammonia concentration at two irradiance levels (A = 0.05, B = 0.20 times surface sunlight irradiance) for (A) *Coccolithus huxleyi* and (B) *Skeletonema costatum*.

fixation occurs at all, but a few cases where fixation supplies up to 50 percent of the annual nitrogen input have been reported (see Chapter 2). Even in the typical case where fixation makes only a small contribution to the total loading, however, the process is still significant in maintaining nuisance blue-green algal blooms in lake surface waters.

Denitrification occurs in the anoxic hypolimnia of stratified eutrophic lakes, and can represent a significant term in lacustrine nitrogen balances (see Appendix A and Chapter 2). Denitrification also occurs in the anoxic sediments of lakes. The source of nitrate for sediment denitrification may be upward seepage of groundwater, downward diffusion of nitrate from the lake water column, or nitrification in the oxygenated surface layer of sediment. Sediment denitrification can occur in oligotrophic lakes, since their sediments are also anoxic. However, Chen et al. (1972) reported much higher rates in sediments from a hard water eutrophic lake than in those from a soft water oligotrophic lake.

Form of Nitrogen Inputs to Lakes

It is difficult to generalize about the percentage of the total nitrogen loading to lakes that is contributed as nitrate. Nutrient budgets are generally presented by source (streams, rainfall, sewage effluents, etc.) rather than by nitrogen form. Lake Wingra, Wisconsin (see Appendix A, Section 2) represents one of the few cases where nitrogen loading rates have been broken down according to form. Table A.6 indicates that 47 percent of the total nitrogen loading to Lake Wingra was in the form of nitrate.

Inorganic nitrogen forms in lake water are so readily interconvertible that there is probably little to be gained from detailed analysis of this topic. Measured concentrations of ammonia and nitrate in rainfall are roughly comparable, although large short-term, local, and regional variations occur (see Chapter 6). Rainfall in industrialized and urbanized regions has exhibited increasing nitrate levels over the past several decades (Likens 1972). Urban runoff and sewage effluents vary widely in their nitrogen composition, making generalizations tenuous. Kluesener and Lee (1974) summarized average nitrogen component concentrations from several urban runoff studies (see Chapter 6). The grand means of the data they collected are: NH_3-N, 0.44 mg/l; NO_3^--N, 0.51 mg/l; organic nitrogen, 2.0 mg/l.

In summary, the specific contribution of nitrate to eutrophication is uncertain, because of a relative lack of data on nitrate inputs per se, and because of the ease of interconversion of nitrogen forms. Nitrogen inputs from human activities can promote increased biological productivity in aquatic systems, but the role of nitrogen in eutrophication is understood much less quantitatively than the role of phosphorus. The effects that nitrogen inputs may have on productivity, phytoplankton succession, and other processes of aquatic ecosystems are certain to be influenced by other variables, such as light and temperature; but few quantitative statements about the relationships among these factors can be supported with present knowledge.

EFFECTS OF ACIDIC NITRATE AEROSOLS AND NITRIC ACID IN PRECIPITATION

The role played by nitrate in the increased acidity of rainfall over much of the eastern part of North America in recent years was reviewed in Chapter 6. Most controlled experiments on the biotic effects of acid rain have emphasized the sulfuric acid component of simulated rainfall; only the most recent research has attempted to reproduce the actual chemical composition of rainfall.

Acidic aerosols, formed largely from emissions of sulfur and nitrogen oxides (see Chapter 2), contribute to acidic rainfall and to associated effects on vegetation, but may also produce deleterious ecological effects themselves. Whether their deposition in dry periods further aggravates the effects of acidic precipitation is not known. Mannion (1976) noted that, since acidic aerosols are precursors of acid precipitation, respiratory problems in humans and other biological effects of such aerosols might be expected in regions that are experiencing acid rainfall.

Knowledge of the extent and severity of the effects of acid rainfall and nitrate aerosols on terrestrial ecosystems is limited, but clear evidence exists for deleterious effects on aquatic ecosystems.

Effects on Terrestrial Ecosystems

Soils

Norton (1976) has reviewed the potential effects of acid rain on soils (Table 8.8). Most of the available information is from northern latitudes; much less is known about soils of temperate regions, where the largest increases in rainfall acidity are presently occurring. The types of effects that have been observed are destabilization and solution of clay minerals, loss of cation exchange capacity, increased rates of mineral losses, and consequently, increased rates of podzolization. Overrein

TABLE 8.8 Potential Effects of Acid Precipitation on Soils

Effect	Comment
Increased mobility of most elements	Mobility changes are essentially in the order: monovalent, divalent, trivalent cations.
Increased loss of existing clay minerals	Under certain circumstances may be compensated for by production of clay minerals which do not have essential (stoichiometric) alkalies or alkali earths.
A change in cation exchange capacity	Depending on conditions, this may be an increase or a decrease.
A general proportionate increase in the removal of all cations from the soil	In initially impoverished or unbuffered soil, the removal may be significant on a time scale of 10 to 100 years.
An increased flux nutrients through the ecosystem below the root zone	

SOURCE: Derived from Norton (1976).

(1972) has provided perhaps the most extensive studies of effects of acid precipitation on soils. Both accelerated leaching of calcium and loss of the capacity of the soil to buffer pH have been observed in lysimeter studies.

Sensitivity to leaching and to loss of buffer capacity varies according to the type of parent material from which a soil is derived. Buffer capacity is greatest in soils derived from sedimentary rocks, especially those containing carbonates, and least in soils derived from hard crystalline rocks such as granites and quartzites (Gorham 1958). Soil buffer capacity varies widely in different regions of the country (see Chapter 6, Figure 6.26). Unfortunately, many of the areas now receiving the most acidic precipitation also are those with relatively low natural buffer capacities.

The effects of acid precipitation on soils are potentially long-lasting. Odén (1971) has estimated that rainfall at pH 4.0 would be the cation equivalent of 30 kg Ca^{+2}/ha, which represents a considerable potential loss of cations essential for plant growth. McFee et al. (1976) calculated that 1000 cm of rainfall at pH 4.0 could reduce the base saturation of the upper 6 cm of a midwestern U.S. forest soil by 15 percent and lower the pH of the A1 horizon by 0.5 units if no countering forces are operating in the soil. They note, however, that many countering forces could reduce the final effect of acid precipitation, including the release of new cations to exchange sites by weathering and nutrient recycling by vegetation.

Reuss (1976) makes an excellent case for placing the incoming H^+ in the perspective of the H^+ produced within the soil from carbonic acid formation, sulfur oxidation, and nitrification. Cole and Johnson (1977) found that although rain pH was substantially lowered by anthropogenic emissions, the influx of H^+ in rainfall was small compared to that produced within a Douglas fir ecosystem.

If they occur, effects of such pH changes in agricultural soils could be offset by extensive soil liming, in regions where that is practical (Frink and Voigt 1976; also, see Chapter 11).

Lowered soil pH also probably influences the availability and toxicity of metals to plants. In general, potentially toxic metals become more available as pH decreases. Comprehensive reviews have been published on this subject (Barrows 1966, Wright 1976).

Little is known about the effects of acid precipitation on soil microorganisms. Lower soil pH generally favors fungal populations over bacterial populations; such selective effects can alter rates of decomposition and remineralization of elements essential to plant growth. Densіon et al. (1976) found that the application of dilute sulfuric acid solutions to litter and soil led to decreased nitrogen fixation.

Vegetation

The loss of nutrients from the soil through leaching by acid rain could have major impacts on plant growth unless corrected by fertilizer applications. Other direct effects on higher plants are summarized in Table 8.9 and include necrosis, loss and/or reduction of leaf area (Wood and Bormann 1974), accelerated loss of elements from foliage (Fairfax and Lepp 1976), and erosion of cuticular surfaces (Shriner 1976), as well as some stimulation of growth in response to a "fertilizer effect" of the nitric acid in rainfall (Wood and Bormann 1976). Rather drastic pH regimes of 3.0 or less have been shown to produce morphological and anatomical abnormalities in the pinto bean, Phaseolus vulgaris, as well as physiological changes, such as increased evolution of oxygen, increased respiration, and reduced carbohydrate content and yield (Ferenbaugh 1976).

Lower plants such as mosses and lichens are particularly sensitive to changes in precipitation chemistry, because they meet many of their nutrient requirements directly from precipitation. These plant forms are typically absent from regions with high chronic air pollution and acid precipitation. Excellent recent reviews on this topic are available (Gorham 1976, Giddings and Galloway 1976).

Sparse information is available on the effects of acidic precipitation on plant symbiotic or parasite-host relationships. The most complete work is that of Shriner (1976), who found that rainfall at pH 3.2 inhibited root nodulation by Rhizobium on common beans and soybeans. A number of plant parasites were influenced positively or negatively by acid precipitation, depending upon the status of infection, the condition of the plant and the timing of the precipitation events. The vigor of the host plant appears to be the key to the response of the plant to a pathogen. The potential for serious additive or synergistic effects of acid precipitation and pathogens on host plants is great and merits high priority in future research.

The effects of acid precipitation on entire terrestrial communities or ecosystems are unknown. Several investigators have suggested that acid precipitation is the major cause of observed declines in forest growth (Whittaker et al. 1974, Jonsson and Sundberg 1972). Quantitative relationships have not been established, however, and must await additional research. The effects of acid precipitation on forest growth are difficult to separate

TABLE 8.9 Potential Effects of Acidic Precipitation on Vegetation

Effect	Reference
Direct Effects	
Damage to protective surface structures such as cuticle	Shriner (1974) Sharma (1976)
Interference with guard cell function (potential disruption of gaseous exchange processes)	
Poisoning of plant cells after diffusion through stomata or cuticle	
Disturbance of normal metabolism without tissue necrosis	
Alteration of leaf- and root-exudation processes	Shriner (1976), Fairfax and Lepp (1976)
Interference with reproductive processes	
Synergistic interaction with other environmental stress factors	
Indirect Effects	
Accelerated leaching of substances from foliar organs	Fairfax and Lepp (1976)
Increased susceptibility to drought or other stress factors	
Alteration of symbiotic associations	Shriner (1976)
Alteration of host-parasite interactions	Shriner (1976)

SOURCE: Derived from Tamm and Cowling (1976).

from the many other factors that may also limit growth. For example, the depression in forest growth observed by Whittaker et al. (1974) in an area affected by acid rain also corresponded to a severe drought in the northeastern United States. Studies are needed to determine whether a trend toward slower forest growth will continue in years when rainfall is more abundant. The geographic pattern of rainfall pH exhibits a series of gradients across the eastern United States. The existence of these gradients should permit comparative long-term studies of forest growth, and such research should be initiated.

Another major uncertainty in estimating effects of acid rain on forest productivity is the large capacity of forest soils to buffer against leaching by hydrogen ions. Where the evidence is strongest for a direct effect of acid precipitation on forest growth (e.g., Sweden), the soils are already highly leached, and the buffer capacity has been reduced. For much of the eastern United States, however, the soils still retain a greater portion of their natural buffer capacity. This may explain why effects are not yet apparent in this region. Many questions remain unanswered on this subject, including the rate of forest soil degradation, the ultimate consequences of this degradation to forest productivity, and the time frame in which those consequences will occur under the present rates of hydrogen ion leaching.

Effects on Aquatic Ecosystems

Algae

Limited data are available on the effects of pH on algae. Giddings and Galloway (1976) reviewed work by Moss (1973a, 1973b) and Sorokin (1962), and concluded that lowered pH of lakes would favor species normally excluded by lack of free CO_2. They state that below pH 4.5, growth of most species would be reduced; the result would be erratic blooms by the few tolerant species remaining.

Aquatic Invertebrates

Giddings and Galloway (1976) reviewed the effects of pH on aquatic invertebrates. A number of pH preference patterns are apparent, and organisms can be grouped according to such responses as the width of their tolerance limits, or sensitivity at different stages of their life cycles. With some exceptions, pH values below 5.0 pose a serious threat to aquatic invertebrates. Because invertebrates are important components of aquatic food webs, and because the observed pH in areas affected by acid precipitation is often below 5.0 (see Figure 6.22 in Chapter

6), potentially serious effects on aquatic ecosystems seem likely and could be much more widespread than is currently appreciated.

Fish and Amphibians

Numerous observations are available on the effects of pH on aquatic vertebrates. Table 8.10 summarizes some general patterns of pH effects on fish. Of note are the differences in effects according to species and stages of life history in a given species. Clearly, a significant pH change can cause substantial and rapid changes in the composition of an aquatic community. Our understanding of the mechanism(s) of pH effects on fish is incomplete, but effects on the metabolism of calcium, sodium, and other elements have been strongly implicated.

Effects at the Ecosystem Level

The effects of acid precipitation on aquatic ecosystems have been dramatic and well-documented. Giddings and Galloway (1976) list three conditions that strongly influence the susceptibility of lakes to acidification:

(1) location downwind from a major pollution source;

(2) location in base-poor areas (for example, lakes with adjacent podzol soils, or formed on hard crystalline rock); and

(3) low watershed:surface area ratio (Likens and Bormann 1974, Schofield 1975).

Observed effects include: depauperate phytoplankton communities of low productivity (Stokes and Hutchinson 1976); similarly impacted macrophyte communities; declining fish populations (Beamish 1976); and, particularly in extremely poorly buffered lakes, community changes that further reduce the availability of nutrients because of decreased remineralization of detritus (Grahn et al. 1974). Gorham and Gordon (1963) reported that levels of dissolved heavy metals were elevated in waters receiving acidified precipitation; but they could not determine the relative contributions to this effect of leaching due to rainfall acidity and of fallout of metallic contaminants from a nearby smelter complex. If acidity does in fact lead to higher levels of potentially toxic cations, the secondary biological effects of such changes in the pH of rainfall could be substantially multiplied.

Likens (1976) reviewed the effects of acid precipitation on lakes and concluded that widespread loss of biological

TABLE 8.10 Summary of Effects of pH Changes on Fish

pH	Effects
3.0 - 3.5	Toxic to most fish; some plants and invertebrates survive
3.5 - 4.0	Lethal to salmonids. Roach, tench, perch, pike survive
4.0 - 4.5	Harmful to salmonids, tench, bream, roach, goldfish, common carp; resistance increases with age. Pike can breed, but perch, bream and roach cannot
4.5 - 5.0	Harmful to salmonid eggs and fry; harmful to common carp
5.0 - 6.0	Not harmful unless > 20 ppm CO_2, or high concentrations of iron hydroxides present
6.0 - 6.5	Not harmful unless > 100 ppm CO_2
6.5 - 9.0	Harmless to most fish
9.0 - 9.5	Harmful to salmonids, perch if persistent
9.5 - 10.0	Slowly lethal to salmonids
10.0 - 10.5	Roach, salmonids survive short periods, but lethal if prolonged
10.5 - 11.0	Lethal to salmonids; lethal to carp, tench, goldfish, pike if prolonged
11.0 - 11.5	Lethal to all fish

SOURCE: European Inland Fisheries Advisory Committee (1969), Water Quality Criteria for European Freshwater Fish: Report on Extreme pH Values and Inland Fisheries. Water Research 3:593-611. Reprinted by permission of Pergamon Press, Ltd.

and potential economic productivity has occurred in several regions. In Norway, populations of fish, especially trout and salmon, have been decimated south of 63° north latitude. Although such losses were initially noted 50 years ago, they have increased sharply during the past 15 years, a period that coincides with increases in fossil fuel combustion. Similar changes have been observed in Sweden. About 10,000 lakes have been acidified to a pH value less than 6.0, and 5000 below pH 5.0. Declines in fish populations have been correlated with the acidity of the lakes (Figure 8.9). A recent survey of the Adirondack Mountains of New York has revealed that 50 percent of the lakes above 600 m elevation have pH values below 5.0, and that 90 percent of those lakes are devoid of fish; a similar survey in the 1929 to 1937 period showed that only 4 percent of the same lakes had a pH <5 or were devoid of fish (Likens 1976). While it is clear that adverse effects have occurred, it is not now possible to identify the loadings of acidity that are critical for such effects.

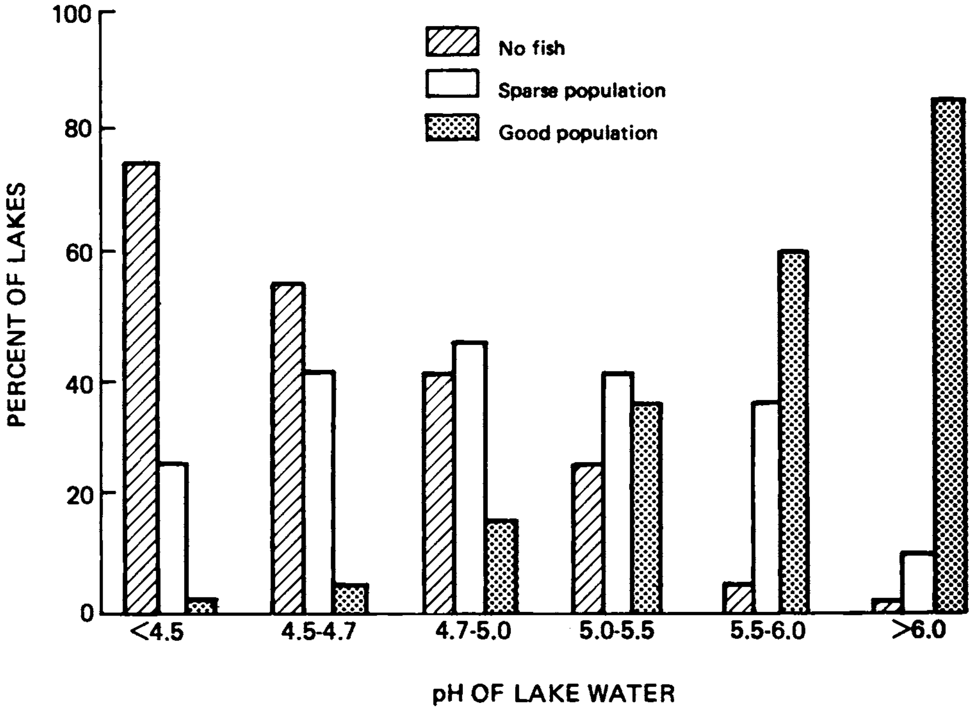
Little information is available on reclamation of acidified lake ecosystems, but addition of lime has produced beneficial effects in some lakes. Much of the experimentation with liming has been done in Scandinavia. Wright (1976) reviewed an early attempt in which addition of chalk to Swedish lakes increased pH and led to increased phytoplankton growth and improved fish survival. Addition of $CaCO_3$ and $Ca(OH)_2$ to two acidic lakes in Sudbury, Ontario increased pH, decreased heavy metal concentrations, and caused a temporary decline in chlorophyll (Michalski and Adamski 1974, cited in Wright 1976). Reviews of liming experiments in Norway, cited by Wright (1976), concluded that this practice would be feasible only for small ponds and streams.

ECOLOGICAL EFFECTS OF DEPLETION OF STRATOSPHERIC OZONE

Chapter 7 describes a range of possible short-term and long-term impacts on the stratospheric ozone layer that might result from human manipulation of the nitrogen cycle. If such depletion of ozone occurs, it will be accompanied by increased ultraviolet (uv) irradiation of the earth's surface, and a concomitant potential for impacts on biological organisms and on climate.

Effects on Organisms

Potential effects of elevated uv radiation on living organisms other than man have been reviewed recently in connection with the environmental impacts of stratospheric flight (NRC 1975). That review concluded that present knowledge is severely limited in this area. Ambient levels



SOURCE: Likens (1976).

FIGURE 8.9 Status of fish populations in Norwegian lakes in relation to pH of water.

of uv radiation vary widely in nature, with latitude being the most important determinant. The range of natural variation far exceeds changes that might result from stratospheric aviation or elevated nitrous oxide input to the atmosphere.

To test the effects of a change in exposure to uv, biota adapted to uv levels of a specific locale can be moved to other regions with different uv exposures. However, such organisms are adapted to soil, climate, and biological communities of their place of origin, which usually cannot be replicated elsewhere. Two other experimental approaches are presently feasible: supplementation of the uv spectrum, and selective deletion of uv. Field data involving supplemental uv are sparse; the most reliable data are from growth chamber and greenhouse studies. Plants in greenhouses exposed to supplemental uv corresponding to the effect of a 50 percent reduction in the ozone layer exhibited a 20 to 50 percent reduction of growth (NRC 1975); similar experiments in the field showed smaller but statistically significant decreases for some species. The greenhouse studies correlated declines in chlorophyll content with the reduced growth, while plants exposed in the field developed degenerative structural changes in some cells. Seedlings appear to be more sensitive to uv than are mature plants.

A wide range of variation in sensitivity to uv damage has been noted among the plant species that have been tested; Table 8.11 lists plant varieties according to their sensitivity to such injury. Tolerance was measured by determining the minimum radiation exposure needed for leaf-kill (Cline and Salisbury 1966a, 1966b). As the table indicates, many of the vegetable varieties tested are among the sensitive species, while those strains of major grain crops tested (wheat and corn) proved more resistant.

Information on the effects of uv radiation on terrestrial and aquatic animals is less well developed. Supplemental uv has been correlated with increased mortality of insect larvae in cages; however, in nature these larvae are likely to be sheltered from direct irradiation. Other reported effects on terrestrial animals, as summarized by Koslow (1977), include genetic damage in insects; increased synthesis of vitamin D in the skin of mammals; eye cancer in mammals; and possible disruption of navigation, communication, or other behavior in insects, which have photoreceptors sensitive to uv. However, limited studies of the last of these effects, using supplemental uv, have failed to produce statistically meaningful results (NRC 1975).

It is difficult to assess the effects of uv on aquatic systems because of uncertainties in determining the extent

TABLE 8.11 Sensitivity of Selected Plants to Injury by Ultraviolet Radiation

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Very Sensitive[a] (1-5 cal/cm²)

- *Pisum sativum*, var. *arvense* Poir. (Colorado White Pea)
- *Lycopersicon esculentum* Mill. (Oxheart Tomato)
- *Phaseolus vulgaris* L. (Bean)
- *Cucurbita pepe* L. (Small Sugar Pie Pumpkin)
- *Hibiscus esculentus.* (Perkins Mammoth Okra)
- *Allium cepa* L. (White Southport Onion)
- *Cichorium endivia* L. (Green Curled Endive)
- *Citrullus vulgaris* Schrad. (Sugar Baby Watermelon)
- *Cucumis sativus* L. (Niagara Cucumber)
- *Brassica rapa* L. (Purple Top White Globe Turnip)
- *Beta vulgaris* L. (Sugar Beet)
- *Beta vulgaris*, var. *crassa* L. (Garden Beet)
- *Tetragonia expansa* Thunb. (New Zealand Spinach)
- *Lactuca sativa* L. (Prizehead Lettuce)
- *Solanum melongena*, var. *esculentum* Nees. (Fort Myers Market Egg Plant)
- *Trifolium pratense* L. (Medium Red Clover)
- *Pharbitis nil* Chois (*Ipomoea nil* L. Roth.)
- *Coleus blemei* Benth.
- *Scrophularia marilandica* L.
- *Mimosa pudica* L.
- *Euphorbia splendens* Bajer.
- *Dieffenbachia amoena*
- *Equisetum arvense* L.
- *Cyclamen persicum* Mill.

Sensitive (6-25 cal/cm²)

- *Cucumis melo*, var. *cantaloupensis* L. (Hales Jumbo Canteloupe)
- *Brassica oleracea*, var. *italica* L. (Green Sprouting Calabrese)
- *Brassica oleracea*, var. *botrytis* L. (Early Snowball "A" Cauliflower)
- *Brassica oleracea*, var. *acephala* L. (Georgia Collard)
- *Pastinaca sativa* L. (Hollow Crown Parsnip)
- *Raphanus sativus* L. (Cherry Belle Radish)
- *Chichorium intybus* L. (Large Rooted Chicory)
- *Daucus carota*, var. *sativa* L. (Streamliner Carrot)
- *Achillea lanulosa* Nutt.
- *Crassula aborescens varigata*
- *Pelargonium hortorum*
- *Hymenoxys grandiflora* (T. & G.) Parker
- *Bryophyllum daigremontiana* x *tubiflora*
- *Gynura aurantica* DC
- *Xanthium pennsylvanicum* Wall.

Moderately Sensitive (26-100 cal/cm²)

- *Alopecurus pratensis* L. (Meadow Foxtail)
- *Hordeum vulgare* L. (Memei Barley)
- *Nephrolepsis exaltata bostoniensis* Schott. (Boston Fern)
- *Lilium longiflorum* Thunb.
- *Potentilla diversifolia* Lehm.
- *Geum turbinatum* Rydb.
- *Yucca filamentosa* L.

Moderately Resistant (100-400 cal/cm²)

- *Aloe* sp. (Oxtongue)
- *Aloe varigata* L.
- *Bouteloua gracilis* (H.B.K.) Lag.
- *Dianthus caryophyllus* L. (Carnation)
- *Picea pungens* Engelm.
- *Pseudotsuga taxifolia* (Poir.) Britt.
- *Sansevieria hahnii*
- *Secale cereale* L. (Balbo Rye)
- *Sporobolus cryptandrus* (Torr.) A. Gray
- *Triticum vulgare* Vill. (Coleraw Wheat)
- *Zea mays*, var. *saccharata* (Golden Bantam Corn)

Resistant (400-1200 cal/cm²)

- *Dioön spinulosum* Dyer. (Cycad)
- *Juniperus sabina* var. *tamariscifolia* Ait.
- *Juniperus scopulorum* Sarg.
- *Opuntia* sp.
- *Pachycereus marginatus* Brit. and Rose
- *Pinus contorta* var. *murrayana* (Balf.) Engelm.
- *Sansevieria laurentii* Wildem.

Very Resistant (1200-3000 cal/cm²)

- *Agave* sp.
- *Pinus nigra* Hort.
- *Pinus ponderosa* Dougl.

---

[a] Sensitivity to uv at wavelength 2537 Å. Energy values stated for each category represent the minimum radiation exposure necessary for leaf-kill.

SOURCE: Modified from Koslow (1977).

of uv penetration into water. The National Research Council report (1975) concluded that the effects of increased uv on aquatic systems cannot now be predicted.

No direct evidence of effects of increased uv at the ecosystem level is available. Deleterious effects of uv on species make some ecosystem effects likely, but it should be recognized that significant effects on ecosystem functioning are not a necessary consequence of effects on individual species. Ecosystems are characterized by complex homeostatic mechanisms that to a limited extent tend to maintain stable functioning in the face of external stress.

Effects on Climate

Global surface temperature is controlled in an unknown manner by a temperature inversion at the base of the stratosphere. In addition to direct biological effects from increased global uv levels, depletion of the ozone layer probably would cause global climatic changes that could alter the biogeography of continents (NRC 1975). The most immediate ramifications of such changes for human welfare would be shifts in crop regions. More specific assessments of this potential threat would require coupling of climatic modeling capabilities with models of natural and agroecosystems and with empirical knowledge. Such coupling is presently not feasible, and more quantitative estimates of the effects must await the results of future research. However, an economic analysis of the potential consequences of climatic change, based on studies by the Climatic Impact Assessment Program of the U.S. Department of Transportation, is presented in Chapter 11 of this report.

ECOLOGICAL EFFECTS OF NITRITE

The occurrence of excessive nitrate in the environment carries with it some risk of elevated nitrite levels. Nitrite is produced as an intermediate in the process of nitrification. Normally, only trace amounts of nitrite are found in soils or aquatic environments; however, when conditions occur that promote nitrification (e.g., the release of ammonia-bearing wastes), potentially high nitrite levels may occur. The extent of increase in nitrite concentrations depends on the degree to which nitrification is completed prior to discharge.

Effects on Fish

Russo and Thurston (1976) have reviewed nitrite toxicity to fishes. They concluded that differences in tolerance exist among species and that size appears to influence toxicity. Few data on nitrite toxicity are available, and most are from static tests of short duration. Some published results are summarized in Table 8.12. As the table shows, some species are killed by acute exposures to less than 1.0 ppm of nitrite-nitrogen. Chronic exposure at still lower concentrations might be expected to have adverse impacts on at least some fraction of a fish population; also, the tolerance of adult fish to toxicants is often greater than that of fry, and other variables, such as reproductive state, can increase sensitivity (Sprague 1971). It seems likely, therefore, that levels of nitrite that can occur in the environment under some conditions pose a toxic hazard to at least some fish. Very little is known about the influence of water conditions on nitrite toxicity, but some unpublished data of Russo and Thurston suggest that pH and salinity may influence response. In a related study, Smith and Russo (1975) reported nitrite-induced methemoglobinemia in rainbow trout. (See Chapter 9 of this report for discussion of methemoglobinemia in livestock and humans.)

Effects on Plants and Bacteria

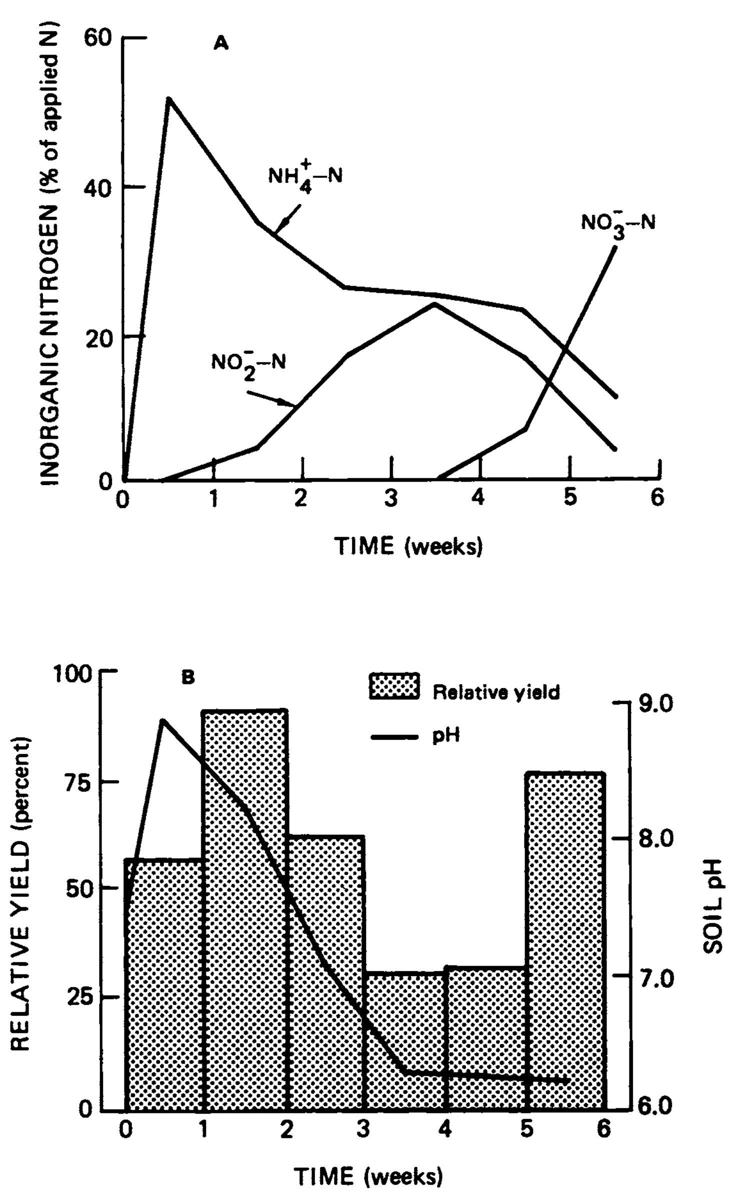
Significant quantities of nitrite rarely occur in soils; however, under conditions of high pH, potentially phytotoxic levels of nitrite may accumulate (Viets 1965). Applications of ammonia or urea fertilizers can elevate soil pH to a point that growth of the nitrite-oxidizing bacterium Nitrobacter is suppressed, while nitrate oxidizers are unaffected. Critical variables related to the accumulation of nitrite are the amount of ammonia present, and soil alkalinity. Nitrite does not accumulate at pH below about 7.2 (Morrill 1959, Stojanovic and Alexander 1958). Figure 8.10 illustrates the changes in pH and concomitant accumulation of nitrite in an alkaline soil amended with urea, and (b) of the figure shows the associated decrease in growth of corn planted in the same soil. Growth was depressed both at high pH, from ammonia toxicity, and at elevated nitrite concentrations (Court et al. 1962).

Bingham et al. (1954) found that nitrite concentrations of 10 ppm NO_2^--N or greater in soils are likely to be toxic to plants, and that the phytotoxicity of nitrite was greatly enhanced by low pH (about 4 to 6); Figure 8.10(b) also supports that observation. Since nitrite accumulates only at high pH, phytotoxicity from nitrite would not appear to be a major agronomic problem.

High concentrations of nitrite, in the range from 200 to 2500 mg/l, can inhibit some bacteria, especially nitrifiers (Walker and Newman 1956, Whiteside and Alexander 1962). De Marco et al. (1969) found that 5 mg/l of NO_2-N introduced into soil produced a lag effect in nitrification. Very

TABLE 8.12 Toxicity of Nitrite to Fishes

Species	Endpoint	Nitrite Concentration (mg N/l)	Reference
Log Perch	death; <3h	5	McCoy (1972)
Common White Sucker	"survival"; >48h	100	McCoy (1972)
Mosquito-fish	LC_{50}; 96h	1.5	Wallen et al. (1957)
Minnow	"fatal"; 14d	10	Klingler (1957)
Channel Catfish	LC_{50}; 96h	7.5 12.0	Konikoff (1975) Colt (1974)
Rainbow Trout	LC_{50}; 96h	0.14-0.15	Russo et al. (1974)
Cutthroat Trout	LC_{50}; 96h	0.4	Russo and Thurston (1975)
Chinook Salmon	40% mortality; 24h LC_{50}; 96h	0.5 0.88	Smith and Williams (1974), Westin (1974)



SOURCE: Modified from Court et al. (1962). Reproduced from Soil Nitrogen, ASA Monograph No. 10, pages 540 and 541 (1965), by permission of the American Society of Agronomy.

FIGURE 8.10 Changes with time in the forms of nitrogen (A), and in soil pH and relative dry weight accumulation by corn seedlings (B), in a sandy loam soil amended with 560 ppm of urea at an initial pH of 7.4. Yields expressed as percent of an unfertilized control.

little other information is available about the possible bacterial inhibition that might occur at the low levels of nitrite typically encountered in the environment.

EFFECTS OF PEROXYACYL NITRATES

A portion of the nitrate in urban atmospheres is in the form of photochemical reaction products, peroxyacyl nitrates (PANs) (see Chapters 2 and 3 of this report). The most abundant member of this family (although not necessarily the most toxic) is peroxyacetyl nitrate (PAN). Data on effects of PANs on higher plants have been derived almost exclusively from laboratory and controlled field exposures, because effects of PANs under ambient conditions are difficult to separate from the effects of other oxidants. On the basis of available information, the U.S. EPA Summary Report on Atmospheric Nitrates (1974) concluded that ozone is the most important phytotoxicant of the photochemical complex. Ozone concentrations are generally 10 to 20 times higher than the levels of PANs in smog (Mudd 1975).

Peroxyacyl nitrates produce similar symptoms of damage irrespective of the hydrocarbon moiety, suggesting that the mechanism of damage is a result of the oxidizing ability of the peroxy portion of the compounds. Table 8.13 summarizes the effects of PANs on plants. Damage following exposure to PANs develops fairly slowly (over about 72 hours). Plant species that are sensitive to PANs include lettuce, oats, and pinto beans. Tobacco and wheat are intermediate in sensitivity, while corn, cotton and cucumbers are resistant.

Because PANs primarily are products of urban air pollution and are relatively unstable in the atmosphere (see Chapter 3), vegetation damage from this class of organic nitrates is likely to be concentrated in regions near major metropolitan areas. Damage from oxidant pollution, primarily ozone, has been detected in remote areas (NRC 1977c); it is unlikely, however, that PANs contribute substantially to such effects. For a critical review of current knowledge of the effects of PANs on plants and other organisms, see the report of the National Research Council's Subcommittee on Ozone and Other Photochemical Oxidants (NRC 1977c).

EFFECTS OF N-NITROSO COMPOUNDS

Some nitrosamines and other N-nitroso compounds are discharged into the environment by human activities; these compounds also may be formed in the air, water, soil, or in vivo in animals when the appropriate amine and nitrite precursors are present (see discussion in Chapter 2 of this report). Human exposure to nitrosamines and precursors, and

TABLE 8.13 Effects of Peroxyacyl Nitrates on Plants

Function Affected	Effect and Exposure Conditions	Reference
Carbohydrate metabolism	Inhibition of growth in *Avena* (oat) coleoptiles	Ordin (1962)
	Inhibition of cellulase synthetase in *Avena* coleoptiles, 35 to 50 ppm, 4 hours	Ordin and Hall (1967)
	Starch mobilization in darkness	Hanson and Stewart (1970)
	Cellulose synthesis in tobacco leaves, 0.85 to 0.97 ppm, 1 hour	Ordin et al. (1971)
Hormonal regulation	In vitro oxidation of indoleacetic acid, with loss of hormonal properties	Ordin and Propst (1962)
Photosynthesis	Inhibition of photosynthesis (evolution of O_2) in *Chlamydomonas sp.*, with recovery after low doses	Gross and Dugger (1969)
	Lowered sulfhydryl content of cells and differential destruction of pigments, especially carotenoids and chlorophyll A	Gross and Dugger (1969)

the potential health hazards represented by such exposures, are assessed in Chapter 9. It seems likely that other organisms in the environment are also at some risk of adverse effects from nitrosamines. Most N-nitroso compounds are carcinogens, and nitrosamines have induced cancer in every species of animal tested. For example, one or more nitrosamines produced tumors in rats, mice, hamsters, guinea pigs, rabbits, dogs, monkeys, mink, hedgehogs, grass parakeets, and rainbow trout. Some N-nitroso compounds have been shown to produce teratogenic effects, and more than 40 members of this class of compounds have been found to be mutagenic in microbial test systems. (See Chapter 9 for additional discussion and references.)

While these toxic properties of N-nitroso compounds provide an obvious basis for concern about their potential effects on wildlife, information on the actual environmental exposures that any organisms might encounter is virtually nonexistent. Similarly, the uptake, metabolism and toxicity of N-nitroso compounds in species other than those listed above have not yet been studied. Until more is known of the occurrence and/or formation of these compounds in polluted and relatively pristine environments, assessment of any ecological hazards they may pose will remain highly uncertain.

EFFECTS OF NITRATE AEROSOLS ON MATERIALS

Corrosion scientists have long recognized that atmospheric particles can promote and accelerate the corrosion of many metals (U.S. EPA 1974), but only a few studies have been conducted on the effects of individual chemical compounds. The corrosion rate of steel under conditions of high humidity is accelerated by sodium and ammonium nitrates, but the magnitude of this increase is less than that caused by chlorides and sulfates (U.S. EPA 1974, Preston and Sanyal 1956).

The only well-documented study of the effects of nitrate aerosols on corrosion is that of Bell Laboratories (Hermance 1966; McKinney and Hermance 1967). Premature failure of nickel-brass wire-spring relays in California led to field observations and tests that strongly implicated some component of airborne particulate matter. Only nitrates were found capable of causing cracking at low humidities (<75 percent), and the rate of crack growth was correlated to nitrate concentration. The corrosion problem could be mitigated by using zinc-free alloys, installation of filters, or humidity control (Hermance et al. 1971). Another corrosion problem, involving the formation of bright greenish deposits on nickel-brass-palladium-capped contacts, has also been attributed principally to nitrates (Hermance et al. 1971).

Estimates of the effects of airborne nitrates on degradation of calcareous building materials are much less certain. Neither our review nor environmental assessments by others (F.G. Taylor, Oak Ridge National Laboratory, personal communication, 1977) unearthed any published quantitative data on this problem. Widespread damage of this sort has been noted in many cities; but it is difficult to separate the effect of nitric acid from the effect of sulfuric acid, which usually occurs in polluted air at even higher concentrations than does nitric acid (see Chapter 6). Solubility data for various materials are available, but detailed experiments on environmental weathering apparently have not been conducted. This issue deserves closer attention, and appropriate research seems warranted, since damage to materials is an economically significant problem.

Precise, comprehensive estimates of the costs of corrosion caused by acidic aerosols are not available, and it is impossible to assess the costs attributable to separate chemical components of these aerosols, such as nitrate. Likens (1976), cited an estimate by V. Kucera of the Swedish Corrosion Institute that corrosion of metals by atmospheric sulfur pollutants cost $7.00 per person in 1970. Sulfate and nitrate are roughly comparable in corrosive strength; if one assumes that nitrate represents approximately 30 percent of airborne acidity, the annual per capita cost due to corrosion by nitrates would be $3.00. Even if these are significant overestimates, the costs of corrosion caused by nitric acid are likely to be high. A cost estimate of hundreds of millions of dollars is in line with estimates for other damage by air pollutants. The recent report on nitrogen oxides by the National Research Council (1977b) estimated that fading of fabric dyes induced by NO_x costs U.S. consumers more than $100,000,000 annually.

SUMMARY AND CONCLUSIONS

Effects of nitrogen anthropogenic inputs on ecosystem productivity can be described qualitatively, but quantitative relationships seldom can be established with present knowledge. Even an intensely studied response, such as the effect on crop production of nitrogen fertilizers, can rarely be predicted with great accuracy, because so many other variables also affect crop yields. Fixed nitrogen in precipitation can be a beneficial nutrient input to some ecosystems. In agricultural systems, this input is equivalent to a relatively small part of the nitrogen assimilated annually by vegetation, but in some pristine forests and oligotrophic lakes, atmospheric inputs may represent a significant fraction of the total. Although it cannot be estimated now, the effect of such inputs on productivity might be important.

The role of nitrate in eutrophication can seldom be specifically quantified. However, nutrient loading rates for nitrogen and phosphorus can be examined with respect to physical characteristics of the aquatic system, such as mean depth and hydraulic residence time. Although they are based on many simplifying assumptions, nutrient input-output balances can be used to develop critical loading functions, which do provide a rough quantitative guide for the management of lake water quality. Cultural eutrophication has been observed in some estuarine environments enriched with nitrogen, and further attention to the role of nitrogen in eutrophication of coastal waters seems warranted.

A number of direct effects of acidic precipitation on both terrestrial and aquatic biota have been reported. The effects include tissue damage and physiological impairment in plants, lethal effects on fish, and possible impacts on host-parasite or pathogenic processes. These effects may occur at specific short periods during an organism's life cycle, or may develop after repeated exposure. The ecological consequences of effects on specific terrestrial organisms or on the quality of soils have not been well measured, and the extent to which synergisms may occur between acid precipitation and other forms of environmental stress is unknown. The long-term effects of acidification on aquatic ecosystems have been better documented. These effects are widespread, regionally and globally, and can include decimation of fish populations. Little is known about the recovery of ecosystems from such effects, but liming of soils and lakes has been successful in a limited number of cases.

Little is known about the direct biological effects of acidic aerosols, but some adverse effects could be expected because of the irritant properties of these pollutants. Effects of airborne particulate nitrates on metals are qualitatively similar to those produced by sulfates. Some specific effects of nitrates on electronic transmission equipment have been described, but less is known of the effects of acidic nitrate aerosols on calcareous materials. Corrosion damages to materials are substantial and economically important, but it is not now possible to attribute appropriate fractions of the damages to the different corrosive aerosols present, chiefly sulfates and nitrates.

Depletion of the stratospheric ozone layer could have adverse biological effects, especially on terrestrial plants. However, the climatic effects likely to result from small changes in temperature in the earth's atmosphere and at the surface, while unknown, are likely to pose a more severe threat than direct biological effects of enhanced uv.

The toxicity of nitrite to fishes varies widely according to species. The acutely toxic concentration (LC_{50}) for the most susceptible species, chinook salmon and rainbow trout, is less than 1 mg NO_2-N/l. Under some conditions, some fish may be sensitive to chronic effects at concentrations significantly lower than the reported LC_{50}. It seems likely, therefore, that nitrite poses a toxic hazard to fish in some polluted environments. The effects of nitrite in soils on plants and soil microorganisms are not well understood, but available data do not suggest any major adverse impacts.

Recent evidence that N-nitroso compounds are present in the environment or are formed in vivo, and the demonstrated carcinogenicity of nitrosamines in many species of mammals and in some birds and fish, suggest a potential hazard to wildlife that may be exposed to these compounds. Because no information is available on actual levels of exposure in ecosystems, however, further assessment of the magnitude of this risk is not possible now.

Organic nitrate air pollutants, for the most part PANs, contribute in some measure to the injury to plants caused by photochemical oxidants. While it is difficult to separate the effects of PANs from those of other pollutants present simultaneously, the other phytotoxic agents, especially ozone, are believed to play a greater role than PANs in causing smog-related vegetation damage.

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CHAPTER 9

HEALTH EFFECTS OF NITRATES, NITRITES, AND N-NITROSO COMPOUNDS

INTRODUCTION

Although nitrate compounds in the environment can have direct adverse effects on the health of humans and animals, the potential effects of nitrite and carcinogenic N-nitroso compounds, of which nitrate may be a precursor, appear to be much more serious. The chief emphasis of this chapter therefore is on the toxic properties of nitrite and nitrosamines. Nitrates also can contribute indirectly to other health problems, through complex chains of environmental events. One such sequence is the possible depletion of the stratospheric ozone layer by nitrous oxide produced by denitrification (discussed in Chapter 7). A short review of the possible health effects of increased exposure to ultraviolet radiation is included here. The hazards to health associated with certain other nitrogen compounds, particularly ammonia and oxides of nitrogen, have been thoroughly reviewed in other recent NRC studies, and were excluded from consideration in this report.

Adverse effects of nitrate and its derivatives may be acute (where a short exposure to a large dose produces a rapid response) or chronic (where exposure is extended, small doses are often repeated, and injury develops over a period of months or years). Short-term, high-dose exposures also may produce effects that appear only after a long latent period. These distinctions are important for at least two reasons: first, it is usually more feasible to demonstrate causal relationships for acute effects than for chronic diseases; and second, the acute toxicity of nitrate and its derivatives usually is reversible therapeutically, while chronic effects may be refractory to clinical treatment.

EXPOSURE TO NITRATE, NITRITE, AND N-NITROSO COMPOUNDS

Sources of Ingestion of Nitrates and Nitrites

The principal route of human exposure to nitrate and nitrite is ingestion. White (1975) estimated the average daily ingestion of nitrate and nitrite in the United States, using U.S. Department of Agriculture data on per capita food and water consumption, and chemical analyses of foodstuffs; similar calculations have been reported by Selenka and Brand-Grimm (1976) for the German Federal Republic.

Variations among individuals are certain to be large, but White's calculations are sufficient to indicate the major sources of these two ions in the American diet (Table 9.1). Vegetables supply almost 90 percent of daily ingested nitrate (approximately 86 mg NO_3^- per person per day), but only about 2 percent of the nitrite. About 9 percent of the ingested nitrate and 20 percent of the nitrite is from cured meats. Less than one percent (about 0.7 mg NO_3^- per person per day) of the nitrate comes from drinking water, based on average values from a survey in 1962 of the 100 largest public water supplies in the United States (Durfor and Becker 1964). Some smaller water supplies and private wells contain nitrate far in excess of the amounts found in public drinking water supplies (see Chapter 3). Nitrate concentrations as high as 100-500 mg N/l have been reported in polluted wells; individuals using such private supplies could consume up to 3000 times more nitrate from water than the average person using a public water supply. In such cases, 95 percent of the daily ingested nitrate could come from the drinking water.

Saliva

Saliva frequently is cited as the major source of ingested nitrite (Tannenbaum et al. 1974). According to White's calculations (1975), saliva accounts for three fourths of the average daily ingestion. Nitrite is produced in the oral cavity by bacterial reduction of nitrate in ductal saliva, and the amount of nitrate in the saliva depends directly on the amount of nitrate ingested (Spiegelhalder et al. 1976, Tannenbaum et al. 1976). White (1975) estimated that up to 9 mg of nitrite per person per day can be ingested in saliva. Although this amount is large compared to other sources, ingestion from saliva is spread over 24 hours and the amount entering the stomach at any one time is quite small, especially in comparison to the amounts of nitrite ingested in meals containing cured meats or certain vegetables. The timing of ingestion of doses of nitrite is especially important because of the reversibility of formation of methemoglobin and because the nitrosation of amines in the stomach is a function of the square of the concentration of nitrite (Mirvish 1970, 1975; see also Chapter 2).

TABLE 9.1 Estimated Average Daily Ingestion of Nitrate and Nitrite for Residents of the United States

	Nitrate		Nitrite	
Source	mg	%	mg	%
Vegetables	86.1	86.3	0.20	1.8
Fruits, juices	1.4	1.4	0.00	0.0
Milk and products	0.2	0.2	0.00	0.0
Bread	2.0	2.0	0.02	0.2
Water	0.7	0.7	0.00	0.0
Cured meats	9.4	9.4	2.38	21.2
Saliva	30.0[a]		8.62	76.8
Total	99.8	100	11.22	100

[a] Not included in total (see text).

SOURCE: White (1975).

Foods

Concentrations of nitrate in vegetables are highly variable and depend on many factors, including climate, soil, and species. Tomatoes, cucumbers, and asparagus usually contain only a few ppm NO_3^--N, while spinach, celery, lettuce, radishes, and beets can contain more than 600 ppm NO_3^--N (Jackson et al. 1967, Brown and Smith 1967). Because of the relatively frequent consumption of lettuce, celery, and white potatoes, these products contribute the largest proportion of nitrate to the daily diet (White 1975).

Most fresh vegetables contain less than 1 ppm nitrite (as the anion); exceptions include beets, 6 ppm; spinach, 2.7 ppm; and corn, 2 ppm (White 1975). Nitrate can be reduced to nitrite by bacteria in improperly stored, cooked, or frozen vegetables. Schuphan (1965) observed an increase in nitrite concentration from 30 ppm in fresh spinach to 3550 ppm after four days of storage. Phillips (1968) reported a 70 to 75 percent loss of nitrate in spinach after four days of storage at 21°C and almost a complete loss by the eighth day; only small increases in nitrite were seen. Similar but quite variable results were seen in spinach stored under refrigeration, although the reduction of nitrate to nitrite was delayed and more limited. Little or no reduction to nitrite occurred in spinach frozen up to five months. Thawing up to 15 hours did not increase nitrite levels, but in thaws up to 39 hours levels of NO_2^--N rose from less than 1 ppm to 30 ppm (see also Raineri and Weisburger 1974).

Cured meats (such as ham, bacon, corned beef, and sausages) and some fish and cheese products contain nitrite as a preservative and color and flavor enhancer. The Animal and Plant Health Inspection Service of the U.S. Department of Agriculture has pending federal regulations to eliminate the use of nitrate in cured meat products. The use of nitrite also will be restricted to a level not yet determined; the level now permitted in cured meat products is 200 ppm as the sodium salt.

Drinking Water

Municipal drinking waters in the United States seldom exceed the U.S. Public Health Service standard of 10 mg NO_3^--N/l (see Chapter 3). For example, a survey of 969 public water supplies serving 18 million people in the United States showed that only 19 exceeded the drinking water standard (U.S. Public Health Service 1970). Water from private wells is more often high in nitrate, especially water from shallow wells (less than 15 m) in regions with impermeable soils (e.g., Larson and Henley 1966; see Table 3.3 of this report).

Air

Nitrate occurs in the atmosphere in inorganic aerosols and in organic products of smog, and some uptake of these substances can occur by inhalation. Comprehensive reviews of problems related to atmospheric nitrogen oxides and nitrates are available (U.S. EPA 1974, NRC 1977; also see Chapter 3). In urban air, the most abundant form of nitrate is peroxyacetyl nitrate, PAN, a photochemical product of air pollution (see Chapter 2). Aerosols of inorganic nitrate salts occur to a smaller extent. In rural air, the predominant forms are nitric acid and nitrate salts. Quantitative analysis of nitrates in the atmosphere is difficult (see Chapter 4), but nitrate levels in various regions have recently been estimated (U.S. EPA National Aerometric Data Book and CHESS program, unpublished results; see Figure 3.8). Nitrate levels in urban and rural air, and PAN and alkyl nitrate concentrations in urban air are given in Table 3.6. Quantitative measurements of nitrite in urban air are not available.

Adult humans breathe about twenty cubic meters of air per day. If we assume that all inhaled nitrate is absorbed, an adult in Los Angeles could inhale and absorb on the order of 150 μg inorganic nitrate, 4000 μg PAN, and 120 μg alkyl nitrate per day, or a total of approximately 500 μg nitrate-nitrogen per day.

N-Nitroso Compounds

Formation

Where nitrite is present there is a potential for the formation of N-nitroso compounds. Nitrosation of secondary and tertiary amines can occur in the air, soil, and water, and in vivo in humans or animals. The reactions that form nitrosamines are discussed in Chapter 2. Too little information is available to estimate the extent to which nitrosation may take place in soil, water, and air, but research on this topic is active and such information should be forthcoming.

Sources of Precursors

Sources of nitrite, and of nitrate that can be reduced to nitrite, have been reviewed above. Sources of secondary and tertiary amines are also important and much more extensive.

Amines may occur in water as a result of the discharge of industrial and municipal wastes, the decomposition of natural organic materials in water, and runoff from feedlots and farmlands. Sources of amines in the soil include decomposition of natural organic materials (crop residues, manures, soil humus), decomposition of sewage sludge, and addition of nitrogenous pesticides (e.g., atrazine, carbaryl, thiram). Simple aliphatic amines are ready substrates for microbial metabolism; they occur in water and in soil in nanogram-to-milligram per kilogram amounts. More complex amines such as pesticides are considerably more persistent in water and soil than are aliphatic amines. Many of the amines that occur in the environment are primary amines, however, and not the secondary or tertiary amine compounds that may be precursors of N-nitrosamines.

Addition of secondary or tertiary amines and nitrite or nitrate to soil, water, and sewage, in amounts far in excess of known ambient levels, results in the formation of N-nitroso compounds (Ayanaba et al. 1973, Ayanaba and Alexander 1974). Simple dialkyl nitrosamines are not readily degraded in soil, lake water, or sewage, and therefore are expected to persist in natural environments (Tate and Alexander 1975, 1976).

Amines have been detected in the air near chemical plants and feedlots, but little quantitative information is available on the amine content of air in other locations. Several possible pathways have been proposed for the formation of N-nitroso compounds in the atmosphere, but neither experimental data nor environmental measurements are available to determine whether, and to what extent, such reactions occur (Hanst et al. 1976, U.S. EPA 1976; see Chapter 2 for discussion).

Nitrite can serve as a precursor for nitrosamines in the food supply. Ender et al. (1964) demonstrated the formation of dimethylnitrosamine (DMN) in herring treated with sodium nitrite as a preservative; the herring was a source of dimethylamine in the nitrosation reaction.

Exposure

Some recent data have been published on concentrations of nitrosamines in industrial and urban air. Fine et al. (1976, 1977a) detected dimethylnitrosamine, and on a single occasion, diethylnitrosamine (DEN), but no other N-nitroso compounds in such environments. Reported levels in ambient air at most sites monitored were less than one $\mu g/m^3$; within 800 m of an industrial source, however, readings of from 0.03 to 3.0 $\mu g/m^3$ were measured. Readings up to 36 $\mu g/m^3$ were detected on the site of an industrial plant, where DMN was used in the manufacture of 1,1-dimethylhydrazine, a rocket propellant. The extent to which the N-nitrosamines detected in the air were derived from nitrosation of airborne amines is unknown. The U.S. EPA has monitored the air near sources of amine emissions in several cities; to date, very few samples have contained detectable amounts of nitrosamines (see Chapter 2).

The human stomach provides conditions favorable for the generation of nitrosamines; the gastric juice is low in pH, and nitrite and amines from ingested foods, drugs, and water mix readily with it (Sander 1967, Sen et al. 1969). Sources of ingested amines include food and water, pesticides in foods, and pharmaceuticals, but the amounts ingested from each source have not been quantified. Sander and Seif (1969) demonstrated the nitrosation of diphenylamine to diphenylnitrosamine, which is not a known carcinogen, by nitrite in the stomachs of human volunteers; nitrosation of a secondary amine also has been measured in the stomachs of rodents (Sander et al. 1968) and dogs (Mysliwy et al. 1974).

Preformed nitrosamines have been found in tobacco (Hoffman et al. 1974, Hecht et al. 1974) and in tobacco smoke (Neurath 1967, Klus and Kuhn 1973). There are also several reports of nitrosamines in human foods; some of these reports, where chemical identity has been confirmed, are summarized in Table 9.2. The concentrations of these compounds are low, usually near the limit of chemical detectability. Too few food samples have been analyzed to comment on the frequency of nitrosamine contamination of the human food supply; also, the present analyses have been confined largely to the volatile nitroso compounds and will have to be extended to include those of lower volatility.

Fine and coworkers (1977b) recently demonstrated in vivo formation of DMN and DEN in one adult subject after ingestion of a large bacon, spinach, and tomato sandwich, and beer. The lunch contained 1600 ng of preformed DMN and an unspecified amount of nitrosopyrrolidine. DMN was detectable in the man's blood before lunch at a level of 2000 ng in the total blood volume. Total DMN in the blood peaked at 4350 ng 35 minutes after ingestion of the sandwich, but fell to below pre-lunch levels after 162 minutes. DEN also was measured, with a pre-lunch level of 510 ng in total blood and a peak concentration 65 minutes after lunch of 2600 ng in total blood. Although nitrosopyrrolidine was present in the lunch, it was not detected in the blood. Because the amounts of nitrosamines absorbed from the blood or exhaled were not estimated, the above values represent the minimum amounts of nitrosamine in the subject. When the same subject had a diet low in nitrate and nitrite and high in ascorbate for 24 hours before blood analysis, no DMN was detectable in his blood.

An ad hoc study group of the Science Advisory Board of the U.S. Environmental Protection Agency recently reviewed available information on human exposures to nitrosamines and on their toxicological properties, as part of a risk

TABLE 9.2 Nitrosamines in Human Food Products

	Nitrosamine Concentration, μg/kg[a]						
Food Product	Dimethylnitrosamine		Nitrosopyrrolidine		Diethylnitrosamine		Reference
Bacon		1-4		up to 40		1	Crosby et al. (1972)
Bacon, uncooked	(1/8)	30		0			Sen et al. (1973)
Bacon, fried	(6/8)	2-5	(7/8)	4-25			"
Bacon, fried						1.5	Alliston et al. (1972)
Bacon, uncooked				10-108			Fazio et al. (1973)
Ham		5					"
Frankfurter	(3/34)	11-84					Wasserman et al. (1972)
Salami		20-80					Sen (1972)
Dry sausage		10-20					"
Souse	(6/7)	3-63	(1/7)	19			Fiddler et al. (1975)
Blood and tongue	(2/2)	7,45					"
Various cured meats[b]	(29/80)	2-35	(17/80)	13-105	(9/80)	2-25	Panalaks et al. (1973)
Salami, Hungarian		1-4					Crosby et al. (1972)
Luncheon meat		1-4					"
Pork, Danish		1-4					"
Haddock, fried		1-9					"
Hake, fresh or fried		1-9					"
Codfish, fresh, salted, fried		1-4					"
Cod		1		6		1.5	Alliston et al. (1972)
Liver, pig, raw						1.5	"
White herring		50-100					Fong and Chan (1973)
Yellow croaker		10-60					"
Anchovies		20					"
Croaker		20					"
Cheese, Cheshire						1.5	Alliston et al. (1972)
Cheese, Grinland, Danish blue, Gouda, St. Paulin, Norwegian Tilsit, and Norwegian goat's milk		1-4					Crosby et al. (1972)

[a] Number of positive samples/number of samples analyzed in brackets.
[b] Only 5 samples confirmed by mass spectroscopy.

assessment for these compounds (U.S. EPA 1976). The study group concluded that available information on the amounts of preformed N-nitroso compounds and their precursors in the environment was too limited to estimate human exposure. The extent of contributions to the human body burden of N-nitroso compounds from in vivo reactions in the stomach and other tissues, especially the lung, is unknown. However, available information on the kinds and amounts of precursors in the environment and on the rates of formation of N-nitroso compounds suggests that in vivo formation could be the largest single source of these carcinogens in the general population.

Sources and Exposures: Summary

In summary, the chief source of the nitrate body burden, except in the newborn, is ingested vegetables, unless rural well water high in nitrate is consumed. Great variation exists within populations with respect to the relative importance of different sources of exposure to nitrate.

On a daily basis, the major source of nitrite is saliva. However, this dose is presented to the body as a continuous, low-level input, and the relatively high concentrations over short periods resulting from ingestion of cured meats are probably more important in terms of potential hazards to health.

The principal sources of preformed nitrosamines appear to be diet and tobacco smoke, but urban and industrial air may prove to contribute much to the exposure to preformed nitrosamines. Insufficient data exist to quantify the importance of in vivo nitrosation of secondary and tertiary amines ingested from air, soil, water, and food, but the greatest potential for the formation of N-nitroso compounds and exposure to them appears to be in food. In vivo formation of nitrosamines could be the largest contribution to body burden in the general population.

ACUTE EFFECTS OF EXPOSURES

Nitrate

Nitrate poisoning in humans is uncommon; in most cases, the acute toxicity of nitrate depends on its reduction to nitrite. Fassett (1973) describes acute nitrate poisoning in man as a rapid, severe gastroenteritis with abdominal pain, blood in the urine and stool, weakness and collapse. This can be induced in an adult by ingestion of 8 to 15 grams of sodium or potassium nitrate, and repeated doses may cause dyspepsia, mental depression, headache, and weakness. The mechanism for this toxicity is not known. Inorganic nitrate is rapidly absorbed by the stomach and lungs and rapidly excreted in the urine; the latter fact undoubtedly contributes significantly to the low toxicity of nitrate itself.

Little is known about the direct acute toxicity to animals and humans of the nitrate component of urban air pollution (principally as peroxyacyl nitrates and inorganic nitrate aerosols). Unpublished results from the U.S. Environmental Protection Agency CHESS program (French et al. 1974) suggest that in the New York-New Jersey metropolitan area, increased occurrence of asthmatic attacks is associated with increased amounts of suspended nitrates when temperatures exceed 10°C (U.S. EPA 1974). Interpretations of the results are complicated by the presence of other air pollutants with the nitrates. Shy et al. (1970) associated an increase in acute respiratory disease in Chattanooga, Tennessee with nitrogen dioxide pollution, but they cautioned that high nitrate levels could possibly contribute to the health effects.

Czechoslovakian children living in an industrially polluted area with high atmospheric levels of nitrate and sulfur dioxide had higher than normal levels of methemoglobin, but the drinking water also was high in nitrate. When airborne nitrate was eliminated, methemoglobin levels returned to normal, leading Peter and Schmidt (1967) to conclude that inhaled nitrate was responsible for the methemoglobinemia. Increased methemoglobin levels also were reported in a Polish population living near a nitrogen fertilizer factory, but no analysis was made for nitrate and nitrite in the drinking water or diet (Szponar and Belezuk 1973).

Peroxyacetyl nitrate is a strong irritant to the eye at a concentration of approximately 1 ppm in air. The median lethal concentration (LC_{50}) of PAN for mice exposed for 2 hours is 106 ppm, similar to the LC_{50} of nitrogen dioxide, but death is delayed to a greater extent in PAN toxicity (Campbell et al. 1967). No observations on gross or histologic pathology were reported. In further studies on mice, Campbell and coworkers (1970) demonstrated a dose-related depression of voluntary wheel-running activity at concentrations of 2.8 to 8.6 ppm PAN in air.

Smith (1965) studied the effect of PAN on cardio-respiratory parameters in 32 college men (average age 21 years) before, during, and immediately after exercise. A concentration of 0.3 ppm PAN in air was used to approximate a heavily polluted urban atmosphere. Most subjects experienced increased oxygen uptake during exercise and to a lesser extent during recovery, but not during rest; Smith suggested that the increased oxygen uptake may be caused by increased airway resistance. PAN had no effect on respiratory rate, exhalation volume, or heart rate.

Tobacco smoke contains organic nitrates such as methyl nitrate and various nitrohydrocarbons, but more importantly, it also contains known carcinogens such as dimethylnitrosamine, nitrosonornicotine, and benzo-a-pyrene. Relative to the potential hazards posed by the latter compounds, the risk to health associated with nitrates in tobacco smoke is probably negligible.

Gelperin et al. (1975) examined the relationship between fetal and infant mortality rates and the nitrate content of the drinking water in selected Illinois communities. Nine communities (total population: 270,000) with nitrate concentrations consistently between 9 and 28 mg N/l in the water supplies were compared to seven communities (total population: 600,000) where water nitrate levels were high (8.9 to 10 mg N/l) only during the spring and nine communities (total population: 1,500,000) in which the water nitrate levels were consistently low (concentrations not given). No correlation between nitrate levels in drinking water and fetal/infant death rates could be demonstrated.

Nitrite

Nitrate can be reduced to nitrite by the intestinal flora of some animals (Tillman et al. 1965); reduction also can occur in the human infant during the first three to four months of life. Microbial activity in spinach and animal forage can reduce the large amounts of nitrate present to nitrite.

Several comprehensive reviews are available on acute nitrite toxicity in animals and humans (Lee 1970, Phillips 1971, NRC 1972, Shuval and Gruener 1972, Deeb and Sloan 1975).

Methemoglobinemia

Nitrite is rapidly absorbed from the stomach into the blood and readily oxidizes the iron of hemoglobin to the ferric state, forming methemoglobin. Any agent that can oxidize the iron in hemoglobin theoretically should increase the amount of methemoglobin in the blood. Aniline, aminophenols, sulfonamides, and perchlorate also can cause methemoglobinemia (Bodansky 1951, Lee 1970).

Methemoglobin cannot function in oxygen transport. When more than 5 percent of the hemoglobin is converted to methemoglobin in children, cyanosis can be observed (Knotek and Schmidt 1964). If 30 to 40 percent of the hemoglobin is oxidized, the child will be hypoxic but usually will survive. If the methemoglobin level exceeds 50 percent, death is likely.

Infants in the first three months of life are particularly susceptible to nitrite-induced methemoglobinemia. At this age the infant's gastric pH is high (between 5 and 7) and does not inhibit the growth of nitrate-reducing bacteria, which otherwise are usually confined to the intestine (Walton 1951). As a result, ingested nitrate can be reduced to nitrite in the stomach before it is absorbed into the blood. In older children and adults, nitrate is absorbed from the stomach before it can reach the reducing bacteria of the intestine. Nitrate does not oxidize hemoglobin and is rapidly excreted in the urine, usually without injury.

Fetal hemoglobin (hemoglobin F) is more readily oxidized to methemoglobin than is adult hemoglobin (Betke et al. 1956). In addition, infant erythrocytes demonstrate less NADH-dependent methemoglobin reductase activity than do adult red blood cells. This enzyme is responsible for the normal reduction of methemoglobin (Ross and DesForges 1959). Newborns are therefore at a higher risk of methemoglobinemia than older infants, children, or adults for three reasons: (1) greater opportunity for reduction of nitrate to nitrite in the stomach; (2) hemoglobin more readily oxidized to methemoglobin; and (3) lower activity of the enzyme system that restores the oxygen-transporting capability of the blood pigment.

Methemoglobinemia in newborn children has only rarely resulted from eating processed vegetables (spinach puree, Holscher and Natzschka 1964, Sinios and Wodsak 1965; carrot juice, Keating et al. 1973) or cured meats containing excessive amounts of sodium nitrite (frankfurters and bologna, Orgeron et al. 1957, Bakshi et al. 1967, Henderson and Raskin 1972; nitrite-treated fish, Singley 1962). The low incidence of food-induced infant methemoglobinemia probably reflects both the rarity of ingestion of nitrate/nitrite from such sources during infancy and the slower absorption of the ion from foods than from water. Almost all cases of nitrate-induced methemoglobinemia in the United States have resulted from the ingestion of private well water used to make infant formula (Lee 1970).

Comly (1945) was the first to demonstrate that most cases of infant methemoglobinemia were associated with the use of well water containing more than 10 mg NO_3^--N/l. Sattelmacher (1962) found that only 3 percent of 473 cases of infant methemoglobinemia were associated with drinking water containing less than 9 mg NO_3^--N/l. In an analysis of

745 German cases of methemoglobinemia caused by nitrate in water, Simon et al. (1964) reported that more than 97 percent of the cases had private wells as their water source. Of those cases, 84 percent involved water containing more than 22 mg NO_3^--N/l, and 10 had nitrite in the water. Only 2 percent of the cases involved infants older than three months of age. The mortality rate was 8.6 percent of the ill children.

Shearer et al. (1972) studied infant methemoglobinemia and high nitrate groundwater in California and suggested that babies with respiratory illness or diarrhea, who can have methemoglobin levels exceeding 6 percent independent of dietary nitrate, are at a much greater risk from nitrate-induced methemoglobinemia.

Kohl (1973) has pointed out that additional subsets of the population may be unusually susceptible to nitrite-induced methemoglobinemia. The occurrence of the disease is elevated among Alaskan Eskimos and Indians (Scott and Hoskins 1958) because of a lack of NADH-methemoglobin reductase activity in the red blood cells in those populations (Scott and Griffith 1959). The distribution of this hereditary deficiency is independent of sex and age. Of 203 people examined, three lacked in reductase activity and were methemoglobinemic, and 22 had about half the normal activity of the red blood cell NADH-methemoglobin reductase (Scott 1960).

Erythrocyte glucose-6-phosphate dehydrogenase deficiency has been demonstrated in approximately 7 percent of black males in the U.S. (Carson et al. 1956, Gross et al. 1958) and in some Caucasian ethnic groups, including Sardinians, Sephardic Jews, Greeks, and Iranians (see Tarlov et al. 1962). Individuals with this deficiency are believed to be less able to reduce methemoglobin to hemoglobin, and thus should be more sensitive to nitrite poisoning. Kohl (1973) examined nine black males who were deficient in this enzyme, but found no elevated methemoglobin levels; however, the subjects had not been exposed to high nitrite intake and might have responded differently under nitrite stress.

Pregnant women also may be at higher risk. Skrivan (1971) found methemoglobin levels as high as 10 percent of total hemoglobin in pregnant Czechoslovakian women in their third trimester, but he did not determine environmental levels of nitrate and nitrite. In contrast, Kohl (1973) was unable to demonstrate elevated methemoglobin levels in pregnant women who used drinking water containing 5 to 9 mg NO_3^--N/l or less.

Kohl (1973) pointed out that individuals with chronically reduced stomach acidity caused by such diseases as gastric ulcer, pernicious anemia, adrenal insufficiency, chronic gastritis, or gastric carcinoma would be more susceptible to bacterial reduction of nitrate to nitrite in the stomach, and therefore could be at greater risk of methemoglobinemia.

Goldsmith and coworkers (1975) measured methemoglobin levels in blood of elementary school children, male high school student athletes, and commuting adults in six areas of the Los Angeles basin. The different areas were selected, in part, on the basis of average levels of air pollution, including nitrates (PANs). Nitrate and nitrite ingestion through foods and drinking water was not measured. In the school children (sample size of 262), mean methemoglobin levels, expressed as percent of total hemoglobin (± standard deviation), ranged from 1.37 (±0.50) percent in one area of the basin to 2.11 (±0.37) percent in another area; for the athletes (sample size of 136), the means ranged from 1.38 (±0.39) percent to 2.09 (±0.77) percent. Methemoglobin levels were slightly higher in adults commuting to downtown Los Angeles; over a six-week period, means for that group ranged from 1.67 (±0.21) percent to 3.40 (±0.31) percent. All three populations demonstrated an unexplained asymmetric distribution of methemoglobin levels; 5 to 10 percent of the population had levels above approximately 2.5 percent. Methemoglobin levels did not correlate well with either air pollutant levels or cigarette smoking.

Shuval and Gruener (1972) point out that although water supplies may contain large amounts of nitrate, the drinking habits of the population must be considered in risk assessments. For example, no difference in methemoglobin levels was found between infants in areas of Israel with 1 mg NO_3^--N/l of drinking water and infants in areas with 10 to 20 mg NO_3^--N/l, probably because only 6 percent of the infants were fed powdered milk reconstituted with tap water; the other infants were breast-fed or given whole cow's milk.

Gelperin et al. (1971) demonstrated a trend of lower methemoglobin levels in small groups of Illinois mothers and their newborn infants with lower levels of nitrate in the drinking water. However, no estimates of water intake or dietary nitrate levels were given.

In the most comprehensive study available on the incidence in the United States of infant methemoglobinemia caused by ingestion of water containing nitrate, Walton (1951) summarized data reported by the American Public Health Association (see Table 9.3). The data were obtained by a questionnaire survey of state health agencies. Efforts were made to restrict the results to those cases definitely associated with water supplies containing nitrate. Despite the shortcomings of the study in terms of clinical diagnosis and water analysis, the table demonstrates the rarity of

TABLE 9.3 Reported Cases of Nitrate Water-Induced Infant Methemoglobinemia Classified According to Nitrate-Nitrogen Concentration of Water Used in Feeding Formula

	Methemoglobinemia		Number of Cases Associated with Indicated Ranges of NO_3-N Concentration (ppm)						
State	Reported Cases	Reported Cases	0-10	11-20	21-30	31-50	51-100	100+	Number of Cases for Which Data are Available
California	1	0	0	0	0	0	1	0	1
Georgia	6	3	–	–	–	–	–	–	0
Illinois	75	6	0	1	2	2	12	11	28
Indiana	1	0	0	0	0	0	1	0	1
Iowa	Several	11	0	0	0	0	1	1	2
Kansas	13	3	0	0	1	1	2	8	12
Michigan	7	0	0	0	0	0	0	7	7
Minnesota	139	14	0	2	25		53	49	129
Missouri	2	0	0	0	0	0	0	2	2
Nebraska	22	1	0	1	0	4	9	8	22
New York	2	0	0	0	0	0	1	0	1
North Dakota	9	1	0	1	1	0	0	6	8
Ohio	0	0	0	0	0	0	0	0	0
Oklahoma	0	0	0	0	0	0	0	0	0
South Dakota	Several	0	–	–	–	–	–	–	–
Texas	0	0	0	0	0	0	0	0	0
Virginia	1	0	0	0	0	0	1	0	1
TOTAL	278+	39	0	5	36		81	92	214
Percent of Total			0.0	2.3	16.8		37.8	43.1	100.0

SOURCE: APHA (1950).

methemoglobinemia in populations where nitrate-nitrogen concentrations in drinking water are below 10 mg/liter.

Infants less than 60 days old normally have methemoglobin levels averaging 2.7 percent of total hemoglobin, independent of nitrate in drinking water (Shearer et al. 1972). Clinical signs of cyanosis are apparent when methemoglobin levels exceed 5 percent. Newborns weigh between 2.5-4.5 kg and drink 400-700 ml water a day; three-month-old infants, weighing 4.5-7.5 kg, drink 700-1100 ml water a day (calculated from growth and water requirements given in Ziai et al. 1975). With these facts in mind, Winton et al. (1971) estimated the amount of nitrite needed to oxidize 10 percent of the total amount of hemoglobin in an infant, and converted this figure to the amount of nitrate required to provide the nitrite. Their results indicated that a one-month-old child would have to consume approximately 13 mg of nitrate-N per day to develop clinically recognizable cyanosis, the first detectable sign of methemoglobinemia. For two-month-old infants, approximately 10 mg of NO_3^--N per day would be required, and for three-month-old babies the amount is about 11 mg NO_3^--N. Although these estimates are based on many untested assumptions and should not be interpreted literally, they suggest that infants in the first three months of life may get all the nitrate they can tolerate just from drinking water that contains the maximum concentration permitted by present regulatory standards. In contrast, the data in Table 9.3 indicate that no cases of methemoglobinemia were associated with drinking water containing less than 10 mg NO_3^--N/l, and only 2.3 percent of the cases were associated with nitrate-nitrogen levels between 10 and 20 mg per liter.

It appears therefore that a level of 10 mg NO_3^--N/l (the current U.S. Public Health Service drinking water standard) affords reasonable protection to the majority of newborns against methemoglobinemia derived from nitrate-contaminated water supplies. Purely from the perspective of preventing methemoglobinemia, there is little evidence to support a more stringent drinking water standard. On the other hand, use of water containing 20 mg nitrate nitrogen per liter or more seems likely to increase significantly the number of infants at risk, unless extensive public education programs alert the appropriate populations to avoid ingestion of high nitrate waters by young infants.

Although methemoglobinemia is well-recognized and unlikely to be a problem in urban areas or areas with adequate medical facilities, it may be more important in poor and underdeveloped areas, in rural areas, and in areas where people do not have access to good health care facilities.

Other Acute Effects of Nitrite in Humans and Livestock

The nitrite ion is a relaxant for smooth muscles and is used pharmacologically to dilate blood vessels in the periphery of the body. Nitrite relaxes all smooth muscles without blocking the reflexes that attempt to compensate for the lowered blood pressure resulting from the vasodilation. These reflex actions can overcome the relaxant effect of the nitrite and the end result can be an increase rather than a decrease in smooth muscle tone. The acutely toxic action of nitrite, other than methemoglobinemia, is almost wholly related to its cardiovascular effects. Decreased blood flow to the brain resulting from vasodilation in the periphery of the body can produce headaches and dizziness, and a rapid lowering of blood pressure may develop when a sudden change in posture occurs. This may be the basis of the "Hotdog Headache" syndrome, discussed by Henderson and Raskin (1972).

Turner and Kienholz (1972) have reviewed nitrate/nitrite toxicity in livestock; the observed effects are qualitatively similar to those seen in humans. The doses that produce toxicity in animals, however, are much higher, and are highly dependent upon rate of food and water consumption (Crawford et al. 1966). The incidence of nitrate poisoning of livestock is thought to be large (NRC 1972), but relatively few reports of such toxicity appear in the literature (Bradley et al. 1940, Jones et al. 1966, Turner and Kienholz 1972, Olson et al. 1972, Deeb and Sloan 1975). Moreover, the veterinary literature has conflicting reports on the effects of nitrate and nitrite on the reproduction of livestock. Some reports suggest that nitrate/nitrite increases the number of abortions in cattle, but more reports fail to support this (Deeb and Sloan 1975).

Shuval and Gruener (1972) found that pregnant rats developed higher methemoglobin levels than non-pregnant rats when both were given drinking water with the same nitrite content. These authors reported a dose-related decrease in litter size, an increase in pup mortality, and a decreased growth rate in the progeny of pregnant rats that were given 2000 or 3000 mg sodium nitrite per liter (406 and 609 mg NO_3^--N/l) in the drinking water.

It is unlikely that under environmental conditions enough N-nitroso compounds could be formed from nitrate or nitrite precursors to provide an acutely toxic dose; therefore, the relation between nitrate and nitrite and toxic effects of N-nitroso compounds is discussed below in the section on chronic effects.

CHRONIC TOXICITY

Nitrate

Little is known about the direct chronic effects of nitrate on biological systems; as is true for acute toxicity, most chronic toxicity of nitrate is thought to derive from its reduction to nitrite. Chronic nitrate poisoning in livestock produces anorexia, dyspnea, restlessness, vasodilation, lowered blood pressure, abortion, and reduced lactation. Induced vitamin A deficiency and thyroid depression also have been attributed to chronic nitrate poisoning (Blood and Henderson 1968, Dollahite and Holt 1970). Nitrate and a number of other anions interfere with the iodide-trapping mechanism of the thyroid of the rat (Wyngaarden et al. 1953, Bloomfield et al. 1961, Lee et al. 1970), but this effect has not been produced in cattle (Jainudeen et al. 1965) or dogs (Kelley et al. 1974). Thyroid abnormalities have been reported in sheep grazed in pastures where fertilization with nitrogen was practiced (Reid et al. 1969).

Chronic toxic effects on the cardiovascular system have been observed among workers exposed to organic nitrates in the explosives industry. The effects reported include severe headaches, elevated diastolic blood pressure, lowered pulse pressure, an increased risk of angina pectoris, and in some cases, sudden death (Carmichael and Lieben 1963, Trainor and Jones 1966).

Petukhov and Ivanov (1970) reported that Russian children aged 12 to 14 years, whose drinking water contained an average of 105 mg nitrate/l (24 mg NO_3^--N/l), responded to various stimuli slightly more slowly over a period of trials than did children whose water supply contained an average of 8 mg nitrate/l (1.8 mg NO_3^--N/l). Other differences in the drinking water and diet were not reported. At drinking water concentrations between 23.7 and 44.6 mg NO_3^--N/l, Petukhov and coworkers (1972) observed cyanosis, lowered blood pressure, and methemoglobin in all sick children and adolescents. Increased pulse rates were observed in children under six years, and increased respiratory rates were found in children under 13 years. These reports require confirmation.

A possible link between inhaled nitrate and cancer has been reported in preliminary form by Ballou et al. (1976), who found that 4 out of 58 Wistar rats that inhaled an aerosol of 0.27 N nitric acid for 30 minutes (approx. 7 times the Threshold Limit Value of 5 mg/m^3 for occupational exposures) developed osteosarcomas. This observation needs confirmation and, if upheld, further study is required to determine whether nitric acid per se is a carcinogen, or whether it leads to the in vivo formation of a different active compound.

Nitrite

Nitrite has been shown to produce reduced motor activity that apparently is unrelated to methemoglobinemia (Behroozi et al. 1971, Shuval and Gruener 1972). Mice given drinking water containing up to 2000 mg sodium nitrite/l (408 mg NO_2^--N/l) showed a dose-related methemoglobinemia and a reduction of overall motor activity. Ascorbic acid lowered the methemoglobin in nitrite-treated animals to near control levels, but motor activity remained low and equivalent to nitrite-treated mice not given ascorbic acid.

The chronic effect of sodium nitrite and potassium nitrate on laying hens was investigated by Tomov (1965). Birds given 100-200 mg sodium nitrite per day for 300 days and then 400 mg for 60 days, or 1-2 g potassium nitrate daily for 300 days then 4 g for 60 days, all showed leg weakness and chronic muscular spasms by the 138th day. The signs were particularly pronounced in groups given acidified drinking water. Postmortem analysis revealed greyish yellow nodules on the esophageal mucosa, as seen in vitamin A deficiency, and atrophy of ovaries and testes. Liver vitamin A levels were depressed, and up to 70 percent of the eggs produced by all treated hens contained blood spots, compared to 2 percent from untreated hens. There was no loss of appetite, and the effects on egg production were not stated.

Rats given 2000-3000 mg $NaNO_2$ (408-612 mg NO_2^--N) per liter in drinking water for two years suffered heart and lung damage, and progeny of pregnant rats drinking this water had high mortality rates and poor growth and development. Rats given 100-2000 mg $NaNO_2$ (20-408 mg NO_2^--N) per liter in drinking water for two weeks or more developed abnormal EEG patterns, which persisted after exposure to nitrite ceased (Shuval and Gruener 1972).

On the other hand, Shank and Newberne (1976) fed two complete generations of rats a diet to which 1,000 mg/kg sodium nitrite was added. Residual in the diet after mixing was 240-460 mg $NaNO_2$/kg or 49-93 mg NO_2^--N/kg. They observed no effects on litter size, infant mortality, growth rate, or longevity. However, the nitrite-fed rats developed a high incidence of lymphoreticular tumors (27 percent compared to an incidence of 6 percent in the control group), often accompanied by infiltrating leukemic cells. The incidence of all tumors was 61 percent in the treated animals versus 18 percent for the controls.

N-Nitroso Compounds

The toxicity of the N-nitroso compounds has been reviewed several times recently (Magee and Barnes 1967, Druckrey et al. 1967, Magee 1971, Shank 1975, Crosby and Sawyer 1976). N-Nitrosamines seem to require metabolic transformation to active intermediates and are most toxic to the liver and kidneys. N-Nitrosamides, on the other hand, tend to decompose at physiological pH, probably to active intermediates similar to those produced from nitrosamines, and thus they often act locally. The acute toxicity of these compounds, expressed as single-dose oral LD_{50} values in adult rats, ranges from 18 mg/kg body weight for methylbenzylnitrosamine to more than 7500 mg/kg for N-nitrosoethyl-2-hydroxylethylamine (Druckrey et al. 1963a). The nitroso compounds are acutely toxic to every animal species tested and also are poisonous to humans (Freund 1937, Barnes and Magee 1954).

Many N-nitroso compounds are mutagenic if assayed by the appropriate system. Bacterial assays for nitrosamines require supplementation with animal-derived enzymes to detect mutagenicity, because the bacteria are not capable of activating these compounds. Nitrosamides, which decompose spontaneously in the bacteriological medium, do not require enzyme activation. More than forty N-nitroso compounds have been shown to be mutagenic in microbial systems (McCann et al. 1975, Montesano and Bartsch 1976), but little testing has been done for the mutagenicity of N-nitroso compounds in mammalian systems.

The toxicity profile of N-nitroso compounds also includes teratogenesis. Von Kreybig (1965) reported fetal death and resorption and malformations of the brain and extremities in progeny from rats given a single dose of 20 mg methylnitrosourea per kilogram body weight on the 13th or 14th day of gestation. Near-LD_{50} levels of N-nitrosoalkylureas and N-nitrosoalkylanilines (but not N-nitrosamines), given to pregnant rats on the 9th or 13th day of gestation, produced malformations of the eye and brain in the progeny (Napalkov and Alexandrov 1968).

The N-nitroso compounds are an important class of chemical carcinogens for several reasons:

- As illustrated in Table 9.4, every vital tissue is susceptible to the carcinogenic action of this class of compounds.

- In several instances, a single exposure of infant animals has induced tumors as the animals reached adulthood (Magee and Barnes 1959, Druckrey et al. 1963b). Single-exposure induction of tumors also can occur in adult rats

TABLE 9.4 Tumor Sites of Some N-Nitroso Compounds

Site	Compound	Reference
Skin	Methylnitrosourea	Graffi and Hoffmann (1966)
Nose	Diethylnitrosamine	Herrold (1964)
Nasal sinus	Dimethylnitrosamine	Druckrey et al. (1964)
Tongue	Nitrosohexamethyleneimine	Goodall et al. (1968)
Esophagus	Nitrosoheptamethyleneimine	Lijinsky et al. (1969)
Stomach	Ethylbutylnitrosamine	Schmähl et al. (1963)
Duodenum	Methylnitrosourea	Druckrey et al. (1963b)
Colon	Cycasin	Laqueur (1965)
Lung	Diethylnitrosamine	Dontenwill and Mohr (1961)
Bronchi	Diethylnitrosamine	Dontenwill and Mohr (1961)
Liver	Dimethylnitrosamine	Magee and Barnes (1956)
Pancreas	Nitrosomethylurethane	Druckrey et al. (1968)
Kidney	Dimethylnitrosamine	Magee and Barnes (1959)
Urinary bladder	Dibutylnitrosamine	Druckrey et al. (1962)
Brain	Methylnitrosourea	Druckrey et al. (1965)
Spinal cord	Nitrosotrimethylurea	Ivankovic et al. (1965)
Thymus	Nitrosobutylurea	Yokoro et al. (1970)
Lymph nodes	Ethylnitrosourea	Vesselinovitch et al. (1971)
Blood vessels	Nitrosomorpholine	Bannasch and Mueller (1964); Shank and Newberne (1976)
Bone	1-(1-hydroxyethyl)-1-nitrosourea	Pelfrene et al. (1976)

SOURCE: Adapted from Shank (1975).

that are pregnant (Druckrey and Ivankovic 1969) or recovering from a partial hepatectomy (Craddock 1971).

- N-nitroso compounds can induce cancers transplacentally. Brain and spinal cord tumors (Ivankovic and Druckrey 1968) and renal tumors (Wrba et al. 1967) were found in progeny of pregnant rats treated with N-nitrosoethylurea. Diethylnitrosamine has induced transplacentally tracheal papillomas in rats (Mohr et al. 1966).

- Carcinogenic N-nitroso compounds have been demonstrated to be contaminants of urban air (Fine et al. 1976, 1977a) and the food supply (see Crosby and Sawyer 1976, and Table 9.2).

Epidemiological Assessment

A few epidemiological studies have attempted to associate environmental nitrates, nitrites, and nitroso compounds with human cancer. A problem common to all the early studies was the inability to measure with high specificity N-nitroso compounds in biological samples. For example, African studies associating esophageal cancer with a nitrosamine in a local alcoholic beverage (McGlashan 1969) and a study relating carcinoma of the cervix with nitrosamine formation in the vagina of South African women (Harrington et al. 1973) were done without the advantage of mass spectroscopic confirmation that is needed to identify the nitrosamines.

The International Agency for Research on Cancer has investigated the possible association between N-nitroso compounds in the diet and esophageal cancer in specific areas of Iran and France, where these tumors occur at a high rate, and in nearby areas where the tumor rates are not elevated (Bogovski 1974). Complete studies of possible sources of exposure to the carcinogens have not been made, but 15 of 29 samples of cider contained 1 to 10 μg/kg DMN and two samples also contained DEN (less than 1 μg/kg). Correlations between dietary intake of N-nitroso compounds and incidence of esophageal cancer have not yet been made.

The Chinese conducted a similar study in the Anyang region, where it is claimed that approximately 20 percent of all deaths (not just cancer deaths) result from esophageal cancer (Coordination Group 1975). Twenty-three percent of the food samples from areas with the highest cancer rates were reported to contain DMN, DEN, and methylbenzyl nitrosamine. However, confirmation of this analysis by gas chromatography and mass spectroscopy is required before the finding can be accepted. Dietary nitrite levels were higher in areas of high cancer incidence than in low incidence areas. Chickens in areas where there were high rates of esophageal cancer in humans also had a high incidence of similar tumors, suggesting an environmental etiology for the disease.

Zaldivar and Wetterstand (1975) demonstrated a linear regression between death rates from stomach cancer and the use of $NaNO_3$ as fertilizer in various Chilean provinces. Fertilizer use was presumed equatable to human exposure to nitrates and nitrosamines, but no actual exposure data were reported. Armijo and Coulson (1975) have shown similar correlations. These reports suggest that nitrate from fertilizer enters the diet in meat, vegetables, and drinking water, is reduced to nitrite by microbial action, and thus is available for in vivo nitrosation of secondary amines in the diet, to form carcinogenic nitrosamines, which induce stomach cancer. As yet, no scientific data have been gathered that support this hypothesized etiology, and the suggested causal relationship remains highly speculative.

Hill et al. (1973) correlated differences in rates of stomach cancer with the nitrate content of drinking water in two English towns; but again, the evidence required to demonstrate a causative role for nitrate is not available. Gelperin et al. (1976) compared death rates ascribed to cancer of the gastrointestinal tract and liver with nitrate levels of drinking water in the same three unmatched population groups in Illinois used in the infant mortality study cited earlier in this chapter. No significant differences in cancer rates were found among the three groups (the level of significance was not stated). It is doubtful, however, whether the available mortality data permitted an analysis that could have detected an effect in the high-nitrate population.

Increased rates of stomach cancer have been observed in Japan in occupational groups and other populations characterized by an unusually high consumption of salt-preserved foods (Sato et al. 1959); presumably, these foods are high in nitrate and perhaps in nitrite.

Appendix B of this report presents a statistical analysis that correlates the incidence of cancer mortality with estimated exposures of urban populations in the United States to various environmental and dietary factors. Strong positive correlations were shown between the aggregate rate of cancer mortality and components of the diet, particularly nitrite and protein; however, insufficient biological evidence is available to confirm the hypothesized causal pathway (involving formation of N-nitroso compounds from nitrite and amines, reacting in the stomach). While the reported correlations offer some grounds not to reject that hypothesis, the statistical analysis cannot provide positive evidence of such an etiology, nor can it indicate the magnitude of the possible role of nitrate and nitrite.

Toxicological Assessment

A qualitative judgment of the risk of human exposure to a substance can be made on a toxicological basis when sufficient data are available. N-nitroso compounds are carcinogenic in every species tested, including rats, mice, guinea pigs, rabbits, dogs, monkeys, grass parakeets, and pigs (Schmähl and Osswald 1967), hamsters (Dontenwill and Mohr 1961), hedgehogs (Graw et al. 1974), mink (Koppang and Rimslatten 1975), and trout (Halver et al. 1962).

Considerable evidence exists to indicate that the mechanism of carcinogenic action of nitrosamines involves their metabolism to intermediates which alkylate DNA at specific sites. Montesano and Magee (1970) observed that human liver slices metabolize dimethylnitrosamine to a DNA-methylating agent at a rate only slightly slower than do rat liver slices. There appears to be no toxicological reason why humans should not be sensitive to the carcinogenicity of N-nitroso compounds.

Little information is available on the dose-response characteristics of the carcinogenicity of any N-nitroso compound in test animals. Terracini et al. (1967) reported a liver tumor in one rat out of 26 fed a diet containing 2 mg/kg (2 ppm) DMN. Moiseev and Benemanskii (1975) found an increase in the incidence of malignant liver and kidney tumors in male but not female rats (and not in mice of either sex) when the animals continuously inhaled air containing 0.2 mg/m^3 of DMN for more than two-thirds of their lifetime (17-month exposure for mice, 25-month exposure for rats), but a concentration of 0.005 mg/m^3 produced no increase in tumors. Mink, the most sensitive species to DMN toxicity and carcinogenicity, developed tumors when fed the toxin at a daily dose of 50 μg/kg of body weight, twice a week (Koppang and Rimslatten 1975).

These dose-response data do not support reliable extrapolation to a no-effect level of exposure (especially in humans), but the question of "safe" exposures can be approached from the basis of the probable mechanism of carcinogenic action. It is conceivable that a single exposure could alter the DNA of a cell in such a way (e.g., alkylation of DNA) that the daughter cell would be capable of forming a tumor, and thus, the only "no-effect" exposure would be no exposure at all. This view is probably unrealistic because it does not consider the natural protective mechanisms of the body: the tumor cell could be destroyed immunologically, or the aberrant (alkylated) DNA could be restored enzymatically to its original template.

Kleihues and Margison (1976) and Pegg (1977) have demonstrated that DNA alkylated in animals treated with nitroso compounds is more efficiently repaired when only a single low dose is given, and that the efficiency of DNA repair diminishes rapidly as the dose increases or if the dose is repeated daily. Maher et al. (1977) and McCormick et al. (1977) have shown that at high doses the carcinogen 7,8-dihydrodiol-9,10-epoxybenzo(a)pyrene binds to DNA in human fibroblasts, causing mutations and cell death, but at low doses the DNA is repaired before the cells divide, and the mutagenic effect does not occur. Such results strongly support the hypothesis that protective mechanisms are significant when cells are exposed to low doses of toxicant, but become saturated, overloaded or inhibited at higher doses.

It seems likely also that in some instances the metabolic detoxication pathway may be rapid compared to the activation pathway. In such cases, low doses of a precarcinogen would follow only the detoxication pathway, and sufficient substrate would be available for activation to the ultimate carcinogen only when higher doses were administered; the activation of vinyl chloride appears to exhibit such a dose dependency (Hefner et al. 1975). These examples of dose-dependent pharmacokinetics for cellular interactions of carcinogens argue in favor of the concept that some low exposure to a carcinogen can occur that will not lead to an unalterable course of carcinogenesis. There is not yet sufficient knowledge, however, to permit a determination of the minimum effective carcinogenic exposure.

It can be argued that the formation of a tumor can be traced back to the interaction of a single molecule of carcinogen with DNA to transform the cell. While such a mechanism cannot be ruled out, it does not mean that any exposure of an animal to a carcinogen will necessarily produce a tumor. The number of molecules of a carcinogen that constitute an exposure that will bring about the transformation of a single cell is a statistical question; it is a key question to be dealt with in a risk assessment.

Quantitative Estimation of Risk

It is presently impossible, for reasons discussed above, to make a scientifically reliable estimate of the risk of human cancer posed by actual environmental exposures to nitrates and N-nitroso compounds. Nevertheless, an attempt to make even a gross, first-order approximation of this risk may be valuable, if only to place the environmental hazard posed by these pollutants in some perspective.

Several models are available to estimate the risks to humans of low-dose exposures to carcinogens by extrapolation from data on effects of high-dose exposures in animal species (Hoel et al. 1975, Guess and Crump 1976, Crump et al. 1976). The use of such models requires many assumptions that have not been (and perhaps cannot be) scientifically verified. For instance, it must be assumed that humans and the animal species tested are essentially similar in the way they metabolize a carcinogen and in their sensitivity to its effects. The mathematical form of the dose-response function (e.g., linear) must be assumed. If it is further assumed that the curve passes through the origin, the effects of the body's defense mechanisms, discussed above, may not be accounted for. Such models also cannot account for the genetic heterogeneity and variable susceptibility of the human population; nor can they deal with the possible interactions of simultaneous exposures to the many agents in the environment. Although it is clear that research is still needed to advance the methodology, the techniques have produced results of some value when they have been applied to specific environmental contaminants. (See, for instance, the report of the Panel on Low Molecular Weight Halogenated Hydrocarbons, NRC 1978).

Despite the above deficiencies and the lack of adequate information on human exposure to carcinogenic N-nitroso compounds, we have attempted a crude, preliminary assessment of the risk of human cancer posed by nitrosamines. Details of the assumptions and methods used in that assessment are presented in Appendix C of this report. In brief, two different approaches were used to estimate human exposure to nitrosamines derived from ingested nitrate and nitrite. A mathematical model described in Guess et al. (1977) was then used to estimate the risk of cancer represented by the calculated rates of exposure. Some limited data on DMN levels in air (Fine et al. 1977a) permit a rough estimate of possible human exposure by that route; but dose-response data on cancer from inhaled nitrosamines are not adequate to support an assessment for such exposures (see Appendix C).

When an exposure estimate based on measured DMN levels in the blood of one individual (Fine et al. 1977b) is used, the calculated risk of liver cancer is extremely small. If exposure to nitrosamines is calculated from estimates of average ingestion of nitrate and nitrite in food and water, and from arbitrary assumptions about the efficiency of in vivo conversion of nitrate to nitrite and synthesis of nitrosamines from nitrite and amines, a larger estimate of risk results (see Appendix C). To reiterate, however, a great many assumptions must be made in order to conduct such an analysis; and the scientific evidence is not available that would permit us to judge the validity of most of those assumptions. These uncertainties prevent our knowing which of the two estimates might better reflect the actual risk associated with ingestion of nitrate and nitrite, or in fact, whether either estimate is accurate even within one or two orders of magnitude. A more credible quantitative assessment of risk must wait for research to answer a number of pertinent questions. Until such knowledge is available, we believe it is prudent to make every reasonable effort to minimize human exposure to carcinogenic N-nitroso compounds.

REDUCTION OF STRATOSPHERIC OZONE AND SKIN CANCER

The possible effects of nitrates on the stratospheric ozone layer are discussed in Chapter 7. The biological impact of decreasing the ozone in the atmosphere has been reviewed in detail elsewhere (Urbach 1969; Emmett 1973; NRC 1973, 1975), and only an overview is presented here.

Solar radiation is both beneficial and detrimental to life on earth. The most detrimental radiation is in the wavelength range of 286-320 nm. Oxygen and ozone in the atmosphere absorb solar ultraviolet (uv) radiation, and virtually no radiation below 286 nm reaches the earth's surface. A decrease in the amount of ozone in the atmosphere would result in an increase in the intensity of radiation of wavelengths between 225 and 320 nm at the earth's surface; an increase in the incidence of biological disorders sensitive to this detrimental radiation probably would follow such a change.

Sunlight has many harmful effects on humans, including sunburn, wrinkling and drying ("aging") of the skin, and phototoxicity, which is an increase in the sensitivity of skin to uv caused by photoactivation of a variety of environmental chemical agents. Sunlight is involved less directly in Lupus erythematosus, porphyria, psoriasis, Herpes simplex, xeroderma pigmentosum, and many other skin-related disesases. The most serious effect, however, is the induction of skin cancer.

Several lines of evidence support, but do not prove, an etiologic role for sunlight in the development of skin cancer:

- Skin cancer is much more common in Caucasians than in races with more pigmented skin. The skin pigment melanin absorbs uv radiation that penetrates the skin and thereby protects adjacent cells in the skin. Sunlight stimulates pigment production (suntanning) in most Caucasians, but people of Celtic origin, who do not tan readily, have higher rates of skin cancer (Gellin et al. 1965, 1969; Lee and Issenberg 1972).

- Skin cancers occur more often on areas of the skin that are frequently exposed to sunlight and among people who are more often exposed to sunlight because of habit, occupation, climate, or geography (Auerbach 1961, Siverston and Searle 1970, Lee and Merrill 1970).

- Repeated exposure of mice to uv radiation (296-313 nm) results in dose-related incidences of skin cancer (e.g., Blum et al. 1941, Rusch et al. 1941). Radiation treatments produce epidermal (the superficial layer of skin) and especially dermal (deepest layers of the skin) tumors in mice (Grady et al. 1941). In humans, skin cancers are of epidermal origin only (Blum 1940). Mouse epidermis from the ear, the site of uv-induced tumors, transmits several times more uv radiation between 296 and 320 nm than does human epidermis; thus, more radiation in this energy range reaches mouse dermis than reaches human dermis (Lucas 1931, Kirby-Smith et al. 1941).

- Deoxyribonucleic acid (DNA), the genetic material of the cell, absorbs and is damaged by ultraviolet light (Wacker et al. 1960, Setlow 1966, Johns et al. 1962). The photochemical dimerization of pyrimidines in DNA is thought to be largely responsible for the transformation of a normal cell to a cancer cell.

Skin cancer is the most frequent form of cancer in the United States, afflicting from 50 to 200 of every 100,000 white males per year (American Cancer Society 1969). However, skin cancer accounts for less than 2 percent of all cancer deaths (Segi and Kurihara 1972). Three epidermal cell types are involved in human skin cancer: squamous cells, basal cells, and melanocytes. The outermost layer (stratum corneum) is made up of flattened, anucleated, cornified cells that are dead and do not give rise to tumors. In the thicker portions of skin, the stratum granulosa contains a few layers of living diamond-shaped cells, but these have not been shown to be involved in skin cancer. The thickest layer of skin, the stratum spinosum, is composed of cuboidal cells that undergo mitosis during skin regeneration after injury. The squamous cell carcinomas that arise from this portion of the epidermis are common malignant tumors of the skin. In white U.S. males, the average yearly rate of this form of skin cancer is about 12 per 100,000, and the mean age of incidence is about 70 years (Haenszel 1963). In sunny areas, the incidence can be 10 times higher (Schreiber et al. 1971). Because of effective therapy, only about 1 percent of the squamous cell carcinoma cases are fatal. Histologically similar tumors that occur in the stratum spinosum are the rapid-growing and often remissive keratoacanthomas.

The most common form of human skin cancer (38 to 200 cases per 100,000 white U.S. males per year; Haenszel 1963) is the basal cell epithelioma (a carcinoma) which arises from a single layer of cylindrical cells on the basement membrane. This form of cancer rarely metastasizes and can be treated effectively. Also present in the deepest layer of the epidermis are melanocytes, the pigment-producing cells; transformation of these cells results in highly malignant, rapidly metastasizing melanomas. These tumors occur much less frequently than squamous cell carcinomas or basal cells epitheliomas. A rate of from two to three cases per 100,000 white U.S. males per year has been reported (Lee and Merrill 1970); rates up to 16 per 100,000 per year may occur in Queensland, Australia (Davis et al. 1966). Melanomas, however, are much more often fatal (about 40 percent of the patients die within 5 years); as a result, the mortality rate from melanoma is comparable to the rate from all other types of skin cancer. The mean age for malignant melanoma is about 20 or more years younger than for the other forms.

The induction of all three cell types of skin cancer appears related to sunlight. The correlation is stronger for squamous cell carcinoma and basal cell epithelioma. Susceptibility to these forms of cancer is related to inability to tan and lightness of skin color (Gellin et al. 1965); the latter (but not the former) has also been correlated with susceptibility to melanoma (Gellin et al. 1969). However, resistance to sunlight-induced skin cancer is not wholly a matter of skin pigmentation. As is true for other tissues, skin contains enzyme systems capable of detecting and repairing damaged DNA. The extent and integrity of the DNA repair system are in part genetically determined; however, it is not known whether this system is inducible, so that it could increase in activity to maintain the fidelity of genetic material under a stimulus of environmental change. If the system were inducible, a slow but steady increase in the intensity of solar radiation at the earth's surface might be compensated for by an increased ability to repair the radiation-induced damage. It appears from indirect evidence, however, that this may not be the case. The incidence of skin cancer is lower in populations living at high latitudes, where stratospheric ozone is high and solar uv radiation low, than in populations closer to the equator, where stratospheric ozone concentration is lower and uv radiation intensities are higher (Auerbach 1961). Apparently, populations at lower latitudes have not developed an increased capacity to repair skin DNA.

A recent study completed by the Climatic Impact Committee of the National Research Council contains several estimates of increases in the incidence of human skin cancer that would result from reduced stratospheric ozone concentrations (NRC 1975). Although there are many uncertainties in deriving such estimates, one conclusion seems inescapable: a reduction of the ozone concentration in the stratosphere will result in some increase in the intensity of solar uv radiation at the earth's surface, which in turn will increase the incidence of human skin cancer (squamous cell carcinoma, basal cell epithelioma, and malignant melanoma). The report concludes:

> "The only relationship that has been found consistently to be applicable to a number of different data sets from different sites is log incidence (or mortality) linearly dependent on uv irradiance. A 10 percent decrease in stratospheric ozone causes about a 20 percent increase in melanoma mortality. However, while a 1 percent decrease in stratospheric ozone causes roughly a 2 percent increase in the incidence of skin cancer, a 10 percent decrease in stratospheric ozone appears to give more than a 20 percent increase in the incidence of skin cancer--possibly a 30 percent increase."

The Council for Agricultural Science and Technology (CAST 1976) concluded that if the stratospheric level of NO_x were to double, the stratospheric ozone concentration would be reduced about 20 percent. A 10 percent reduction in the ozone concentration was estimated to increase the intensity of solar ultraviolet radiation at sea level by 30 percent, and probably to increase the rate of human skin cancer by 50 percent. Green et al. (1976) recently examined several models to estimate the biological amplification factor in the dose-response relationship between an increase in uv exposure and the resulting increase in non-melanoma skin cancer. All models gave values greater than unity for the factor, which is defined as the ratio of the percent increase in the incidence of non-melanoma skin cancer to a 1 percent increase in the dose of ultraviolet radiation. For the population of the central United States, the amplification factor is approximately 1.8, but it is as high as 2.5 in regions of higher radiation doses and as low as 1.5 in regions of lower doses. Obviously, the major difference in estimates of the impact a given depletion of stratospheric ozone will have on the incidence of human skin cancer is the biological amplification factor used.

The reduction in stratospheric ozone that could result from fertilizer use was estimated in Chapter 7 at from 1.5 to 3.5 percent by the year 2100, with a wide range of uncertainty (see Table 7.3). Assuming biological amplification factors of from 1.5 to 3.0 for the increase in incidence of skin cancer and 2.0 for the increase in skin cancer mortality following such a change, the health impacts of this ozone reduction can be calculated as follows. The incidence of skin cancer (squamous cell carcinoma, basal call epithelioma, and malignant melanoma) is approximately 50 to 200 patients per 100,000 people per year, depending on geographic location (exposure to the sun). An increase of from 2 to 10 percent in this rate would raise the incidence to 51 to 220 per 100,000 per year, or 2,000 to 40,000 additional skin cancer patients per year, assuming a white population of 200 million. The 1967 mortality rate for all forms of skin cancer in the white U.S. population was 2.6 per 100,000 per year (Segi and Kurihara 1972). A 3 to 7 percent increase in this rate would give an expected 150 to 350 extra deaths per year in a population of 200 million.

If the "preferred estimate" in Chapter 7 of a 1.5 to 3.5 percent reduction of the ozone layer should prove to be valid, the resulting changes in skin cancer rates would be a health consequence of major importance. If, instead, the effect on the ozone layer should be much smaller, as Table 7.3 indicates it could be, the increase in cancer mortality might be an order of magnitude smaller, but could still lead to perhaps 15 to 35 added U.S. deaths per year. If, on the other hand, the decrease in ozone approached the upper limits suggested by Table 7.3, the consequences in terms of skin cancer could be catastrophic, although the full impact would not be felt for several centuries.

While this discussion has emphasized the impacts of ozone depletion on skin cancer morbidity and mortality in the United States, a change in the ozone layer would have global consequences for human health, and other nations at lower latitudes would be likely to experience larger increases in skin cancer rates (NRC 1975).

SUMMARY

Environmental levels of nitrate occurring in the United States rarely have a reported <u>direct</u> harmful effect on the health of humans or livestock.

Nitrite, the reduction product of nitrate, can present a serious risk to the health of infants who are less than three to six months old by inducing methemoglobinemia. This hazard, well recognized by the medical and public health communities, can be readily diagnosed and treated, and can be prevented by avoiding high-nitrate vegetables and drinking waters in preparing infant diets.

To establish and quantify causal relationships between environmental contaminants and disease, it is desirable to have mutually supporting evidence from several lines of investigation: toxicological experiments on laboratory animals; biochemical and pharmacological evidence of mechanisms of toxicity; and data drawn from human populations connecting observed clinical disease with exposure to the suspected agent. For nitrite-induced infant methemoglobinemia, adequate congruent evidence of these kinds is available and some clear dose-response relationships have been established. In contrast, the possible contribution of nitrates in the environment to exposures to N-nitroso compounds, and the quantitative impact of such exposures in terms of increased risk of cancer, at present cannot be clearly defined.

Certain foods, urban air in some locations, and tobacco smoke are the sources of most of the known human body burden of preformed carcinogenic N-nitroso compounds in the United States. Although the carcinogenicity of nitroso compounds has been amply demonstrated in laboratory animals, and in vivo formation of nitroso compounds in humans from nitrate and amine precursors seems likely to occur, the few epidemiological studies to date have been inadequate to establish any correlations between exposure to nitrate and cancer as valid causal relationships. Sufficient toxicological data are available, however, to indicate that humans are likely to be susceptible to the carcinogenicity of N-nitroso compounds. In our view, therefore, every reasonable effort should be made to minimize this body burden.

The contribution to that body burden by nitrosation reactions of precursors in the stomach, lungs, and other organs, although not yet quantified, may be greater than the other sources combined. Any action directed toward prevention of possible adverse effects on health should be based on knowledge of the relative significance of different routes of exposure. Much more information is needed before a quantitative evaluation of the risk inherent in human exposure to nitrates and nitrites can be made.

Available data on the relative importance of N-nitroso precursors (nitrate/nitrite and certain secondary and tertiary amines) to the formation of carcinogens in water supplies and the atmosphere are insufficient upon which to base a risk assessment.

Two estimates of human exposure to nitrosamines derived from dietary nitrate and nitrite, calculated from different assumptions, gave values that differ by a factor of more than 200. Risk assessments based on these calculated exposures gave comparably divergent estimates of the potential expected excess incidence of liver cancer that might result from nitrate and nitrite ingestion (see Appendix C). Both estimates were based on assumptions that lack the scientific evidence necessary to judge their validity. Whether either estimate approaches the actual risk associated with nitrate/nitrite ingestion is wholly undetermined.

The possible decrease in stratospheric ozone caused by anthropogenic nitrogen fixation could increase the incidence of human skin cancer by an amount proportional to the decrease in ozone that actually occurred. Various estimated magnitudes of impacts on the ozone layer attributable to this cause would be expected to lead to up to several thousand extra deaths from skin cancer per year in the United States, with much larger increases in skin cancer morbidity. The impact of the "preferred" projection of ozone depletion, 150 to 350 added deaths from skin cancer per year in the United States, although not imminent, would be a serious consequence.

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CHAPTER 10

TECHNIQUES AND STRATEGIES FOR THE CONTROL OF NITRATES IN THE ENVIRONMENT

INTRODUCTION

Society may choose to attempt to reduce the risk of adverse impacts on the ozone layer, ecosystems, or human health described in the preceding three chapters, by reducing the amounts or inputs of nitrogenous compounds in various compartments of the environment. This chapter briefly reviews the large body of information available on control techniques for specific nitrate pollution problems, and evaluates the effectiveness of different techniques for abating adverse environmental impacts. The estimated costs of control measures are reviewed here; some of these costs and the benefits of controls are also discussed in Chapter 11.

In general, there are three basic options for the control of any pollutant: (1) reduce pollution at the source by making or using less of the substance(s); (2) use best management practices in industrial or natural systems to minimize leakage or loss, or to maximize the cleansing effects of natural processes; and (3) collect and treat wastes to prevent pollutants from being discharged to the environment. Table 10.1 summarizes some applications of each basic control option to the major categories of nitrate sources.

In addition to the options presented in the table, other non-technical approaches may merit consideration in specific cases. For instance, if the objective is to reduce the risks to health of humans or livestock posed by high levels of nitrate in groundwater, the most effective solution might be to control exposures by providing an alternative supply of low-nitrate drinking water, rather than to attempt to control the sources of the nitrate contamination.

The control of nitrate-related environmental problems is difficult and complicated, and some control measures directed at preventing one problem may create others. For example, removal of nitrate from wastewaters can increase releases of ammonia or nitrous oxide to the atmosphere, or

TABLE 10.1 Options for the Control of Nitrogen Pollution

	Control Options		
Problem	Source Reduction	Process or Management Practices	Treatment
Point Discharges			
Sewage	Pretreatment of industrial waste	Separate sewage and storm water	Conventional treatment; nitrification/ denitrification; desalination; physical separation; chemical reaction; land disposal
Industry	Reduce product loss	Good housekeeping; process changes	Chemical reaction; biological treatment
Nonpoint Sources			
Fertilizers	Regulate rate, frequency and amount applied	Minimize runoff and leaching	Collect runoff and hold in ponds or wetlands
Farmlands	Use manure for fertilizer	Reduce erosion and runoff by vegetation, harvest and cultivation practices, structural devices	Collect and treat
Forest lands	Control use of fire retardants	Proper design of roads	Collect and treat
Urban lands	Sweep streets, control litter		Collect and treat
Combustion			
Stationary	Combustion modifications	Location of power plant	Catalytic or noncatalytic reduction with NH_3
	Staged combustion; combustion temperature control	Type of fuel	Scrubbing
Mobile	Increase miles per gallon	Shift from cars to mass transit	Three-way catalyst
	Eliminate pollution controls that increase NO_x		Adjust combustion temperature

create a solid waste problem; and measures that reduce runoff of surface water can increase infiltration and leaching of nitrate, and can promote denitrification in moist soils. On the other hand, some nitrate problems result from basic characteristics of our national lifestyle and economy, and changes in social patterns could affect more than one nitrate-related issue. For instance, if the size of the U.S. cattle population were reduced as a result of either a decline in per capita beef consumption or an economic policy decision to rely increasingly on imported meat, both the amount of nitrogenous animal wastes produced and the amount of grain grown for cattle feed would be reduced. As a result of the latter change, the demand for fertilizer to produce grain and the total amount of nitrogen fixation would decrease.

Most of the control techniques listed in Table 10.1 are not specific for nitrogen, but often reduce pollution by phosphorus and other substances as well. When evaluating the costs of control options, it is important to take into account the multiple objectives that can be attained by each one. It does not appear to be feasible at present, however, to allocate a specific portion of the costs to a single pollutant such as nitrate.

Although this chapter describes a wide range of control techniques that theoretically can be applied to specific nitrate problems, the choice of control measures is usually very site-specific, and is affected by a number of important considerations. In most instances, there is inadequate scientific knowledge to establish accurately the causal chains between specific activities involving nitrates and associated health, environmental, or economic impacts. Similarly, it is seldom possible to predict the beneficial effects of control measures accurately.

A second practical consideration is that national policies on pollution abatement may limit the number of options available for dealing with specific nitrate-related environmental problems. Several different national strategies could exist, each with different implications for control measures directed at nitrates:

1. Identify problems and control them at the local level;

2. Establish national environmental quality standards, but leave the choice of strategies to attain them to the state or local level;

3. Establish national abatement procedures (specific mandates for treatment standards, process-weight standards, effluent charges, or the like).

National policies typical of each of these strategies have been adopted, or may be adopted, for different classes of sources; for instance, strategy (2) has been adopted for atmospheric emissions of nitrogen oxides, and strategy (3) has been applied to point sources of sewage and industrial wastes.

Controls for Point and Nonpoint Sources

Chapter 6 of this report described the sources of nitrate-related pollution problems. The characteristics of sources vary widely, and a parallel variety in applicable control techniques exists. Although point sources of nitrogen compounds are responsible for only a small fraction of the nitrate input to soil and aquatic systems on an aggregate regional or national basis, their local impacts generally require effective controls. Stationary combustion sources, in contrast, produce most atmospheric nitrate loading and consequently most regional and national impacts of nitrate in precipitation. Techniques for the treatment of nitrate-related nitrogen from point sources have been extensively reviewed (Metcalf and Eddy 1976, U.S. EPA 1975b, Teixeira 1976). These comprehensive surveys of the literature have shown that control methods for point-source nitrogen discharges to the air, water, or soil have been proven effective in the laboratory, but are not yet well demonstrated in full-scale tests. Whether costs of such controls will exceed perceived benefits, and what investment strategy should be pursued in further development of practical control measures, are major national policy issues for the near future. These issues provide the framework for the evaluation of currently available control techniques in the sections on sewage and industrial wastes and combustion emissions, below.

The largest and most troublesome nitrate-related environmental impacts are associated with diffuse (nonpoint) sources such as agricultural croplands, feedlots, urban areas, and forests (see Chapter 6). The nonpoint pollution problems that have attracted the most attention are nitrogen oxide emissions from mobile combustion sources and transport of nitrogen into surface waters by stormwater runoff. However, ammonia losses by volatilization, production of nitrous oxide by denitrification, and leaching of nitrate into groundwater also pose potentially important nonpoint pollution problems.

The broad options for control of nitrogen from nonpoint sources are summarized in Table 10.1. They range from reduction of problems at the source, such as limiting fertilizer application rates or dispersing cattle on pastures and range, to the collection of runoff or wastes and subsequent treatment as for point sources. Intermediate measures include management practices to regulate nitrogen transformations (e.g., to facilitate nitrification and denitrification), and measures to increase the amount of nitrogen taken up by plants. Surface contours and vegetation patterns also can be modified to reduce the volume or velocity of runoff. The effectiveness of such controls depends on local weather, soil, and vegetation patterns. Specific applications of the general control options are discussed in relation to pollution from croplands, livestock wastes, urban stormwater, septic tanks, and other nonpoint sources of nitrate pollution in the sections that follow.

TREATMENT OF DOMESTIC SEWAGE

The control of nitrogenous materials in municipal wastewaters has been a growing concern in the past decade, and a number of reviews of available technology have appeared recently (e.g., Reeves 1972; Barnard 1973; Wilson and Riddell 1974; Schroeder 1974, 1975; Christensen and Harremoes 1975; and Metcalf and Eddy 1976). Significant advances have been made in the development and demonstration of techniques to remove organic nitrogen, ammonia, and nitrate from wastewaters; and sufficient knowledge is now available to design highly effective treatment systems. Table 10.2 summarizes the available techniques and their effectiveness in removing nitrogen. The U.S. Environmental Protection Agency's manual for the design of nitrogen control systems (U.S. EPA 1975b) presents detailed design and performance data for nitrification, denitrification, and ammonia removal facilities; according to that manual, information was insufficient to prepare such a compendium as recently as 1972. The selection of a treatment alternative in a given case depends on factors such as (1) the form and concentration of nitrogen compounds present, (2) the required quality of the treated effluent, (3) other treatment processes to be employed, and (4) the cost, reliability, and flexibility of each option. Most of the attention in developing control techniques for nitrogenous compounds in municipal wastewater has focused on ammonia. Reasons include the high proportion of ammonia-nitrogen in wastes, the large biochemical oxygen demand (BOD) created by ammonia compounds, and the toxicity of ammonia to aquatic life. Control techniques for ammonia emphasize nitrification, and the potential that this trend may pose for creating or aggravating nitrate-related water quality problems needs to be carefully evaluated. Coupled systems using nitrification/denitrification are the most common treatments for decreasing the total nitrogen content of sewage; however, the significance of increased denitrification, as a sink for a potentially useful resource and as a source of nitrous oxide, also needs to be examined.

TABLE 10.2 Effects of Various Sewage Treatment Processes on Nitrogen Compounds

	Effect on Constituent			Percent Removal of Total Nitrogen Entering Process
Treatment Process	Organic N	Ammonia	Nitrate	
Conventional Treatment Processes				
Primary	10-20% removed	no effect	no effect	5-10
Secondary	15-25% removed[a] urea → NH_3/NH_4^+	<10% removed	nil	10-20
Advanced wastewater treatment processes				
Filtration[b]	30-95% removed	nil	nil	20-40
Carbon sorption	30-50% removed	nil	nil	10-20
Electrodialysis	100% of suspended organic N removed	40% removed	40% removed	35-45
Reverse osmosis	100% of suspended organic N removed	85% removed	85% removed	80-90
Chemical coagulation[b]	50-70% removed	nil	nil	20-30
Land application				
Irrigation	→ NH_3/NH_4^+	→ NO_3^- → plant N	→ plant N	40-90
Infiltration/percolation	→ NH_3/NH_4^+	→ NO_3	→ N_2	0-50
Major nitrogen removal processes				
Nitrification	limited effect	→ NO_3^-	no effect	5-10
Denitrification	no effect	no effect	80-98% removed	70-95
Breakpoint chlorination	uncertain	90-100% removed	no effect	80-95
Selective ion exchange for ammonium	some removal, uncertain	90-97% removed	no effect	80-95
Ammonia stripping	no effect	60-95% removed	no effect	50-90
Other nitrogen removal processes				
Selective ion exchange for nitrate	nil	nil	75-90% removed	70-90
Oxidation ponds	partial transformation to NH_3/NH_4^+	partial removal by stripping	partial removal by nitrification-denitrification	20-90
Algae stripping	partial transformation to NH_3/NH_4^+	→ cells	→ cells	50-80
Bacterial assimilation	no effect	40-70% removed	limited effect	30-70

[a] Soluble organic nitrogen, in the form of urea and amino acids, is substantially reduced by secondary treatment.

[b] May be used to remove particulate organic carbon in plants where ammonia or nitrate are removed by other processes.

SOURCE: Modified from U.S. EPA (1975b).

Conventional Treatment Processes

Conventional processes for sewage treatment are well documented in many texts and design manuals. Such processes were developed to remove suspended solids and oxygen-demanding organic matter, rather than nitrogenous compounds, and as a result, conventional sewage treatment is relatively ineffective for the control of nitrogen forms in wastewater. As shown in Table 10.2, primary sedimentation removes part of the particulate organic matter, representing about 10 to 20 percent of the total nitrogen in sewage. Secondary (biological) treatment removes additional particulate organic nitrogen and some ammonium, and transforms some of the organic nitrogen to ammonium ion and other inorganic forms. Sludges from primary and secondary settling tanks are usually treated further by anaerobic digestion, to decrease and stabilize the organic matter. Much of the organic nitrogen in sludge is converted to ammonia in this process, and is transferred with the digester supernatant back into the main waste stream. As a result, anaerobic digestion of sludge is rather inefficient for removing nitrogen. At best, secondary treatment removes about 10 to 20 percent of total nitrogen in raw sewage, and a conventional primary-secondary facility usually achieves at most 30 to 40 percent removal.

Advanced Wastewater Treatment Processes

Some advanced treatment processes designed to remove constituents other than nitrogen also remove some nitrogen, primarily in particulate forms, but overall removal efficiency is rarely high. Tertiary filtration can remove suspended organic nitrogen, and carbon adsorption will also remove organic nitrogen compounds. Electrodialysis may remove about 40 percent of the ammonium or nitrate in wastewater, and reverse osmosis about 80 percent, but neither process is commonly used for treating municipal sewage effluents. Chemical coagulation is useful for removing particulate matter, including particulate organic nitrogen. Land disposal, another option, is discussed later in this chapter, and may be suitable for towns and small cities that have land available nearby for disposal of such effluents.

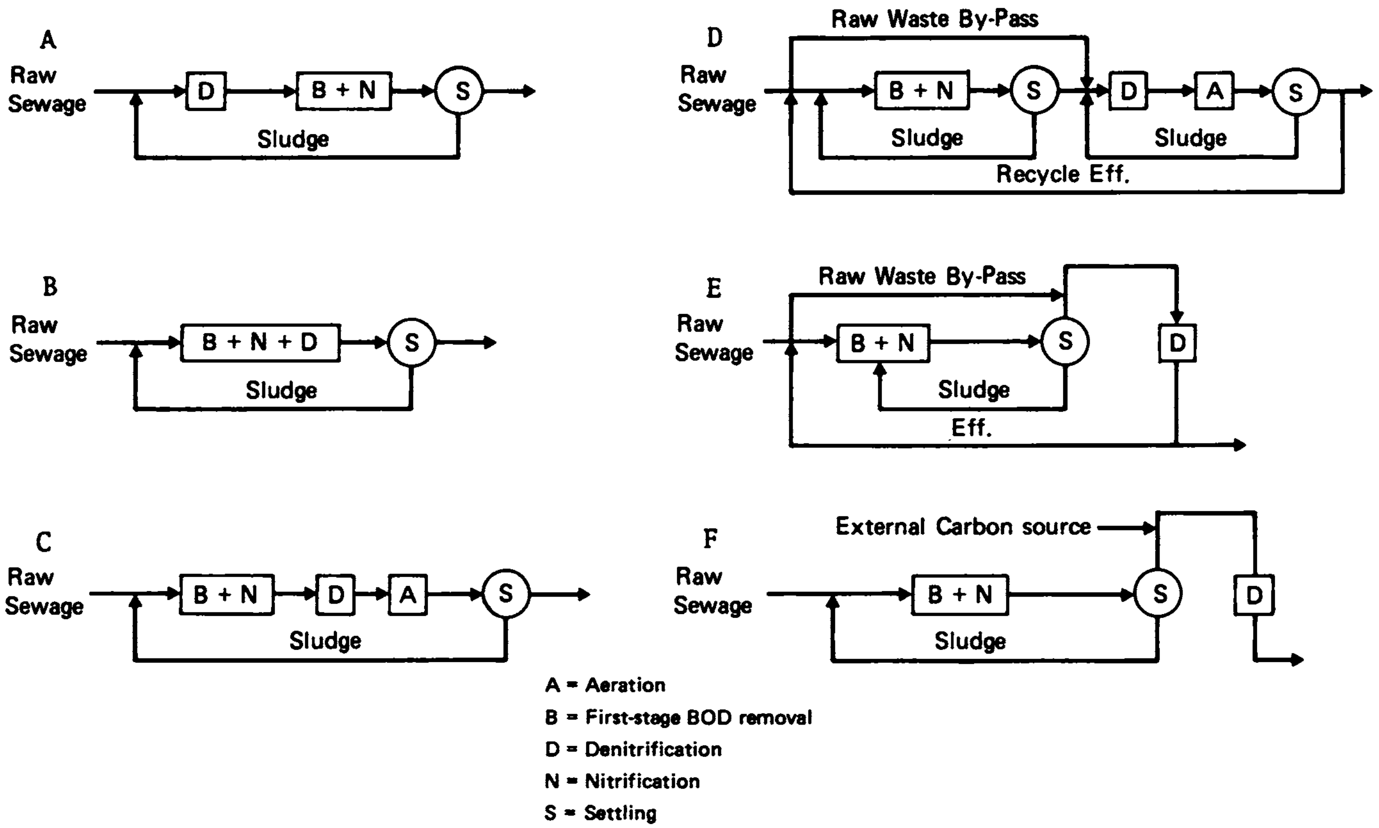
Major Nitrogen Removal Processes

While phosphorus can be readily removed from wastewater by precipitation or adsorption onto coagulants, nitrogen forms are more difficult to remove. A variety of chemical and biological schemes for nitrogen removal have been developed, but few have advanced beyond the pilot plant scale. Only the biological nitrification-denitrification process removes nitrogen as nitrate; the other processes either require the nitrogen to be present as ammonia, or remove all of the nitrogen forms present (e.g., land disposal).

Biological Nitrification-Denitrification

Biological nitrification is used to transform ammonia to nitrate, especially in cases where it is essential to reduce the oxygen demand of ammonia-rich wastes. Nitrification does not reduce the nitrogen content of the waste stream, but converts it to a form that can be denitrified. Reeves (1972), Barnard (1973), Schroeder (1974, 1975), Francis and Callahan (1975), and Christensen and Harremoes (1975) reviewed the state-of-the-art and concluded that the biochemistry and microbiology of nitrification-denitrification systems are sufficiently understood now to permit full-scale application of the method.

Nitrification can be carried out in either suspended growth reactors (activated sludge) or attached growth reactors (such as trickling filters). The same alternatives exist for denitrification except that the environment must be anoxic. Some of the variations that can be used are shown in Figure 10.1. Because nitrification does not occur to any significant extent until most of the organic matter in waste has been consumed, little oxidizable organic substrate is available in highly nitrified effluents. The carbon required for subsequent denitrification can be supplied either by diverting some of the raw waste directly to the denitrification chamber or by adding carbon substrate from an external source. Methanol is the least costly and most widely used carbon supplement for denitrification systems. Some pilot studies recently have used elemental sulfur as the energy source for sulfur-oxidizing denitrifiers such as <u>Thiobacillus</u> <u>denitrificans</u> (Sikora and Keeney 1976b). Combined processes can be used in which the bacterial cultures are alternately nitrifying and denitrifying (Figure 10.1 A, B, and C), but systems in which the nitrifying and denitrifying flora are kept separate (Figure 10.1 D, E, and F) may be easier to maintain and more efficient. If the pH of the system is above 7.0, denitrification will produce nitrogen gas almost exclusively, but a lower pH will result in increased production of nitrous oxide. Temperature has a pronounced impact on nitrification and a lesser effect on denitrification. Nitrification rates in suspended cultures can change by a factor of 4 for each 10°C change in temperature, and treatment plants in cold climates experience difficulty in producing highly nitrified effluents in winter (Christensen and Harremoes 1975; see Chapter 2 of this report for further discussion of factors that affect nitrification and denitrification).



SOURCE: Modified from Christensen and Harremoes (1975).

FIGURE 10.1 Alternative systems for biological nitrification/denitrification. (A), (B), and (C), suspended combined-culture denitrification; (D), suspended separate culture denitrification with an internal carbon source; (E), attached-growth, separate sludge denitrification with an internal carbon source; (F), a similar scheme to (E) but with an external carbon source.

Pilot plant studies have established that secondary treatment facilities can be effectively modified to provide biological oxidation of organic matter and subsequent nitrification and denitrification, through control of the oxygen content. Conversion of ammonia to nitrate can be as high as 98 percent. Depending on the extent to which organic nitrogen has been removed or converted to ammonia at earlier stages of treatment, the overall removal efficiency of a nitrification-denitrification plant may be 70 to 95 percent, with effluent concentrations of less than 1 mg N/l of ammonia and 1 to 5 mg N/l nitrate.

Breakpoint Chlorination

If sufficient chlorine is added to a waste stream, ammonia-nitrogen will be oxidized to nitrogen gas, by reactions of the type:

$$3Cl_2 + 2NH_4^+ \text{------>} N_2 + 6HCl + 2H^+$$

Although the above reaction theoretically requires approximately 3 moles of chlorine for every two moles of ammonia, in practice, Cl:N ratios as high as 10:1 may be required because of the high chlorine demand of organic matter present in the wastewater. The acidity produced by chlorination must be neutralized with lime or caustic soda, adding to the total dissolved solids in the effluent and to the cost of the treatment. Breakpoint chlorination can reduce ammonia-nitrogen concentrations to near zero, but it does not remove nitrate or nitrite. Mixed results have been obtained in removing organic nitrogen. Because of the high cost of chlorine and the hazards posed by formation of toxic chloramines and substituted organochlorine compounds, breakpoint chlorination is a relatively unattractive candidate for nitrogen removal.

Selective Ion Exchange

Ammonium ions can be removed with an efficiency of more than 90 percent by passing wastewater through a column of clinoptilolite, a naturally occurring zeolite. This process does not remove other forms of nitrogen, and disposal of the concentrated ammonium brine produced in regenerating the zeolite column poses a major problem.

Air Stripping for Ammonia Removal

Ammonium ions can be converted to molecular ammonia by addition of sufficient lime to raise the pH of wastewater to

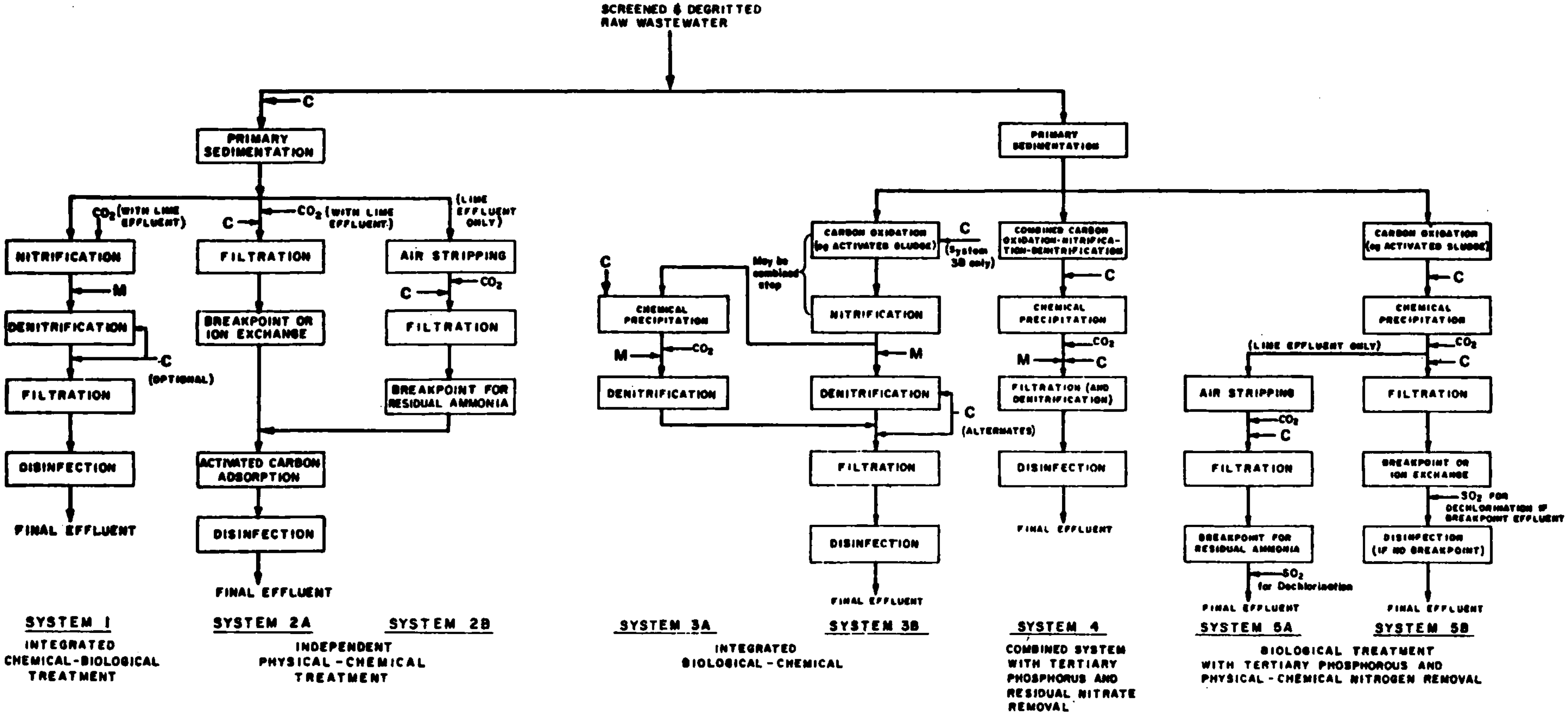
10 or 11; the ammonia can then be stripped from the water by mixing a fine spray of the effluent with a large volume of air (up to 500 ft^3/gal [3.7 m^3/l] of waste). A drawback to this method is the requirement for large volumes of air, which implies a relatively large energy input (Culp and Culp 1971). By comparison, conventional activated sludge treatment requires only a few cubic feet of air per gallon of wastewater. Similarly, the high pH requirement for this process implies high chemical costs for lime and for acid to neutralize the stripped wastes. In cold climates, ice formation in stripping towers in winter has created problems. Finally, ammonia stripping may merely transform a point source problem into a diffuse source problem by dispersing the stripped ammonia over downwind watersheds where it may return to earth in rainfall or by gaseous deposition. An air-stripping facility for ammonia was operated at the South Lake Tahoe advanced wastewater treatment facility for several years, but finally was abandoned because of unsatisfactory results (Dean and Forsythe 1976).

Other Nitrogen Removal Processes

Several additional methods of removing nitrogen from wastewaters are at least theoretically possible. Anionic exchange resins have been tested for removing nitrate from irrigation return flows, but inadequate selectivity of resins for nitrate over chloride and disposal problems with nitrate-laden regenerants have limited the usefulness of this technique. Wastewater lagoons and oxidation ponds can remove up to 85 percent of total nitrogen, apparently through assimilation by algae and bacteria, loss of ammonia to the atmosphere, and denitrification by bacteria in the anaerobic bottom layer. Addition of a carbon source (glucose or methanol, for instance) can increase the rate of incorporation of nitrogen into bacterial cells; this approach, however, increases the volume of sludge produced and creates a problem of disposal of nitrogenous solid waste.

Preferred Systems for Nitrogen Removal

EPA's design manual (U.S. EPA 1975b) presents several process sequences as alternatives to conventional primary/secondary treatment with nitrification/denitrification. Figure 10.2 presents some of those alternative systems, and Table 10.3 summarizes the effluent nitrogen concentrations from demonstration plants that employ some of the systems illustrated in the figure. The data indicate total effluent nitrogen concentrations of 1.5 to 4.5 mg/l, or removal efficiencies of 90 to 95 percent of the total nitrogen in municipal wastewaters. Most of the results in



C = Coagulant, usually lime, iron, or aluminum
CO_2 = Carbon dioxide, added only when lime is the coagulant
M = Methanol, carbon source for denitrification
SO_2 = Sulfur dioxide, used in dechlorination after breakpoint chlorination

SOURCE: Modified from U.S. EPA (1975b).

FIGURE 10.2 Alternative process sequences for systems to remove nitrogen and phosphorus from wastewaters.

TABLE 10.3 Effluent Nitrogen Concentrations in Various Advanced Waste Treatment Systems

Type and process sequence	Location	Scale mgd (m^3/sec)	Average effluent nitrogen, mg/l				
			Organic N	NH_4^+-N	NO_3^--N	NO_2^--N	Total N
Nitrification-Denitrification							
Lime treatment of raw sewage, nitrification denitrification	Contra Costa, California	0.5 (0.022)	1.1	0.3	0.5	0.0	1.9
Primary treatment, high rate activated sludge, nitrification, denitrification, filtration	Manassas, Virginia	0.2 (0.0088)	0.8	0.0	0.7	0.0	1.5
Primary treatment, roughing filters, nitrification, denitrification, filtration	El Lago, Texas	0.3 (0.0132)	0.8	0.9	0.6	0.0	2.3
Ion Exchange							
Lime treatment of raw wastewater, two-stage recarbonation, filtration, activated carbon, ion exchange	Blue Plains, D.C.	0.05 (0.0022)	na	3.6	na	na	4.5[a]
Lime treatment of raw wastewater, recarbonation, filtration, activated carbon, ion exchange	East Bay Municipal Utilities District, Ca.	Pilot scale	2.4	0.5	--	--	2.9[a]
Breakpoint Chlorination							
Lime treatment of raw wastewater, two-stage recarbonation, filtration, breakpoint chlorination, activated carbon	Blue Plains, D.C.	0.05 (0.0022)	na	na	na	na	3.3
	Same, digital control	0.05 (0.0022)	na	na	na	na	1.6
Lime treatment of raw wastewater, filtration, activated carbon, breakpoint chlorination, and dechlorination by activated carbon	Owosso, Michigan	0.02 (0.0009)	0.58	1.42	--	--	2.0[a]
Primary treatment, oxidation ponds, algae removal by alum-flotation, filtration, breakpoint chlorination	Sunnyvale, Ca.	0.01 (0.0004)	2.6	0.2	0.4	0.0	3.2

[a] Estimated

SOURCE: Modified from U.S. EPA (1975b)

Table 10.3 are for pilot plants of less than a million gallons per day (1 mgd, or 0.044 m^3/sec) capacity, however, and they do not guarantee similar efficiency of removal by full-scale plants.

In summary, adequate theory and design concepts are available for the effective removal of nitrogen from municipal wastewaters, but the operation of full-scale treatment facilites is in its infancy, and problems with disposal of residuals of the treatment processes have not been fully resolved. Further evaluation is required to determine the relative environmental consequences and economic feasibility of alternative treatment systems that produce ammonified, nitrified, or denitrified effluents from nitrogen-laden wastewater.

Costs of Control

The firm of Metcalf and Eddy (1976) surveyed the costs of removal of nitrogen from municipal wastewaters; Table 10.4 summarizes estimated removal costs. In general, removal of nitrogen increases costs by less than 50 percent of the costs of secondary treatment. To facilitate comparisons, it is useful to calculate the cost of removal of nitrogen from wastewater on a unit basis. Daily generation of wastes averages about 15 grams of nitrogen per capita in 100 gallons (4 g/100 liters) of wastewater (U.S. EPA 1973c). According to Table 10.4, treatment costs range from 2 to 50 cents per 1000 gallons (0.5 to 13 cents per 1000 liters), and the costs of nitrogen removal by the different processes range from $0.60 to $1.20 per pound ($1.32 to $2.64/kg); except for electrodialysis, however, no process costs more than $0.70 per pound ($1.54/kg). It is noteworthy that many of the processes remove other pollutants as well as nitrogen, and it is therefore somewhat inequitable to regard these estimated costs as the price of control of nitrogen alone.

Much of the nitrogen removed by wastewater treatment is captured in sludge, and control costs should include the costs of sludge management. Sludges normally contain less than 10 percent solids, and require dewatering and thickening prior to disposal. Many options are available for disposal of sludges, including incineration, composting, land spreading, ocean disposal, and other methods; the selection of one or more methods depends on the volume and properties of the sludge, geographic location, and many other considerations. The National Research Council recently assessed problems of management of municipal sludge for EPA (NRC 1978), and reviewed the literature on disposal costs (see Table 10.5). Costs per ton of sludge are much lower for large sewage treatment operations (i.e., >100 tons of sludge produced per day) than for smaller treatment

TABLE 10.4 Treatment Costs for Removal of Nitrogen from Domestic Sewage[a]

Treatment Process	Percent of total nitrogen entering process removed by treatment	Costs of removal, by plant capacity[b] 1 mgd	10 mgd	100 mgd	Cost in $ per pound of nitrogen[c,d]
Conventional Treatment			(cents/1000 gal)[d]		
Primary	5-10	33	19	8	2.30
Secondary	20-40	73	76	8	1.06
Nitrogen Removal Process (in addition to conventional treatment)					
Nitrification	5-10	8	2	4	.66
Denitrification	70-95	8	2	2	.60
Chlorination	80-95	12	2	5	.70
Ion Exchange	80-95	10	2	3	.63
Electrodialysis	35-45	50	30	20	1.20

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[a] Data from Metcalf & Eddy (1976).

[b] Assumes capital recovery factor of 0.1.

[c] Calculated for a 100 mgd facility, assuming that raw wastewater contains ~0.35 lbs N/1000 gallons (15 g N, 100 gal wastewater per capita per day).

[d] Metric equivalents: 1¢/1000 gal = 0.27¢/m^3; $1/lb = $2.20/kg.

TABLE 10.5 Estimated Costs of Sludge Management at Several U.S. Cities

	Cost for Indicated Option for Sludge Management[a]										
City	Pyrolysis	Wet Oxidation	Incineration	Drying	Oil-Dehydration	Composting	Landfill	Liquid Application on Land	Dewatered Application on Land	Ocean Disposal	Lagoon
New York City	51-88	113		87	116						
Washington, D.C.	48-60		57	60-73	41-80	71-86			81-82		
Washington Suburban Sanitary District			69-111				83-99				
Corpus Christi, Texas			111	68				46-59	54-76		
Boston, Massachusetts		59	44				63				
Knoxville, Tennessee			58	67		81	64-78	125			
Southern California Region			33			22	27-53	64		9	
East Bay MUD, California			138	134				117	130	61	138
Denver, Colorado			76-98			135-177		77	87-104		
Sacramento, California			95				60-74	56			
Tampa, Florida			173	101-128			121-141	158-160			

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[a] Cost in dollars per ton of dry solids, adjusted to January 1976, Engineering News Record Construction Cost Index.

SOURCE: NRC (1978).

facilities (Metcalf and Eddy 1976). Costs of sludge management for typical medium-to-large cities range from $9.00 to $177 per ton of dry solids (about $10 to $195 per metric ton), and most commonly are between $50 and $100 per ton. Sludge disposal is required for many reasons, and control of nitrogen pollution rightfully can account for only a small fraction of the cost. Typical sludges contain from 1.5 to 6 percent nitrogen on a dry weight basis (NRC 1978); if an average nitrogen content of 4 percent is assumed, the costs of disposal of nitrogen in sludge would range from $0.36 to $7.08 per ton of sludge, or from 0.45 to 8.85 cents per pound (1 to 19 cents/kg) of nitrogen. Most typically, costs would probably fall in the range of $2 to $4 per ton, or 2.5 to 5 cents per pound (5.5 to 11 cents per kg) of nitrogen. These costs represent an increment of a few percent above the costs of treatment for removal of a unit of nitrogen.

TREATMENT OF INDUSTRIAL WASTES

Industrial production of ammonia, manufacture of fertilizers, nitric acid, and innumerable chemicals, and production of pulp and paper are important sources of nitrogen-laden wastewaters (see Chapter 6). The major forms of nitrogen in industrial effluents are ammonia, ammonium nitrate, nitric acid, and urea. Industries that produce complex organic nitrogen compounds discharge a very small fraction of the industrial nitrogen waste load; however, monitoring and control of such wastes is essential, since many of the organic nitrogen compounds may be carcinogenic or otherwise toxic in small quantities (U.S. EPA 1973c).

A study by the U.S. EPA (1971) concluded that most nitrogen-related industries (e.g., ammonia synthesis or fertilizer production) used dilution as the only control method for their wastewaters at that time. Most of the water used in such industries is used for cooling; the amount of wastewater discharged depends on the extent to which cooling water is recycled, and to which process water is used for cooling (U.S. EPA 1971). Control techniques for wastewaters from such operations have focused on solids, oils, and heavy metals. According to a report by the Development Planning and Research Associates (DPRA 1975), only 5 percent of 400 nitrogen industry plants surveyed met standards of Best Practicable Technology (BPT). DPRA concluded that many plants could recycle cleaner waters for process use and use process waters for cooling; the result would be to decrease the volume and increase the nitrogen content of the wastewater requiring treatment. As described in Chapter 6, wastewater from nitrogen industries may be produced in volumes ranging from 50 to several thousand gallons per ton of product, and may contain nitrogen (ammonia) concentrations ranging from that of domestic wastewaters (20 to 40 mg/l) to more than 1000 mg/l.

The same techniques described for removing nitrogen from sewage effluents are applicable to industrial wastes, although the design of treatment systems must take into account the low BOD of some wastes, the often high concentrations of nitrogen, and the nature of the industrial effluents in each specific case, which may involve combined streams from many different processes. The literature reviews cited above on sewage treatment also describe methods for removal of nitrogen from industrial wastes. Biological digestion in treatment ponds and ammonia stripping are the most commonly used methods for removing ammonia; EPA has recommended ion exchange methods, but these are not in use at present in many industries. Hutton and LaRocca (1975) reported that biological treatment removed 90 percent of the nitrogen from fertilizer plant wastewaters containing 600 mg/l ammonia-nitrogen. Antomi (1974) reported that other contaminants in wastewaters, such as phenols, chromium, zinc, lead, or cadmium in concentrations of a few mg/l, can inhibit the oxidation of ammonia. Voets et al. (1975) found inhibition of biological oxidation of nitrite, and accumulation of nitrite, in highly nitrogenous wastewaters; the nitrite can subsequently be reduced by aerobic or anaerobic microbial action, or it can be removed chemically by acidification and addition of urea or sulfuric acid. Michael and Jewell (1975) reported that plug flow reactors, such as anaerobic submerged filters, have a far greater capacity for denitrification than do completely stirred reactors, such as anaerobic activated sludge, for treatment of wastes with high nitrate concentrations.

Ammonia stripping of industrial wastes must include recovery of ammonia so that it is not discharged to the atmosphere. This is feasible with wastewaters that typically have ammonia concentrations in the thousands of parts per million, such as some industrial wastewaters, supernatants from sludge digesters, and feedlot wastewaters. Nitric acid wastes can be combined with ammonia wastes to produce ammonium nitrate, a byproduct that can be sold as fertilizer (DPRA 1975).

In general, controls for nitrogen in industrial wastewaters have been implemented only where product recovery provides an economic justification. Careful management and maintenance to control leaks and spills and to decrease water use can significantly reduce nitrogen discharges from industry.

Costs of Control

The cost of removing nitrogen from industrial wastes is difficult to estimate, since the percentage of product lost in wastewater may vary from 0.1 to 1 percent. A study by DPRA (1975) estimated the costs of removal of nitrogen from wastewater for the fertilizer industry (see Table 10.6). The data reveal few economies of scale in these treatment systems. Industrial wastewaters generally have higher nitrogen concentrations than municipal wastes; as a result, costs of removal of nitrogen are correspondingly lower. If it is assumed that treatment is 90 percent effective in removing nitrogen and capital costs are spread over 10 years, a range of costs of from about 5 to 50 cents per pound of nitrogen removed can be calculated from the information in Table 10.6.

LAND DISPOSAL OF NITROGENOUS WASTES

Sewage, food processing wastes, sludges containing organic nitrogen, and manures are all amenable to disposal on land. In some areas, spray irrigation or incorporation into soils may be, or could become, the chief treatment method. Land disposal potentially could transform a point-source problem into one of nonpoint-source pollution, but properly managed land disposal systems can provide cost-effective and energy-efficient alternatives to technological treatment methods. Assimilation of nitrogen by natural systems also recycles nutrients in useful form.

The transport and transformations of nitrogen in wastes applied to land are reviewed in Chapter 6. Intermediate storage of wastes in lagoons or oxidation ponds can minimize ammonia losses by volatilization. The extent to which land disposal can provide an effective alternative to conventional treatment without creating other pollution problems is the subject of active study. The Cold Regions Research and Engineering Laboratory (CREL) of the Army Corps of Engineers has evaluated several systems for application of sewage to land. A low-rate system that depends on volatilization of ammonia and uptake of nitrate by crops was found to absorb 112 to 224 kg N/ha-yr. Overland flow systems assimilated 560 to 1680 kg N/ha-yr, and high-rate systems using sandy loam soils were reported to absorb as much as 27,000 kg N/ha-yr, when an alternating cycle of drying and flooding was used to create the aerobic/anaerobic conditions for nitrification and denitrification (Bouwer 1974). An important management consideration with high-rate systems is the need to maintain a C:N ratio high enough to provide adequate carbon for denitrification. In the absence of adequate carbon, nitrification may proceed faster than denitrification, and excessive nitrate may be leached below the denitrification zone. Bouwer (1974) found that a cycle

TABLE 10.6 Estimated investment and Annual Operating Costs of Water Pollution Controls for the Fertilizer Industry

		BPT[a]		BAT[b]	
Product	Plant Capacity (1,000 tons)	Capital Investment	Operating and Maintenance[c]	Capital Investment	Operating and Maintenance[c]
		(x $1,000)			
Ammonia	50	81	47	33	2
	105	127	93	51	3
	210	191	170	77	6
	350	260	266	105	9
	525	332	380	134	13
Ammonium Nitrate	50	34	20	211	93
	105	72	43	336	157
	160	82	59	428	212
	350	135	119	687	374
Urea	52	128	66	19	1
	105	194	121	29	2
	160	267	179	44	3
	350	432	358	73	6
Mono-Ammonium Phosphate[d]	50	330	100	133	12
	105	529	190	264	26
	350	1,324	560	503	57
Diammonium Phosphate[d]	50	245	73	117	11
	78	404	120	194	18
	150	522	194	250	26
	350	966	419	463	53

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[a] BPT = best practical treatment.

[b] BAT = best available treatment; costs are incremental costs of going from BPT to BAT.

[c] Not including interest and depreciation. Sulfuric acid not included because its discharges are not covered by standards. Nitric acid not included due to no discharge of process pollutants.

[d] Sizes in 1,000 tons of P_2O_5.

SOURCE: DPRA (1975).

of two to three weeks of flooding followed by two- to three-week drying periods could maximize denitrification; some soils could remove up to 9000 kg N/ha-yr under this regime.

Odum et al. (1975) and Kadlec et al. (1975) have shown that wetlands also have good potential for recycling sewage. The generally high biological productivity of wetlands, coupled with their proximity to many urban areas or other sites of accumulation of wastes, make such areas attractive as disposal sites. Disposal efficiencies (e.g., percent removal of BOD, phosphorus, and nitrogen) are comparable to other systems. However, while high nitrogen removal rates have been reported for wastewater applied to cypress wetlands (Dierberg and Brezonik 1978), it is not known whether the ultimate sink for nitrogen is sediments or assimilation in tree growth. Furthermore, some wetland ecosystems may have limited capacities to assimilate nutrients and may release excess nitrogen to adjacent coastal waters (see Chapter 3).

Although land disposal at appropriate sites appears to be an effective alternative to other methods for removing and recycling nitrogen from waste streams, the ultimate environmental impacts of such practices still need to be carefully assessed (see Chapter 6). Furthermore, because appropriate disposal sites are relatively scarce and transportation costs to such sites are significant, the feasibility of land disposal for large urban areas remains to be demonstrated. However, land disposal does have some economic advantages over conventional biological nitrification-denitrification systems for smaller cities.

The costs of land disposal vary with the system design, location and management procedures. Allender (1972), as reported by Nesbitt (1974), developed general cost information. Capital costs for the distribution system, lagoon, pumping station, pipeline and land, were estimated to range from $440,000 to $2,430,000 (in 1967 dollars) for systems with capacities of 1 mgd and 10 mgd (0.044 and 0.44 m^3/sec), respectively. Annual costs, which included amortization (at 6 percent for 20 years), were approximately 10 percent of capital costs. The cost of disposal ($0.07 per 1000 gallons, or $8.00 per dwelling unit per year) did not decrease appreciably at flows above 6 mgd.

Similar cost information is available for sewage disposal in a Florida cypress dome (Odum et al. 1975). Operating costs for a 25,000 gal/day system were $0.27/1000 gal, and 45 percent of the cost was for maintenance of the lift station. For a given system, cost reductions can be achieved with increases in loading rate.

CONTROLS FOR NITROGEN OXIDE EMISSIONS

Most atmospheric nitrates related to human activities originate as combustion products, i.e., oxides of nitrogen (see Chapters 2 and 6), and control methods must deal with these precursors. Nitrogen oxides (NO_x) are produced in high-temperature combustion by the oxidation of atmospheric nitrogen and nitrogen compounds in the fuel. The scientific knowledge needed to control of NO_x emissions appears to be available, but development and demonstration of the control techniques are still needed. In general, controls can be designed more effectively for new units than for existing units, and large combustion facilities (e.g., power plants of capacities >25 megawatts) are more readily controlled than are smaller units. The Los Angeles Air Pollution Control District has adopted emission standards for NO_x, and demonstration units have been built that meet the standards. National emission standards have been promulgated by EPA for new combustion sources and some noncombustion operations, but many existing boilers (e.g., power plants) are not yet subject to regulations.

The discussion that follows is intentionally succinct, and relies on recently published review documents. In brief, there are two basic methods to control NO_x emissions: (1) modification of combustion conditions to decrease the formation of NO_x, and (2) removal of NO_x from exhaust streams by chemical or physical methods. The state-of-the-art for control of NO_x emissions has been reviewed by the National Research Council (1973, 1975, 1977), and by the Electric Power Research Institute (Teixeira 1976). EPA has updated the 1970 NAPCA publications on control techniques for NO_x emissions (U.S. DHEW 1970a, 1970b), and publishes a periodical, _NO_x Control Review_, to communicate recent advances in the field. A recent review by Kircher et al. (1977) surveyed control options for nitrate and other acidic aerosols.

Controls for Mobile Sources

The 1973 study by the NRC presents an extensive discussion of controls for NO_x emissions from mobile sources. Since that report was published, advances in the technology of automotive emission control have been summarized annually in the reports of the Council for Environmental Quality (CEQ 1975, 1976). Modification of combustion to reduce peak temperatures and oxygen concentrations can effectively lower NO_x emissions from conventional internal combustion engines. However, the modifications that can accomplish this reduction (spark retardation, lean combustion, low compression ratio, injection of water, recirculation of exhaust gases) also tend to impede engine performance and increase emissions of other pollutants. Less conventional engines (such as diesels, gas turbines, the Wankel rotary engine, and stratified charge engines) and alternative fuels (alcohol, hydrogen, or other fuel blends) produce lower NO_x emissions than current engines and fuels, and could have a beneficial impact, if widely adopted. Most attention at present, however, has been focused on catalytic removal of NO_x from exhaust, using a three-way system designed to meet carbon monoxide, hydrocarbon, and NO_x emission standards. Deterioration of catalysts and considerations of fuel economy have posed the largest problems in the development of this control technology. The controls used on 1968 to 1972 model-year automobiles to reduce emissions of hydrocarbons and carbon monoxide led to increased emissions of NO_x (CEQ 1976); however, controls using exhaust gas recirculation (1973 and 1974 model years) and catalytic converters (1975 and later model years) have reduced overall NO_x emissions. NO_x emissions from catalyst-equipped vehicles are about half of those from the 1968 to 1972 models (CEQ 1976). Recently, objectives for future reductions of NO_x emissions from motor vehicles have been relaxed in favor of increased fuel economy, through revisions of the Clean Air Act. Table 10.7 summarizes the history of NO_x emission standards for automobiles. The ultimate emission standard for NO_x (0.4 g/mi) appears to be achievable by some available technologies, such as the Japanese stratified-charge engine or the three-way catalytic system developed by Volvo (CEQ 1976).

Controls for Stationary Sources

Emissions of nitrogen oxides from stationary sources currently exceed those from mobile sources (see Chapter 6), and increased use of coal for industrial fuel and power generation could lead to a doubling of present NO_x emissions from stationary sources in coming decades. Although many of the scientific aspects of the issue are unresolved, it is likely that NO_x emissions from the tall stacks of stationary sources play a larger role than mobile source emissions do in contributing to atmospheric nitrate loadings (see Chapter 6).

The primary control techniques currently used to reduce NO_x emissions from power plants, industrial boilers, and other stationary combustion sources involve modifications of boiler design and/or operating conditions. Reduction in the amount of excess air, staged combustion, injection of over-fire air, recirculation of flue gases, injection of water, and altered design of firing chambers all can reduce the peak temperature of combustion and thereby reduce the formation of nitrogen oxides from atmospheric nitrogen (Teixeira 1976). The first two techniques may also reduce the formation of NO_x from organic nitrogen in the fuel.

TABLE 10.7 Legislative History of Automobile Emission Standards for Oxides of Nitrogen

	Model Years to Which Standards Apply			
	Emission Standards, grams NO_x/mile			
Legislation	3.1	2.0	1.0	0.4
Clean Air Amendments of 1970	1976	1977		1978
Schedule in effect, January 1976	1976	1977		1978
1977 Clean Air Amendments		1977-1980	1981& later[a]	[b]

[a] The Administrator of EPA may waive standard to 1.5 g/mi for up to 1 percent of autos manufactured, in order to permit development of innovative power trains or emission control systems, and may waive standard to 2.0 g/mi for small manufacturers after finding that certain specified conditions are met.

[b] The Administrator of EPA must conduct research to determine the need for an emission standard of 0.4 g NO_x/mi, and the public health, cost, and technical implications of attaining such a standard, and report his findings to Congress by 1980. The development of an automobile engine system with NO_x emissions lower by 90 percent than those of a 1971 (uncontrolled) auto is established as a national research objective.

The control of combustion temperature is reported to be effective at reducing NO_x emissions from low nitrogen fuels, but this technique is less effective for liquid petroleum fuels, and ineffective for fuels, such as shale oil and coal, that contain more than 1 percent organic nitrogen. Some form of fuel-rich combustion stage is required to convert the organic nitrogen in such fuels to N_2 (Teixeira 1976).

Flue gas treatments to remove NO_x by scrubbing or catalysis have been tested in some pilot plants and are in operation in some Japanese plants. Two techniques now being investigated are the selective noncatalytic reduction of NO_x with ammonia at 950°C, and catalytic reduction of NO_x with ammonia at 430°C. Both methods convert NO_x to N_2, but release excess NH_3. Wet scrubbing of NO_x produces liquid wastes that contain N_2O, nitrite, and nitrate; the waste nitrogen has in effect been concentrated, but not removed. Such flue gas treatments will not be practical until these and other problems have been resolved, and they are not economically competitive with modifications of combustion. A more comprehensive discussion of this subject was presented in the 1975 study by the National Research Council, cited previously.

Use of a fuel with a lower organic nitrogen content, substitution of natural gas for fuel oil, catalytic processing of fuels to remove nitrogen, gasification of coal, and vaporization of liquid fuels all have the potential to reduce NO_x emissions, but most of these have not been demonstrated in full-scale applications. The current trend toward increased use of coal because of past or projected shortages of natural gas or petroleum, however, seems to preclude any control strategy based on the use of fuels with low nitrogen contents. There is currently inadequate information to determine whether the conversion of coal to liquid or gaseous fuels would result in fuels with lower nitrogen content than the coal itself.

The hypothesis that combustion of wood may be a significant source of NO_x to the global atmosphere is examined briefly in Chapter 6. For the United States, the use of wood as fuel is a minor source of NO_x emissions; less than 2 percent of domestic energy consumption is derived from wood (Hayes 1977), and most of that occurs in the lumber industry, as the major use of sawdust and scrap. The NO_x emissions from such sources might be subject to regulations applied to industrial boilers, but it is doubtful that any control could be attained over NO_x emissions from the residential use of firewood or from combustion of biomass in land clearing. On a global scale, the NO_x from wood burned as fuel or in slash-and-burn agriculture may be a relatively more important source; the only methods to reduce this input would be to switch to fuels with lower nitrogen content and to introduce modern land-clearing techniques. However, the feasibility of such options for the underdeveloped nations in which most of the wood burning occurs is doubtful.

Noncombustion Stationary Sources

A small fraction (about 1 to 3 percent) of NO_x emissions from stationary sources comes from noncombustion processes, chiefly the manufacture and use of nitric acid. These emissions can be controlled by catalytic removal of NO_x from the tail gas; some techniques permit economic recovery of NO_2 for use in nitric acid production. Specific methods for control and some cost data are discussed in reviews by the NRC (1975) and the National Air Pollution Control Administration (U.S. DHEW 1970a, 1970b).

Costs of Control of NO_x Emissions

Costs of NO_x controls for automobiles, based on catalytic converters capable of meeting the 0.4 g/mile emission standard, may be as much as $50-$100 per vehicle. The CEQ (1975) summarized the costs of abatement measures for automobile emissions up to 1975. The costs of decreased fuel economy and of maintenance of the pollution control devices were estimated by CEQ to be greater than actual costs of the equipment, at least through 1974 (CEQ 1975).

Capital costs for different control techniques for stationary sources have been reviewed by the National Research Council (1975) and by others. For coal-fired utility boilers, for example, the cost may be up to about $10/kilowatt, or $200 to $300 per ton of NO_x removed; costs depend on the control technique employed, the size of the unit (smaller units being proportionally more costly to control), and whether the unit is new or controls are added to an existing plant (the latter being more costly). Substitution of fuels, if alternate fuels are available, may be less costly than modification of boiler design in some instances. An average cost of $1.50 per ton of acid produced has been cited for the control of NO_x from nitric acid production (NRC 1975).

CONTROL OF POLLUTION FROM AGRICULTURAL CROPLANDS

Knowledge of the processes of transport and transformation at specific sites in agricultural regions is generally inadequate to quantitatively determine specific sources of excess nitrogen or the potential for adverse environmental impacts, even in intensively studied crop systems (see Chapter 6). It is clear that much additional research is needed before the consequences of nitrogen use on croplands are fully understood, or can be effectively controlled. Nevertheless, in areas where nitrate-related environmental degradation is a problem and remedial action is warranted, best available information must be used.

Techniques for minimizing nitrogen losses from croplands are many and diverse; they include established practices of efficient agricultural management, innovative applications of agricultural technology, regulations limiting fertilizer applications, and possibly even changes in fundamental patterns of land use and crop production. A brief summary of these diverse control options is presented in Table 10.8. The sections that follow briefly examine each of these approaches, the conditions under which they may be applied, and their implications for environmental quality and agricultural production.

Storage and Treatment of Runoff from Agricultural Lands

Where watershed terrain and precipitation patterns make it feasible to contain runoff, storage and treatment of nutrient-enriched effluents from agricultural lands may be a viable control strategy. Huber et al. (1976) used a simulation model to examine the potential effectiveness of several alternatives for storage and treatment of agricultural runoff from the Kissimmee River Basin, in Florida. When runoff waters were fed into a marshland with adequate storage capacity to detain 80 percent of the flow for two days, nutrient removal by the natural system was estimated to be 70 percent. Although the applicability and effectiveness of this approach must be evaluated for each area on a site-specific basis, such treatment of agricultural runoff may be a feasible method for preventing impacts on downstream water quality.

Agricultural Best Management Practices

The contiguous 48 states contain about 178 x 10^6 hectares of cropland, nearly all of which is classified as suitable or highly suitable for agriculture according to the land capability classification system of the U.S. Department of Agriculture (USDA 1971). According to this system, classes I to III are excellent to adequate for crop production, with little to moderate erosion potential; class IV soils are marginal, and require special management for cultivation; and classes V to VIII are generally not suitable for cultivation. There are about 19.5 x 10^6 ha of class I soils (2.5 percent of the total U.S. land area) and 114 x 10^6 ha of class II land (14.7 percent) in the United States, and about 56 percent of the land is in classes V to

TABLE 10.8 Potential Methods for the Control of Nitrate Pollution from Croplands

Method	Comment
Containment and/or Treatment of Runoff	This option is feasible for only a limited number of sites.
Management of Cropping Practices	
Soil conservation to minimize erosion	Most techniques involve already-proven methods, each with advantages beyond pollution control.
Water conservation; minimal irrigation	
Crop rotation (e.g. corn/soy beans)	
Use of cover crops to scavenge nitrogen	
Management of Fertilizer Use	
Improved estimation of crop nutrient needs through soil and tissue testing	Most techniques involve experimental or still-developing methods, not yet fully demonstrated to be technically or economically feasible for widespread use, or for use on more than a few crops.
Use of slow-release fertilizers	
Timing fertilizer applications to correspond with crop needs.	
Placement of fertilizer to improve efficiency of uptake	
Mulching to retard leaching losses	
Foliar application of fertilizers	
Addition of carbon to soils to immobilize residual nitrogen	
Chemical treatments to inhibit nitrification or urease activity	
Regulations to Restrict Rates of Fertilizer Applications	Technical and economic feasibility remain unproven, and political acceptability is doubtful.
Fundamental Changes in Agriculture	
Improvements in symbiotic nitrogen fixation (e.g. fixation by cereals)	Still only a theoretical possibility.
Changes in relative proportions of major crops (e.g. less corn, more soybeans)	All would necessarily be tied to large scale changes in dietary and consumption patterns. Neither the environmental nor the social impacts of such changes can be evaluated accurately.
Reduction of total land area cultivated	
Shift from major crop monoculture to mixed crop/livestock farming	

VIII. As Stewart and Woolhiser (1976) point out, restriction of agricultural production to lands in classes I to III would minimize environmental impacts; effective land use is thus an important aspect in the control of agricultural impacts of nitrogen.

Management practices that decrease soil erosion and surface runoff will also reduce the amount of nitrogen lost from croplands via these routes. Some of these practices are commonplace; some are proven but their adoption is limited by tradition, economics, or local soil conditions; and some are in developmental stages. Some practices may be effective in controlling one problem but may have deleterious effects on other aspects of the nitrogen cycle.

Best Cropping Practices

Soil Conservation. Various methods that protect soil from wind and water erosion limit the movement of soil nitrogen (especially the particulate fraction) from the land. Such measures do not necessarily control other nitrate-related problems, such as leaching into groundwater. Soil conservation practices are designed to hold the topsoil in place by increasing infiltration and reducing the velocity and quantity of runoff water. This may be done by physical manipulations, such as contouring and terracing; by leaving crop residues on the soil surface; by using no-till or low-tillage methods that minimize soil disturbance (Baeumer and Bakermans 1973); and by changes in cropping patterns so that plant cover is on the soil during periods of high potential for erosion. Nearly 2 million hectares of corn were cropped by no-till methods in 1977; most of this land is concentrated in a narrow band from Maryland and Virginia to Kentucky. While some projections suggest that nearly half the cropland of the United States could be managed by no-till techniques within the next 25 years (USDA 1975), Gersmehl (1978) recently argued that climatic, economic, and other factors are likely to limit widespread adoption of this practice outside its present geographic region. Gersmehl re-analyzed trends in no-till corn production and concluded that the practice would be adopted on at most 10 percent of the corn cropland in the United States. The effects of changes in cropping systems are discussed later in this chapter. Since control of runoff generally increases infiltration, nitrate leaching may be enhanced by these methods (Thomas et al. 1973). The resulting higher water content in the root zone and subsoil may increase denitrification, but data are not available to quantify this effect.

Water Conservation. In irrigated crop systems, the flux of nitrate to groundwater via leaching and to surface waters via return flows is a function of both the volume of water moving through the soil and its nitrate concentration (see Chapter 6). By increasing the efficiency of water use, it may be possible to substantially reduce the mass of nitrate leaving the root zone, but the concentration of nitrate in the smaller volume of effluent may be quite high.

A recent study of water and nitrogen balances in a sprinkler-irrigated potato crop grown on lysimeters (Saffigna et al. 1977) showed that a "minimal leaching" approach reduced drainage by 35 percent, and lowered nitrate losses from 185 to 104 kg/ha, without adversely affecting crop yields. Nitrate concentrations in leachate at a depth of 1.5 m were lowered from 23 to 16 mg N/l.

The irrigation systems commonly used in agriculture are flooding, sprinkler, and furrow (Taylor and Ashcroft 1972). Flood irrigation involves leaching under saturated soil conditions, which is regarded as less efficient for solute leaching than is unsaturated flow (Nielsen et al. 1972:169-170). Flood irrigation also offers more opportunity for denitrification. Furrow irrigation can lead to inefficient nitrogen use, since this method involves both lateral and upward water movement into the row between the furrows. Nitrate carried with this water may accumulate in the dry surface soil of the row, where it is not available to the plants (Taylor and Ashcroft 1972). Subsurface application and drip irrigation are two recently developed methods that may reduce the quantity of water needed for irrigation. Both methods involve frequent applications of small amounts of water to soils, and both permit addition of fertilizer with the irrigation water. Subsurface irrigation requires a highly permeable surface soil underlain at 2 to 3 m by a relatively impermeable subsoil. This method can result in severe salinity problems (Taylor and Ashcroft 1972). Drip irrigation involves transport of water under pressure through buried mains and laterals to surface-placed emitters, which release the water at a slow rate (Marsh et al. 1975). The method has low operating costs, but problems are encountered with clogging of the emitters and with accumulation of salts in the soil.

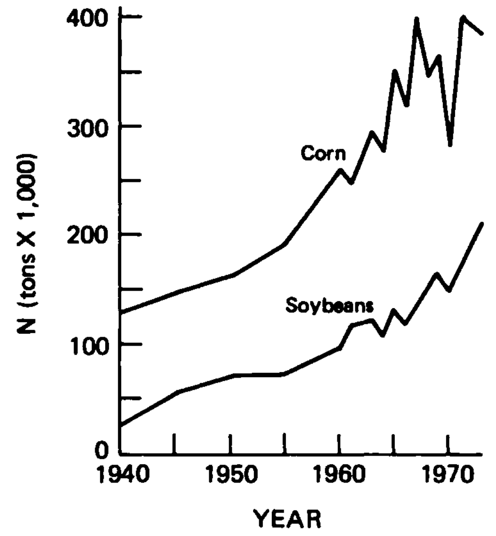
While minimal irrigation techniques have potential for controlling nitrate losses, the economic feasibility of the more careful (and labor-intensive) management required has yet to be evaluated for many crops and soils.

Water conservation and irrigation practices can have unforseen secondary impacts. For example, terracing of cropland in Texas resulted in the desired increased water retention, but also increased leaching of nitrate, which was present below the root zone as a result of several decades of dryland farming (Kreitler and Jones 1974). Similarly, Boyce et al. (1976) found high concentrations of nitrate from 7 to 30 m below the soil surface in a deep loess mantle in southwestern Nebraska. This nitrate, apparently formed during the recent geologic past, is now being leached into the groundwater as irrigation practices are increasing in the region.

Cropping Sequence. The practice of planting different crops on a field in successive years remains quite common, although the types of rotations have changed considerably with the increased use of fertilizers and pesticides and with the advent of more specialized farming. For example, the general farm of the pre-World War II days often was a self-contained unit, with some dairy or beef cattle and poultry. Forage and grain needed for the livestock often were produced and used on the farm. Rotations of corn, oats, and meadow (e.g., alfalfa and clover) were common, with a typical rotation consisting of two to four years of meadow, and one to two years of corn. Little if any chemical fertilizer was required, as nitrogen was adequately supplied to the corn crop by manure and legume residues. Because corn yields were less than half the present yields, requirements for nitrogen by the corn crop were substantially lower than present needs. Ideally, this crop rotation practice provided more economic stability, since the farmer's income was not predicated entirely on one or two crops. Erosion, crop diseases and pests also were minimized by rotation. Further, the deep-rooted legume had the potential of scavenging nitrate from the soil profile.

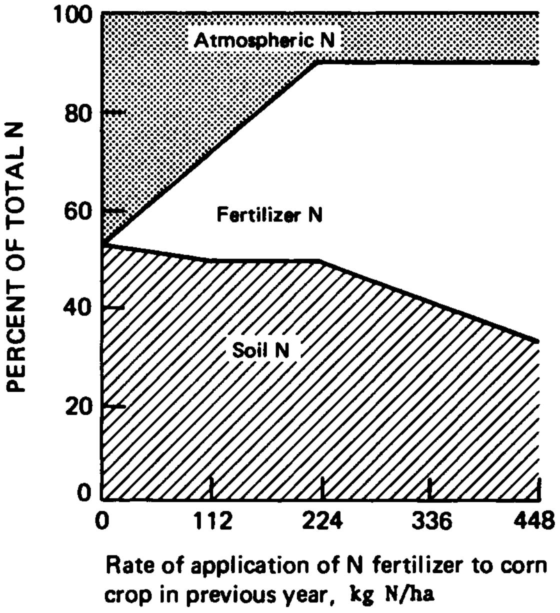
Management practices in American agriculture, however, have changed markedly in the last few decades. Farming today requires high inputs of energy and capital, and produces relatively low returns. As a result, dairy operations have moved (except for supplies to local municipalities) to areas on the northern fringe of the corn belt and to the Northeast (Stewart et al. 1975), where grain production is less profitable because of weather and soil limitations.

Economic considerations and the general compatibility of the crops have made corn-soybean rotation increasingly common in the midwestern United States. In Illinois, for example, the area in corn and in soybeans was nearly equal in 1973 (Johnson et al. 1974). In addition to their other advantages, soybeans, a nitrogen-fixing legume, can scavenge residual fertilizer from the corn crop, as well as use mineralized and symbiotically fixed nitrogen. Johnson et al. (1974) estimated that in 1973 soybeans removed 195,000 tons of soil and fertilizer nitrogen from cultivated land in Illinois, or about 56 percent as much as was removed by corn (Figure 10.3). Johnson et al. (1975b) calculated that on corn fields receiving 224 kg/ha, about 40 percent of the nitrogen removed by soybeans came from residual fertilizer (Figure 10.4). However, the primary purpose in growing soybeans is not to remove residual fertilizer nitrogen. A



SOURCE: Johnson et al. (1974).

FIGURE 10.3 Net removal of nitrogen by corn and soybeans in Illinois.



SOURCE: Johnson et al. (1975b), J. Environ. Qual. 4:204. Used with permission of the American Society of Agronomy.

FIGURE 10.4 Sources of nitrogen used by soybeans.

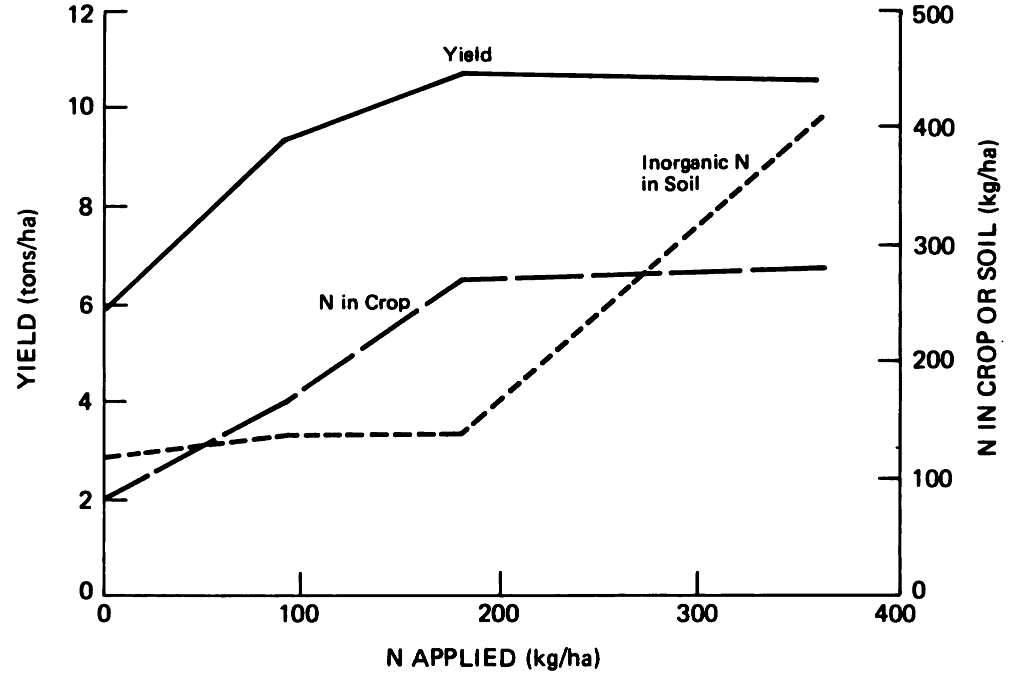
more effective rotation for removing residual nitrogen might use a rapidly growing grass or cereal crop such as oats, rye, or barley. However, to get an economic return from these crops requires a growing season that overlaps with the corn season, and they mature too late for a second planting the same year. Further, they may remove so much soil water that yields of the main crop are adversely affected.

While considerable data are now available for corn and corn-soybean rotation (see Chapter 6), long-range, comprehensive evaluation of the rate and extent of nitrate leaching and efficiency of fertilizer use is needed for various other crop rotation systems. New rotation systems using grass or grain crops such as adapted sorghum-sudan, or sudan grass, should also be considered. Adoption of such rotations would clearly have impacts on other farming practices, and those impacts also must be evaluated.

Cover Crops. Cover crops, particularly rye, are sometimes planted after the principal crop has been removed, to control erosion. These crops can also take up residual inorganic nitrogen. When the green crop is plowed back into the soil at the time of seedbed preparation in the spring, the nitrogen in the cover crop is at least partly available for subsequent crops. Studies in Illinois showed that a rye crop, planted after the fall corn harvest, effectively scavenged residual nitrogen (Welch 1974). However, adverse fall weather often prevents planting or fall growth of a cover crop. In addition, its presence prevents fall plowing, and the planting costs (seeding cost is about $8 to $9 per acre for rye) at present are disincentives to use such cover crops strictly for nitrogen conservation. Another possible approach is to interseed a low-cost crop such as oats late in the corn season. However, problems with seedling sowing and establishment would seem to preclude such an approach on a wide scale. Furthermore, the fate of the organic nitrogen in the plowed-down cover crop is uncertain. It is possible that under some circumstances the nitrogen would not be mineralized until too late in the growing season to be utilized by the corn crop.

Improved Management of Crop Nutrients

In general, nitrate accumulation occurs in agricultural systems when fertilizer inputs greatly exceed amounts that can be efficiently used by crops. This statement has been supported by many investigations of application of nitrogen fertilizer to nonleguminous crops, at rates ranging from those expected to show marked yield responses to rates far above expected crop utilization (and usually much greater than typical farm application rates). Figure 10.5 illustrates this concept. Yields increased at fertilizer inputs up to 180 kg N/ha, and little fertilizer nitrogen was



SOURCE: Broadbent (1976).

FIGURE 10.5 Yield, removal of nitrogen by crop, and residual nitrogen in soil after harvest at different rates of application of nitrogen fertilizer.

retained in the soil. At an input of 360 kg N/ha, however, a residual of at least 162 kg N/ha was removed by leaching and/or denitrification. In a similar study at a different site, crop yields were maximized at application rates of about 220 kg/ha, and residual inorganic nitrogen in the soil increased steeply at application levels above that value (Broadbent and Carlton 1976).

If fertilizer applications were always at the most efficient dose-response levels (see Chapter 8), losses of nitrate from fertilized croplands would be minimal. However, given the economic climate of agriculture today, this appears unlikely. Maximum economic efficiency of production requires inputs of fertilizer nitrogen in excess of the amount taken up by the crop. Even under favorable conditions, the efficiency of fertilizer nitrogen recovery by crops is seldom more than 70 percent, and the average value is probably nearer to 50 percent (Allison 1965, Viets 1965). In addition, the optimum rate of fertilizer application is influenced by a multitude of site-specific conditions, about which information is generally inadequate (see Chapter 8 for discussion).

Despite the inherent difficulties in prediction of the dose-response curve and hence of optimal application rates, surveys in Illinois indicate that few farmers are applying excessive amounts of nitrogen fertilizer, relative to experimentally determined maximum economically efficient rates (Taylor and Swanson 1973, Swanson et al. 1973). Unfortunately, data on application rates are not very reliable, especially at the farm or watershed level. Recent evidence strongly suggests, however, that fertilizer nitrogen makes a significant contribution to nitrate loads of some Illinois surface waters, even in areas where fertilizer use is generally at or below the maximum economically efficient level (Klepper 1976; see Chapter 6).

One possible way of minimizing such pollution is to restrict nitrogen fertilizer applications to rates that do not exceed the economic optimum. It may also be possible to use other practices to increase the efficiency of fertilizer use, or to reduce losses of the unused portion. Numerous areas exist in which the efficiency of use of fertilizer nitrogen can be improved without the introduction of new technology. For example, nonuniform application of fertilizer will limit yields; low application rates and low yields in one area are not compensated for by higher yields in other areas with excessive rates (Voss 1976). On the other hand, many of the techniques proposed to increase efficiency of fertilizer use are relatively recent developments, and their impacts on crop production and on nitrate-related environmental quality have yet to be evaluated in full-scale field studies.

Soil and Tissue Testing

While no definitive studies have been conducted, the efficiency of fertilizer use might be improved by placing more emphasis on effective field testing and educational programs. Such programs have traditionally been conducted by state agricultural extension personnel, often in conjunction with privately owned soil and tissue testing laboratories.

Problems with the use of soil tests for predicting the amount of soil nitrogen available for a crop were discussed in Chapter 4. With annual crops such as corn, tissue tests for nitrogen are difficult to interpret (Jones and Eck 1973), and tissue analysis has the added disadvantage that it is often done too late in the growing season to correct a deficiency that might be revealed. However, considerable success has been reported in the use of tissue tests for prediction of nitrogen needs in commercial fruit production. Embleton et al. (1974) reported that the availability of commercial leaf analysis in California has led to reductions of up to 50 percent in nitrogen fertilizer use in orange groves. The amounts of residual nitrogen available for leaching from orchard soils were reduced by up to 80 percent.

Nitrogen fertilizer recommendations involve, first, an estimate of crop needs, which in turn requires that the potential yield be known with some accuracy. Secondly, the amount of soil organic nitrogen mineralized during the growing season, its availability to the crop, and the amount of any residual soil inorganic nitrogen must be estimated. Third, the efficiency of use of the applied fertilizer must be evaluated. This procedure is difficult at best, and has often led to rather simplified approaches where the amount of nitrogen added is equated to the amount removed in the harvested crop. This approach does not account for mineralization of soil nitrogen or for inefficiencies in fertilizer use (Stanford 1973).

Agricultural experiment station data are usually available to provide a first approximation of nitrogen removals by crops in a given area. Further, experimental data are usually adequate to estimate fertilizer efficiency. However, predicting the supply of nitrogen released from soil reserves is very difficult (see Chapter 4), and in practice soils are not routinely tested for mineralization rates. However, in more arid regions such as the Great Plains, consideration of the nitrate remaining in the root zone after harvest or at planting time can greatly improve the accuracy of fertilizer recommendations (Dahnke and Vasey 1973). Until more reliable soil tests are developed, fertilization recommendations for annual crops (especially long season crops such as corn) will require considerable skilled judgment on the part of the extension agronomist and the farmer. Efforts should be made to provide farmers with as much information as possible to avoid using more fertilizer than the soil and crops require, and continued long-term, on-farm research on soil and tissue testing for crop nitrogen needs is essential.

Slow-Release Fertilizers

If nitrogen is supplied in a form that becomes available for crop uptake slowly over the growing season, the amount available for leaching at any time will be reduced. Natural organic sources (soil humus, manure, or plowed-under legume crops) are in this category, since the process of mineralization is gradual. Inorganic fertilizers that solubilize slowly also have been developed; e.g., organic formulations (such as substituted ureas) and inorganic preparations (such as plastic-coated pellets).

Slow-release substituted ureas and sulfur-coated urea (SCU) have been used mainly on specialty crops and turf and lawn grasses, and are not especially suited to field crops such as corn, which require large amounts of nitrogen over short periods (Parr 1973). Sulfur-coated urea (Prasad et al. 1971) recently has received extensive agronomic evaluation; yield results have been mixed in comparison to yields with urea or anhydrous ammonia. Saffigna et al. (1977) found that much more of the nitrogen from NH_4NO_3 appeared in lysimeter leachate from irrigated potatoes during the early part of the growing season than in a comparable lysimeter with SCU. The SCU dissolved slowly, and some particles remained even after plant harvest. According to Parr (1973), SCU is likely to cost 25 to 40 percent more per unit of nitrogen than uncoated urea, and thus a substantial increase in crop yield would be needed to justify its use. It would appear that SCU has its main application to high-value crops and turf, and to soils where leaching is high. In these cases, its slow release characteristics can be used to economic benefit. On the other hand, many of the yield comparisons have been conducted at nearly optimal fertilization rates, but the benefits of a slow-release material would be more pronounced at suboptimal rates.

An alternative to the use of only one slow-release material is to blend materials of varying solubility to provide a product that would have a specific nitrogen release rate (Prasad et al. 1971, Parr 1973). Further research and development seem warranted in this area.

Use of Animal Manures

More effective use of animal manures would reduce the demand for chemical fertilizer somewhat; however, the nitrogen presently available in all manures is only about 10 percent of that used in fertilizers (CAST 1975), and under present farming systems, manure cannot possibly be regarded as a total or even a major substitute for fertilizer. Handling and application of manure is costly and has little economic return; this is especially true in the northern United States, where weather conditions dictate storage during winter, since runoff from applied manure can be minimized only if the manure can be worked into the soil. Further, it is difficult to estimate the amount of available nitrogen that is in applied manure (Frere 1976), and thus difficult to prescribe appropriate spreading rates.

Timing of Applications

The most logical approach to increasing fertilizer efficiency is to supply nitrogen as it is needed, i.e., to match applications closely to the nitrogen uptake curve throughout the growing season (Stanford 1973). Theoretically this could be accomplished with slow-release fertilizers, but these require further development before their use is practical. Alternatively, fertilizer can be supplied in several applications to match crop needs (Frere 1976). However, each application increases operating costs, and the use of field equipment compresses soil, consumes energy, and usually is limited to early in the growing season. With crops irrigated by sprinkler or drip irrigation, nitrogen can be supplied in the irrigation water.

Fall fertilization with anhydrous ammonia on heavier-textured soils is a relatively common practice in some areas (see Chapter 6). Under some weather and soil conditions, much of the fertilizer nitrogen can be lost. For example, a wet, warm spring could result in leaching and denitrification of nearly all of the fall-applied nitrogen, since nitrification of anhydrous ammonia is nearly complete by mid-spring. Fall application of nitrogen therefore should generally be discouraged as an environmentally unsound and economically wasteful practice.

An alternative practice in the corn belt is to supply some nitrogen (75 to 100 kg/ha) at or just before planting, and to add more as a sidedressing early in the growing season. Usually one, and sometimes two more supplemental applications are made. This practice is desirable in that fertilizer rates can be adjusted to take into account weather conditions and anticipated yields, but since incorporation of the fertilizer into the soil is usually required, root damage may result from the later applications (Kurtz and Smith 1966). Nitrogen fertilizer also can be supplied as a foliar solution, or as solid pellets by airplane. Foliar application has many problems (see discussion below), and application by air is expensive and may lead to inefficient fertilizer use.

Fertilizer Placement

Some benefits may be gained from more effective placement of fertilizers. For example, significant losses may result if urea or ammonia solutions are applied to the soil surface (Kurtz and Smith 1966), unless rain or irrigation water washes the nitrogen into the soil. However, little is gained from deep (>15 cm) placement of volatile fertilizers, and some damage to crops can occur if urea or ammonia is placed too close to the germinating seed.

Techniques to Minimize Leaching on Coarse-Textured Soils

Several techniques have been tested on experimental plots to reduce water infiltration and/or leaching. For example, Snyder et al. (1974) examined the effect of a plastic mulch and a water-repellent silicone applied over a fertilizer band to reduce nutrient leaching in a coarse-textured soil. They found the silicone to be as effective as the plastic mulch and much superior to an organic mulch. These and similar techniques require further economic evaluation before they can be recommended for field crops.

Foliar Applications

Ammonia and urea are effectively absorbed by plant leaves (Wittwer et al. 1963, Porter et al. 1972, Searsbrook 1965, Viets 1965). Urea has been used most often in foliar treatments because of its rapid penetration. This practice has been used for many years as a nitrogen supplement on high value truck crops, citrus, and deciduous orchards. It is most convenient and economical with crops that require frequent spray treatments with micronutrients or pesticides. The practice has not been widely adopted for field crops such as corn and wheat, primarily because severe leaf burn occurs if the concentration of urea in the spray solution is greater than 1 to 3 percent. Biuret (a condensation product of urea that commonly occurs in manufactured urea fertilizers) must be less than 0.25 percent of the urea for foliar applications (Viets 1965).

The maximum amount of nitrogen applied at any one time by foliar spray is usually 10 to 20 kg/ha. Since corn requires as much as 2 to 3 kg/ha-day during maximum growth, foliar feeding would need to be practiced once or twice a week. Obviously this is not economical at present. Also, application of the solution to corn or other row crops by conventional means (tractor-sprayer equipment) would be quite difficult by mid-season.

Yields of navel oranges in California were comparable with equivalent applications of nitrogen to leaves or to the soil, and a lemon crop produced 8 percent more fruit with foliar applications of 128 kg N/ha-yr than with soil applications of 484 kg N/ha-yr (Jones and Embleton 1965, Jones et al. 1970). Soil applications of up to 200 kg N/ha-yr did not increase the amount of nitrogen leaving the root zone, but applications in excess of 200 kg/ha-yr led to greater nitrate leaching. In contrast, foliar applications appeared to have no effect on nitrate movement, down to a soil depth of four meters. Because more than 200 kg/ha-yr of nitrogen is required for economic citrus production, foliar sprays might be used as supplements to soil applications of 200 kg/ha-yr, to meet crop nitrogen needs without greatly increasing pollution potential.

Foliar application of urea leads to some loss of nitrogen as ammonia, at a rate that depends on the time of day the urea is applied and on the weather (Viets 1965). Further research, development and educational efforts on foliar feedings of high value crops seem warranted. At present, this approach appears to offer little promise as a general practice to increase fertilizer efficiency in field crops. In addition, the limited supply of low-biuret urea has restricted the expansion of the practice even in cropping systems where its value is established, such as California citrus (T. Embleton, University of California, Riverside, personal communication, 1976).

Carbon Supplements

The incorporation of large amounts of organic carbon into soils can minimize leaching of residual nitrate from fertilizer applications by immobilization of inorganic nitrogen in the biomass of soil microflora. Corn stalk residues (including cobs) are commonly plowed back into the soil under current practices. With high-yielding corn, this residue may amount to as much as 5000-10,000 kg/ha of dry matter, with a C/N ratio of from 40:1 to 60:1. Such a high C/N ratio is quite favorable for immobilization of nitrogen (Bartholomew 1965). Immobilization of nitrogen by incorporated crop residues would tend to be minimal soon after fall harvest, because of cool temperatures. In most cropped systems, however, the return of crop residues is the major source of maintenance of reasonable organic carbon levels in soils.

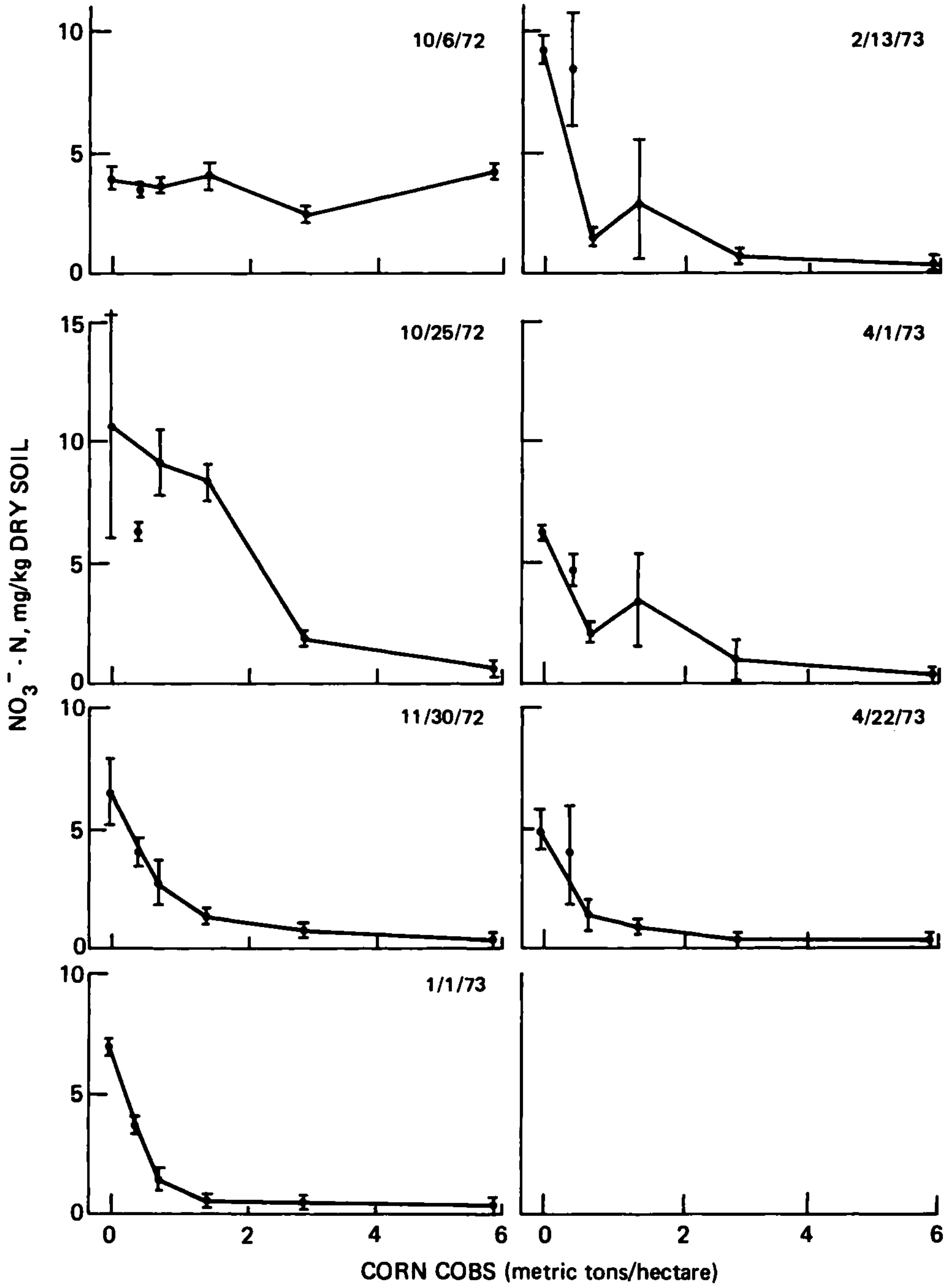
Steelman (1974) evaluated the advantages of incorporation of additional carbon as ground-up corn cobs or paper in amounts from 0.7 to 5.9 metric tons/ha (Figure 10.6). As expected, significant decreases in the concentrations of nitrate in the soil were obtained. Corn yields were not depressed except at the highest level of carbon supplementation. Although the effectiveness of carbon in immobilizing nitrogen is clear, this approach is probably not feasible for the great expanse of cropped soils. The greatest limitation is the lack of a ready supply of organic carbon material, available at low cost to the farmer (Steelman 1974). The research demonstrates, however, the advantages of a high C/N ratio wherever nitrogenous wastes are applied to soils. Use of cover crops would seem to be a more cost-effective method of immobilizing nitrogen and increasing the organic matter content of the soil.

Immobilized nitrogen will be released as the organic matter goes through the mineralization phase of the nitrogen cycle. It is likely that the nitrogen will be released at a time other than the period of maximum uptake by crops, and increased losses by leaching and denitrification could result. Additional studies need to be carried out to examine the fate of nitrogen in carbon-supplemented soils over intervals of several years, but given the limited applicability of carbon supplements, such research does not warrant high priority at present.

Urease and Nitrification Inhibitors

Anhydrous ammonia and urea are the predominant forms of nitrogen in fertilizer. Urea accounts for about 10 percent of the U.S. market at present, and its use is expanding rapidly. In recent years, there has been considerable interest and research into chemicals that retard the rate of hydrolysis of urea and/or the rate of nitrification of ammonia. The rationale for this approach is that retention of nitrogen in these forms reduces losses by leaching of nitrate or denitrification; in the case of urea, losses by volatilization of ammonia also are reduced. While considerable success has been achieved in inhibiting urease activity in laboratory studies, this technique has not been demonstrated to be effective in the field.

The formulation of fertilizers containing nitrification inhibitors offers promise for improving the efficiency of use of fertilizer nitrogen. The only compound currently registered by the U.S. EPA and approved for sale in the United States is nitrapyrin, the common name for 2-chloro-6-(trichloromethyl)-pyridine. Nitrapyrin is the active ingredient in N-Serve®, a product of the Dow Chemical Company (Mullison and Norris 1976). The compound inhibits



SOURCE: Modified from Steelman (1974).

FIGURE 10.6 Effect of carbon supplements on levels of leachable nitrate in a field that was planted to soybeans in 1972 and corn in 1973.

the activity of autotrophic ammonia oxidizers, specifically Nitrosomonas. Laboratory and field studies have shown that this compound effectively inhibits nitrification for at least 4 to 6 weeks in the field (e.g., Goring 1962, Hughes and Welch 1970, Briggs 1975).

The available evidence indicates that nitrapyrin (formulated as N-Serve®) presents few health hazards to nontarget species. Unpublished results of toxicological tests by the manufacturer indicate that the product has only moderate to low toxicity by all exposure routes (Mullison and Norris 1976). The acute oral LD_{50} for rats is more than 1000 mg/kg, and dogs can be fed up to 600 mg/kg with no ill effects. The toxicity to fish and other aquatic organisms is low, and the compound does not exhibit biological concentration in aquatic environments. Tests also indicate that nitrapyrin has no apparent adverse effects on soil microorganisms other than nitrifiers (Laskowski et al. 1975). Nitrapyrin degrades rapidly (within a few days to weeks) by chemical and biological pathways in plants, animals, and soils. Its only significant chemical residue is 6-chloropicolinic acid. Toxicological studies indicate that the latter compound has lower toxicity (acute oral LD_{50} of >2000 mg/kg for rats) than the parent product. Nitrapyrin is volatile (Briggs 1975) and soluble only in anhydrous ammonia and certain organic solvents. It is applied most easily by dissolving it in anhydrous ammounia.

Since treatment of soil with nitrapyrin enhances retention of ammonium ion in the root zone, plant growth in the presence of this agent depends in part on the ability of the crop to use NH_4^+ as effectively as NO_3^-. The shift towards ammonium nutrition can result in anion and cation imbalances and can affect the availability of other elements such as Ca, P, Mg, and K (Kirkby and Hughes 1970, Dibb and Welch 1974). Corn and a variety of other crops appear to be well adapted to NH_4^+ nutrition.

Increases in yield have been observed following use of nitrapyrin (e.g., Huber et al. 1974). The increases are usually attributed to lower losses of nitrogen by leaching or denitrification; however, reductions in plant diseases also appear to be a factor (Warren et al. 1975). For example, stalk rot on corn is more common in nitrate-enriched than in ammonium-enriched systems. Several no-response or negative effects of nitrification inhibitors also have been reported. For example, Keeney et al. (1976) found that nitrapyrin-treated plots showed either no effect or lower yields compared to non-treated plots of irrigated potatoes on a sandy soil. Favorable responses to nitrapryin apparently involve a combination of factors, including fertilizer practices, soil type, weather, and crop species.

The variable results with nitrification inhibitors thus far indicate that more research is needed to evaluate the conditions in which these compounds are best used. Possible side effects on soil microbial ecology need further study. Nitrification inhibitors are presently being promoted in part as a means of decreasing the losses of fall-applied ammonia fertilizer. The effectiveness of nitrapyrin in this regard has not been proven yet in field-scale experiments throughout the corn belt. Innovations such as this one, because they could increase the amount of fertilizer applied in the fall, must be viewed with caution at present.

Other inhibitors such as the pesticide Terrazole® (marketed by Olin Industries) and soil sterilants such as CS_2 (Briggs 1975) need more evaluation. As experience is gained with these and with yet-to-be-developed biological inhibitors, significant progress may be made in tailoring the rate of nitrogen transformations, particularly nitrification, to crop needs. However, it remains to be seen whether these materials will be cost-effective, or will significantly diminish nitrate pollution problems on croplands.

Limitations on Rates of Fertilizer Applications

A control option that has been the subject of considerable research and public policy debate in recent years is the restriction of nitrogen fertilizer applications to rates that are lower than the economic optima. Implicit in such a proposal is a judgment that some sacrifice in efficiency of crop production might be acceptable as a cost of maintaining or improving environmental quality. Applications of fertilizer nitrogen could be restricted, in theory, by several policy mechanisms. These include imposing regulatory limits, zoning land according to allowable fertilizer input rates, taxing fertilizer, selling rights to use fertilizer, and subsidizing farmers for losses in production that might result from reduced fertilizer use. This section reviews previous studies on the relationship between the degree of restriction of fertilizer use (by any policy mechanism) and the quality of the environment. A later section evaluates the economic and social impacts of such control measures.

The possibility of restricting fertilizer applications has been most widely studied in Illinois, and most of the following discussion is based upon what has been learned about the possible consequences of fertilizer regulations in that state. Although the problems and implications of such actions might be vastly different in other parts of the country, a comparable base of research does not exist for any other region.

It should be noted that the Illinois data are also far from conclusive. The Illinois Pollution Control Board has twice (in 1972 and again in 1975) considered the imposition of such restrictions, and in both cases it rejected the proposal on the grounds that an adequate scientific basis did not exist to select any particular limits (IPCB 1972, 1975). In order to augment the limited fund of scientific knowledge, researchers at the University of Illinois and at the Center for the Biology of Natural Systems (CBNS) at Washington University in St. Louis have studied the potential impacts of fertilizer limits on water quality, on crop production, and on the economy of the region (e.g., Aldrich et al. 1975, Parker et al. 1974).

Parker et al. (1974) correlated historical data on nitrate concentrations in surface waters of Illinois with data on agricultural practices and other factors that might explain the variation in nitrate levels. Using the coefficients thus obtained, they calculated the effects of differing degrees of fertilizer restrictions on water quality (see Table 10.9). One of the major findings of the study was that different regions of the state could achieve a given water quality objective with quite different degrees of restriction of fertilizer use; uniform statewide limitations would not have uniform impacts. Limitations required to meet the 10 ppm nitrate water quality standard 95 percent of the time varied from 100 lb/acre (112 kg/ha) to no restriction, depending on the region and the fraction of land in corn production.

Both the authors of the CBNS study and other scientists who have reviewed it recognize that some limitations in existing methods make the results much less definitive than the values in Table 10.9 might appear. The available data on water quality and fertilizer applications for the most part were gathered for other purposes; the data base is often incomplete, and contains many uncertainties and possible sources of error that hinder both research and policy making. Some important variables in agro-ecosystems inevitably show extreme degrees of colinearity, making an analysis of their independent explanatory power impossible. In an attempt to compensate for this difficulty, the CBNS study used some substitute measures; for instance, acreage in soybeans was used as a proxy for total acreage in row crops. The representativeness of such proxies can be questioned. The CBNS study also did not consider possible changes in land use, such as cultivation of additional acreage, that might occur as a consequence of fertilizer restrictions, or the impacts of such changes on water quality.

Largely unavoidable uncertainties in the analysis limit the confidence that can be attached to predictions of the relationships between proposed limits on fertilizer use and

TABLE 10.9 Estimated Limitations on Applications of Nitrogen Fertilizers to Corn Needed to Meet a 10 mg N/l Water Quality Standard for Nitrate in Illinois Surface Waters

		Fertilizer application limits required to meet standard				
		Percent of time standard exceeded				
Region of Illinois	Fraction of Land in Corn	1	5	10	20	50
		(lbs N/acre corn)[a]				
North	.50	90	110	120	130	160
	.45	110	130	140	170	***[b]
	.40	120	170	***	→	→
	.35	160	***	→	→	→
	.30	***	→	→	→	→
West Central	.50	100	130	140	170	***
	.45	120	160	300	***	→
	.40	150	***	→	→	→
	.35	***	→	→	→	→
	.30	***	→	→	→	→
East Central	.50	80	100	100	110	120
	.45	90	110	120	130	150
	.40	110	130	140	160	260
	.35	120	170	260	***	→
	.30	170	***	→	→	→
	.25	***	→	→	→	→
Southwest	.50	90	110	120	120	150
	.45	100	120	140	160	***
	.40	120	160	240	***	→
	.35	160	***	→	→	→
	.30	***	→	→	→	→
Southeast	.50	100	130	140	170	***
	.45	120	160	***	→	→
	.40	150	***	→	→	→
	.35	***	→	→	→	→
	.30	***	→	→	→	→

[a] Metric equivalent: 100 lbs/acre = 112 kg/ha.

[b] *** = no application limit required.

SOURCE: Modified from Parker et al. (1974).

resulting water quality. The CBNS is continuing to obtain more definitive information, by making more detailed examination of fertilizer use and water quality for 16 tributaries within a single watershed (Klepper 1978). It seems likely, however, that the complexity of agricultural systems will make definitive analysis impossible for many years. If fertilizer limitations are to be established, a large degree of uncertainty will have to be accepted and weighed as part of the policy decision.

Fundamental Changes in Agriculture

In addition to the improved management practices and regulatory approaches discussed above, some basic shifts in patterns of agricultural production can be envisioned that would reduce nitrate-related environmental pollution. These changes include development of more efficient varieties of crops, development of capabilities for nitrogen fixation in corn and other nonfixing crops by "genetic engineering," improvements in efficiency of fixation by legumes, improvements in crop rotation patterns, and a return to mixed livestock-field crop farming practices in which manures are used at least partially to replace chemical fertilizers. None of the changes is likely to be pursued solely for the sake of control of nitrogen losses, and in most cases there has been little research to indicate the quantitative effects of any of these measures on environmental problems. Nevertheless, both the environmental implications and the economic and social consequences of such changes deserve to be examined.

Improved Crop Varieties

The recent increases in fertilizer prices, which are closely related to increases in energy prices, already have stimulated considerable research on improving nitrogen fertilizer technology. Research also should be initiated to develop crop varieties capable of more efficient use of fertilizer nitrogen. For example, corn breeding efforts should perhaps concentrate on obtaining varieties that use residual soil nitrogen more efficiently and give good yields in the 50 to 150 kg N/ha range. Improvements in this area are limited, however, since a corn crop removes about 0.8 lb N/bushel of grain, and thus a minimum of 100 lb N/acre (112 kg N/ha) is needed to produce a crop of 120 bu/acre.

Symbiotic Nitrogen Fixation by Corn and Other Cereals

The possibility exists that the genetic information for the synthesis and control of nitrogenase can be transferred from plant species that fix nitrogen to those that do not. Research to accomplish this is being pursued in several laboratories (Hardy and Havelka 1975). While such a breakthrough could be at least a partial solution to the environmental and economic problems asociated with intensive use of chemical fertilizers, its success is very speculative at present. Furthermore, widespread fixation of nitrogen by cereals could lead to even greater increases in fixed nitrogen levels in croplands than at present.

Another approach currently being studied is the use of nitrogen-fixing free-living bacteria in the root rhizosphere. Again, many problems exist, not the least of which are the high energy requirement for nitrogen fixation and the numbers of bacteria needed. A plant-algal symbiosis in rice fields with the small aquatic plant *Azolla* and *Anabaena* has been reported to fix from 60 to 140 kg N/ha (Hardy and Havelka 1975; see Chapter 2).

Increased Nitrogen Fixation by Legumes

Considerable research effort is currently being expended to increase nitrogen fixation by legumes, mainly through genetic engineering of *Rhizobium* (Hardy and Havelka 1975; see Chapter 2). These efforts, if successful, could result in major shifts in American agriculture in the next two decades, toward less dependence on chemical fertilizers. The farming systems that might evolve from these research efforts will need to be evaluated with respect to their potential for environmental nitrate pollution.

Changes in Crop Patterns

A shift to increased acreage of soybeans, alfalfa, and other legumes and decreased acreage of corn would reduce the amount of chemical fertilizer used. However, information on the exact environmental consequences of major shifts in cropping patterns is not available. Substantial alterations in the relative production of various forage crops could occur only in conjunction with changes in livestock production, land use, and possibly in the human diet. Similarly, improvements in the direct use of plant protein for human foods could also have large impacts on dietary habits, and thus on the markets for specific crop products. The environmental and social consequences of such adjustments in the agricultural system are difficult to project.

"Organic" Farming

Commoner (1977) has suggested that farms that combine production of field crops and livestock and return animal manures to croplands are environmentally preferable to farms that produce only grain (the majority of farms in the corn belt), because of the reduced use of chemical fertilizers and the recycling of animal wastes to the soil. Some commercial farms presently rely exclusively on organic sources of nitrogen, and a research team from the CBNS recently compared energy use, crop yields and crop production costs on 14 large-scale "organic" farms and 14 "conventional" farms (Lockeretz et al. 1976). The average corn yield per acre on organic farms was 87 percent of that on conventional farms, and the organic farms had less cropland in corn. For other crops, the yield ratios ranged from 82 percent (wheat) to 100 percent (soybeans). Gross income per acre on organic farms was only 90 percent of that on conventional farms, but because of lower costs of production, the net return per acre was the same over a two-year period for both groups. These results led Commoner (1977) to suggest that organic farming techniques, supplemented by relatively low additions of inorganic fertilizer, could attain per acre production rates on cropped areas equivalent to those of conventional farms, while minimizing fertilizer-related nutrient losses. No data are currently available on losses of nitrogen from croplands farmed "organically," however, and quantitative assessments of the environmental impacts of a shift toward organic techniques cannot be made. Furthermore, Lockeretz et al. (1976) point out that organic farms add less potassium and phosphorus than they remove, and that eventually these soil reserves may be sufficiently depleted to require fertilizer additions. A similar situation may exist for nitrogen, although balance sheets for such operations are difficult to construct accurately. The long-term net effect could be reduced crop production.

Mixed-system farming has largely disappeared from the corn belt for numerous reasons (see the earlier discussion of crop rotation), and its reintroduction would require large shifts in technology, economics and diet. No study has yet been conducted to assess the aggregate social impacts of the large changes in farming patterns that would be required to maximize the use of the manure resource.

Reduced Area in Cultivation

Aldrich (1972) suggested that the total amount of land in cultivation may be as important in explaining nitrate levels in surface waters as are fertilizer application rates. Cultivation increases the rate of mineralization of soil organic nitrogen and thus may contribute to nitrate leaching even in the absence of added fertilizer. Researchers at the CBNS, however, found no statistically significant relationship between water quality and soybean acreage (Parker et al. 1974). This suggests that the mineralization of soil organic nitrogen is probably not the major source of nitrate in surface waters, and that the area planted in heavily fertilized crops, rather than the total cultivated area, may be the most critical land-use variable.

A reduction in total area planted, or in areas planted to corn, if not accompanied by an offsetting increase in fertilizer applications, would reduce total fertilizer inputs, and thereby mitigate some nitrate contamination problems. Again, however, detailed analysis of the environmental consequences of such changes has not been performed. Any substantial reduction in cultivated area would almost certainly be accompanied by a reduction in total production of crops. About 85 percent of the corn grown in Illinois is used as livestock feed. Major changes in cattle feeding practices, (i.e., increased use of pasture and range instead of feedlots), a reduction in the size of cattle populations, or increased reliance on imported grain for cattle feed would probably be associated with any large reductions in crop acreage. The environmental, economic, and social implications of such changes cannot be evaluated at this time.

Costs of Controls for Croplands

Analysis of the costs of controlling nitrate pollution from agricultural lands requires evaluation of a very complex system, in which changes in one variable can affect many others. Control costs include not only the direct costs of implementing control measures (such as equipment costs, labor, and administrative costs of enforcement or education), but also the costs of such secondary impacts as potential losses in crop production, changes in land use, water use, and energy consumption (with associated environmental impacts), effects on costs of crop production and on farm income, effects on the kinds and prices of food available, and effects on the distribution of income. The selection of appropriate control measures requires the analysis of multiple trade-offs among these effects, and comparison of costs with an equally complex array of benefits. The perception of the trade-offs involved and of the social value attached to specific consequences can change dramatically in a few years (Viets 1975). For instance, control measures that lead to denitrification of fertilizer may preserve water quality, but the cost of such measures in terms of the risk of effects on stratospheric ozone has only recently entered the evaluation.

Because the analysis is so complicated, and many control techniques are still in the experimental stages of development, little information on costs is available. The most important exception is the cost of limitations on rates of fertilizer application, which have been studied fairly extensively.

Runoff Controls

The costs of storage and treatment of runoff from agricultural lands should be similar to the costs of controlling runoff from urban lands (discussed in a later section of this chapter). In some cases, management of existing flood control systems to provide adequate detention time for removal of nutrients may be the only control required. However, the costs of building storage reservoirs where none exist (which is the case for most croplands) probably would be very large in proportion to even the multiple benefits gained from controls.

Best Management Practices

Agricultural practices such as erosion control and crop rotation have their own economic justification, and any control of nitrate problems that can be achieved by these methods should involve minimal additional costs. More careful management of irrigation might cost a few dollars per hectare for increased monitoring and regulation of flows, or up to twelve dollars per hectare for the installation of sprinkler irrigation, lined canals, or desalination of return flows (Toups Corporation 1975). These costs might be partially offset by reduced water consumption. The use of cover crops involves expenses for seed, labor, equipment, added uses of pesticides and energy, and perhaps some adverse impact on planting the spring crop; however, comparisons of these costs with the benefits of various cover crops on specific sites are generally not available.

Improved Fertilizer Management

In general, practices that improve the efficiency of crop use of fertilizer should have economic benefits in terms of lower fertilizer costs. Whether these savings would offset more expensive formulations of fertilizers or increased costs of management cannot be determined from present information. Carbon supplementation of soils would involve added costs of obtaining and applying the carbonaceous material; however, Steelman (1974) could identify no available high-volume source of the material. Nitrogen retained in soil because of carbon additions would probably lower future needs for fertilizer, but according to Steelman (1974), it is doubtful that this saving would offset the initial costs. Nitrification inhibitors require further evaluation also, to determine the ratio between the costs (for chemicals, equipment, and labor, as well as possible impacts on production) and the benefits (reduced loss of fertilizer and possibly increased efficiency in the use of equipment and labor).

Regulation of Fertilizer Applications

It can be reasonably assumed that, should such an approach be attempted, restriction of fertilizer applications to levels below the maximum economically efficient rate would decrease productivity per unit of land area. Because of the complexity of factors that determine crop yields on a given site in a given year, the magnitude of the expected decrease cannot be estimated with any accuracy (see Chapter 8). Some loss in yield might be offset by the substitution of manures for chemical fertilizers, or some of the other management techniques discussed above; but the impact of such practices on costs of production would need to be considered. A decline in per-acre yield could lead to planting of increased acreage, with corresponding increases in erosion, loss of organic soil nitrogen, and pesticide and energy uses (Taylor and Swanson 1975). The increases in these environmental impacts would be disproportionately greater if the land brought into cultivation were of lower quality than land currently being cropped (Aldrich 1972). Expansion of cultivated acreage would decrease the uses of such land for other purposes, such as recreation or wildlife habitat. The combination of effects likely to result from fertilizer restrictions probably would affect the costs of production, the prices of agricultural commodities, the income of farmers, and the distribution of income, on several scales.

If fertilizer limits were imposed by regulation, additional governmental costs would be incurred in the adminstration of control programs; enforcement would be difficult and expensive at best. Alternatives with a lower administrative cost might be the imposition of an excise tax on fertilizer, or the establishment of a market for rights to use nitrogen fertilizer (Taylor 1975a, 1975b). The taxation approach assumes that the economically optimum rate of fertilization would decrease automatically if a tax were imposed on fertilizer, but in reality this is not the case, because crop prices fluctuate. Taxation thus would need to be coupled to the price of corn, which is not reliably known at the beginning of the season. Selling rights to fertilizer use, on the other hand, could lead to inequitable allocation of fertilizer rights. Research to date has been inadequate to support definitive estimates of the costs of these latter two approaches, but Taylor's (1975a, 1975b) analysis suggests that the market rights approach may be a viable alternative.

The most thoroughly studied control options from the standpoint of economic impacts are those based on statutory limitations of per-acre fertilizer applications. Taylor and Swanson (1974, 1975) used a linear programming model to examine the effects of state (Illinois) and national restrictions on the areas planted to different crops, on total fertilizer use, on crop yields, and on the costs of production. According to their model, a limit of 150 pounds of nitrogen fertilizer per acre (168 kg/ha) imposed in Illinois would cause fertilizer use to decline by 9 percent, but farm income would rise by 0.4 percent, primarily because of reduced expenditures for fertilizer (see Table 10.10). If the limit were 100 lb/acre (112 kg/ha), fertilizer use would drop 29 percent. While the area planted would not change significantly, yields would decline, and farm income would fall off by about 4 percent. At a restriction to 50 lb/acre (56 kg/ha), the effects would be more drastic. Fertilizer use would be reduced by 81 percent; the area in corn in Illinois would decline by 49 percent; the area in soybeans would increase by 78 percent; and per-farm income would be reduced by 17 percent.

A similar study by the CBNS (Parker et al. 1974) projected the impacts of fertilization limits on corn production and farm income for different regions of Illinois. Table 10.11 shows the results of (a) regional and (b) statewide limits intended to meet the 10 mg N/l water quality standard for nitrate 95 percent of the time. To achieve that goal, a 130 lb/acre (146 kg/ha) limit would have to be imposed in only one region of the state (east central Illinois), and only 37 percent of the farms in the region would be affected. Corn production would decline 1.1 percent in the region, and 0.5 percent in the state. Gross farm income would be lowered by an average of $539 per farm affected in the region, but net income would be only 1.7 percent lower. If a statewide limit of 130 pounds/acre were imposed, impacts on production and income across the state would be approximately doubled, without a correspondingly increased benefit to water quality.

The results of the separate studies of the University of Illinois and CBNS groups are quite similar in many respects. Fertilizer application limits of 100 or 130 lb/acre are projected by both studies to have only modest effects on corn production and on farm income. The economic impacts of a 50 pound/acre limit would be much more severe, but there is little basis for supposing that such a restrictive policy would ever be needed to achieve acceptable environmental quality. A 150 lb/acre limit, on the other hand, might have beneficial economic effects by eliminating some wasteful use

TABLE 10.10 Projected Consequences of Several Alternative Policies to Control Fertilizer Use in Illinois

	Policies						
	Fertilizer limitations, (maximum lbs N/acre)			Excise tax, (¢/lb N)		Market for rights (million lbs N sold)	
Variable affected	150	100	50	12	24	672	395
Percent change in fertilizer use	-9	-29	-81	-61	-76	-61	-76
Change in area in corn, 10^6 acres	+0.03	+0.04	-5.7	-5.7	-7.7	-5.7	-7.7
Change in area in soybeans, 10^6 acres	+0.02	+0.03	+4.4	+6.6	+8.8	+6.6	+8.8
Corn production, as percent of production with no restrictions	99.7	95.8	41.7	--	--	--	--
Soybean production, as percent of production with no restrictions	100.3	100.4	194.8	--	--	--	--
Price of corn, cents per bushel	47.94	48.33	51.14	--	--	--	--
Percent change in net farm income	+0.4	-4.0	-17.0	-9.6	-12.3	-9.6	-12.3

SOURCE: Derived from Taylor (1975b) and Taylor and Swanson (1975).

TABLE 10.11 Projected Consequences of Two Regulatory Approaches to Control Surface Water Pollution by Nitrogen Fertilizers in Illinois

	Consequences, by regions of Illinois					
Variable	North	West Central	East Central	Southwest	Southeast	Entire State
Percent of area in corn, 1971	31	36	39	21	16	29
(A) Variable limitations, to meet water quality standard 95 percent of the time (see Table 10.10)						
Fertilizer limits, lbs N/acre	none	none	130	none	none	--
Percent of farms affected	0	0	37	0	0	13
Percent reduction in corn produced	0	0	1.1	0	0	0.5
Decrease in gross income per affected farm ($/yr)[a]	--	--	539	--	--	539
Percent decrease in net income for affected farms	--	--	1.7	--	--	1.7
Total decrease in gross farm income (million $)	0	0	6.64	0	0	6.64
(B) Uniform statewide limitation on fertilizer applications						
Fertilizer limit, lbs N/acre	130	130	130	130	130	130
Percent of farms affected	23	24	37	23	13	27
Percent reduction in corn produced	0.6	0.7	1.1	1.6	0.7	1.0
Decrease in gross income per affected farm ($/yr)[a]	417	429	539	573	386	503
Total decrease in gross farm income (million $)	1.54	1.37	6.64	2.41	0.58	12.54

[a] Price of corn was assumed to be $1.25/bushel.

SOURCE: Modified from Parker et al. (1974).

of fertilizer. In each case, the consequences would not be uniform; some farmers would be more severely affected than others. Although it can be assumed that increased costs of production traceable to regulation of fertilizer would eventually be matched by higher commodity prices, some farmers might be heavily affected by the short-term disequilibrium.

Despite the relative agreement of the two analyses, there are a number of major uncertainties and limitations on the confidence that can be placed on these projections of economic effects. There are few good yield-response data upon which to base estimates of production declines due to restrictions on fertilizer use (see Chapter 8). Both studies relied largely on data compiled from decade-old experiment station results by Ibach and Adams (1968). Taylor and Swanson (1975) attempted to adjust the data to match actual current yield-response relationships on commercial farms, but uncertainties remain. It is interesting to note that although Klepper (1978) calculated an economic optimum application rate for corn in the Sangamon (Illinois) watershed of 170 to 190 lb N/acre, and Swanson et al. (1973) and Taylor and Swanson (1973) estimated the optimal rates to be 200 or more lb/acre for several regions of Illinois, the actual fertilizer application rates in the state are estimated at 115 to 125 lb N/acre in recent years (see Chapter 6). The estimates of nitrogen applications may be low, because of failure to include manure and other possible weaknesses in the data. It appears, however, that current practices on many farms in Illinois amount to underfertilization and that statutory limits on fertilizer use rates could prevent the attainment of higher levels of production.

S.R. Aldrich (Department of Agronomy, University of Illinois, Champaign-Urbana, personal communication, 1976) has pointed out that flat limitations of fertilizer applications, even within a region, may be inequitable. Some of the highest rates of application may occur on farms where production is most efficient, and where careful management allows the farmer to make maximum use of fertilizer applications while minimizing losses of nitrogen to the environment. More serious nitrate pollution problems may result from lower application rates that are combined with less effective management practices, on other farms. These essentially intuitive observations seem reasonable, but no research data are available to indicate the impacts of regulations on individual farms with differing management capabilities. Although the most equitable approach might be to tie fertilizer regulations to the practices and management efficiencies of single farms, the economic and administrative costs of such a strategy have not been estimated.

In summary, the existing analyses of the economic impacts of restrictions of fertilizer applications provide some useful information for comparing policy alternatives. The economic models used rest on many assumptions that may be invalid, although without them the system would be too complex to be analyzed. As a result, the projected economic effects of limits on fertilizer applications are far from conclusive. If firm cost data are lacking for such limits in Illinois, where problems are largely tied to a corn monoculture, it is not surprising that virtually no estimates have been made of the costs of fertilizer limitations in states with more diversified agriculture, such as California.

Fundamental Changes in Agriculture

The economic and social impacts of the fundamental changes in agriculture described earlier would in all likelihood be far-reaching and significant. At present, the large number of important connections among agricultural and economic variables that would need to be examined have not even all been identified, let alone translated into credible quantitative coefficents. Although it is important to pursue efforts to obtain such information, it is not possible now even to speculate as to the magnitude of costs (and benefits) of such changes.

CONTROLS FOR POLLUTION BY LIVESTOCK WASTES

A study by the U.S. EPA (1974) identified 18 different subcategories of livestock feeding operations, and recommended zero discharge of effluents (except during catastrophic storms) for all categories except ducks. EPA proposed regulations for feedlots in 1975 (U.S. EPA 1975a), and such sources are now subject to the regulations that were subsequently adopted.

The most favored options for control of pollution from feedlots are land spreading of manures, and anaerobic or aerobic treatment of collected wastes in lagoons or oxidation ponds. Often the two methods can be combined, with land disposal of effluents from holding facilities.

Simple containment facilities for solid manures can be highly effective in controlling runoff from feedlots in arid regions, but they may achieve only 50 to 80 percent control in other areas, because of higher volumes of runoff (NCWQ 1976). The higher cost and lower effectiveness of runoff controls in high rainfall areas make it likely that zero discharge regulations will accelerate movement of the feedlot industry to the southwest (Viets 1971).

Anaerobic and aerobic treatment methods also have been evaluated for managing animal wastes (Moore 1970, Nye 1973). Anaerobic lagoons can create odor problems, and sludge build-up is a further deterrent to their use. Aerobic treatment overcomes the odor problems, but adds to the complexity and expense of treatment. Both methods produce effluents that are too concentrated for discharge to streams, but are suitable for land disposal. Erickson et al. (1972) described a nitrification-denitrification method for treating animal manures. The system used a soil mound for nitrification, an anaerobic barrier beneath the mound for denitrification, and molasses as a supplemental source of energy. This approach apparently has not been developed for full scale operation.

Land disposal is presently the most feasible method for handling livestock wastes. Coote et al. (1975) reviewed various strategies for land spreading of manures for dairy farms in New York (see Table 10.12). Guidelines for animal waste disposal have also been developed for other areas of the United States (e.g., Meek et al. 1975). The area required for land spreading and the preferred management practices depend on the climate, soil types, terrain, and other parameters of specific sites. If manures are applied at rates of nitrogen input equivalent to recommended fertilizer applications, and if they are mixed into the soil to minimize ammonia losses, the environmental impacts (chiefly leaching of nitrate) should be no greater than in farming operations that rely on nitrogen fertilizers.

While land spreading and containment/treatment of runoff can reduce the direct impact of livestock wastes on surface water quality, neither technique prevents ammonia losses, odors, or leaching of nitrate into the soil profile. Lagoons also accumulate sludges, which pose an additional disposal problem.

Several other alternatives exist to alleviate some pollution from livestock wastes, but none of them appear to be economically competitive and/or capable of absorbing much of the enormous tonnage of manure produced each year. These techniques include composting, dehydration, pyrolysis, incineration, and recycling the nitrogen into the food chain by using manure as feed for livestock or for organisms (algae, invertebrates) that can be fed to livestock (Nye 1973).

Costs of Controls

The U.S. Department of Agriculture conducted a number of studies of the potential economic impact of EPA's proposed regulations on discharges from feedlots (USDA 1974, 1976; Johnson et al. 1975a); the economic analyses were done

TABLE 10.12 Restrictions Imposed on Disposal of Solid Manure for Two Hypothetical New York Dairy Farms

Parameter	Restriction level 1	Restriction level 2
Application rates of manure	50 tons/acre (112 mt/ha)	Expected plant uptake of N plus allowance for organic matter maintance and denitrification minus allowance mineralization
Slope	n.a.	No manure on slopes >20%
Distance from surface water capable of leaving farm	n.a.	No manure <30 m if sodded or <60 m if cultivated
Time of year	n.a.	No manure during December-April.
Distance to dwelling or public access	No manure within 30 m of dwellings or public access	No manure <150 m from dwellings or public access; no storage <150 m from dwellings or 75 m from from public access
Minimum land area	0.04 ha/animal unit	0.2 ha/animal unit

SOURCE: Adapted from Coote et al. (1975), with permission of the New York State College of Agriculture and Life Sciences at Cornell University.

before final regulations were adopted, and were based on assumptions about the numbers of operations that would be subject to control. As is true for other sources, only a fraction of the total cost of control can reasonably be assigned to prevention of nitrogen-related pollution problems. According to Johnson et al. (1975a), investment costs for control of wastes from beef cattle feeding operations in the 18 leading beef producing states would be $132 to $136 million, and annual operating costs would be $20 million. An earlier study (USDA 1974) estimated that effective control of wastes from swine operations (511,000 farms, producing 89 percent of the marketed hogs and pigs) could require investments of up to $290 million, and annual costs of $36 to $44 million. An analysis by USDA (1976) of the impacts of EPA's proposed regulations for the beef, dairy, and swine industries concluded that about 200,000 operations would be affected; total costs were estimated at up to $365 million.

Each of these economic analyses has emphasized that the costs of control fall disproportionately heavily upon smaller operations. About half of the marketed beef and more than 70 percent of the dairy and pork production affected in the USDA analysis is produced in small feedlots (<100 beef cattle, <70 dairy cows, or <250 swine). Investments per unit of production could be more than 10 times higher for small operations than for large feedlots. While the USDA saw no long-lasting adverse impact on the industry as a whole or on prices of livestock products, the analysis emphasized that many small farmers could be hurt by short-term impacts, and some would undoubtedly be put out of business. Relocation was found to be the least-cost solution for an estimated 10 percent of the operations affected by EPA's regulations (USDA 1976).

CONTROLS FOR URBAN RUNOFF

Several alternatives are available to control urban stormwater pollution. At present, storage-treatment techniques are emphasized (Lager and Smith 1974). Storage options include in-line sewer storage as well as off-line storage in ponds and surface or subsurface reservoirs. The provision of storage reservoirs can be useful both for regulating the flow of runoff into receiving waters (reducing peak runoff), and for collecting runoff prior to wastewater treatment. The treatment employed may be one of the techniques listed in Table 10.2; or stored runoff may be released at controlled rates to a lake, river, wetland, or land disposal site. The efficiency of nitrogen removal by storage/treatment will depend on many factors, including the percentage of runoff that can be treated. Primary treatment of stormwater can be obtained using swirl concentrators, micro-strainers, dissolved air flotation, or sedimentation.

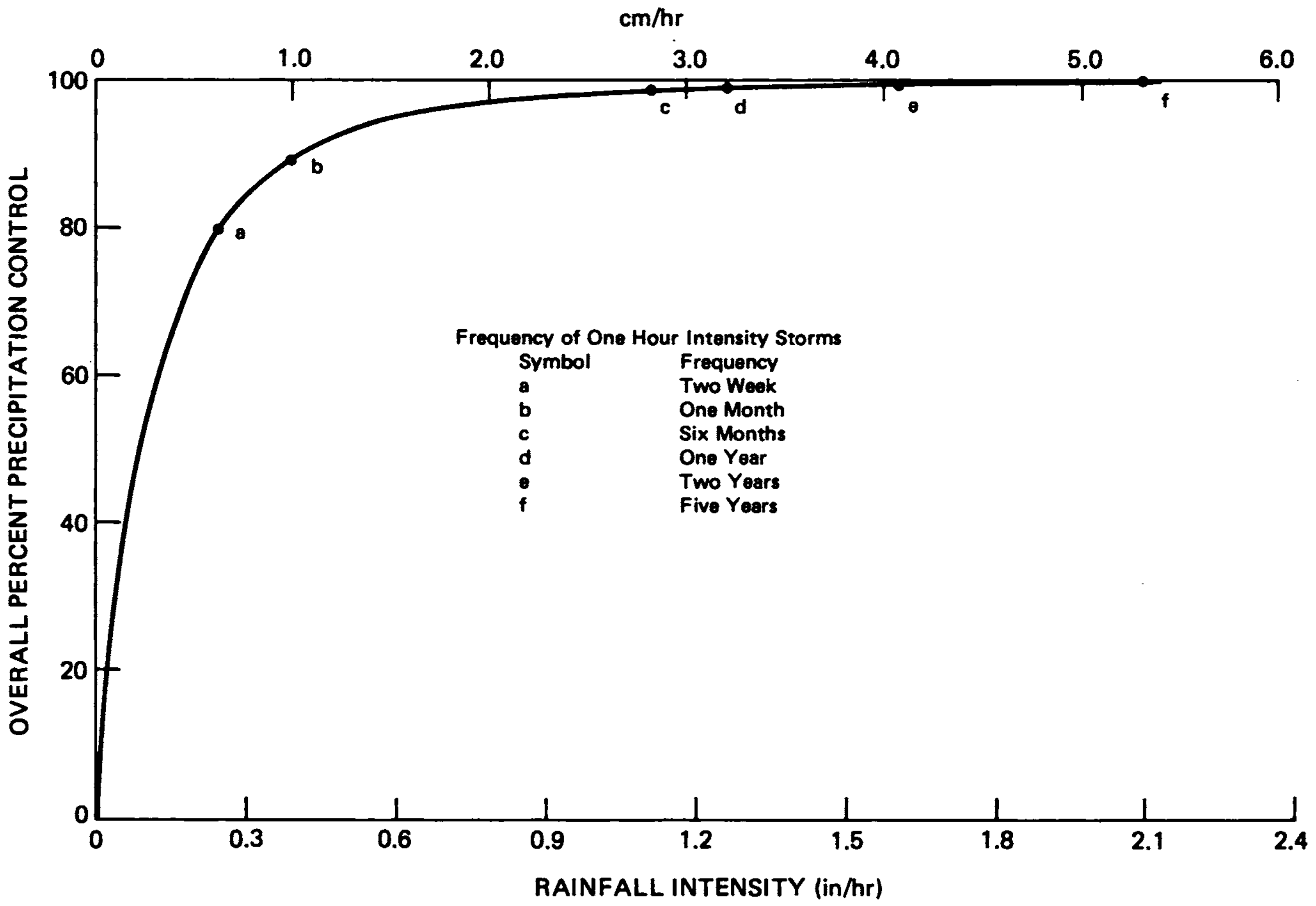
Contact stabilization or physical-chemical methods can be used to obtain higher degrees of removal.

Preventive measures, such as source and collection system controls, may be used to reduce the need for storage-treatment, and a combination of both approaches may provide a more cost-effective pollution management package than either would separately. Source and collection system controls are often referred to as "best management practices" (BMPs); examples include street sweeping, combined sewer flushing, erosion control, and catch-basin cleaning. Little is known regarding the ability of the above control alternatives (both BMPs and storage-treatment techniques) to remove nitrogen; most of the information that does exist focuses on control of BOD. EPA (1976a) has reviewed available techniques for control of urban runoff.

Costs of Control

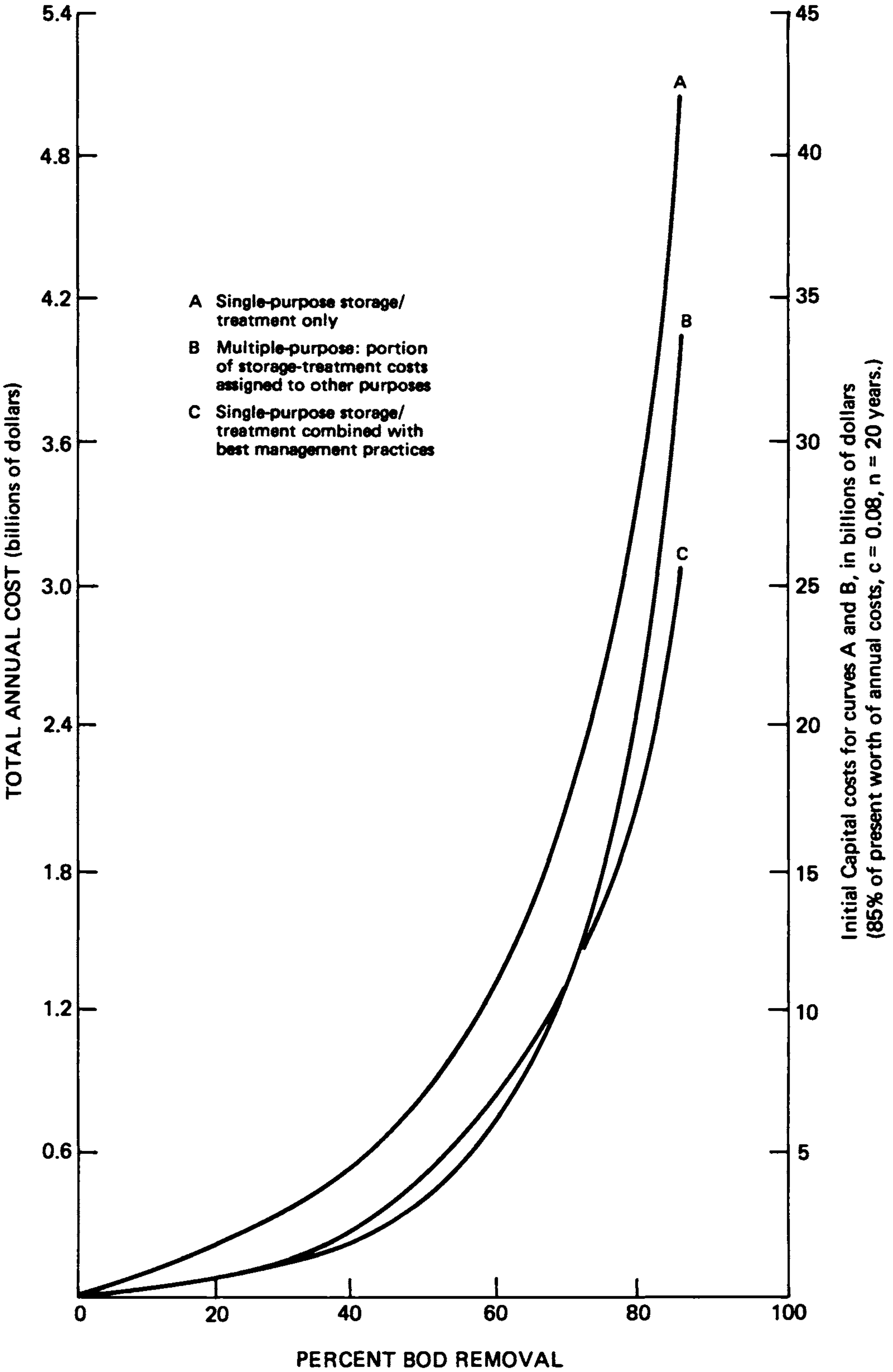
Following the tradition of designing storm drainage systems based on a specified design "event," early efforts to estimate wet-weather control costs arbitrarily selected a "design storm," to size the control units. Recently published studies for the National Commission on Water Quality used a two year, one hour storm as the control criterion. Heaney et al. (1976) assessed the costs of controlling stormwater runoff for the United States, using varying levels of control of total annual runoff volume as control criteria, and derived much lower control costs than the NCWQ estimates. As shown in Figure 10.7, relatively little additional pollution control is obtained by containment of runoff from storms that occur less frequently than every few months. Thus, the choice of a "design storm" has a very significant impact on total costs.

The projected nationwide costs of stormwater runoff control using a variety of treatment and BMP options are shown in Figure 10.8. For storage/treatment alone (curve A), marginal costs increase at higher levels of control, because of the disproportionately greater amount of storage required to capture runoff from less frequent, larger storms. Significant savings can be realized, however, when some costs of storage can be allocated to drainage control and when wet- and dry-weather treatment facilities are used jointly (curve B). Further substantial savings in control costs can be obtained by including BMPs as partial alternatives to storage-treatment devices (curve C). Flushing of combined sewers and sweeping relatively dirty portions of urban areas are cost-effective control options. The control cost curves for nitrogen alone should have the same shape as the curves for overall control of runoff, shown in Figure 10.8; those total costs could reasonably be apportioned among control of several pollutants.



SOURCE Heaney et al. (1977).

FIGURE 10.7 Comparison of intensity of rainfall events and efficiency of control systems required to contain runoff from storms of different intensities and frequency. Data from Atlanta, Georgia, 1948-1972.



SOURCE: Modified from Heaney et al. (1977).

FIGURE 10.8 Costs of control of urban stormwater runoff for the United States.

CONTROL OF POLLUTION FROM SEPTIC TANKS

The septic tank soil disposal field is the principal means of disposal of household wastes in nonsewered areas. About 25 percent of the population of the United States lives in such areas (NRC 1972), and about 0.3 million metric tons of nitrogen is disposed of annually in septic tank soil disposal systems. The septic tank is essentially an inefficient anaerobic digester with a detention time of one to five days. Some particulates are settled out, and the raw effluent, which typically contains 200 to 300 mg/liter of BOD and 50 to 75 mg/liter of nitrogen, primarily as ammonium (75 percent) and organic nitrogen (25 percent), flows by gravity to the soil disposal field. The field usually is constructed of tiles or perforated pipe, set in a gravel bed about 1 to 1.5 m below ground surface. The effluent percolates through the soil, resulting in essentially complete removal of BOD, pathogenic microorganisms, and usually phosphorus (Bouma et al. 1972). However, the nitrogen is nitrified and moves down with the effluent to the groundwater. Much of the particulate organic nitrogen, along with biological material, is deposited at the gravel-soil interface, forming a semipermeable crust. This nitrogen also is mineralized and subsequently nitrified. Hence, septic tanks are potential nonpoint sources of nitrate (see Chapter 6 for discussion).

Septic tank-soil disposal field systems are plagued with problems. The most serious is the fact that they often have been installed where the soil is unable to accept the water flow because of low permeability, or where insufficient soil is available over bedrock to purify the waste adequately.

Research to overcome these problems has led to development of "fill" or "mound" systems (Bouma 1974), wherein the disposal field is placed in a specially designed mound above the soil. These systems, while more expensive, have been successful and could permit more widespread development of suburbs in unsewered areas. Nitrification also is quite efficient in the mound systems, and small scale research on denitrification of the nitrified effluent has shown that the process is technically feasible, using either methanol or elemental sulfur as energy sources (Sikora and Keeney 1976a, 1976b). Problems with the methanol system involve the need for maintenance and the high cost, while the elemental sulfur system results in high concentrations (50 to 60 mg/l) of sulfate in the effluent.

The only presently feasible means of controlling nitrate output from septic tank disposal fields is through proper land use and zoning controls, which either limit the density of housing or prohibit development unless sewer connections are available. Technical solutions such as the small scale treatment plants described here, or denitrification of the disposal field effluent, are expensive and are probably not feasible on a long-term basis because of maintenance problems.

CONTROLS FOR MISCELLANEOUS SOURCES

Nonpoint sources not already discussed include silviculture, mining, construction sites, recreational sites, and similar land use activities. Most of the nitrogen in runoff from such sources is in organic forms in eroded soil particles. Some forest lands are fertilized, and some fire retardants are composed of ammonium compounds. Fertilizer from golf courses, human wastes from heavily used camping or picnic sites, and animal wastes from grazing on forest and range lands may also contribute to nitrate loads in runoff or leaching water. Although the quantitative importance of these sources is not readily ascertained, it is safe to say that they are quite minor in comparison to croplands, feedlots, and urban stormwater runoff. Nevertheless, such sources may contribute to local degradation of water quality (U.S. EPA 1973b).

Control techniques for such sources are generally soil conservation practices designed to minimize erosion from logging, burning, recreation, or the construction of roads and trails. Where problems are the result of concentrated human wastes, the solution may be to install or improve the design and location of septic tanks. An array of effective control measures for this category of non-point sources has been reviewed by EPA (1973a, 1973d, 1976; J.M. Montgomery Inc. 1976). Typical expenditures for minimizing runoff and erosion from construction sites range from about $400 to $800 per hectare (U.S. EPA 1973a). As is the case with all other nonpoint source controls, the cost of controlling nitrate per se is just a small part of the cost of the control plan.

LIMITING EXPOSURES OF SENSITIVE POPULATIONS TO NITRATES

In many cases, the principal environmental problem associated with nitrate pollution is the risk of adverse health effects in humans or animals who ingest excessive amounts of nitrate or nitrite. Where this is true, one control option is to identify the population at risk and protect it against excessive exposures, rather than to attempt to reduce the amount of nitrate in the environment through control of sources, transport, or transformation processes. Control of exposures is likely to be a viable course of action only in relation to certain hazards, specifically health risks. On the other hand, if measures to reduce exposures to health hazards are implemented, the perceived urgency of nitrate-related problems in general may be reduced, and the attainment of other environmental quality objectives could be retarded.

The costs of control methods that focus on protecting receptors are likely to vary according to the size of the population to be protected, the degree of protection desired, and the techniques used to achieve protection. Few studies of such costs have been published; it seems advisable, however, to examine the cost-effectiveness of these options before embarking on source-control programs, which may themselves be quite expensive.

Nitrates and Nitrites in Foods

The largest route of exposure to nitrates and nitrites for the general population is food, including cured meats and certain vegetables that accumulate nitrate from the soil (see Chapter 9). The U.S. Department of Agriculture appointed an expert panel in 1973 to examine the need for and the feasibility of reducing the allowable limits of nitrate and nitrite in meats. That panel considered health hazards both of these compounds and of nitrosamines, and recommended the complete elimination of nitrate and the reduction of residual nitrite to the lowest practical levels in cured meat products (U.S. EPA 1977). Regulations were proposed, and met vigorous resistance from the meat processing industries; a final decision was still pending as this report went to press.

Control of nitrate and nitrite levels in vegetables (the largest source of dietary intake) is more difficult, because of the variety of conditions that promote nitrate accumulation (see Chapter 3) and the impossibility of monitoring every batch of several high-volume products for excessive nitrate levels. Similarly, to protect livestock from the toxic levels of nitrate and nitrite that may accumulate in forage plants under some conditions (see NRC 1972), the available options include monitoring of forage samples and reduction of intake of contaminated feed, as well as crop management to prevent the build-up of nitrate in forage. To protect both humans and animals, public education programs might be pursued; for example, mothers of young infants might be advised to avoid feeding their babies any vegetables known to accumulate nitrate, and warnings could be issued to livestock producers when conditions favorable to accumulation of nitrate in forage occurred.

Few estimates of the costs of preventing exposures to nitrates and nitrites in foods are available. The expense of surveillance and information systems could be as large or as small as the risks seemed to justify; in many cases, monitoring for nitrate hazards might simply be added to existing public health or agricultural extension programs, with little increased expense. A more difficult cost to assess is the increased risk of food poisoning (botulism) that might be associated with reduced nitrite levels in cured meat. The limits recommended by the USDA expert panel are intended to minimize that risk, while lowering exposures to precursors of nitrosamines.

Nitrates in Drinking Water

Some ground and surface waters that are used for drinking contain excessive nitrate (see Chapter 3), and because of time lags in transport or the economics of agricultural production, many of these water supplies seem destined to remain high in nitrate (see Chapter 6). Unless and until improved management of croplands reduces the flow of nitrate into ground or surface waters, other approaches may be required to protect against possible hazards of excessive nitrate intake.

The available options include removal of nitrate from drinking water, provision of an alternative, low-nitrate supply of water, and educational and informational programs to increase awareness of the potential hazards. There is currently no well-proven, economical method to remove nitrate from water supplies. Conventional water treatment does not affect nitrate levels. Tertiary techniques for removing nitrate from sewage effluents (described earlier in this chapter) can be used for treating water supplies; anion exchange equipment has been installed for this purpose in at least one Long Island city (Gregg 1973). The expense of such measures is substantial, however; and while they might be used for municipal water supplies, they could be prohibitively expensive for private wells, which appear to be the source of most exposures to high-nitrate waters.

Provision of alternative supplies is likely to be a more feasible approach than nitrate removal. Protection of human populations may be accomplished by drilling new wells to tap uncontaminated aquifers (if such are available), development of piped water systems for rural areas, or furnishing bottled water to persons at risk. In one portion of the claypan region of Illinois, a piped water system now exists and has alleviated some problems from high nitrate in groundwater (E. Dickey, University of Illinois, personal communication, 1976). In other areas, until such options are available, the provision of bottled water, at least to families with small infants, coupled with an educational program to alert those at risk, deserves consideration.

Although the costs of providing alternative, low-nitrate drinking water supplies have not been evaluated formally, they would probably be relatively modest. Where farm ponds of acceptable quality already exist, their use for livestock watering adds little if anything to the operational expenses of the farm (Dickey and Mitchell 1975). Where new ponds or wells must be dug, however, the costs to individual farmers could be a burden. The provision of bottled water should be a relatively low-cost alternative, if the water is supplied only to the subset of the population at greatest risk (i.e., formula-fed infants in the first three months of life). On the other hand, the provision of bottled water to entire populations could be quite expensive. Since adults are not likely to be affected by methemoglobinemia, the principal justification for such a measure would be to reduce risks associated with nitrate as a possible precursor of nitrosamines. Given the importance of dietary sources of nitrate (see Chapter 9), the degree of reduction of exposure provided by the use of bottled water would need to be evaluated carefully to determine whether this approach were cost-effective in any given case.

Other Protective Measures

When no effective control of exposures is possible, prophylaxis, diagnosis, and treatment can offer some control over acute hazards (methemoglobinemia) in livestock and man, and may provide some protection against long-term (carcinogenic) risks. For example, ascorbic acid (vitamin C) is effective in reducing methemoglobin in the blood (NRC 1972), and may also inhibit nitrosation reactions in the stomach (U.S. EPA 1977). The possibility of adding ascorbate to cured meats (along with nitrite) is currently being studied by the USDA and the Food and Drug Administration. Vitamin A protects poultry from nitrate and nitrite toxicity (NRC 1972), but similar data on other animals are lacking.

When methemoglobinemia occurs in humans or in animals, the disease can be reversed readily by the administration of methylene blue, which rapidly reduces methemoglobin. The critical point in such treatment is the diagnosis of methemoglobinemia. In humans, diagnosis is relatively straightforward when cyanosis is present; but when symptoms are less severe, or when a baby is ill from other causes, methemoglobinemia may go unnoticed (NRC 1972). Knowledge of the symptoms of methemoglobinemia in livestock has improved substantially in recent years, with the result that serious outbreaks of nitrate-related mortality are now considered quite unlikely (see NRC 1972). Detection and treatment of less severe or chronic effects in animals, however, are more difficult, and careful surveillance of nitrate/nitrite exposures may be the surest way to avoid adverse impacts on the health of livestock.

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CHAPTER 11

ECONOMIC ANALYSIS OF SOME ISSUES RELATED TO NITRATES IN THE ENVIRONMENT

The actual or potential impacts of nitrates and related nitrogenous compounds in the environment on health, ecosystems, productivity, and property, described in previous chapters, suggest a number of specific problems for economic analysis. Where both damages resulting from exposure to nitrates and costs of control are quantifiable in economic terms, benefit/cost analysis can help in framing environmental decisions. While in general only order-of-magnitude estimates can be made of the costs of environmental damages, a comparison even of these rough estimates with costs of control or with the value of beneficial uses of nitrates often is helpful.

The literature contains very few published analyses of economic aspects of the specific nitrate-related issues examined in this study. For the most part, the state of knowledge on scientific and technical questions has not permitted much economic analysis of these issues prior to now. We believe it is important for economic and scientific assessments to develop hand-in-hand, as research enlarges the information base for future decision making. This chapter is therefore largely an exploration of some useful methods for conducting economic analysis of nitrate-related environmental issues. Although the numerical results of the analyses presented here are far from definitive, we feel that the approach taken illustrates some ways in which economic analysis can be very useful, once research has answered some of the critical scientific questions.

Using the methodology outlined below, this chapter examines the economic aspects of (1) effects of nitrogen fixation on the ozone layer, (2) effects of nitrogen oxides and acid precipitation, and (3) health hazards of ingested nitrates. Initial consideration also was given to assessing the costs and benefits of measures that might be adopted to prevent nitrate-related impacts on surface water quality; however, this issue ultimately proved resistant to analysis. Health hazards of nitrate in drinking water primarily involve groundwater, rather than surface waters, and the role of nitrogen in eutrophication has not been well quantified (see Chapters 9 and 8). It therefore did not seem feasible to estimate the benefits of a reduction of nitrogen loadings of surface waters, or to compare the possible costs of controls of nitrogen sources (discussed in Chapter 10) with any realistic array of damages that such controls might prevent.

METHODOLOGY

Economic analysis of environmental questions first attempts to quantify costs imposed through the environment on receptors; that is, to attach an economic value to adverse effects. Such estimates of costs, or damages, are needed to estimate the benefits of control measures that could prevent or reduce the risk of adverse effects; the estimated benefits, in turn, can be compared with the costs of the control measures. One useful method for making such a comparison is to consider the consequences of imposing the damages on those individuals or entities that are responsible for causing the problem. Whether this is done directly (e.g., through an emission tax) or through some regulatory mechanism that achieves an equivalent outcome, economic theory predicts that the result will be a reduction in those actions that create the environmental damages (Kneese 1977). Theoretically, such an analysis can define a point at which the net benefits of control are maximized and the "external" environmental damages are "internalized." (Note that the concept of maximizing net benefits of control leads to a solution in which the excess of avoided damages over costs of control and lost production is maximized, and that this need not imply a total elimination of adverse environmental effects.)

In practice, however, economic analysis cannot define such an "ideal" level of control. Scientific understanding of environmental impacts generally is neither complete enough nor clear enough to permit the exact causes of adverse effects to be determined accurately. Further, both scientific uncertainties and lack of adequate economic measures of value prevent precise quantification of the costs of most adverse effects. Similarly, the consequences of control measures can rarely be fully known in advance, either in terms of their impacts on environmental proceses or in terms of their direct and indirect costs. The effectiveness of policies intended to impose damages on those responsible for them thus cannot be predicted with much confidence. Finally, even if economic analysis could specify an "ideal" level of control as defined earlier, society might choose to pursue another goal as the objective of social policy.

Because of these limitations, the best result that environmental economic analysis can achieve often is a comparison of rough estimates of costs and benefits of control. The outcome of such analysis is seldom definitive, but the exercise itself has several valuable consequences. First, economic analysis provides a framework for organizing both scientific and economic data that is readily adapted for comparing alternative policy options (see Chapter 12). At the same time, the analysis usually identifies many critical information gaps, and often can suggest the relative value of research that could answer different questions, by indicating the sensitivity of the economic analysis to the missing information. Finally, economic analysis may show either a large excess of benefits over costs, or the reverse, for a given control measure. Results of this sort, even if crude, are useful in screening options. In practice, economic analysis proceeds in iterative stages: more detailed analysis is devoted to a limited number of control options once the most appealing candidate measures have been identified and as more definitive scientific data are amassed.

This chapter draws on the scientific and technical assessments of relationships that link nitrates and other nitrogenous compounds to specific effects, presented in earlier chapters, and on the review of control techniques in Chapter 10, for its definition of environmental impacts and possible countermeasures. Next, appropriate economic measures of damages done by nitrates are identified. Losses in goods and services are easily accepted as appropriate measures for property damages; in contrast, however, the value of health damages, including the risk of mortality, is especially difficult to assess. Costs of illness (morbidity) can be calculated both as lost productivity and as the cost of required medical services, but these measures exclude losses from pain and suffering. Ecological and aesthetic impacts are often the most difficult types of damages to quantify. Loss in recreation benefits is one measure used; however, some important components of the analysis, such as the demand for preservation of a scenic area by non-users, cannot be quantified directly (Krutilla 1967). Finally, the direct costs of pollution control, based on economic engineering cost analysis, and the possible loss of economic benefits derived from the use of a commodity that may be restricted by control are assessed.

Estimating the latter kind of cost, in particular, is a complex and difficult procedure. For instance, in order to calculate the benefits of fertilizer use it is necessary to know the precise increments in crop yields that result from fertilizer applications, the value to society of those incremental yields, the extent to which high production under optimum fertilizer applications frees crop lands for other uses, and the value of those other uses to society. Information on these or other critical relationships usually is lacking, but economists can use the aggregate producers' or consumers' willingness to pay for the commodity as a reasonable proxy for benefits measured more directly (see Willig 1976). That is, knowledge of the aggregate demand function for a commodity allows calculation of benefits foregone if use of the commodity is restricted, and can suggest changes that would occur in the level of use of a product if its price were increased by the internalization of costs of environmental impacts. The most important economic measure for making that calculation is the elasticity of demand for a commodity (the percentage of reduction in use that would follow a given percentage increase in cost to the user).

POTENTIAL IMPACTS OF ANTHROPOGENIC NITROGEN FIXATION ON THE OZONE LAYER

Chapter 7 describes the potential for depletion of the stratospheric ozone layer that is related to anthropogenic nitrogen fixation, chiefly by cultivated legumes and as chemical fertilizer for use in crop production. The health effects, environmental damage, and possible climatic changes that could follow a decrease in stratospheric ozone are reviewed in Chapters 8 and 9. If further research resolves current scientific uncertainties and substantiates the hazard to the ozone layer represented by nitrogen-fixing cultural activities, the only effective control approach that society could implement to reduce that hazard would be to reduce the anthropogenic contribution to global nitrogen fixation. This section estimates the economic damages associated with the degrees of depletion of ozone described in Chapter 7; those costs are then compared with the economic benefits of agricultural uses of nitrogen, which are estimated by using demand as a proxy measure, as discussed in the earlier section on methodology.

Damages from Ozone Depletion

Two recent research efforts have attempted to quantify the economic damages associated with changes in stratospheric ozone and possible changes in climate. These are the Climatic Impact Assessment Program (CIAP) undertaken by the U.S. Department of Transportation (U.S. DOT 1975, Volume 6), and a study of the environmental and economic effects of the use of fluorocarbons, sponsored by the U.S. EPA (d'Arge et al. 1976). The damage estimates provided in these studies relating impacts on health, property, and productivity to the percentage of ozone depletion are used with the relationships between nitrogen fixation and ozone depletion described in Chapter 7 to calculate the damages associated with each ton of nitrogen used as fertilizer.

The damages that would result from ozone depletion would accrue over a long period of time (decades to centuries), and the damages must be properly discounted. For example, if fixation of one metric ton of nitrogen in 1978 causes $50 per capita of damages 75 years hence, and if $1.18 placed in a bank now at 5 percent compound interest would grow in 75 years to $50, $1.18 is the discounted present value of damages of $50 75 years hence, with a 5 percent discount rate. The equity of such a discounting procedure is suspect, however, unless a mechanism actually exists by which funds to compensate future generations are in fact invested in a bank or in some sort of insurance policy. (The likelihood of continued existence of such financial institutions must also be accounted for to justify the procedure--a consideration typicaly ignored.) Moreover, because successive generations cannot negotiate together, future generations are unrepresented in such decisions (Page 1977). The issue of choosing appropriate discount rates has received much attention but has not been resolved (Baumol 1968, Usher 1969). As a result, in this analysis a range of discount rates of from 3 to 8 percent is employed.

In Chapter 7, we used preferred values for the relevant parameters and estimated that continuation of the current rate of nitrogen fixation for fertilizer (79 Mt/yr) could result in a 1.5 percent reduction in stratospheric ozone by the year 2100. If, however, fertilizer use increases to the projected level of 200 Mt N/yr, a 3.5 percent ozone reduction is projected over the same period. Because world use of nitrogen fertilizer is expected to continue to expand, we have chosen the larger of these two estimates as the more probable long-term rate of anthropogenic nitrogen fixation, and used the consequent 3.5 percent ozone depletion in damage calculations.

The results of the CIAP study (as adapted by d'Arge et al. [1976]) that pertain to the environmental costs of a 3.5 percent ozone depletion are shown in Table 11.1. According to other studies that were part of the CIAP, a change of this magnitude in the ozone layer would lead to an 8 percent increase in exposure to ultraviolet radiation at the earth's surface, and to a change of +0.037°C in the average global temperature. The CIAP study calculated discounted total damages on the basis of an ozone depletion projection similar to our preferred case--a relatively long approach to equilibrium, in the neighborhood of 120 years; however, d'Arge et al. projected an ozone depletion of 7 percent. The damages asociated with ozone depletion increase approximately linearly with the magnitude of the depletion;

TABLE 11.1 Hypothetical Global Environmental Costs of a 3½% Decrease in Stratospheric Ozone (Present value in millions of 1971 US dollars)

Discount rate	3%	5%	8%
Environmental Cost of +.037°C Change in Temperature			
Urban	42,985	13,913	3600
Marine	-702.5	-330.5	-114
Forest	-14,897.5	-5,530	-2,421.5
Corn	423	134.5	35
Cotton	-21.5	-8	-2.5
Total	27,786.5	8,179	1,097
Environmental Cost of 8% Increase in Ultraviolet Exposure			
Skin Cancer	85 - 339	26 - 103	7.5 - 30.5
Materials Weathering	779.5	284.5	96
Total	864.5 - 1,118.5	310.5 - 387.5	103.5 - 126.5
Grand Total	28,651 28,905	8,489.5 - 8,566.5	1,200.5 - 1,223.5

SOURCE: d'Arge et al. (1976).

the damages shown in Table 11.1, therefore, are half as large as those derived by d'Arge and coworkers.

The damages associated with climatic impacts are quite speculative. The effects of ozone depletion on world climate are uncertain, and existing knowledge implies a number of contradictory (and possibly offsetting) impacts. The National Research Council (1976) concluded that a slight net positive change in temperature might occur. The costs associated with an increase in temperature are primarily the net costs of changes in urban cooling and heating patterns, and the result of projected losses in corn production, which exceed the projected benefits to marine and forest productivity and to world cotton production. The CIAP concluded that any change in temperature or rainfall, no matter what its direction, imposes enormous costs on a socioeconomic system adapted to existing patterns of climate. In contrast, the damages of depletion of ozone in terms of materials weathering and skin cancer costs can be estimated with more confidence. The individual studies upon which Table 11.1 is based can be found in the CIAP report, Volume 6 (U.S DOT 1975).

The projected damages in Table 11.1 can be translated into annualized equivalents, which represent the constant yearly payment in perpetuity that has a present value equal to discounted damages, as opposed to actual damages that are nonconstant over time. The annualized damages, which are equal to the present value of damages times the appropriate discount rate, can then be expressed in terms of damages per ton of nitrogen fixed for use as fertilizer by dividing the total by 200 Mt (Table 11.2). Since damages as shown in Table 11.1 are approximately linear in proportion to the magnitude of ozone depletion, the values in Table 11.2 can also be interpreted as marginal damages associated with agricultural use of a ton of nitrogen. As the table shows, at a 3 percent discount rate, and if one accepts the validity of the projection of climatic impacts, damages are $4.34/ton of nitrogen; but if the 8 percent discount rate is used and the uncertain climatic effects are excluded, the damages could be as low as $0.05/ton.

Costs of Control: Benefits of Fertilizer Use

Some economists would argue that, in order to "internalize" the environmental costs associated with fertilizer use, the damages should be added to the price of fertilizer. We do not propose this as a policy approach; but the concept is a useful analytical construct that allows us to examine the effects of such a "price increase" on the use of nitrogen fertilizers, and on consequent environmental hazards. In reality, this approach would be inadequate,

TABLE 11.2 Estimated Annualized Damages of Depletion of Ozone by Fertilizer Nitrogen, Using Various Discount Rates

	Damages, in 1971 Dollars per metric ton of Fixed Nitrogen		
Discount Rate (%)	Climatic Impact	Effects of u.v.	Total Damages
3	4.17	.17	4.34
5	2.04	.10	2.14
8	.44	.05	.49

since more than 40 percent of the nitrogen used as fertilizer worldwide is fixed by cultivated legumes, rather than through manufacture of chemical fertilizers, and different mechanisms determine the prices of nitrogen from each source. In theory, however, some means could be devised to include environmental costs in the price of any ton of nitrogen that was fixed for use as fertilizer. For this analysis, rather than attempt to differentiate between leguminous nitrogen and chemical fertilizer nitrogen, we have assumed that the two forms are comparable and that agricultural users of nitrogen would respond in an equivalent manner to an increase in the price of either cultivated or manufactured fertilizers.

As noted in the section on methodology at the beginning of this chapter, knowledge of the elasticity of demand for fertilizer nitrogen is necessary to project the consequences of including social costs of fertilizer use in the price paid by users. Rausser and Moriak (1970) reviewed demand for fertilizers, and found that from 1949 to 1964, elasticities increased from -0.5 towards -1.0. This suggests that as fertilizer use increased dramatically its incremental productivity dropped substantially, making demand increasingly elastic for high levels of use. Taylor (1975) presents a demand curve for nitrogen fertilizer for Illinois which also bears out this hypothesis; the elasticity is in the neighborhood of -1.58 for current use levels, but decreases (becomes more inelastic) to about -0.6 for levels of use less than half of those currently employed. As a reasonable working assumption, we have used a demand elasticity of -1.0 for developed nations, and an average elasticity of -0.5 for developing nations, since the latter have lower rates of fertilizer use. However, since we have also assumed that world consumption of nitrogen fertilizers will increase to 200 Mt N/yr, the average elasticity of demand for the entire world may also approach -1.0 in the future.

The 1975 price of nitrogen fertilizer was 6¢/pound, or about $132/metric ton (Taylor 1975). If the upper limit of damages per ton of nitrogen (Table 11.2) of $4.34/ton is adjusted for inflation, it becomes $5.46 in 1975 dollars. Adding that amount to the price of a ton of fertilizer nitrogen would represent an increase of about 4 percent. The damages calculated using larger discount rates (see Table 11.2) are equivalent to from less than one-half to about two percent of the 1975 price of fertilizer. With an elasticity of demand of -1.0, a 4 percent increase in price would result in a 4 percent decrease in use of nitrogen fertilizers. In those nations where the elasticity is only -0.5, the projected decrease in use would be only 2 pecent; as noted, however, an elasticity of -1.0 (and a 4 percent, or 8 Mt/yr, decrease in use) may be a more appropriate maximum for the long-term global average.

In summary, the long-deferred nature of the adverse effects of depletion of the ozone layer makes the current discounted value of the future damages small. (The caveats concerning the equity of the discounting procedure, stated earlier, should be recalled at this point.) If the value of the damages were added to the current price of fertilizer, our analysis indicates that this "internalized" cost would lead to only a small reduction of the worldwide use of nitrogen fertilizer.

NITROGEN OXIDES AND ACID RAIN

Some of the adverse effects associated with nitrogen oxide emissions were reviewed in Chapter 8, including adverse impacts of nitric acid in precipitation on fisheries and forest yields, on agricultural soils, and on materials. Nitrogen oxides also have quantifiable aesthetic effects (on visibility), and pose a hazard to health. Although our concern is primarily with nitrates, control of atmospheric nitrates requires control of NO_x emissions, and such controls would apply to all the potential hazards, not just those attributable to nitrates. This section attempts to estimate approximate damages from NO_x emissions and nitrates, and to compare these damages with costs of control.

Damages from NO_x Emissions

Chapter 6 reviews current understanding of trends in nitrate in precipitation and of the contribution of nitric acid to the decrease in pH of rainfall in the eastern United States. As Figure 6.22 shows, virtually the entire area east of the Mississippi River now receives precipitation with a pH less than 5.0, and the average pH of rainfall in much of the Northeast is 4.5 or below. Nitrogen oxide emissions from the tall stacks of stationary sources may be responsible for a significant part of the acidity of precipitation in the Northeast, and are likely to be an increasing concern in the future, because in comparison with emissions of sulfur oxides, such NO_x emissions are now relatively uncontrolled. Table 11.3 summarizes emissions of NO_x in 1972 for the eastern United States. (The discussion of emission trends presented in Chapter 6 suggests that the level of NO_x emissions today is approximately equal to the level in 1972; see Figure 6.15).

Table 11.4 presents estimates of the values of forest and sport fishery yields for the early 1970s in the eastern

TABLE 11.3 Estimated Emissions of NO_x in 1972 for Four Regions of the United States

Region	Total NO_x Emissions, Tons/yr[a]	Emissions from Stationary Fuel Combustion	Percent of total
New England	730,000	370,000	51
Mid Atlantic	5,800,000	2,000,000	34
Great Lakes	6,700,000	4,800,000	72
Southeast	3,600,000	1,700,000	48
Total	16,800,000	8,900,000	53

[a] Data from U.S. EPA regional source inventories, compiled in NRC (1975). Estimates rounded off to two significant figures.

TABLE 11.4 Estimated Values of Forest and Fishery Production for the Eastern United States

Region	Value in $\$10^6$/yr	
	Forest[a]	Sport Fishery[b]
New England	24	187
Mid Atlantic	32	488
Great Lakes	43	1,077
Southeast	800	NA
Total	899	1,752

[a] U.S. Department of Commerce (1971); assumes stumpage price of $32/1000 board-ft.

[b] Assumes each fisherman-day is valued at $8.00 and that each fisherman is associated with 20.4 fisherman-days (U.S. DOI 1972).

United States. These values may be at risk now or in the future because of the effects of acid rain. A problem in this analysis is the time period over which acidification of land and fresh inland waters will take place, given the natural buffering ability of soils in the region; this period cannot be estimated with current knowledge. This implied lag in the impact of acid precipitation is ignored in the analysis here, but it should rightfully be included, and damages should be discounted over the appropriate interval.

Losses in forest yield from acid precipitation have been studied most closely in Scandinavia. Losses in Sweden over the period from 1945 to 1965 have been estimated at 0.3 percent of annual production (United Nations 1971), and projected cumulative impacts by the year 2000 range up to a 15 percent decrease in yield.

Chapter 8 concludes that a quantitative estimate of the potential loss in forest yield from acid precipitation in the United States can not be made with current knowledge. Further, it is impossible to estimate accurately the fraction of such damages that is attributable to NO_x emissions, or to emissions from stationary fuel combustion, for reasons discussed in Chapter 6. Nevertheless, the qualitative conclusion of both chapters is that acid precipitation is a serious environmental problem with important potential adverse ecological effects, and that NO_x emissions, especially those from tall stacks of stationary sources, makes a major contribution to the acidity of precipitation. In order to proceed with this economic analysis, therefore, we have had to make some arbitrary assumptions. For forestry losses, we assume that the long-term impact of acid rain in the eastern United States will be a 5 percent reduction in yield. We have arbitrarily allocated one-third of that effect to the nitrate component of the acidity. Damages were then calculated for each region of the eastern United States, using the estimates of the regional value of forestry (Table 11.4). Those damages are displayed in Table 11.5.

To estimate damages to fisheries, we assume that fish production decreases linearly from 100 to 0 percent as the pH of rainfall over a region decreases from 5.0 to 4.0 (see Figure 8.9 and discussion in Chapter 8), and assumed further that the value of a fishery is directly proportional to its yield. Since some loss of fisheries occurs when the pH of lakes is below 6.0, these assumptions may be conservative. We then assume that the average pH of rain over the eastern United States is 4.5, although some sites have recorded lower pH values. (Since pH is a logarithmic function and fishery losses are assumed to be a linear function of pH, a change in acidity from pH 5.0 to 4.5 would result in about a

TABLE 11.5 Estimated Damages to Forest and Fishery Production by Acid Precipitation for Four Regions of the United States

Region	Damages, x $\$10^6$	
	Forestry	Sport Fishing
New England	0.40	13.3
Mid Atlantic	0.53	34.7
Great Lakes	0.72	76.9
Southeast	13.30	NA
Total	14.95	124.9

22 percent decrease in fishery value.) Again, one-third of the effects of acidity is attributed to nitrates. The estimated value of fishery losses for each region is shown in Table 11.5.

Given our assumptions, the potential damages of acid rain to forests total about $15 million per year, and potential annual damages through sport fishery losses are at least $125 million. The latter figure does not include an estimate for the southeast region, because data on the value of sport fisheries in that region were not available. However, unless we assume that damages from losses of sport fisheries in the southeast are negligible (and this assumption seems unreasonable), total losses in this category must be higher than the $125 million indicated.

Also, it is unlikely that the estimates of loss in production of marketable timber adequately capture all of the potential values of a forest ecosystem that are threatened by acid rainfall. At present, credible scientific or economic estimates are not available of the impacts of acid precipitation on the value of forests as reservoirs of biotic diversity, as habitat for wildlife, or as functional components of natural biogeochemical cycles. Knowledge that some of these functions of ecosystems may be threatened by acid rain (see Chapter 8) suggests, however, that the full costs of impacts on forest systems may be substantially greater than $15 million/year, although they cannot be more accurately quantified.

On the other hand, the nitrate content of precipitation is also a source of nutrient input that might tend to <u>increase</u> biotic productivity (see Chapter 8). The significance of such a nutrient flux to lake or forestry yields, or the extent to which the beneficial impacts of nitrate as a nutrient might offset the damage of nitric acid, cannot be estimated; but this confounding aspect requires consideration.

The damages shown in Table 11.5 can be expressed on the basis of each ton of NO_x emitted, for comparison with costs of control. Table 11.3 shows that about 16.8 million tons of NO_x are emitted each year in the eastern United States. The average nitrate-related damages for the eastern United States thus are $0.89 per ton of NO_x for losses in forest yield, and $7.44 per ton for losses of sport fisheries. Although it would be possible to calculate damages per ton of NO_x emissions within each of the regions listed in the tables, such an estimate would not be especially useful. The long-range transport of pollutants associated with the acid rain problem (see Chapter 6) makes it unlikely that there is any direct correspondence between emissions and adverse impacts within a single region. Until site-specific damages can be linked to specific sources, averages for the entire eastern part of the country are probably the most appropriate measures.

As Table 11.3 indicates, 8.9 million tons of NO_x emissions, or 53 percent of the total for the eastern United States, comes from stationary combustion sources. Because some of these sources, especially large industrial boilers and utility power plants, may contribute more directly through tall-stack emissions to the regional dispersion of pollutants that acidify rainfall than do ground-level (e.g., automobile) sources, a disproportionately larger share of the damages may be attributable to this category of emissions. However, it cannot be determined yet what fraction of the acid rain problem can be traced back to each category of sources (see Chapter 6). For lack of a better estimate, damages may be apportioned according to the relative contributions of different sources to total emissions (see Figure 6.13 and Table 6.13).

Another important effect of acid rain is the acidification of agricultural soils. Nisbet (1975) assumed that 50 percent of emissions fall as acid rain on agricultural land, and that soil pH is maintained by the common practice of liming. Taking the price of lime as \$14-\$18 per ton and the amount of additional lime required to offset acidification as 12 million tons, Nisbet calculated 1980 damages (costs of additional liming) of \$200 million for the sulfate fraction of acid rain. If we assume that by 1980 the nitrate fraction of acidity will be 40 percent, liming costs attributable to nitrates would be about \$133 million per year. Projected emissions of NO_x for the U.S as a whole by 1980 may be about 30 million tons (see Chapter 6); calculated damages per ton (as liming costs) therefore may approach \$4.40.

Nitrogen oxides also have aesthetic impacts on visibility; however, the economic value of these effects has been measured only for the southwestern United States and for emissions from large, coal-fired power plants. Such sources emit large quantities of nitric oxide (NO), which is rapidly converted to nitrogen dioxide (NO_2), a reddish-brown gas that has a major impact on scenic visibility in the region. Brookshire et al. (1976) surveyed recreators in the region of the planned Kaiparowits power plant in southeastern Utah, and determined that recreational users of the area were willing to pay \$1.2 million per year (annualized) to avoid aesthetic losses from the plant. Similar studies (with comparable results) have been conducted in relation to emissions in the Four Corners region by Randall et al. (1974) and Blank et al. (1977). Although such damage estimates apply only to this particular region, which is noted for its sweeping scenic vistas, they indicate that the value of visibility impacts can be substantial in comparison to some other sources of damage.

It is not a simple matter to determine what portion of the damages from loss of visibility can be attributed to NO_x emissions. Sulfur oxides and particulates, which are also emitted from power plants and smelters in the southwest, also contribute to visibility reduction, and some visibility-reducing pollutants may be transported into the region from distant sources. Current EPA regulations impose stringent restrictions on emissions of SO_x and particles from newly-constructed power plants, but smelters and some other industrial sources still emit large quantities of SO_2. However, NO_x emissions from such sources are less stringently controlled. In the Kaiparowits study, which may not be typical, it is reasonable to assume that the coloration of the sky by NO_x would be the major visibility-related impact on the region. Given projected NO_x emissions of 80,000 tons/yr from the power plant, the estimate of $1.2 million of potential losses in aesthetic value translates to $15.00/ton, if damages are allocated entirely to NO_x. This figure can be taken as a regionally-specific upper boundary for potential aesthetic damages from NO_x emissions.

The National Research Council (1974) has previously summarized estimates of the economic damages related to potential impacts of NO_x emissions on health and materials. The NRC estimated that annual damages from health impacts (mortality) from NO_x could be $160 to $900 million nationally. Using the NRC's estimate of national emissions from all sources in 1972 of 24.4 million tons/yr, damages then range from $6.56 to $36.93 per ton. Jackson et al. (1976) reported a similar range of health damages in a study of the benefits and costs of auto emission controls. The study by General Motors (Jackson et al. 1976) also estimates nitrogen-related air pollution damages to materials to be from $135 to $542 million per year nationally. Again, using total national emissions of 24.4 million tons of NO_x, the estimated damages are from $5.54 to $22.21 per ton.

The benefits of controlling nitrogen oxides in terms of damages per ton are summarized in Table 11.6. Some of the benefits shown in the table are specific to regions of the country; the total benefit from NO_x control therefore varies regionally. Also, not all of the benefits are comparably related to controls of different classes of sources. For example, emissions from large stationary combustion sources in rural locations contribute to visibility reduction and acid rain, but because they are distant from population centers they have smaller impacts on health or materials than emissions other sources, such as automobiles in urban areas. Thus, control of urban NO_x emissions from automobiles could have benefits of $60 or more per ton

TABLE 11.6 Benefits of NO_x Control

Effects	Region	Damages, \$/Ton NO_x
Forestry	East	0.89
Sport Fisheries	East	7.44
Agriculture	U.S.	4.40
Aesthetic	Southwest	up to 15.00
Health	U.S.	6.56 - 36.93
Materials	U.S.	5.54 - 22.21

(comprised of high estimates for health and materials damages and value for some aesthetic impact). The benefits of control of NO_x from a rural power plant in the Southwest might total about $20 per ton (including only damages from acidification of agricultural soils and major aesthetic impacts), while a similar power plant in the more densely populated Northeast might have significant impacts in every category except aesthetic damages, and control benefits of up to $70 per ton.

Costs of Control

Control of NO_x emissions from stationary sources often is costly, especially for large, older boilers (see NRC 1975 and Chapter 10 of this report). Although costs will vary widely according to the characteristics of a given source, the cost of controlling NO_x emissions is estimated to fall in the range of \$30 to \$300 per ton of NO_x. For automobiles, if we assume that the pollution control devices now required will reduce NO_x emissions from a pre-control average of 5 g/mi to an average of 1 g/mi, and that an 80 percent reduction in NO_x emissions would cost about \$100 per vehicle (see Jackson et al. 1976), the cost per ton of NO_x controlled is about \$225 (assuming a lifetime of 100,000 miles for the average automobile). Costs of maintenance and possible losses in fuel economy are not included in this estimate, but such costs might increase the total substantially.

Given the number of assumptions needed and the very rough nature of the estimated costs and benefits, no great significance can be attached to the differences between estimated costs and benefits of NO_x controls. Although it appears that, in general, the estimated costs of control exceed the estimated benefits, it should be recalled that not all benefits could be included in the estimates. The uncertainties in estimates of both dimensions imply that there is a potentially broad range of overlap of costs and benefits. Calculations for specific regions are likely to produce a better-defined cost/benefit picture, and may show an excess of benefits over costs in some cases.

INGESTED NITRATES AND HUMAN HEALTH

Estimates of the economic damages related to hazards of cancer and methemoglobinemia associated with nitrate and nitrite are particularly important for an analysis of possible measures to control exposures. Such estimates can be based on calculated costs to individuals of the increased risk of death that could result from controllable exposures. Unfortunately, the concept of "cost of risk" has been confused by attempts to value life. In this section, therefore, the theoretical development of the concept of valuing risk is discussed briefly, and some preliminary empirical results are noted. The remainder of the section then discusses the evidence on possible relationships between nitrates and cancer and methemoglobinemia, focusing on how economic analysis *might* be used if better dose-response relationships are developed.

Placing a Value on Risk

The relationships between exposures to nitrate and nitrite and the risk of methemoglobinemia and cancer were reviewed in Chapter 9. Some estimates of the economic value attached to that risk by people who are exposed to nitrates can be derived from observing society's behavior in the market place. While the idea of placing a dollar value on a human life provokes understandable objections, it is a fact that people die as a result of certain activities, many of which can be controlled to some extent through the market. Without some theoretically sound economic measure of the value of safety, the value assumed in policy making may be either far lower or far higher than the market behavior of individuals and institutions reflects.

Economists in the past have attempted to value human life as the sum of the present value of future earnings over an individual's lifetime (see for example Rice [1966], and Lave and Seskin [1970]). This approach, however, is no longer viewed as acceptable. In the first place, it assumes that the value of life can in fact be measured--a point certainly open to debate. Secondly, it implies that the lives of children, housewives, retired and other unemployed individuals are worth less than the lives of employed heads of households.

Two other measures are now used to value safety or risk to life. These are equivalent variation (EV) and compensating variation (CV). An EV measure of the value of life is the amount of money an individual would pay to escape from or prevent certain death; in theory, a rational individual would part with all his available wealth to save his life. CV, in contrast, measures the compensation required to induce an individual to accept voluntarily a situation where the probability of death is increased. As the probability of death approaches unity, the CV measure can be taken as an estimate of the value the individual places on his life. Logically, though, the value of life measured this way must be infinite, because as the probability of death approaches certainty, the probability of enjoying any compensation offered (and thus the value of the compensation) approaches zero. Thus neither EV (which requires coercion) nor CV (which makes the value of life immeasurable) provides a wholly satisfactory way of estimating the dollar costs of mortality in real world situations that involve risk. An elaboration of the CV concept, however, can provide a useful measure of the compensation necessary to induce an individual to accept a slight increase in the probability of death. For assigning a dollar value to risk derived from exposure to nitrates or other environmental pollutants, this approach seems more useful than attempts to place a dollar value on a particular human life.

Some fairly well established economic theory exists for describing the behavior of individuals with respect to risk. One case that has been thoroughly analyzed is the observed behavior of individuals and employers in regard to high-risk jobs. The existence of a "market" for risk of death can be inferred from the existence of compensating differences in wage rates for different job classifications with different work-related probabilities of death and injury. When the market is in equilibrium, the difference in wages between high-risk and low-risk jobs corresponds to the value of the increased risk. For example, Thaler and Rosen (1975) determined from empirical data that, in a case where 1000 workers are employed in a job that entails an increased risk of death of 0.001 per year, each individual must be paid from $176 to $260 more per year than would be required if the added risk were zero. Collectively, the risk of one death per year in 1000 employees would cost the employer from $176,000 to $260,000 in extra wages. Again, it should be emphasized that this figure is <u>not</u> the value of a life, but is a measure of the compensation required for a small increase in the risk of death, or the value of a small increase in safety. In addition, because Thaler and Rosen's data were drawn from a selected group of high-risk jobs that may attract individuals with a low aversion to risk, their study may have underestimated the value of risk to the average person. Nevertheless, the study does provide a lower bound for estimates of this value.

Nitrates and Cancer

To demonstrate how the methodology discussed above might be used to assess the cost of risk associated with use of nitrates, a study by Kneese and Schulze (1977) is briefly described here (also, see Appendix B). This study used multiple regression analysis to develop statistical correlations between cancer mortality and dietary and environmental variables, including several that are related to nitrate. The objective was to assess the overall cost of environmentally induced cancer; however, no specific attribution of damages to nitrates is possible from the results (see Appendix B).

The statistical model developed by Kneese and Schulze assumes that the risk of cancer death for each category of cancer considered is a linear function of the level of dietary, environmental, and socioeconomic variables among a sample of 60 cities. The categories of cancer mortality, the variables examined, their units of measurement, and the regression results are shown in Table 11.7. Several explanatory variables were chosen because of their potential relationship to nitrates, including consumption of beef, pork, and cigarettes, and exposure to atmospheric ammonium, NO_2, and nitrates in drinking water. Time-lagged data were used wherever possible to account for the delayed nature of the possible effect (cancer); unfortunately, this was impossible for some of the variables. Other environmental variables were included both to investigate their effects and to produce a more detailed model and reduce the likelihood of spurious statistical correlations.

The coefficients in each column of Table 11.7 relate 1972 cancer mortality by category to each of the explanatory variables listed on the left. For example, a positive variation of one pound per week in the 1959 per capita consumption of pork products was statistically related to a positive variation of 0.82 deaths from all categories of

TABLE 11.7 Environmental Factors in Cancer Mortality (Mortality in Deaths per Thousand)

Independent Variables		Linear Regression Equations[a] Estimated Coefficients with *t*-Values in Parentheses[b]								
Name	Mean Units	Mortality	All Cancers	Digestive	Respiratory	Breast	Genital	Urinary	Leukemia	All Other Cancers
% Change in Population (1960–1970)	—	−.048 (−2.02)	−.0033 (−1.16)	−.0027 (−3.13)			−.0012 (−2.46)			
Median Age of Population (1970)	Year	.52 (3.38)	.104 (7.25)	.004 (4.20)	.025 (6.65)	.01 (4.35)	.01 (3.06)		.0059 (4.95)	.026 (5.49)
% Nonwhite of 1970 Population	—				.000086 (1.37)	.000054 (1.27)			−.00002 (−1.08)	−.00008 (−1.09)
1969 Mean Family Income	Dollars		−.000003 (−1.2)		−.0000012 (−1.8)					−.000001 (−1.76)
1959 Per Capita Beef Consumption	1.4 Lb/Person/Week	−2.86 (−1.34)						.039 (1.79)	.034 (1.66)	
1959 Per Capita Pork Consumption	1.09 Lb/Person/Week		.68 (2.36)		.18 (1.89)	.108 (1.83)	.204 (2.99)		.079 (2.61)	.22 (2.06)
1956 Per Capita Cigarette Consumption	110.0 Packs/Person/Year			.002 (2.85)	.00074 (1.33)	.00085 (2.31)				
NO_x (in the air)	1.15 Micrograms/m^3								−.18 (2.05)	
SO_x (in the air)	43.04 Micrograms/m^3								−.00008 (−1.73)	.0003 (1.90)
Ammonium (in the air)	.09 PPM		.07 (2.89)			.02 (3.01)				.032 (3.42)
Suspended Particulate	114.8 Micrograms/m^3			.00062 (1.48)	.00046 (1.63)		.00035 (1.45)			
Sulfate (air)	10.79 Micrograms/m^3					−.0057 (−3.03)		.001 (1.54)		
Beta Radioactivity	.26pC$_i$/m^3	9.25 (2.14)							.057 (1.73)	
UV Radiation	18.79 Microwatts/cm^2	.052 (2.26)								.001 (1.49)
Nitrate in Drinking Water	2.45 PPM	.15 (1.67)				.0023 (1.56)				
Constant		−3.11	−1.82	−.436	−.399	−.32	−.31	.019	−.22	−.44
R^2		.38	.71	.63	.58	.41	.45	.09	.44	.63
SSR		367.7	2.902	.5464	.2439	.095	.1733	.044	.019	.2619
DF		53	54	55	53	52	56	57	46	46

[a] Independent variables with *t*-values below 1.0 excluded from final estimated forms.

[b] Significance level: 85%: $1.04 < t < 1.28$; 90%: $1.28 \le t \le 1.68$; 95%: $1.68 \le t \le 2.33$; 99%: $2.33 \le t$ (one tailed *t* test)

SOURCE: Kneese and Schulze (1977).

cancer per thousand people across the 1972 sample of 60 major cities. This was perhaps the most striking statistical result--a strong correlation between 1959 pork consumption and several categories of cancer mortality. These results and others are discussed in more detail in Appendix B.

If we assume that the coefficients shown in the table are valid indicators of causal relationships, damages can be calculated for the urban United States population (about 150 million individuals). (This assumption is tenuous, for reasons discussed in Appendix B. However, it is made here, in order to illustrate the procedure for calculating damages of cancer risk.) In the regression equations relating various possible sources of carcinogens, the coefficients of the variables multiplied by the mean values of those variables give the probability that a typical individual in the urban population will die of cancer. That probability can be multiplied by $260,000, the higher of Thaler and Rosen's estimates of the value of a small increase in the risk of death, to place a value on the risk to the individual. This in turn may be multiplied by the size of the urban population to estimate the total value of the risk.

These calculations were performed for each of the dietary and environmental variables that showed correlations with statistical significance at or above the 95 percent level. Table 11.8 summarizes the calculated damages.

Appendix C presents two estimates of the potential risk of human liver cancer induced by exposure to dimethylnitrosamine. The risk estimates, which are based on limited data and some untested theoretical assumptions about possible in vivo formation of nitrosamines, translate to cancer mortality rates of from 0.03/yr to 1700/yr in a population of 200 million that is exposed for an average 70-year lifetime. These estimates are not thought to be scientifically justifiable; however, if they are taken as the basis for calculating damages, using Thaler and Rosen's value for the risk of mortality, the estimated cost to society of this particular form of nitrosamine-induced cancer would range from $7,800 per year to $440 million per year. Even this upper estimate does not compare with the cost suggested by the Kneese-Schulze study (which included all forms of cancer). However, these results indicate that, should the larger estimate of risk prove to be remotely accurate, the damages of nitrosamines would be a very large cost, but if the smaller estimate of risk proves valid, the value of that risk to society could reasonably be regarded as trivial.

TABLE 11.8 Suspected Damages from Environmental Factors When Relationship is Significant at the 95% Confidence Level

	Cancer Mortality											
Environmental Factors	Digestive	Respiratory	Breast	Genital	Urinary	Leukemia	All Other Cancers	Total Cancer Mortality	x Mean Value	= Deaths per 1000 Population	Deaths for Urban Population	Suspected Damages ($$10^9$)
Beef Consumption					.039	.034		.073	1.4	.1022	15,330	3.986
Pork Consumption		.18	.108	.204		.079	.22	.791	1.09	.8622	129,330	33.626
Cigarettes	.002		.00085					.0029	110	.3190	47,850	12.441
SO_2							.0003	.0003	43.04	.0129	1,935	.503
Ammonium			.02				.032	.052	1.15	.0598	8,970	2.332
Radioactivity						.057		.059	.26	.0153	2,301	.598
Total												53.485

SOURCE: Kneese and Schulze (1977).

Since considerable uncertainty accompanies any assessment of the risk of cancer associated with environmental exposures to nitrates and nitrites (see Chapter 9 and Appendices B and C), it is questionable whether these quantitative economic assessments of damages resulting from nitrite ingestion are meaningful. However, the suggestion from the Kneese-Schulze study that current dietary patterns, and possibly in particular nitrite preservatives in pork products, may have an enormous cost in terms of human health indicates a need for more intensive research to improve the risk assessments.

If we accept the hypothesis that nitrate and/or nitrite in processed meat produces poses some risk of cancer to consumers of such products, the most effective way to reduce that risk is to reduce the amounts of nitrate and nitrite added to meats. The primary costs of such control measures (which are now being implemented--see Chapter 10) are some possible loss of product quality, and a potential increased risk of botulism. Until experience is gained with the production of processed meats containing reduced levels of these preservatives, however, these consequences cannot be effectively quantified, and their economic value therefore cannot be estimated.

Methemoglobinemia

The most important other possible health hazard of nitates is methemoglobinemia resulting from nitrate in drinking water. Chapter 9 indicated that 98 percent of all cases of methemoglobinemia occur in infants of less than 3 months of age; 97 percent affect users of private well water; and 97 percent of the cases involve greater than 40 ppm nitrate. Further, in one sample of cases the mortality rate was reported to be 8.6 percent, where 84 percent of the cases were associated with nitrate levels above 100 ppm. Very few cases of methemoglobinemia have been reported in this country, and serious outbreaks seem unlikely because of the low nitrate levels found in public water supplies (see Chapter 3). The main risk rather is to rural users of private well water, especially young infants. Within this rather scattered population, the risk of mortality cannot be well quantified, but appears to be small in the United States (see Chapter 9). If we assume that the population at risk numbers 10,000, and that 1 percent of that population is less than three months of age, the low mortality rate from methemoglobinemia would lead us to expect no more than 10 or 20 fatal cases each year. In fact, however, reported cases of methemoglobinemia are not even this common, and this estimate is probably high. Using the same value of risk discussed above in relation to cancer, the benefit gained by avoiding the risk of 10 infant deaths from methemoglobinemia would be $2.6 million. Prevention of a hazard of sublethal illness from methemoglobinemia also would have economic value, but the value of avoiding illness in infants cannot be readily determined.

To reduce the risk, rural families may need to be informed of the hazards and encouraged to substitute either breast feeding or bottled water for high-nitrate well water used in formula feeding. If educational efforts are made and proper precautions are taken, the only costs of control would be for informational programs and for bottled water. These costs seem unlikely to exceed the benefits gained by reducing further what is already a small risk of adverse health effects.

SUMMARY AND CONCLUSIONS

Economic techniques exist, with degrees of theoretical support that vary from case to case, for estimating the value to society of most of the assorted adverse environmental effects of nitrates and related compounds, and for estimating the costs of most protective measures. In order to apply those economic techniques, however, the economist needs firm quantitative estimates of the risks of adverse effects and of the consequences of control measures that might be implemented. When the scientific assessment cannot be definitive in estimating the impacts of a change in the environment, the economic assessment inevitably is equally inconclusive. In this chapter, many arbitrary assumptions were made about the likelihood and severity of adverse effects on health, ecosystems, materials, and the ozone layer. Such assumptions were needed to make the economic analysis possible; but the uncertainties in the scientific information base, discussed in detail in other chapters of this report, cannot be escaped. The results of this economic analysis are only as valid as the assumptions about environmental relationships that led up to them, and many of these may eventually be shown to be in error.

That caveat stated, this analysis nevertheless has revealed some interesting points. First, although the potential damages of depletion of ozone by nitrogen fixed for use as fertilizer are projected to be substantial, they would occur at such a distant time in the future that their present value, even with the lowest assumed discount rate, is small. If such damages were "internalized" by an increase in the price of fertilizer nitrogen, our analysis indicates that at most about a 4 percent decrease in world fertilizer consumption would result.

Second, control of nitrogen oxide emissions can be shown to have many beneficial consequences; the magnitude of benefits varies according to where the emissions occur. The largest values to be gained from NO_x control would be protection against adverse health effects and materials damages; also, in some regions, aesthetic benefits would be a major result. The effects of acid rainfall that are attributed to NO_x (insofar as they can be estimated) may be substantial, but appear in general to be somewhat smaller than some of the other classes of damages. Controls of NO_x emissions are relatively costly; however, considering that benefits are likely to be underestimated, the costs and benefits appear to be of about the same order ot magnitude. Because both the benefits and the costs of controls are likely to vary widely from region to region, more detailed estimates for specific locations are needed to provide a more relevant cost/benefit comparison.

Third, acceptable methods exist to place an economic value on the increased risk of death associated with ingestion of nitrate or nitrite and related risks of cancer and methemoglobinemia. However, toxicological and epidemiological data are too limited to support credible estimates of the actual hazard of cancer, and the likelihood of an infant death from methemoglobinemia appears to be very small. Neither the benefits nor the exact costs of possible measures to protect against these hazards can be estimated with any accuracy.

In summary, while the economic analysis here suggests some interesting conclusions, its value for policy making is severely limited by the massive uncertainties in the scientific assessment upon which this analysis is based. Research to answer many of the currently open questions about environmental effects of nitrates and economic assessments of such issues can be expected to evolve gradually to a more definitive level.

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CHAPTER 12

ANALYSIS OF SOME POLICY ISSUES RELATED TO NITRATES IN THE ENVIRONMENT

INTRODUCTION

The accumulation of nitrates in certain compartments of the environment poses some hazards to human health, to ecosystems, and to the ozone layer, and society may choose to attempt to reduce those hazards. To support the selection of appropriate policies to do this, both a scientific and technical assessment of the issues and an analysis of alternative strategies to reduce the hazards are required. The analysis of policy options also provides a context for comparing and weighing different social goals that often appear as competing objectives of policy (e.g., to maintain or increase the productivity of agriculture and to preserve the quality of the environment).

The analysis of policy options includes three critical elements:

(1) Assessment of risks: a quantitative (if possible) estimate of hazards, identification of populations at risk, and estimates of the geographic and temporal scales of the problems;

(2) Assessment of control opportunities: identification of points in the risk-generating process at which intervention could be effective, and evaluation of specific technical or nontechnical methods to control or prevent the environmental hazards; and

(3) Assessment of the economic benefits and costs and of the broader environmental and social consequences of alternative policies.

In short, a sound policy analysis draws together the essential components presented in the ten preceding chapters of this report, and arranges the information in a unified, systematic structure. Ideally, such an analysis identifies uncertainties, points out those areas in which social (political) choices are required, and specifies the value judgments that enter into the analysis. The purpose of the analysis is not to argue for a particular policy. In practice, however, environmental problems are usually complex, and the number of possible policy approaches is so large that a full-scale assessment of all options is impossible. The analysis in such cases proceeds, of necessity, in an iterative manner: an initial and relatively superficial scan is made to identify a manageable number of promising or "preferred" policy approaches, which are then examined in more detail.

A full-scale analysis of the many policy options related to each of the issues addressed in this report was outside the scope of this study. The Panel on Nitrates was constituted primarily to compile and assess scientific and technical information on nitrate-related environmental issues. Nevertheless, a relatively crude analysis of policy issues was attempted early in the study and provided a portion of the structure within which the scientific and technical assessment was organized. This chapter represents the next step in the iterative process: a number of policy issues have been isolated, and the findings of earlier chapters have been compiled into an assessment of the feasibility of different approaches. Our purpose here is to provide a qualitative integration of the diverse findings of this report on major issues related to human-induced excesses of nitrate or related compounds in the environment, and to place those issues in perspective with each other and with broader social considerations. This chapter is, however, only a step in the direction of a more complete analysis, covering a broad range of social goals and values, that might be desirable to support specific policy decisions. Such analysis would probably be valuable, but it would be a difficult and costly task, and it is left to others to pursue.

NITROGEN FIXATION AND DEPLETION OF STRATOSPHERIC OZONE

Policies concerned with preventing the biologic and climatic impacts that could result from depletion of the stratospheric ozone layer by nitrous oxide (N_2O) must deal with the global scale of the effects, and with the massive scientific uncertainties inherent in the risk assessment. Effects on the ozone layer (and consequent impacts on life on earth) would occur worldwide, although they would not necessarily be uniformly distributed; likewise, control measures, if implemented, would need to be pursued at least on a multinational scale, since policies pursued by individual nations could affect only parts of the problem. A wide range of uncertainty remains in estimates of values for several critical variables in the global nitrogen cycle (see Chapter 7 and Appendix A-7). Similarly, the relationships between a change in the concentration of N_2O

in the atmosphere and a change in the ozone layer, and between depletion of ozone and the incidence of skin cancer or other adverse effects, can be quantified only approximately. Also, as the discussion of recent research on the sensitivity of ozone to HO_x and NO_x demonstrates (see Chapters 2 and 7), new research findings can lead to rapid and sometimes radical revision of our understanding of environmental processes.

The projected impacts on the ozone layer of current and future rates of nitrogen fixation by human activities, including fertilizer use and combustion, were estimated in Chapter 7 using "best guess" values for the critical variables. These estimates are tentative and subject to revision; nevertheless, our analysis does suggest several important conclusions. First, on the basis of current knowledge, the projected impact on ozone of anthropogenic nitrogen fixation is smaller than the projected impact of the current level of use of fluorocarbons. Second, it is very unlikely that a large depletion of ozone by N_2O could occur in the near future. If a large effect occurs, it probably will not be fully felt for centuries; and even the smallest effects that seem likely would probably develop over decades. It appears, therefore, that prompt action is not required to reduce the nitrogen-related hazard to the ozone layer. Further research on the critical scientific questions is required to support the future formulation of policies (see Appendix D).

If society determines in the future that measures should be taken to limit production of N_2O, the number of control options is small. In theory, it may be possible to manage the nitrogen cycle in agricultural systems so that either the rate of denitrification or the N_2O/N_2 ratio of the products of the process is minimized. However, neither the feasibility of techniques to accomplish this nor the impacts of such manipulations on the global nitrogen cycle have been investigated adequately. The most effective method to limit N_2O production would be to limit the fixation of nitrogen for fertilizer. This goal might be achieved, in part, by more efficient recycling of fixed nitrogen in wastes. Research to explore the extent to which the nitrogen in manures and sewage could substitute for newly-fixed fertilizer nitrogen on a long-term, global basis therefore seems warranted. If research indicates that nitrogen fixed by combustion is a significant source of N_2O, NO_x emission controls, discussed below in relation to the acid rainfall problem, would also be part of a control strategy to protect the ozone layer.

On the other hand, the growing worldwide demands for food and energy probably will continue to stimulate increasing amounts of nitrogen fixation for fertilizer and by fuel combustion for the foreseeable future. At present, there is no political mechanism capable of implementing a policy to limit global fertilizer production or energy use. More importantly, however, our current understanding indicates that the projected effect of N_2O on the ozone layer is rather small, and is far in the future. In our judgment, and on the basis of this relatively narrowly-defined study, the near-term worldwide benefits of fertilizer and energy use appear to outweigh the hazard to the ozone layer, and the only immediate need is for continued research on the scientific uncertainties.

NITRATE IN GROUND AND SURFACE WATERS

The presence of elevated concentrations of nitrate in ground and surface waters stimulates two major concerns: a risk of adverse health effects on humans or animals through drinking water; and the likelihood of enhanced biotic productivity, with a potential for cultural eutrophication, in aquatic ecosystems. Because of the rapid interconversion of nitrogen forms in aquatic environments and soils, control efforts must be concerned with all forms of fixed nitrogen and not just nitrate.

The U.S. Public Health Service established a drinking water standard for nitrate of 10 mg N per liter in 1962 as a national policy guideline, in order to protect against infant methemoglobinemia. The risk of human methemoglobinemia increases significantly at nitrate levels higher than this standard; however, an accurate dose-response relationship cannot be derived from available data (see Chapter 9). The effect occurs almost exclusively in infants less than six months old and is very rarely fatal. However, the potential for more widespread, subtle effects (e.g., behavioral or mental health impacts) on infants or others from chronic, low-level exposure to nitrate has been inadequately studied. The possible contribution of nitrate in drinking water to exposure to carcinogenic N-nitroso compounds (formed in vivo) is not sufficiently known to estimate the risk this might represent. In general, levels of exposure that are considered safe for humans will also pose no hazards to livestock.

Chapter 9 and Chapter 3 indicated that the largest portion of exposure to nitrate and nitrite for the average person (and for most livestock) is through foods, rather than through drinking water. Situations in which contaminated drinking water is the chief source of ingested nitrate usually are localized; and the total population likely to be affected by nitrate-enriched water supplies is small. These facts suggest that control strategies intended to protect public health from this potential hazard should be designed for implementation at the local level.

The role of nitrogen in eutrophication of surface and coastal waters may be significant in some cases, but quantitative general conclusions cannot be supported with current knowledge. Nitrate concentrations higher than a few hundred μg/l in lakes can stimulate algal growth; however, phosphorus, rather than nitrogen, is likely to be the limiting nutrient in most lakes, except in those that are already highly eutrophic. The extent of water quality problems in eutrophic lakes and in coastal waters depends on many other chemical, physical, and biological variables in addition to the concentrations of these two major nutrients.

The development of control strategies to prevent nitrate contamination of ground or surface waters is hindered by substantial uncertainties about the causes of nitrate pollution. Even in relaitvely well-studied locations, such as the Illinois watersheds described in Chapter 6, the proportional contributions of nitrogen from various sources cannot be determined accurately, and thus the effectiveness of possible control measures cannot be assured. In other cases, the causes may be known, but prevention of nitrate contamination may be virtually impossible. For instance, it is probably not feasible with present agricultural practices to keep nitrate concentrations below 20 mg N/l in groundwater beneath heavily irrigated fertilized croplands in some regions of the country (see Chapter 6).

Policies (e.g., EPA regulations) already exist that will reduce contamination of surface waters from some major sources of nitrate, such as sewage and runoff from feedlots. In some cases the same policies, however, increase the potential for nitrate contamination of groundwater by promoting more widespread use of land disposal for wastes.

Because of limitations in the scientific data base, estimates of the costs and benefits of controls for nitrate water pollution are not available, except in certain narrowly defined cases (see Chapters 10 and 11). The total economic and social impacts of some measures that might be used to reduce nitrate contributions from agricultural activities cannot be reliably estimated, but some are potentially large. On the other hand, the economic value attached to the nitrate-related risks to health, while also difficult to measure, appears to be rather small (see Chapter 11). The economic value of eutrophication of estuaries and coastal waters, however, could be large, because such ecosystems are often critical elements in the productivity of ocean fisheries.

Given the scientific uncertainties about the efficacy of most measures that could reduce nitrate levels in runoff from nonpoint sources, and in the absence of a convincing economic justification for most such measures, some approaches other than source controls for nitrate-related water quality problems merit consideration, and might be evaluated in reference to specific local situations. For example, if drinking water supplies contain excessive nitrate, the most effective solution might be to avoid use of that water and to provide an alternative, low-nitrate water supply, either to the entire population of an area or to selected high-risk subsets of the population (e.g., families with infant children). Another approach might employ land use restrictions to separate nitrate-generating activities from water supplies that are used as drinking water.

Even in the absence of more conclusive data about the hazards to health, the 10 mg NO_3^--N/l drinking water standard has been a useful policy instrument. The existence of the standard has led to extensive monitoring of nitrate levels in water and has stimulated concern over methods to control contributions of nitrate from many different sources. It appears, however, that a degree of control that would allow all water supplies to be of drinkable quality probably is not feasible. Some desirable objectives of future analyses, therefore, might be to determine the extent to which it is necessary to attain drinkable water quality in different cases and to examine strategies for meeting the need in localities where problems exist.

ATMOSPHERIC NITRATES AND ACID PRECIPITATION

Emissions of nitrogen oxides from combustion sources and subsequent chemical reactions in the atmosphere produce organic and inorganic nitrates and nitric acid, which may be transported long distances (see Chapters 2, 3, and 6). Atmospheric nitrates may pose some potential hazard to health, although little specific information is available on effects of inhaled nitrates, other than PAN (see Chapter 9). Atmospheric inputs also may be a significant fraction of the total nitrogen available to support biotic productivity in some ecosystems (see Chapter 8). The most important effects of atmospheric nitrates arise from their contribution to the acidity of precipitation. Acidic aerosols contribute to corrosion of many materials, and acidic rainfall is a major regional problem with a potential for widespread, possibly irreversible, and economically important adverse effects on ecosystems (see Chapters 8 and 11).

Although there are many uncertainties about the relative importance of NO_x and SO_x emissions in causing the acidification of rainfall, nitric acid appears to account for between one-fourth and one-third of the current excess acidity of rainfall in the eastern United States. Knowledge of the linkages among emissions, transport processes, and deposition patterns is insufficiently quantitative to connect specific sources with specific impacts (see Chapter

6). Stationary sources emit about half of the total NO_x. Although SO_x emissions from such sources are now subject to control, and new sources must meet an NO_x emission standard, there are currently no restrictions on NO_x emissions from older units. If this situation persists, the proportional contribution of nitric acid to the acidity of precipitation is likely to increase.

Reduction of emissions is the only practical approach to control of the acid rain hazard. The technology available to reduce NO_x emissions has been tested primarily on pilot-plant and demonstration scales, but neither the effectiveness nor the cost of NO_x controls has been adequately determined for full-scale combustion operations (see Chapter 10). Because of the possible contributions of NO_x to ecological damage and the projected upward trend of NO_x emissions (see Chapter 6) research efforts to further develop effective, economically feasible control techniques seem justified.

NITRATES AND CANCER

Inhaled or ingested nitrate can be converted to nitrite in the body, and nitrite can react with other precursors to form carcinogenic N-nitroso compounds. It is thus possible that nitrates, via nitrosamines, pose some risk of human cancer. This hypothesized etiology, however, is unsupported by concrete evidence that could indicate the magnitude of the hazard represented by typical exposures to nitrate or nitrite in foods, water, or air. Each step in the process of conversion and carcinogenesis is biologically plausible, and each has been shown to occur with relatively high doses of the appropriate agents in laboratory animals. However, there are few comparable data on exposure levels or on in vivo formation of nitrosamines in humans; and neither toxicological studies nor the available epidemiological evidence has reliably indicated any firm connection between exposures to environmental levels of nitrate and human cancer (see Chapter 9). Two other approaches to assessment of this hazard gave conflicting and inconclusive results (see Appendices B and C). Further research, particularly epidemiological studies of populations exposed to different amounts of nitrate and nitrite, therefore seems highly desirable.

When the effect at issue is a serious and irreversible one such as cancer, even a largely speculative risk may be seen as justification for some policy action. In this case, the soundest way to reduce the potential risk of cancer is to reduce exposures to nitrate and nitrite. The largest single source of exposure, and one most readily subject to control, is the consumption of cured meats to which nitrate or nitrite has been added. Regulations currently being promulgated by the U.S. Department of Agriculture will eliminate nitrate as an additive to such products, and reduce the amounts of residual nitrite permitted. Further reductions might be considered; however, since nitrite is used to enhance the flavor and color of the meat products and to inhibit the growth of <u>Clostridium</u> <u>botulinum</u>, such measures could involve some sacrifice of product quality and an added risk of botulism.

Before society can judge the levels of nitrate and nitrite that are acceptable in meats or other products for human consumption, additional information is needed in several areas: (1) the actual magnitude of the risk of human cancer posed by nitrosamines; (2) the proportional contributions to that risk represented by exposures to preformed nitrosamines and by in vivo formation of nitrosamines from ingested nitrate or nitrite; (3) contributions of air, drinking water, and various components of the diet to total exposures to nitrosamines and precursors; (4) methods of controlling exposures for each route that is found to be significant; and (5) alternatives for uses of nitrate and nitrite that lead to human exposure, such as development of other methods to prevent botulism and improve the flavor and color of meat products. A more thorough analysis of policy options and their costs and benefits will require the results of research on these questions; and ultimately, the choice of policies will depend on social value judgments on matters such as the relative acceptability of different risks.

SOCIAL TRENDS AND NITRATE-RELATED ENVIRONMENTAL IMPACTS

Several of the nitrate pollution problems discussed in this report have their roots in fundamental social trends related to the production and consumption of food and energy, and to population growth. Prevention of adverse impacts for the long term is therefore likely to require more than the use of control measures to mitigate localized excessive accumulations of nitrate. For instance, more than 80 percent of the nitrogen fluxes in the agricultural food-and-fiber chains in the United States is associated with the production of meat (see Chapter 5); and per capita consumption of animal protein by Americans increased by about 50 percent between 1930 and 1970, while the population increased by about 80 percent. Similarly, per capita energy consumption in the United States increased by 10 percent between 1970 and 1976, and the trend toward increasing use of coal and oil as sources of electric power is likely to result in a greater rate of growth in NO_x emissions in the future than has occurred in the recent past. On a global scale, the combined effects of rapid population growth, increasing food production, and growing demands for energy and meat, associated with a rising standard of living, seem certain to aggravate nitrate pollution problems (and many other problems, as well).

Some conceivable changes in the ways society meets its needs for food were discussed briefly in Chapter 10. Several fundamental changes, such as substantial reductions in per capita meat consumption or energy use, could have beneficial effects on several nitrogen-related environmental impacts; however, neither the full range of environmental consequences nor the economic and social ramifications of such changes in basic lifestyle patterns can be estimated at present. Furthermore, it is doubtful that any such far-reaching transformations of society would be undertaken primarily for environmental protection; and neither knowledge of how such changes might be brought about nor a policy-making agency capable of assuming responsibility for such complex decisions exists today.

Nevertheless, the fundamental trends inherent in modern society's agricultural/industrial system may well be the dominant factors that determine whether or not the nitrate pollution problems described here can be solved, especially on a global and long-term basis. There would therefore be some value in research to examine the complex origins of such social trends, and to explore possibilities and project the consequences of possible national or international policies on food production, energy use, or environmental protection that might modify those trends that aggravate environmental problems.

INTERCONNECTIONS OF PROBLEMS AND SOLUTIONS

A common feature of each of the major environmental impacts of nitrates examined here is that each can be described in terms of an imbalance (an excessive accumulation or rate of transfer) in some part of the nitrogen cycle on one or more geographic scales. Because the solutions to many of the problems involve diverting the excessive fluxes into other pathways of the nitrogen web, these solutions also can lead to the creation or aggravation of other problems. For example, removal of nitrogen from sewage and industrial wastes can lead to increased production of N_2O by denitrification, or to losses of NH_3 by ammonia stripping, or it may create a sludge disposal problem. The incorporation of manures and other nitrogenous wastes into soils makes likely increases in denitrification, volatilization of ammonia, and leaching of nitrate into groundwater. In a somewhat different vein, reductions in NO_x emissions could have have beneficial effects on the acid rain problem, but might at the same time remove some atmospheric nutrient fluxes that were valuable inputs to some systems.

Such interrelationships cannot be quantified now, but should be recognized as part of the trade-offs that must be weighed in examining the consequences of any "solution" to a specific problem. The analysis of policy options for dealing with nitrates in the environment therefore is often best done within a comprehensive framework, such as a mass-balance assessment, that permits coordinated consideration of the many interwoven processes of the nitrogen cycle.

APPENDIX A

MASS-BALANCE STUDIES FOR NITROGEN

INTRODUCTION

Appendix A presents mass balances for nitrogen that were either developed de novo or summarized from existing balances in the literature by various panel members and consultants. The scales of the mass balances range from local (aquatic and terrestrial ecosystems), to regional (river basins and political states), and ultimately to the entire globe. These mass balances form the basis for the discussion in Chapter 5 on the usefulness of the mass-balance approach in studying the behavior of nitrogen in the environment. In particular, methodological issues that arose from developing or reviewing these mass balances and the major findings of the mass-balance analyses are summarized in that chapter.

The mass balances in this appendix are presented in order of increasing geographical scale. First, mass-balance analyses are presented for three well-studied lakes (Lake Okeechobee, Florida, and Lakes Mendota and Wingra, Wisconsin). Several mass balances covering different years are given for the first two lakes, allowing comparisons to be made of year-to-year variations in various inputs, outputs, and storages. We have gone beyond earlier published mass balances for Lake Okeechobee, and used their findings and supplemental information to calculate by difference the amount of denitrification within the lake system. Partial mass balances on terrestrial ecosystems in several biomes (major climatic regions) are then briefly reviewed. Data for these balances were obtained from the literature; in some cases the original studies were part of the International Biological Program (IBP).

At the regional scale, mass balances for two agricultural river basins in California were reviewed from literature reports, and original mass balances were developed for peninsular Florida and for the state of Wisconsin. The mass balance model for Florida emphasizes the importance of atmospheric fluxes; submodels of various agricultural components are also presented. The model for Wisconsin emphasizes the terrestrial portion of the nitrogen cycle and describes the important agricultural flows in a state that is dominated by dairy, vegetable crop, and grain agriculture.

At the global scale, several existing mass balance models for nitrogen are reviewed, and the storages and flows estimated by different workers are compared. The most recent global model (Söderlund and Svensson 1976) was also revised and updated with some new information.

The different mass balances were authored primarily by the following panel members and consultant: J.J. Messer and P.L. Brezonik developed the balances for Lake Okeechobee, Lake Mendota, and peninsular Florida; D.R. Keeney constructed the mass-balance for Wisconsin and reviewed the global mass balances; Messer, Keeney, and Brezonik worked on the study of Lake Wingra; and W.F. Harris reviewed the terrestrial biome studies and river basin mass balances.

(1) LAKE OKEECHOBEE, FLORIDA

Lake Okeechobee ranks second (after Lake Michigan) in size among freshwater lakes wholly within the United States. At its normal stage (about 14 ft above mean sea level), the lake has a surface area of 730 square miles (1850 km^2). However, it is shallow throughout, with a maximum depth of only 15.5 ft (4.7 m) and a mean depth of about 9 ft (about 3 m). The lake plays a key role in the hydrology and ecology of south Florida and serves as a major water-storage, flood-retention, wildlife, and recreational resource for the region. Normal flow in the 5020-square-mile (13,000-km^2) watershed is from north to south; the Kissimmee River, with headwaters near Orlando, is the lake's main tributary.

Under natural conditions, in former times, the lake had no outflow channel, but during periods of high water, sheet flow occurred over the south shore and into the shallow, sawgrass trough of the Everglades. Outflow from the lake is now controlled by several structures and canals, and the hydrology of the Lake Okeechobee watershed bears little resemblance to natural patterns of water flow and storage. For example, the Everglades Agriculture Area, a 310-square-mile (785-km^2) area south of the lake, is now farmed intensively, primarily for sugarcane; an extensive system of canals and pumps has been constructed in this area for soil drainage, irrigation, and flood control.

Because of extensive channelling in the entire Kissimmee-Okeechobee watershed, upland storage of water has decreased and runoff rates have become more rapid. In order to have sufficient water during dry seasons to supply downstream users, including the Everglades National Park, and still keep the level of the lake at a desired stage, backpumping of water from the Everglades Agriculture Area into the lake and other water conservation measures are carried out.

Lake Okeechobee has been subjected to numerous stresses as a result of human attempts to drain and tame the south Florida wilderness. The lake is moderately eutrophic, and its water quality is thought to be declining, although historical data are inadequate to quantify these trends. Because of the importance of Lake Okeechobee as a regional water resource, concern in the state about its degradation has prompted large-scale efforts to evaluate the present condition of the lake and sources of its pollution (e.g., McCaffrey et al. 1976; MacGill et al. 1976).

Nitrogen Balances for the Lake

At least four nutrient budget analyses have been made for the lake in recent years (Joyner 1974; Davis and Marshall 1975; the National Eutrophication Survey [NES] [U.S. EPA 1975a]; F.M. Davis, South Florida Water Management District, West Palm Beach, Florida, personal communication, 1977). Summaries of the four nitrogen balances are presented in Table A.1, which shows that the range of total nitrogen loading was from 5.86 to 7.95 x 10^9 g N/yr. The mean loading rate for the four studies is 7.15 x 10^9 g N/yr, and the individual values fall within about ±15 percent of the mean. The largest loading occurred in 1969, a year with relatively high rainfall in the drainage basin.

Rainfall directly on the lake surface accounts for 15 to 30 percent of the total nitrogen loading; the Kissimmee River, the principal tributary to the lake, supplies 30 to 39 percent of this loading and is the single most important source of nitrogen. Backpumping of drainage waters from the Everglades Agricultural Area has variable significance as a nitrogen source, depending on rainfall patterns and management practices. In a wet year, the level of the lake is maintained by flows from the Kissimmee River and other northern tributaries of the lake, but in drier years, more backpumping is done to supplement the natural inflows. Thus, in 1969 backpumping accounted for only 10 percent of the total nitrogen load, but in 1973-1975 it represented 24 to 32 percent of the loads. Similarly, surface outflows of nitrogen depend on hydrologic conditions. None of the nitrogen balances is truly comprehensive, however, because they do not include dry fallout or absorption from the atmosphere, and to date no measurements of nitrogen fixation in the lake have been made. Nitrogen release from sediments is undoubtedly important in this shallow lake, but this process is regarded as an internal source of nitrogen and was not considered in the balances shown in Table A.1.

TABLE A.1 Summary of Nitrogen Balances for Lake Okeechobee from Four Studies[a]

Flux	Joyner (1974)	Davis and Marshall (1975)	U.S. EPA (1975a)	SFWMD (1977)[b]
		10^9 g/yr (% of total)		
Sources				
Kissimmee River	3.063 (39)	1.748 (30)	2.744 (39)	2.630 (33)
Other natural streams	1.639 (21)	1.326 (23)	1.239 (18)	1.684 (21)
Agricultural backpumping	0.815 (10)	1.869 (32)	1.866 (27)	1.869 (23)
Rainfall	2.316 (30)	0.915 (15)	1.097 (16)	1.786 (22)
Sewage outfalls	--	--	0.024 (<1)	--
Total inputs (N_{in})	7.833 (100)	5.858 (100)	6.970 (100)	7.951 (100)
Areal loading (g N/m^2-yr)	4.23	3.16	3.76	4.29
Sinks				
Surface outflows (N_{out})	5.204 (66)	1.956 (33)	1.954 (28)	3.816 (48)
Other sinks[c]	1.749 (22)	6.040 (>100)	5.017 (72)[d]	3.750 (47)
Change in Storage (ΔN)	0.880 (11)	-2.138 (--)	--[d]	0.385 (5)

[a] Data for years as follows: Joyner (1974), 1969 data; Davis and Marshall (1975), 1973 and 1974 data (one 12-month span); U.S. EPA (1975a), 1973 data (see Footnote d); SFWMD, 1974 and 1975 data (one 12-month span).

[b] F. M. Davis, South Florida Water Management District, West Palm Beach, Florida, personal communication, 1977.

[c] Calculated by difference from the relationship: $N_{in} - N_{out} - \Delta N$ = other sinks.

[d] Lake sampling did not extend over the entire year of stream sampling; it is therefore not possible to calculate values for other sinks and ΔN separately from this study.

Areal nitrogen loadings reported in the four studies range from 3.16 to 4.29 g N/m² of lake surface per year. These values exceed the critical standards of both Vollenweider (1968) and Shannon and Brezonik (1972), shown in Table A.2, which suggests that the lake should be eutrophic. A eutrophic condition, of course, depends also on the phosphorus loading. Areal loading rates of phosphorus (Table A.2) are also in the range in which eutrophic conditions occur, and the studies mentioned earlier in this section agree that the lake is moderately eutrophic.

The item labeled "other sinks" in Table A.1 includes sedimentation, denitrification, increases in nitrogen storage by macrophytes and fish, and volatilization of ammonia from the lake surface. Assuming that the last three of these sinks are small compared to other components of the nitrogen balance, denitrification in the lake can be estimated from the mass balance data on nitrogen and phosphorus. This method was proposed by Vollenweider (1968) and has been used by several Danish investigators (see Chapter 2). Briefly, the method assumes that total phosphorus is conservative and that phosphorus retained in the lake (input P minus output P), corrected for the change in storage, is equal to the amount of phosphorus lost to the sediment. The total N lost to the sediment can be computed on the basis of knowledge of total N/total P concentration ratios in the surficial sediments, and is then subtracted from the total N retained in the lake (calculated as above for total P) to yield the N lost by denitrification. In equation form, the calculations are:

$$N_{den} = N_{in} - N_{out} - \Delta N_{st} - N_{sed}$$

$$N_{sed} = P_{sed} \times \frac{[N]_{sed}}{[P]_{sed}} = (P_{in} - P_{out} - \Delta P_{st}) \times \frac{[N]_{sed}}{[P]_{sed}}$$

where the bracketed values refer to total N and P concentrations in the sediment.

Table A.3 summarizes calculations of denitrification made from the four nutrient budgets of Lake Okeechobee (Messer and Brezonik 1978). The budgets for 1973 and 1973-1974 yield similar values for the amounts of denitrification (approximately 1.6-1.8 x 10^9 g N/yr, and the budget for 1974-1975 yields a larger value (2.7 x 10^9 g N/yr). These

TABLE A.2 Comparison of Nutrient Loadings for Lake Okeechobee with Permissible and Critical Guidelines[a]

	Nitrogen	Phosphorus
Lake Okeechobee (present situation)[b]	3.86	0.26
Permissible Load (up to) (eutrophication problems not expected)		
Vollenweider (1968)	1.0	0.07
Vollenweider (1975)	---	0.12
Shannon and Brezonik (1972)	2.0	0.28
Critical (in excess of)		
Vollenweider (1968)	2.0	0.13
Vollenweider (1975)	---	0.36
Shannon and Brezonik (1972)	3.4	0.49

[a] All values in g/m^2-yr.

[b] Average of four nutrient budgets in Table A.1 (N) and Table A.3 (P).

TABLE A.3 Calculations of Denitrification in Lake Okeechobee by the Mass-Balance Approach in Four Studies[a]

	Joyner (1974)	Davis and Marshall (1975)	U.S. EPA (1975a)	SFWMD[b]
		$(10^9/\mathrm{g/yr})$		
N_{in}	7.83	5.86	6.95	7.95
$N_{out} + \Delta S_N$	6.08	-0.18[c]	1.95	4.20
$N_{sed} + N_{den}$	1.75	6.04	4.99	3.75
P_{in}	0.679	0.499	0.517	0.218
$P_{out} + \Delta S_p$	0.430	-0.139[c]	0.058	0.067
P_{sed}	0.249	0.638	0.459	0.151
$[N]_s/[P]_s$	7.0	7.0	7.0	7.0
N_{sed}	1.74	4.47	3.21	1.06
N_{den}	0.01	1.57	1.78	2.69
Percent of Input N Denitrified:	0	27	26	34

[a] All values in 10^9g/yr.

[b] F.M. Davis, South Florida Water Management District, West Palm Beach, Florida, personal communication, 1977.

[c] Decrease in storage exceeded outflow losses.

three budgets thus indicate that denitrification is an important sink for the lake, and a larger sink than surface outflows. Furthermore, direct measurements recently have confirmed the occurrence of denitrification in sediments of Lake Okeechobee (Messer and Brezonik 1978).

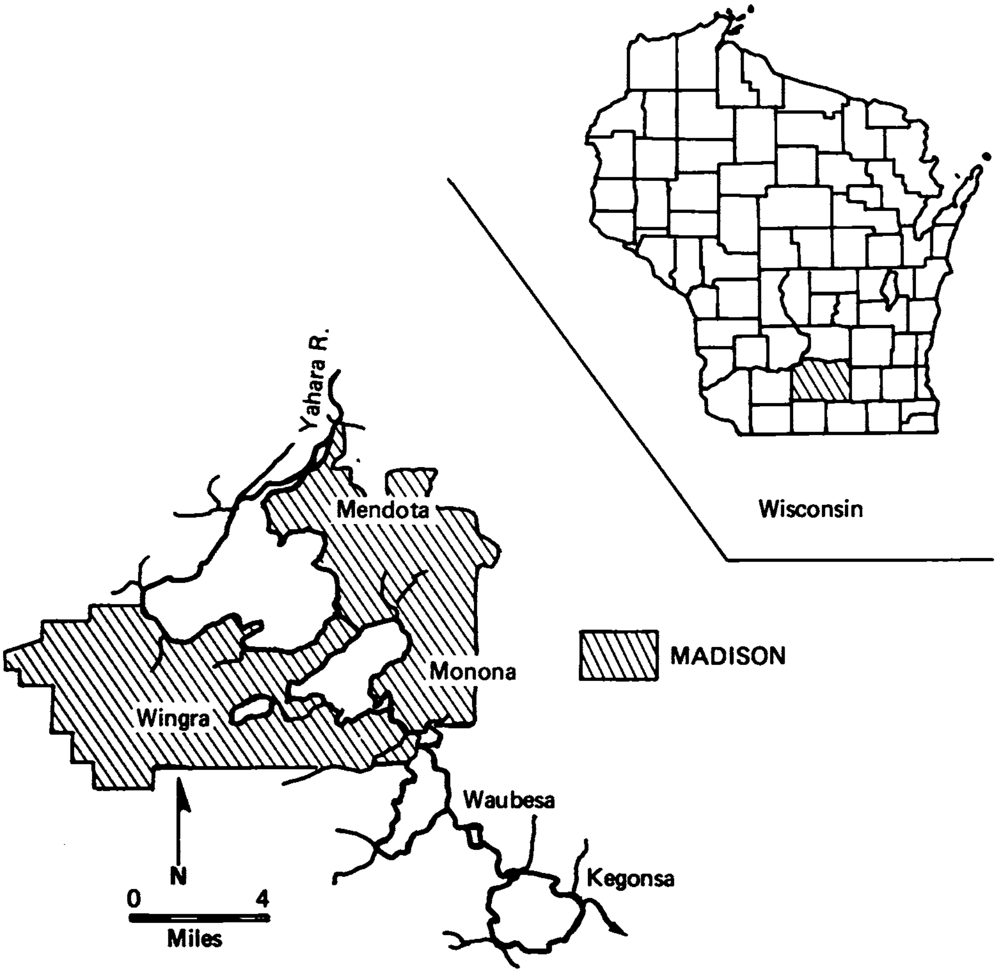
The calculations based on Joyner's (1974) data for 1969, however, yield essentially no denitrification. At the present time, we are unable to evaluate the accuracy of these mass-balance calculations. The differences between the 1969 value and the more recent values possibly represent real differences in the amount of denitrification in the lake. On the other hand, we cannot exclude the possibility that the large range in the values results from inaccuracies in some of the data on individual inputs and outputs, or from unjustified assumptions (e.g., that changes in macrophyte nitrogen storage are small) in the mass-balance technique. It should be noted that the budget for 1969 had the smallest data base of the four budgets, and thus it is probably the least reliable. Chapter 5 discusses the reliability of these estimates and other methodological issues connected with the budgets.

(2) LAKES MENDOTA AND WINGRA, WISCONSIN

Lakes Mendota and Wingra, near Madison, Wisconsin, are among the most studied in the world. Sawyer (1947) pointed out that by the beginning of the twentieth century, nuisance blooms of blue-green algae had prompted a governor's committee to study nutrient inputs to these lakes; thus, a long-term data base exists. The limnologist E.A. Birge, of the University of Wisconsin, conducted many of his pioneering studies on Lake Mendota, and the subsequent attention of researchers in a variety of disciplines at that university to the lake has continued to provide in-depth studies. Lake Wingra and its watershed were part of the IBP Deciduous Forest Biome study, and extensive studies of the lake and its nutrient inputs were conducted in the past decade. The lake was selected for the IBP because its small watershed is in an urban and primarily residential setting. Analysis of nitrogen budgets for the two lakes provides insight into the effects of land-use patterns on nitrogen loading and the suitability of mass-balance modeling of the nitrogen cycle at the ecosystem level.

Description of the Lakes

Lake Mendota and Lake Wingra and their watersheds are depicted in Figure A.1. Lake Mendota is a 3900-ha, hard-water, eutrophic lake, with a mean depth of 3 m and a maximum depth of 23 m (Torrey and Lee 1976). The lake stratifies with an anoxic hypolimnion during the summer.



SOURCE: Modified from Syers et al. (1973).

FIGURE A.1 Map of the watershed of the Madison Lakes, Wisconsin. Inset shows location of Dane County, within which the chain of lakes is located.

Lake Wingra is smaller (133 ha), and shallower, with a mean depth of 3 m and a maximum depth of 5 m. It is easily mixed by wind and fails to stratify stably in the summer (Isirimah et al. 1976). The lake is moderately eutrophic and exhibits frequent algal blooms as well as macrophyte problems.

The Lake Mendota watershed is dominated by rural land on the north and west; only 12 percent of the watershed is urbanized (Sonzogni and Lee 1974). On the other hand, the Lake Wingra watershed is predominantly (68 percent) residential (Isirimah et al. 1976), and about 27 percent of the 1540-ha watershed is covered by impervious surfaces. The remainder of the watershed is in the University of Wisconsin Arboretum and is maintained in a natural state. The land-use pattern in the Lake Mendota watershed is presented in Table A.4.

Nitrogen Balances for the Lakes

An early attempt to determine the cause of algal problems in Lake Mendota, made in 1918 by a consulting engineer to the Madison City Council, blamed agriculture rather than sewage for eutrophication of the lakes downstream from Lake Mendota (Sawyer 1947). In a later study made in 1942-1943, Sawyer did not measure inputs to the lake but reported an average annual concentration of 0.17 mg N/l in the outflow. Bartsch and Lawton (1949) measured nitrogen concentrations and discharges of the ten influent streams to the lake on an irregular basis and reported a total nitrogen load of 9.07 x 10^4 kg N/yr (Table A.5). According to Lee et al. (1966), the flow data of Bartsch and Lawton are suspiciously low, resulting in underestimates of nutrient loadings. Runoff from the 13 percent of the drainage basin not drained by streams was unmeasured. Belter and Calebresa (1949) used more sophisticated flow measurements and estimated annual loadings of 11.7 x 10^4 kg of inorganic nitrogen and 3.98 x 10^4 kg of organic nitrogen for a total load of 15.7 x 10^4 kg N/yr. Both Bartsch and Lawton and Belter and Calebresa reported that nitrogen fluxes were proportional to tributary flow, except in one stream that drains heavily tilled agricultural land and in another creek that receives wastewater from a village. Emelity and Hanson (1949) calculated a nitrogen balance on the lake and found that only 23 percent of the inflow nitrogen left the lake through its surface outlet (the Yahara River). The remaining 77 percent presumably was lost to the sediment or was denitrified. By comparison, Sawyer (1947) found 30 to 60 percent retention of nitrogen in the downstream lakes.

None of the early studies described above considered nutrient fluxes from nonstream sources. The Nutrient Sources Subcommittee of the Lake Mendota Problems Committee

TABLE A.4 Land Use in the Lake Mendota Watershed, 1966 and 1974

	Lake Mendota Watershed			
	Lee et al. (1966)		Sonzogni and Lee (1974)	
Land Use	Area, km^2	Percent	Area, km^2	Percent
Rural	460	81	465	83
Urban	44	7	65	12
Marshland	28	5	24	4
Woodland	40	7	4	1
Total	572	100	558	100

SOURCE: Modified from Sonzogni and Lee (1974).

TABLE A.5 Summary of Nitrogen Budgets for Lake Mendota and Lake Wingra

Nitrogen Budgets	Lake Mendota Bartsch and Lawton (1949)	Belter and Calabresa (1949)	Lee et al. (1966)	Sonzogni and Lee (1974)	Lake Wingra[a]
Total N Loading (10^4 kg/yr)	9.07	15.69	21.69	56.75	1.22
Areal Loading (g/m^2)	2.33	4.03	5.56	14.6	9.17

Detailed Budgets	Lake Mendota Lee et al. (1966)	Sonzogni and Lee (1974)	Brezonik and Lee (1968)	Lake Wingra
Sources	10^4 kg/yr (% of total)			
Wastewater	2.13 (10)	2.72 (5)		
Urban runoff	1.37 (6)	3.31 (6)		0.46 (38)
Rural runoff	2.36 (11)	23.59 (42)		0.11 (9)
Precipitation	4.40 (20)	3.13 (6)		0.22 (18)
Dry fallout		6.12 (11)		
Nitrogen fixation	0.09 (0.4)	3.81 (7)		
Groundwater	11.34 (52)			0.43 (35)
Seepage		7.76 (14)		
Baseflow		6.12 (11)		
Sinks				
Outlet loss			4.13 (16)	
Denitrification			2.8 (11)	
Fish catch			1.13 (5)	
Weed removal			0.33 (1)	
Sedimentation			16.8 (67)	

[a] Based on data from Kluesener (1972), Isirimah (1972), and Isirimah et al. (1976).

(Lee et al. 1966) attempted to estimate these "nonpoint" sources by using data from the literature. The results are given in Table A.5, and the data and assumptions for their calculations are described below.

Domestic sewage loading was based on an average generation of 3.2 kg of nitrogen per capita per year. Limited data were available for nitrogen concentrations in wastewater from a milk company, a cheese plant, a seasonal canning operation, and a car wash. Urban runoff was based on data for Cincinnati, Ohio (Weibel et al. 1964) that were lowered by 10 percent to account for the smaller amount of precipitation in Madison. Nitrogen in runoff from cropland, woodland, and manured pasture was based on various literature values. Values in the literature for areal loadings from manured pasture correlated well with actual runoff measurements in part of the watershed. Both rural and urban runoff values represent only soluble nitrogen.

Although drained marshland was thought to represent a possibly significant source of inorganic nitrogen, quantitative estimates were not possible. Laboratory studies and in situ observations of increases in inorganic nitrogen above the sediment during winter led Lee et al. (1966) to conclude that sediments, as well as sewage sludge deposited on marshland, contribute nitrogen to Lake Mendota. Quantification of these sources was not attempted. Nitrogen fixation in the lake was originally estimated to contribute 3.63×10^4 kg N/yr, based on studies with ^{15}N by Goering (1963), but this figure was revised downward to 908 kg in a 1969 version of the report because of an error in the initial calculations.

Precipitation loading of nitrogen onto the surface of Lake Mendota was based on field measurements by Shah (1962). The groundwater contribution to nitrogen loading was based on the assumption by Cline (1965) that of the 15 cm of rainfall not lost by evapotranspiration, there is 5 cm of runoff, leaving 10 cm of water to percolate to the water table. Given the available flow data, and a balance on the 10 cm of percolate, the total groundwater contribution was calculated at 11.4×10^4 kg N/yr, indicating that groundwater is by far the principal nitrogen source for the lake.

Summing up all the sources, Lee et al. (1966) calculated a total annual loading of 21.69×10^4 kg N to the lake. Expressed per unit of lake volume and area, this loading amounts to 0.45 g/m^3-yr and 5.56 g/m^2-yr, respectively. Brezonik and Lee (1968) measured denitrification in the lake hypolimnion during the summer of 1966 and calculated other components of the outflow side of the nitrogen balance shown in Table A.5.

Changes in patterns of wastewater disposal and advances in measuring and understanding the nitrogen sources to the lake prompted Sonzogni and Lee (1974) to calculate a new nitrogen balance for Lake Mendota. Land-use patterns in the watershed, which are shown in Table A.4, changed little between the two studies, with the major change being the encroachment of suburbia on former woodlands. Baseflow stream contributions of nitrogen were extrapolated from a study by Minshall et al. (1969) on some streams in southern Wisconsin that were thought to be free of pollution. Minshall and coworkers found a mean contribution of 1.1 kg N/ha from a variety of watersheds over a range of flows. Extrapolating to the Lake Mendota watershed, these figures imply an annual yield of 6.12 x 10^4 kg N. Sonzogni and Lee (1974) used a mean annual areal loading rate of 4.5 kg N/ha to calculate a nitrogen loading of 23.6 x 10^4 kg/yr from rural runoff.

Urban runoff and atmospheric loading, including dry fallout, were calculated from the information collected by Kluesener (1972) on the Lake Wingra watershed. Estimates of groundwater flow were not changed from the previous (1966) budget, nor were the industrial wastewater estimates significantly altered. Sonzogni and Lee (1974) altered the annual wastewater loading to 3.63 kg N/capita; together with newer census data, this calculation yielded a total wastewater contribution of 2.72 x 10^4 kg N/yr. Torrey and Lee (1976), who used the acetylene reduction method to obtain the most recent estimate of nitrogen fixation in the lake, reported a contribution of 3.81 x 10^4 kg N/yr and revised the Sonzogni and Lee budget accordingly. The total annual nitrogen loading (56.56 x 10^4 kg) according to the slightly altered estimate of Sonzogni and Lee (1974) is more than twice the loading calculated in the previous study by Lee et al. (1966). The reliability of the four nutrient budgets for Lake Mendota and methodological issues involved in their preparation are discussed in Chapter 5.

The nitrogen contributions to Lake Wingra, based on the research of Kluesener (1972), Isirimah (1972) and Isirimah et al. (1976) also are given in Table A.5. Total nitrogen input to Lake Wingra from all external sources was estimated at 12 t/yr, and Isirimah et al. (1976) estimated that from 3 to 14 t of nitrogen were regenerated yearly from the lake sediments. The streams had about 3 mg NO_3^--N/l, most of it apparently from groundwater sources. The nitrate in urban runoff from storm sewers typically peaked early in a runoff event, reaching a maximum of 2 mg/l, and steadily declining thereafter to about 0.8 mg/l. In general, nitrate-nitrogen in urban runoff exceeded ammonia-nitrogen, except in the spring. Nitrate tended to be higher in urban runoff when rainfall followed prolonged dry periods.

Over the year, nitrate contributed nearly half of the nitrogen input into Lake Wingra, most of it from springs (Table A.6). Dry fallout was as important a source of nitrate as was rainfall (Table A.6), and about 30 percent of the nitrate in urban storm runoff originated in rainfall. Because of the rapid infiltration rates of lawns in the suburbs near Lake Wingra, lawn and garden fertilizers were not an important source of nitrate to surface runoff. About 35 percent of the total nitrogen input came from urban sources; thus, nearly 65 percent came from "uncontrollable" nonpoint sources.

Discussion

Comparison of the nitrogen sources for Lakes Mendota and Wingra reveals some similarities and many differences. The atmosphere contributes approximately 20 percent of nitrogen inputs to both lakes. The magnitudes of contributions from agriculture to Lake Mendota (42 percent) and from urban runoff to Lake Wingra (38 percent) are similar. Lee et al. (1966) estimated that 87 percent of the nitrogen in rural runoff resulted from winter manuring.

Groundwater flow is somewhat more important in the budget of Lake Wingra (35 percent) than in that of Lake Mendota (24.5 percent). The importance of groundwater nitrogen contributions to the lakes is clouded, however, by the role of denitrifying bacteria in the sediments. Keeney et al. (1971) and Chen et al. (1972) demonstrated denitrification in anoxic sediments of Lake Mendota, and Keeney et al. (1971) suggested that 63 percent of the nitrogen in groundwater that seeps into Lake Mendota may be denitrified. However, this calculation is based on sediment samples from lake depths of 7 and 14 m, and may not be typical of the littoral zone, where most groundwater seepage probably occurs (McBride and Pfannkuch 1975), or of channelized flows such as springs. Information on the availability of carbon substrates and on metabolic activity in littoral sediments would help clarify this issue.

Mineralization of sediment nitrogen has been shown to act as an internal nitrogen source for Lake Wingra, and the magnitude of this source may rival the total loading of the lake (Isirimah et al. 1976). In the overall nitrogen balance, however, this sediment loading results from the deposition of detrital nitrogen formed by plankton. Removing inorganic nitrogen inputs to the system may rapidly curtail plankton growth and thus limit the availability of easily mineralized organic nitrogen.

Sonzogni and Lee (1974) provided an explanation for the lower values of stream loadings in the earlier studies. Because the highest concentrations of nutrients in streams

TABLE A.6 Nitrate-N Loadings to Lake Wingra

Source	Kilograms NO_3^--N/yr	Percent Total N as NO_3^--N
Precipitation on Lake Surface	440	40
Dry Fallout	480	22
Spring Flow	4,140	96
Urban Runoff	600	13
Average	---	47
Total	5,660	--

SOURCE: Kluesener (1972).

were associated with periods of high discharge (Shannon and Lee 1966), periodic sampling, as opposed to continuous sampling or sampling done more frequently during periods of high stream flow, would tend to underestimate the transport of nitrogen. This problem was avoided in the recent studies on Lake Wingra. The nitrogen contributions from urban runoff, rural runoff, and sewage reported in Lee et al. (1966) included only soluble forms of nitrogen, and thus underestimated loading. Although a mean areal contribution of 4.5 kg/ha was used to calculate rural runoff, the range of values found by different investigators varies over an order of magnitude (1 to 10 kg/ha-yr). Adoption of the extreme values would result in a range of loadings of from 5.2×10^4 to 52×10^4 kg N/yr; the relative contributions of rural runoff would then range from 14 to 61 percent of the annual nitrogen budget.

Finally, several potentially significant sources of nitrogen were not included in the budgets for these lakes. The potential importance of marshland inputs has been noted by both Lee et al. (1966) and Sonzogni and Lee (1974), but quantitative work on inputs from marshlands is not available. Nitrogen fixation in marshland contiguous to Lake Mendota was found by Lonergan (1973) to average 8.8 kg N/ha-yr, but problems in establishing the fate of this fixed nitrogen and the seasonal variations in marsh transport and transformations obviate calculation of loadings from marshlands (Lee et al. 1975). Atmospheric inputs involving gaseous deposition of ammonia and nitrogen oxides have not been investigated in the Madison lakes, and quantitation of groundwater flows and nutrient contributions is still needed.

(3) TERRESTRIAL ECOSYSTEMS: EXAMPLES FROM SEVERAL BIOCLIMATIC ZONES

Terrestrial nitrogen cycles for ecosystems in several bioclimatic zones (biomes) are summarized in Table A.7. The purpose of this comparison is to illustrate broad bioclimatic trends and variations in nitrogen cycles. Since these studies were confined to specific sites and were not comprehensive surveys of entire bioclimatic regions, estimates of atmospheric input, system outputs, and pool sizes should not be used indiscriminately to characterize major regions. Despite limitations on extrapolation, the data are illustrative of several trends that should be considered in studying these environments.

Terrestrial ecosystems that have evolved naturally accumulate organic matter and essential nutrient elements, including nitrogen. It can be argued that accumulation of organic matter, as living structure or humified organic matter, is a strategic mechanism operating at the system

TABLE A.7 Estimated Nitrogen Balances for Some Bioclimatic Types

	Deciduous Forest[a]	Tundra[b]	Desert[c]	Western Coniferous Forest[d]	Grassland[e]	Tropical Forest[f]
Inputs[g]			16.1	1.1	--	
Wetfall						1.4
NO_3-N	4.0	0.5				
NH_4-N	5.3	0.5				
NH_3	---	5				
Total N	13.0					27.0
Nitrogen fixation	---	2-90	3.6			88.0
Pools						
Plant Tissue	492	90	41	--	8.6%[i]	1230
Detritus	119	32	68	--		126
Soil Organic Matter	5080	3350	162	2809	91%	--
NH_4-N	75	72	--	326	0.4%	
NO_3-N	3	0	--	175		
Internal Fluxes						
Uptake	124.0	11.0	12.7	38.4		102
Mineralization	115.6	11.0[h]	12.7	--		
Losses				0.6		
Streamflow			--			29.0
NO_3-N	0.4					
NH_4-N	1.1					
Total N	3.1	+10.0	--			
Denitrification	--	0	14.2	--		56.0
Ecosystem Residence Time (yr)	1370	--	19	4680		

[a] Henderson and Harris (1975).
[b] Rosswall et al. (1975).
[c] West (1975).
[d] Gessell et al. (1973).
[e] Woodmansee et al. (1976).
[f] Edmisten (1970).
[g] Values in table are kg/ha (pool sizes) or kg/ha-yr (fluxes) unless otherwise noted.
[h] Mineralization of 7 kg/ha-yr to a depth of 10 cm. To meet the demands for nitrogen by plant roots, it is assumed that an additional 4 kg/ha-yr is made available as a result of mineralization of organic matter at depths greater than 10 cm.
[i] Values are expressed as percent of total nitrogen.

level to conserve elements that are essential to life processes (Reichle et al. 1975). Although accumulation of nutrient elements in the organic pool is expensive in terms of energy, accumulation of a stable element supply and an energy base to support its microbial remobilization is ensured.

Terrestrial element cycles tend to be conservative (i.e., inputs far exceed outputs) and residence times (defined as total element pool/output-yr) are long. The total amount of an element and its residence time in an ecosystem generally are correlated with the amount of organic matter, particularly undecomposed or humified soil organic matter. The amount of organic matter is related to the bioclimatic regime and to the developmental age of the ecosystem, particularly the soil component.

In the case of nitrogen, 90 percent or more of the pool is incorporated in soil organic matter except in desert ecosystems, where soil organic accumulation is limited by low rates of detrital input and high rates of breakdown of organic matter. As a result of the slow buildup of organic matter, total nitrogen is generally an order of magnitude less in the desert ecosystem than it is in other ecosystems. In contrast, tundra ecosystems accumulate nitrogen in detrital organic matter, but they still may be nitrogen-limited because of extremely low rates of decomposition.

A common feature of all terrestrial nitrogen cycles is the extremely small fraction of nitrogen that occurs as ammonium and nitrate ions (generally less than 3 percent of the total nitrogen). The small but rapid fluxes of nitrogen through the decomposers are sufficient to support other needs for nitrogen. The rapid activity of decomposers, resulting in a small pool of soluble nitrogen species, serves to minimize losses by leaching from the system. The net result is a long residence time of nitrogen in the ecosystem (e.g., 1000^+ years for nitrogen compared to 50 to 100 years for carbon [Reichle et al. 1975]).

In the absence of large organic accumulations, (e.g., in the ecosystems of arid zones), the nitrogen cycle is much more rapid. Microbial catabolism of detritus is replaced by large annual fixation-denitrification fluxes to accommodate annual utilization (West 1975). In contrast to the nitrogen residence times of greater than 1000 years, noted above, arid zone ecosystems exhibit nitrogen residence times of about 20 years.

Despite emphasis in the past ten years on the analysis of whole ecosystems, there is still a need for additional case studies of local nitrogen cycles. The extent to which geographic variability is understood and quantified remains limited. There are few studies that provide any insights into temporal changes in local mass balance, as the result of either natural processes or human activities. While the nitrogen pool sizes in various compartments of ecosystems are estimated with acceptable precision and accuracy, measurements of fluxes, particularly nitrogen fixation and denitrification, are not so consistently considered, nor are measurement techniques for fluxes comparable between studies.

(4) RIVER BASINS

While mass balances are an intuitively attractive means of studying the dynamic cycling of a material, such studies of entire river basins are difficult to construct and interpret. Difficulties in construction arise from the fact that data bases are often incomplete because basins usually encompass several political units. Considerable resolution of spatial variation is lost in the averaging processes required to construct the balances. Difficulties in interpretation arise from the fact that a complex river basin ultimately is resolved by the researchers into at most a few spatial components. Finally, steady-state mass balances provide only a single window in time.

The importance of land use in controlling the mass movement of nitrogen and other elements in river basins is apparent from a recent study by Omernik (1976). In this study of the eastern United States, watersheds with 100 percent agricultural/urban land use had nitrogen export rates more than fivefold greater than undisturbed forested watersheds (see Chapter 6).

Studies in California

Two recent studies of river basins in California have collected information on mass balances and are compared in this section. Both studies used comparable methodology. The upper Santa Ana River Basin (Ayers and Branson 1973) encompasses 356,000 acres (144,000 ha) and is characterized by shifting land use from citrus to urban and cattle/poultry. Certain areas of the basin are experiencing elevated nitrate levels in groundwater. The southern San Joaquin Valley (Miller and Smith 1976) is a much larger area (1.8 million ha, with 1 million ha under irrigation). This basin has a lower population density, and relatively fewer livestock, poultry, and dairy operations, but much greater production of food and fiber crops compared to the Santa Ana basin.

Tables A.8 through A.10 summarize the storages, mass-loading rates and fates of nitrogen in the two river basins, and Figure A.2 summarizes the nitrogen cycles in the two

TABLE A.8 Estimated Mass of Nitrogen in Various Pools in Two California River Basins

	Mass of Nitrogen (metric tons)[a]	
Pool	Santa Ana River Basin[b]	San Joaquin River Basin[c]
Atmosphere	1.13×10^{10} (99.66)	1.39×10^{11} (99.70)
Land surface	2.64×10^{4} (0.0002)	2.22×10^{5} (0.00016)
Soil	2.59×10^{6} (0.0228)	1.88×10^{7} (0.0135)
Substrata	3.61×10^{7} (0.3175)	3.58×10^{8} (0.2570)
Surface water	5.40×10^{3} (0.00005)	3.81×10^{4} (0.00003)
Groundwater	5.27×10^{4} (0.0005)	5.23×10^{5} (0.0004)
Total	1.134×10^{10} (100.0)	1.394×10^{11} (100.0)

[a] Values in parentheses are percent of total.

[b] From Ayers and Branson (1973). Values modified to correct error in original.

[c] From Miller and Smith (1976).

TABLE A.9 Sources of Nitrogen Inputs and Estimated Annual Fluxes and Loading Rates for Each Source in Two California River Basins

Source	Input flux (mt/yr)		Area affected (ha)		Loading rate (kg/ha-yr)	
	Santa Ana River Basin[a]	San Joaquin River Basin[b]	Santa Ana River Basin[a]	San Joaquin River Basin[b]	Santa Ana River Basin[a]	San Joaquin River Basin[b]
Precipitation (wet & dry)	1,296	690	144,130	1,771,750	8.99	0.39
Sorption of ammonia	648	6,000	144,130	1,771,750	4.50	3.39
Symbiotic N_2 fixation	1,620	46,500	144,130	220,110	11.24	211.3
Nonsymbiotic N_2 fixation	648	5,010	144,130	1,514,900	4.50	3.31
Combustion[c]	4,277	6,900	---	---		
Municipal wastes	3,564	5,040	---	---		
Industrial wastes	74	10,090	---	---		
Manures	4,148	50,910	---	---		
Fertilizers	7,688	118,830	144,130	1,029,300	53.34	115.0
Water (ground + surface)	4,726	37,160	---	---		
Totals for basin	28,689	287,130	144,130	1,771,750	199.0	162.1

[a] From Ayers and Branson (1973). Based on 1960 level of development.

[b] From Miller and Smith (1976). Based on 1971 level of development.

[c] Combustion inputs computed as auto emissions. Not all nitrogen fixed by combustion remains in the basin; some is removed by atmospheric transport, and some is transported into the basin from sources outside the region. See Figure A.2.

TABLE A.10 Estimated Fates of Nitrogen Inputs From Various Sources In Two California River Basins

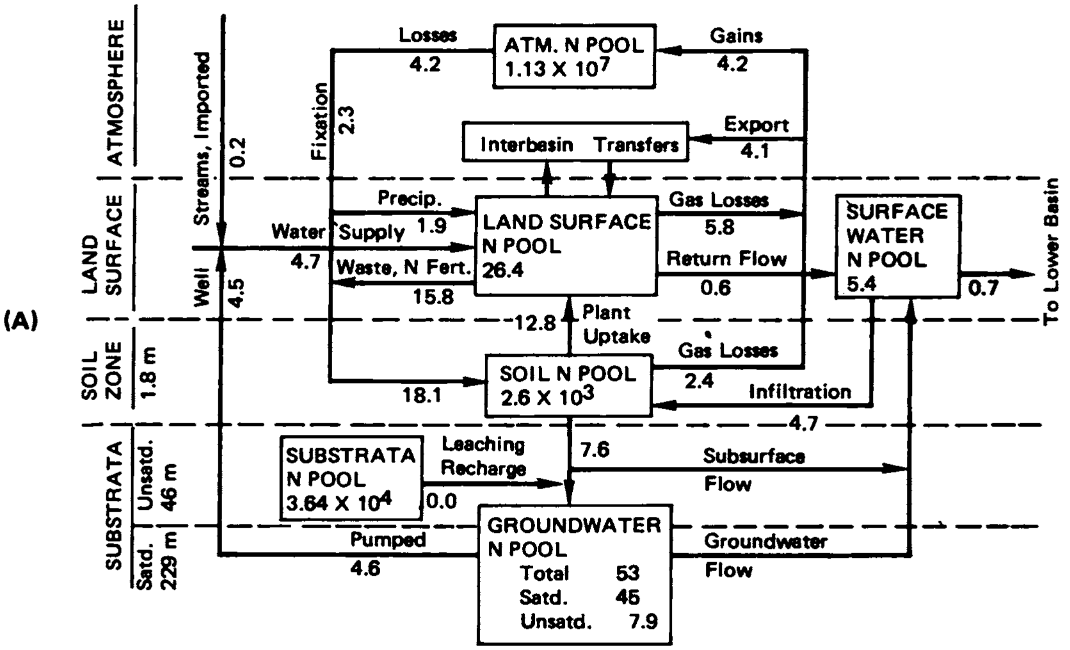
		Fate: Losses, mt N/yr (percent of input)				
Source	Input[a] (mt N/yr)	Volatilization	Denitrification	Crop Uptake	Residual (Potential leachate)	Losses in Surface Water[d]
Municipal wastes						
Santa Ana[b]	3,564	---	356 (10)	356 (10)	2,852 (80)	---
San Joaquin[c]	5,040	---	500 (10)	500 (10)	4,040 (80)	---
Industrial wastes						
Santa Ana	74	---	---	---	74 (100)	---
San Joaquin	10,090	---	1,010 (10)	1,010 (10)	8,070 (80)	---
Manures						
Santa Ana	4,148	1,244 (30)	415 (10)	1,659 (40)	830 (20)	---
San Joaquin	50,910	15,270 (30)	5,090 (10)	25,460 (50)	5,090 (10)	---
Fertilizers						
Santa Ana	7,688	308 (4)	1,153 (15)	4,613 (60)	1,614 (21)	---
San Joaquin	118,830	5,940 (5)	17,820 (15)	59,420 (50)	35,650 (30)	---
Waterborne						
Santa Ana	4,726	---	473 (10)	2,836 (60)	1,417 (30)	---
San Joaquin	37,160	---	3,720 (10)	18,580 (50)	14,860 (40)	---
Nitrogen fixation						
Santa Ana	2,268	---	---	1,815 (80)	453 (20)	---
San Joaquin	51,510	---	---	41,210 (80)	10,300 (20)	---
Precipitation + sorption						
Santa Ana	1,944	---	---	1,555 (80)	389 (20)	---
San Joaquin	6,690	---	---	5,310 (80)	1,330 (20)	---
Total						
Santa Ana	24,412	1,552 (6)	2,397 (10)	12,834 (53)	7,629 (31)	720
San Joaquin	280,230	21,210 (8)	28,140 (10)	151,490 (54)	79,340 (28)	886
Loading, kg N/ha-yr						
Santa Ana	169.4	10.8	16.6	89.0	52.9	5.0
San Joaquin	158.2	12.0	15.9	85.5	44.8	0.5

[a] Combustion inputs not included.

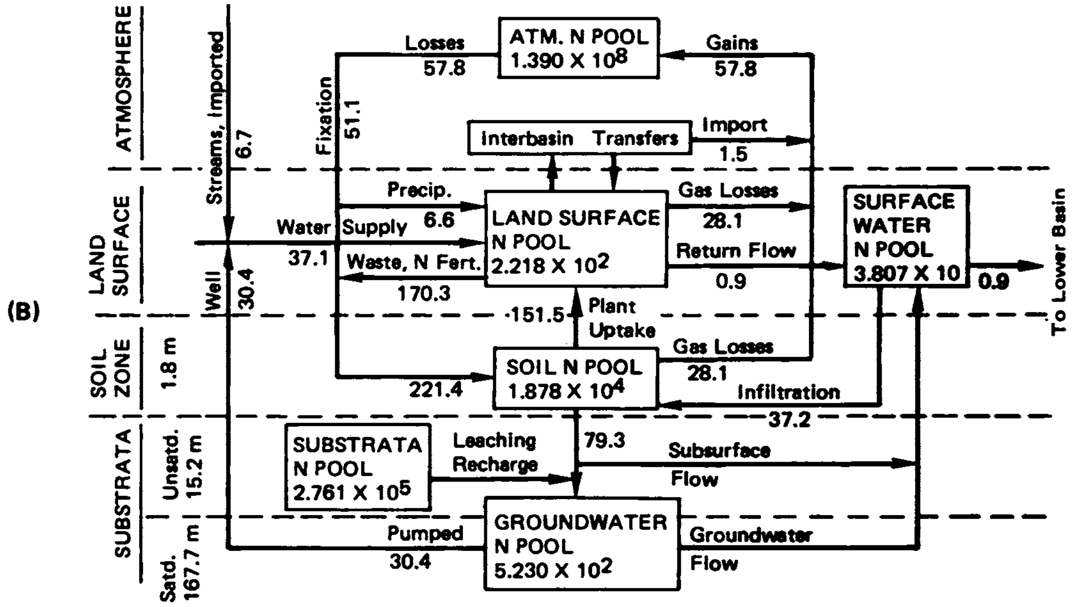
[b] From Ayers and Branson (1973).

[c] From Miller and Smith (1976).

[d] Represents a fraction of residual nitrogen (leachate), shown in adjacent column.



SOURCE: Modified from Ayers and Branson (1973).



SOURCE: Miller and Smith (1976), J. Environ. Qual. 5:276, reproduced by permission of the American Society of Agronomy.

FIGURE A.2 Nitrogen pools and fluxes within (A), the Upper Santa Ana River Basin, and (B), the Lower San Joaquin River Basin, in California. Values of pools and fluxes are in thousands of metric tons and thousands of metric tons per year, respectively. (A) based on 1960 and (B) based on 1971 level of development.

basins. Despite the detail of these analyses, there are still unknown fluxes (e.g., the partitioning of sources of nitrogen in subsurface and groundwater flow). Even with some missing estimates, such a basinwide examination provides for interesting comparisons.

Both basins have comparable areal nitrogen loading rates and potential for leachate loss (Tables A.9 and A.10). Areal surface outflows, however, vary by an order of magnitude. The explanation for this variation is not readily apparent from mass balances alone, but the variable contribution of groundwater to surface water could account for some of the differences that were observed. The nitrate concentration of groundwater that was used to calculate the mass balances for the two river basins varied by nearly an order of magnitude, and the proportion of pumped to imported water varied between the two basins. Other factors such as differences in the size of the basins also could contribute to the differences in surface outflow. The large size of the San Joaquin Basin could provide some buffering capacity. Finally, there is a need to consider spatial distribution of land use, soil characteristics, and other variables that could influence the dynamics of the nitrogen cycle of a basin and result in differences in concentrations of nitrogen in surface water.

There are several methodological difficulties with these two highly similar models; these problems are discussed in general terms in Chapter 5. A major conceptual problem concerns the land surface pool, which is not clearly described in either study. This pool includes the nitrogen in vegetation and animals (including man); it also apparently includes chemical fertilizer and manure. Chemical fertilizer, which would seem to be an input to both systems, is shown to be transferred from the land surface pools to the soil pools, but no inputs of fertilizer to the land surface pools are indicated. The land surface pool is not balanced in either study; whether this was intentional or not is not stated in the original articles. Neither balance lists imports or exports of livestock or crop nitrogen from the land surface pool, although such transfers would seem to be important in mass balances on agricultural systems. Perhaps this information was unavailable; nonetheless, some discussion of these transfers would seem appropriate. Finally, Figure A.2 indicates that nitrogen in streamflow and pumped groundwater is contributed to the land surface pool, rather than to the surface water pool in both models. An amount of nitrogen equal to that imported in water is transferred by infiltration to the soil pool from the surface water pool, but no linkage is described that transfers this nitrogen from the land surface to the surface water pool. Improved definitions of the boundaries of the soil surface pool and of the specific transfer pathways of fluxes into and out of that pool appear to be needed to enhance the usefulness of the models.

At the present stage of development, mass balances of entire river basins appear to be more of a research tool than an aid in policy analysis (see Chapter 5). Such balances systematize available information and appear to be an invaluable aid to guiding research programs, but unfortunately they do not provide unequivocal answers for policy makers.

Hubbard Brook, New Hampshire

A discussion of watershed and river basin models would be incomplete without a brief mention of the Hubbard Brook, N.H., experiment. Extensive ecological and mineral cycling studies have been conducted there for about 15 years. The forested catchments in the watershed are underlain with impermeable granite, and seepage therefore can be ignored; surface outflows are gauged at stem outflows. In contrast to the much larger river basins discussed in the previous section, the Hubbard Brook system contains no agricultural land and no permanent population. Thus, complicated estimates of fertilizer, manure, and wastewater loadings are unnecessary. The most ambitious mineral mass balances in the watershed to date have been for conservative or non-volatile minerals. A preliminary attempt recently was made at a nitrogen mass balance (Bormann et al. 1977) in one of the catchments, watershed No. 6.

This watershed comprises an aggrading beech forest, and the nitrogen mass balance indicated that the system was "tight" with respect to retention of nitrogen. Precipitation delivered 32 percent of the system's nitrogen while (net) biological fixation was calculated by difference to supply the remaining 68 percent. Only 20 percent of the nitrogen escaped the system, while 80 percent accumulated in the system. Of the retained nitrogen, 54 percent was added to living biomass and 46 percent stored as organic matter. Dry gas deposition and denitrification, which were not measured, were assumed to be minor pathways. It is interesting that even though the Hubbard Brook system has been extensively studied for mineral cycling over a 15 year period, several important nitrogen fluxes have not been measured there at all. As a result, Bormann and coworkers had to use literature estimates and difference calculations to complete the balance.

(5) WISCONSIN

Wisconsin is largely a rural state, with a mixed cash grain, dairy, vegetable crop, and general farm-based agriculture. The total area of the state is 14.64 x 10^6 ha, with 54 percent of the area in farmland. There are 105,000 farms, averaging 75.6 ha. Wisconsin has a population of 4.6 million, with a heavy concentration around Milwaukee and its surrounding counties in the south central part of the state. About 179,000 workers are employed on farms. In 1973, gross farm cash receipts were $2,540 million, with dairy and dairy products accounting for $1,198 million and livestock products for $690 million of the gross income (Wisconsin Agricultural Statistics 1975).

This study of the flow of nitrogen in Wisconsin agriculture was conducted using available statistical data and literature estimates, and thus is a relatively low-cost regional mass-balance study. This method has many limitations, one of the greatest of these being a lack of verification of the model. However, it is hoped that this model will highlight areas where data are deficient and serve as a guide to future research efforts.

Nitrogen Inputs

Fertilizer

The use of nitrogen fertilizer has increased rapidly in Wisconsin in the past decade (Figure A.3). Anhydrous ammonia accounts for about 30 percent of the fertilizer nitrogen. The consumption (127 x 10^6 kg) of anhydrous ammonia was about 1.5 percent of U.S. consumption in 1974.

The area in corn silage, about 400,000 ha, has remained roughly constant in recent years. However, the area devoted to corn that is grown for grain increased more than 59 percent in the past decade, and the average fertilizer nitrogen rates have more than doubled (Table A.11). The statewide average yields of corn (about 80 percent of the corn grain is raised in the south and east portions of the state) reflect the effects of weather, however, more than they do nitrogen fertilizer rates. For example, the summer of 1970 was hot and dry, and corn yields suffered from a deficiency of moisture. In 1974, a late spring coupled with an early killing frost resulted in a short growing season and low yields. Hence, in 1974 (the year chosen for this balance) nitrogen removal by corn was considerably below average.

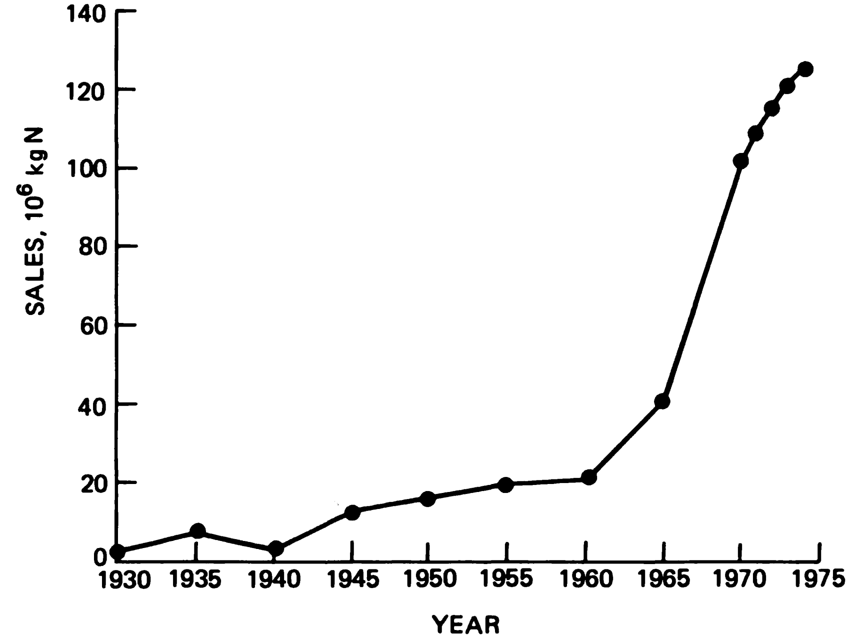


FIGURE A.3 Nitrogen fertilizer sales in Wisconsin, 1930-1975. Data from Wisconsin Department of Agriculture, October 1975.

TABLE A.11 Area in Corn Grain, Rate of Application of Nitrogen Fertilizer, Crop Yield, and Nitrogen Removal in Grain for Wisconsin, 1964-1974.

Year	Hectares	Fertilizer N applied	Average yield	Crop N Removed
			(kg/ha)	
1964	577,000	32	4710	65
1968	710,000	70	5960	82
1970	752,000	76	5150	71
1972	867,000	89	5960	82
1974	919,000	70	4270	59

Nitrogen Fixation

Symbiotic nitrogen fixation, mainly by alfalfa, is a major part of Wisconsin's agricultural nitrogen budget (Table A.12), but the amount of nitrogen added to the soil when an alfalfa stand is plowed under is difficult to estimate. Data on accumulation of nitrogen by plant roots do not exist for stands of alfalfa more than 6 to 9 months old. Several long-term experiments with crop rotation under conditions found in Wisconsin indicate that an alfalfa meadow will supply the equivalent of about 120 to 135 kg/ha of fertilizer nitrogen (Rohweder and Powell 1973, Shrader and Pierre 1966). The availability of nitrogen in legume residues ranges from 28 to 50 percent of the equivalent amount of fertilizer nitrogen (Shrader and Pierre 1966). Assuming that the uptake of fertilizer nitrogen is about 70 percent, the residues of nitrogen in alfalfa amount to about 170 kg/ha. Since these residues accumulate over the lifetime of the average crop rotation (about 3 years in Wisconsin), the input of alfalfa-nitrogen to the soil reserve is estimated at 56 kg N/ha-yr. Mixed hay systems probably add about half this amount (28 kg N/ha-yr). Soybeans fix only about two-thirds of the nitrogen they remove (Johnson et al. 1975).

The rate of nonsymbiotic nitrogen fixation in various ecosystems was estimated by Burns and Hardy (1975) as follows: cropland, 5 kg N/ha-yr; grassland, 15 kg N/ha-yr; forests, 10 kg N/ha-yr (see Chapter 2). Fixation in wetlands and surface waters was estimated at 20 kg N/ha-yr and includes fixation in sediment as well as that by algae in the water (Macgregor and Keeney 1975).

Precipitation

A recent survey of nitrogen in precipitation in Wisconsin (Hoeft et al. 1972) gave a weighted average flux of 3.5 kg NO_3^--N, 3.5 kg NH_4^+-N, and 7.5 kg particulate nitrogen (total N minus inorganic N) per hectare per year. Particulate nitrogen is assumed to be derived largely from soils, and thus its net contribution is zero. Undoubtedly some of the nitrogen in precipitation comes from agricultural activities through volatilization from fertilizers and manure. In this sense, the estimated inputs of nitrogen in Wisconsin precipitation involve some double counting.

Total Inputs

Total inputs of nitrogen for various Wisconsin land uses in 1974 are summarized in Table A.13. Agriculture (categories 1-5) received 585 x 10^6 kg N/ha-yr, with 21 percent from fertilizer, 7 percent from precipitation, 62

TABLE A.12 Nitrogen Removal by Legumes in Wisconsin, 1974

		N Removed[a]		Residual N	
Crop	10^3 ha	kg/ha	10^6 kg	kg/ha	10^6 kg
Alfalfa	1,215	162	197	56	68
Mixed Hay[b]	385	88	34	28	11
Soybeans	88	72	6.3	-24	-2
Snapbeans	25	13	0.4	0	0
Field Peas	53	26	1.4	0	0
Total	1,766		239		77

[a] From estimates in Boone and Welch (1972), Johnson et al. (1975), Welch (1972), and Wisconsin Agricultural Statistics (1975).

[b] Largely red clover and timothy mixture.

TABLE A.13 Estimated Nitrogen Inputs to Wisconsin, 1974

Land Use	10^3 Hectares	Source of Nitrogen (10^6 kg N)[a] Nitrogen Fixation	Fertilizer	Import of Feed Supplements	Inorganic Nitrogen in Precipitation
Grains, Cereals, Potatoes	2,025	10	115	--	14.0
Alfalfa, Mixed Hay	1,600	316	0	60	11.0
Soybeans	88	4	0	--	0.6
Specialty Crops	99	2	12	--	0.7
Pastures	1,795	27	0	--	13.0
Forest and Idle Land	7,573	76	0	--	53.0
Urban	200	1	0	--	1.4
Wetlands and Water	1,260	26	0	--	9.0
Total	14,640	462	127	60	103
Total Nitrogen Added			752 x 10^6 kg/yr		

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[a] From estimates in Welch (1972), Burns and Hardy (1975), Johnson et al. (1975), and Wisconsin Agricultural Statistics (1975).

percent from nitrogen fixation, and 10 percent in feed supplements.

Nitrogen Removal by Crops

Nitrogen removal by nonleguminous crops in Wisconsin was calculated on the basis of nitrogen contents of various crops (Agricultural Research Service 1971, Boone and Welch 1972, Welch 1972) and on the basis of reported yields (Wisconsin Agricultural Statistics 1975). An estimated 144 x 10^6 kg N were removed in 1974 (Table A.14).

Nitrogen Transfers

Some of the crop nitrogen is transferred out of the state in grain and vegetables and in animal products; some is used in the state and reappears in the production of wastes by the animal and human populations. Relatively large amounts of protein concentrate are imported. Estimates for these nitrogen transfers are given in Tables A.14 and A.15.

Analysis of Input, Output, and Transfer Errors

Of the nitrogen inputs listed in Table A.13, the quality of the estimates of fertilizer and precipitation sources can be considered good. In contrast, there is undoubtedly some error in the estimates of symbiotic and nonsymbiotic nitrogen fixation. However, inputs from nonsymbiotic nitrogen fixation are relatively small, particularly in the agricultural sector. Inputs from symbiotic fixation have been estimated from data on crop harvests (Table A.12). Fixation of nitrogen by alfalfa is by far the largest component of such inputs. A range of ±10 percent in the nitrogen content of alfalfa is likely in practice, giving a range in removal of 197 ± 20 x 10^6 kg N. A further source of error is the allocation of residual nitrogen from alfalfa, an important value because it affects the size of the pool of available nitrogen in the balance, as discussed later in this section. Alfalfa also takes up some nitrogen from the soil; accounting for this transfer would reduce the net value of the contribution by legumes through fixation. The estimate used in Table A.12 is based on experimental observation of the relative yield response of corn/alfalfa fields the first year after plowing. The actual value will depend on weather and farm management practices and it is therefore difficult to estimate possible error.

Nitrogen production and transfer estimates (Table A.14) were made by multiplying accepted values for the nitrogen content of each product by the appropriate production,

TABLE A.14 Nitrogen Tranfers for Wisconsin Farm Products, 1974[a]

Product	Annual production as N	Transfers			
		Within state	Exports	Total transfers	Residuals in soil
			(10⁶ kg N)		
Crop Products (nonlegumes)					
Corn Grain	65	40	14	54	11
Corn Silage	31	31	0	31	0
Small Grains	30	23	4	27	3
Specialty Crops	6	3	2	5	1
Pasture	27	27	0	27	0
Total	159	124	20	144	15
Crop Products (legumes)					
Alfalfa	317	238	0	238	79
Soybeans	6	6	0	6	-2
Total	323	246	0	246	77
Animal Products					
Dairy	68	13	55	68	--
Eggs	10	5	5	10	--
Meat	19	18	1	19	--
Feeding and Breeding Livestock	5	0	5	5	--
Total	112	36	66	102	--

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[a] Estimates from Agricultural Research Service (1971), Boone and Welch (1972), Welch (1972), Wisconsin Agricultural Statistics (1975). Corn grain, 138 kg N/1,000 kg; corn silage, 3.3 kg N/1,000 kg; sweet corn, 35 kg N/1,000 kg; wheat, 31 kg N/1,000 kg; barley and rye, 18 kg N/1,000 kg; oats, 20 kg N/1,000 kg; potatoes, 2.8 kg N/1,000 kg.

TABLE A.15 Nitrogen as Human or Animal Wastes Produced Annually in Wisconsin

Producer	Population (Millions)	kg N/yr per unit[a]	Total Produced (10^6 kg N)
Humans	4.6	6.0	28
Cattle	4.64	52.0	240
Swine	1.40	7.0	10
Sheep	0.10	9.0	1
Chickens			
Laying	6.8	0.6	4
Broilers	11.3	0.2	2
Turkeys	4.6	0.4	2
Total Animal			259
Total			287

[a] From estimates in National Research Council (1972) and Taiganides and Stroshine (1971).

consumption, or export data available from Wisconsin Agricultural Statistics (1975). Similarly, nitrogen waste production values were obtained by multiplying accepted per-unit nitrogen excretion values by the populations. The nitrogen transfer and waste production values (Tables A.14 and A.15) are thought to be reliable, with the possible exception of the data for pastures (Table A.14), where nitrogen uptake was equated to nitrogen fixation. This estimate would be low if the nitrogen in the excreta of grazing cattle were considered, and high if considerable immobilization of nitrogen were occurring in the topsoil. On balance, the estimate seems low, since uptake of 22 kg N/ha (40×10^6 kg N/1.8×10^6 ha^2 of pastureland; Tables A.13 and A.14) is equivalent to the production of only about 1500 kg (1.5 percent N in herbage)/ha of dry matter. However, since survey data on the productivity of Wisconsin pastures are lacking, no better estimates are available at present.

Agricultural Nitrogen Balance in Wisconsin

Estimates of the sizes of pools and fluxes of nitrogen in Wisconsin agriculture are presented in Figure A.4. Two models were examined for their applicability in this exercise. One involved consideration of the total soil nitrogen as the receptor of the annual nitrogen flux, assuming steady state in this pool. The pool of organic nitrogen in the soil in Wisconsin was estimated, assuming 0.15 percent N (4000 kg N/ha in 20 cm of soil), for a total of $22{,}500 \times 10^6$ kg N. This pool is several orders of magnitude larger than any of the nitrogen inputs (see Table A.13 and Figure A.4). Thus the steady-state assumption with respect to soil organic nitrogen would have to be extremely accurate to permit estimation of an output by difference (Kohl et al. 1978).

The problem can be overcome in part by considering the pools of available nitrogen and slowly-available organic nitrogen in the soil to be dynamic. The steady-state assumption can be applied with greater accuracy to the soil available nitrogen pool because this would not be expected to vary markedly on an annual basis. This pool, which is essentially the inorganic nitrogen in the root zone, also is of the same magnitude as the annual nitrogen fluxes. Experience has shown, however, that the main problems with the latter approach are in estimating the net mineralization from the soil organic nitrogen pool. This is particularly true in respect to the assignment of mineralization (availability) rates of crop residues and manure, two major inputs to the Wisconsin agricultural nitrogen budget.

Rather than assign separate mineralization values to various inputs of organic nitrogen, we have treated them as

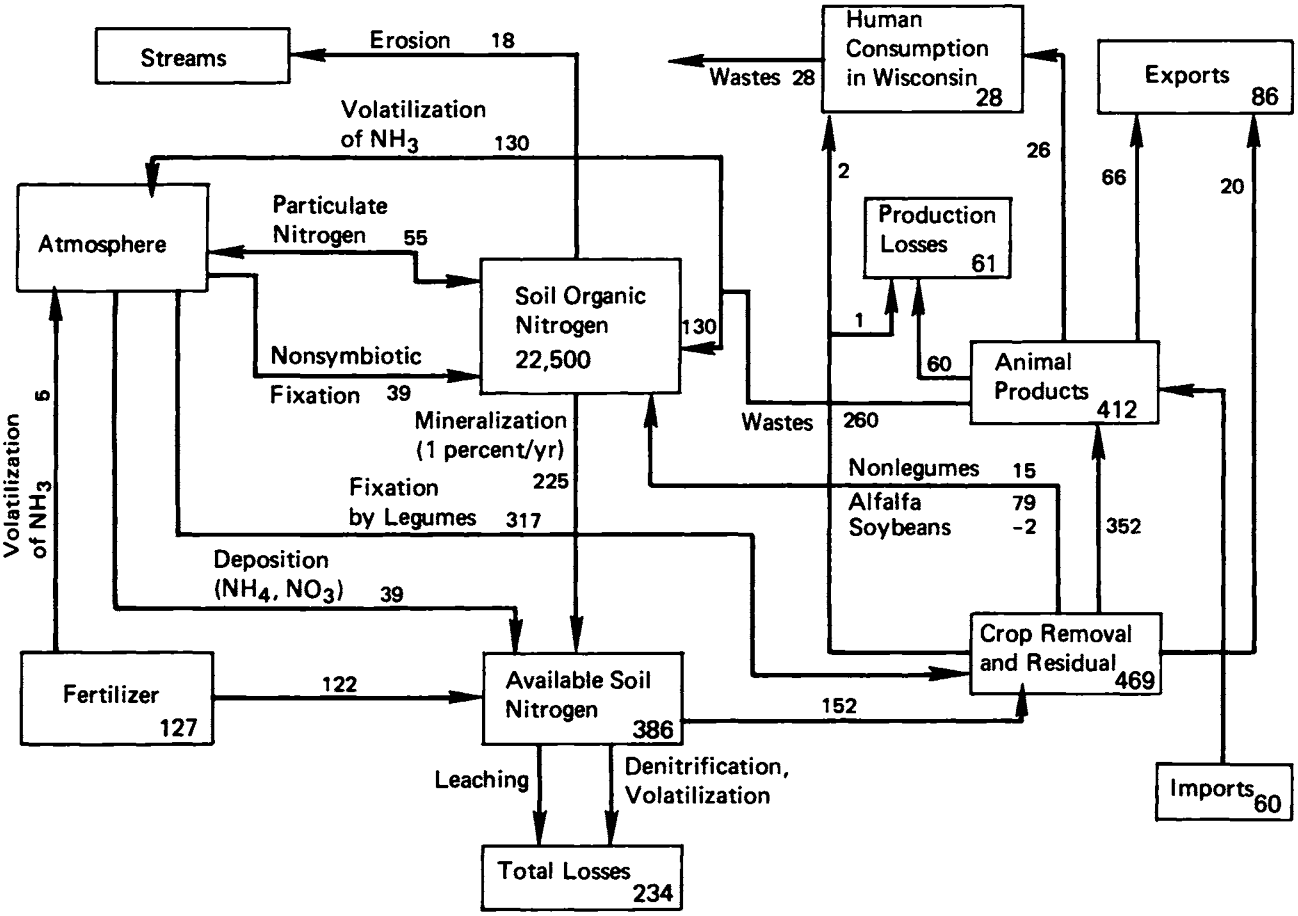


FIGURE A.4 The flow of nitrogen in Wisconsin agriculture in 1974. Pool sizes and fluxes are expressed in 10^6 kg N.

an integral part of the soil pool of organic nitrogen, and estimated a mineralization rate for this pool. It was assumed that inputs of organic nitrogen from crop residues and manure are small relative to the total pool of organic nitrogen in the soil. Net mineralization of nitrogen from the organic pool is normally considered to range between 1 and 3 percent a year (Bremner 1967). Under the cool temperate conditions in Wisconsin, the lower value is probably more realistic. Thus, net mineralization was estimated at 225 x 10^6 kg N/yr. Other inputs to the soil pool of available nitrogen are 39 x 10^6 kg N/yr from the atmosphere and 122 x 10^6 kg N/yr from fertilizers.

The organic nitrogen input from manures was estimated at 130 x 10^6 kg N/yr, assuming 50 percent loss from volatilization (essentially all of the inorganic nitrogen in the manure; see Chapter 6). Total annual input from plant residues was estimated at 94 x 10^6 kg N, and nonsymbiotic fixation was estimated at 39 x 10^6 kg N/yr. The total input of organic nitrogen was thus 263 x 10^6 kg N/yr. Nitrogen outputs by erosion to streams were estimated at 3 kg N/ha-yr (Shrader and Pierre 1966), for a total loss of 18 x 10^6 kg N/yr by that route. Although inputs to and outputs from the pool of organic nitrogen are close to balance, unknown errors in the assumptions are too great to determine net gain or loss in this pool.

The uptake of nitrogen from the pool of available nitrogen in soil was estimated at 152 x 10^6 kg N/yr, or 39 percent of the total flux (386 x 10^6 kg N/yr) in that pool. The value was obtained by the difference between the total for removals and residual nitrogen, and the estimate for fixation by legumes. This estimate is reasonably close to the 50 percent value commonly cited for overall efficiency of nitrogen uptake by crops, especially considering that 1974 (the year for which this balance was done) was a year of relatively poor corn harvests. The remainder of the total flux, 234 x 10^6 kg N/yr, or 41.7 kg N/ha-yr, is assumed to be lost to the environment by leaching and denitrification, but the present data base does not permit apportioning this loss between the two routes. Furthermore, an analysis of potential errors in estimates is difficult. If the estimate of the pool of organic nitrogen were in error by ±10 percent, and if actual net mineralization ranged from 1 to 1.5 percent, the per hectare loss of nitrogen would range from 36 to 66 kg/yr. This loss seems high and could be the result of overestimation of the rate of mineralization of soil organic nitrogen, or of underestimation of the amount of inorganic nitrogen taken up by legumes. The high degree of aggregation also limits the usefulness of the model, which reveals little about possible site-specific problems (e.g., much of the agriculture is in the fertile lands in the southern part of Wisconsin).

As Figure A.4 shows, most of the crop nitrogen is transferred to animals, and the majority of this nitrogen is transferred to wastes; because of losses by volatilization, only 50 percent or less of the nitrogen in wastes is usually retained in the soil system (Frere 1976). Volatilization is estimated to be a major loss of nitrogen from the system. This output has not been balanced by an equivalent atmospheric input, because some of this ammonia is deposited on nonagricultural lands and some is transferred by the prevailing winds across the state boundary.

Human consumption of grain and meat, and exports from the state, account for 114 x 10^6 kg N (27 percent of the harvested plant nitrogen). Human waste production (Table A.15) does not equate exactly with the estimated consumption of food nitrogen (Figure A.4). The difference may be the result of losses in food preparation, or of errors in estimates of the transfer functions. The amount of nitrogen in human wastes that is deposited on land in Wisconsin is negligible.

The nitrogen in the animal products compartment is partitioned into wastes and edible products. Fifty-six percent of the total (260 x 10^6 kg N) was estimated to be transferred as wastes. Production losses, the unaccounted-for portion of the animal products pool, represent about 14.6 percent of the total (60 x 10^6 kg N). This value seems high, and suggests some errors in the analysis.

Conclusion

The complexity of Wisconsin's agriculture and the degree of aggregation limit the usefulness of this state mass balance for making recommendations for management decisions to ameliorate environmental impacts related to nitrate. However, despite problems of unknown errors in the many assumptions of the model, some important points have emerged. The input calculations show that fixation of nitrogen by legumes is an important component of the agricultural nitrogen balance, estimated at about 2.5 times the inputs of nitrogen from fertilizer. The nitrogen fixed by legumes, when cycled through animals and returned as wastes or when plowed under as residues, is a major input to the pools of soil organic nitrogen, and eventually, available nitrogen. Further evaluation of this phase of the cycle, particularly the net mineralization estimate, would seem warranted. This could have important impacts in predictions of available nitrogen in soil and hence in improving the efficiency of use of nitrogen fertilizer.

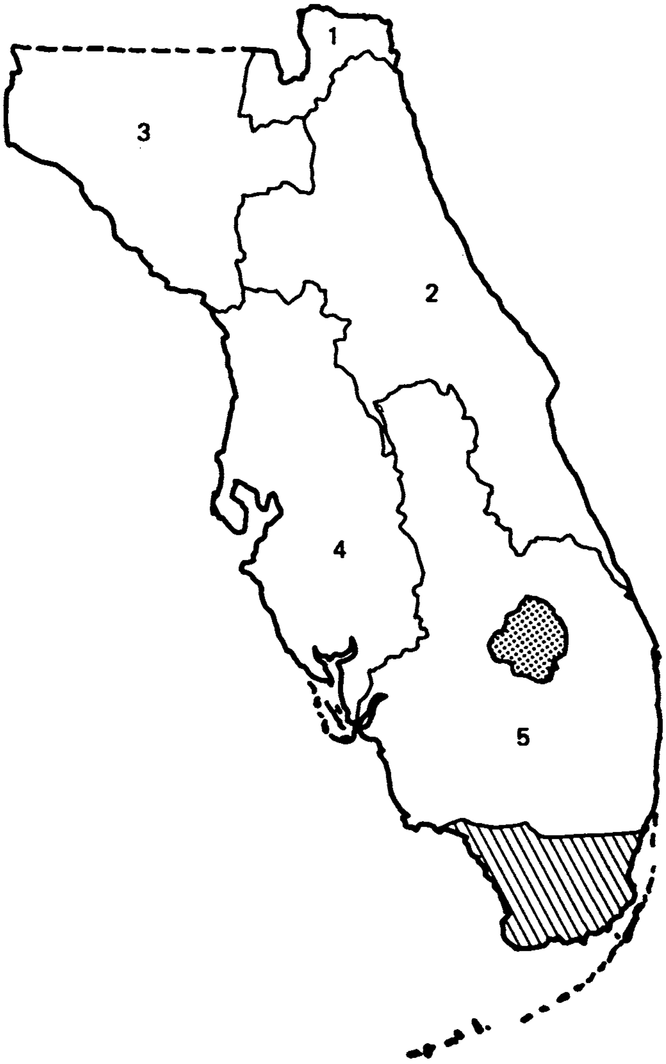
(6) PENINSULAR FLORIDA

Although the qualitative aspects of the nitrogen cycle have been understood for decades, rates of transformations among the forms of nitrogen are known accurately for only a few pathways. Large-scale input-output models attempt to circumvent this problem by treating the system as a "black box," integrating the outputs of complex internal processes that vary considerably in time and space. If a steady state can be assumed, or if changes in storage of nitrogen can be measured, the rates of some processes that are unknown or difficult to measure can be obtained by difference (see Chapter 5).

The accurate calculation of a mass balance for nitrogen at the regional level requires accurate definition of the system boundaries and an adequate data base for fluxes of nitrogen across these boundaries. Peninsular Florida (Figure A.5) may be unique in this regard. For purposes of the model, the region is delineated to the north and west by the Suwannee River and St. Mary's River watersheds. The peninsula, together with a portion of the Suwannee River watershed in south Georgia, is hydrologically isolated from the land to the north, since the groundwater flow in the region of the Georgia-Florida state line is essentially in an easterly or westerly direction (C.W. Hendry, Florida Geological Survey, personal communication, 1976). The movement and quality of surface water is monitored regularly by the U.S. Geological Survey and is sporadically monitored by various state agencies. These data are reasonably abundant for the area north of the Tamiami Canal, which intercepts much of the southward flow of water into the south Everglades. In the vertical dimension, the deep limestone Floridan aquifer is considered the lower limit of the system for this study. A flux of nitrogen into this aquifer thus represents a system storage, as do sedimentation and terrestrial humus formation. The upper boundary of the system was defined to be the top of the plant canopy; thus, volatilized gases which are reabsorbed by plants are not assumed to leave the system.

Major Fluxes of Nitrogen in Florida

Agricultural fluxes of nitrogen that involve the import and export of fertilizer and food usually constitute the greatest anthropogenic movements of nitrogen in a developed region. The need to control citrus pests in Florida has led to the inspection of crops and livestock that cross the state line east of the Suwannee River. Data on these exchanges have been published since 1963 by the Florida Crop and Livestock Reporting Service. Since relatively good data are available to calculate hydrological and agricultural flows of nitrogen, a relatively accurate balance for this



SOURCE: Modified from Conover and Leach (1975).

FIGURE A.5 Drainage basins of peninsular Florida: (1) St. Mary's and Altamaha Rivers; (2) St. John's River; (3) Suwannee and Aucilla Rivers; (4) Peace, Withlacoochee, Hillsborough, and Alafia Rivers; (5) South Florida-Withlacoochee River-Miami Canals and Everglades.

regional system can be constructed. Models of some of the important agricultural subsystems in the state also were formulated. Management implications of the regional model and areas requiring further data collection and research are discussed at the end of this section.

The important sources and sinks for nitrogen in the Florida peninsula are shown in Figure A.6, and the calculated magnitudes of these fluxes, averaged for the period 1970 to 1975, are presented in Table A.16. Hydrologic inputs and outputs were calculated for each U.S. Geological Survey hydrologic accounting unit (numbered 1-5 in Figure A.5). Concentrations of nitrogen in rainfall in various parts of the state have been measured by Brezonik et al. (1969), Fox et al. (1977), Joyner (1974), Hendry (1977), and R.C. Harriss (Florida State University, Tallahassee, unpublished data). The concentration of nitrogen for each appropriate accounting unit was multiplied by the average annual precipitation to give the average annual nitrogen flux from precipitation. These data are presented in Table A.17. Concentrations of nitrogen in rainfall on the St. Mary's Altamaha unit were not available, and they were assumed to be the same as in the St. John's unit. Although some wind-borne particulate nitrogen may be transported outside of the system boundaries, data on this flux are unavailable, and dry fallout was considered an internal loop within the system. Calculations of gaseous deposition of ammonia and oxides of nitrogen are discussed in a later section. The other principal atmospheric input, biological fixation of gaseous nitrogen, was estimated at 38.5×10^9 g N/yr. Discussion of the estimates of nitrogen fixation and of the problems in estimating gaseous nitrogen fluxes is deferred to the section on atmospheric pathways, below.

Although Florida has a thriving agricultural industry, its 8.5 million residents consume more food, particularly meat, than is produced in the state. An agricultural model, discussed below, indicates an annual import of 21.7×10^9 g N in foodstuffs, based on in-state production data and on average per capita consumption of animal and vegetable products during 1970 to 1975. Annual fertilizer use in the peninsula is estimated to be 105×10^9 g N (Florida Department of Agriculture and Consumer Services 1975). Although animal feeds or their precursors, such as cottonseed oil, are imported from other states, the import data are not readily available. Feedlot operations are generally not important in Florida, but feed imported for poultry farms, small cattle lots, and pets may represent a small but possibly significant flux of nitrogen.

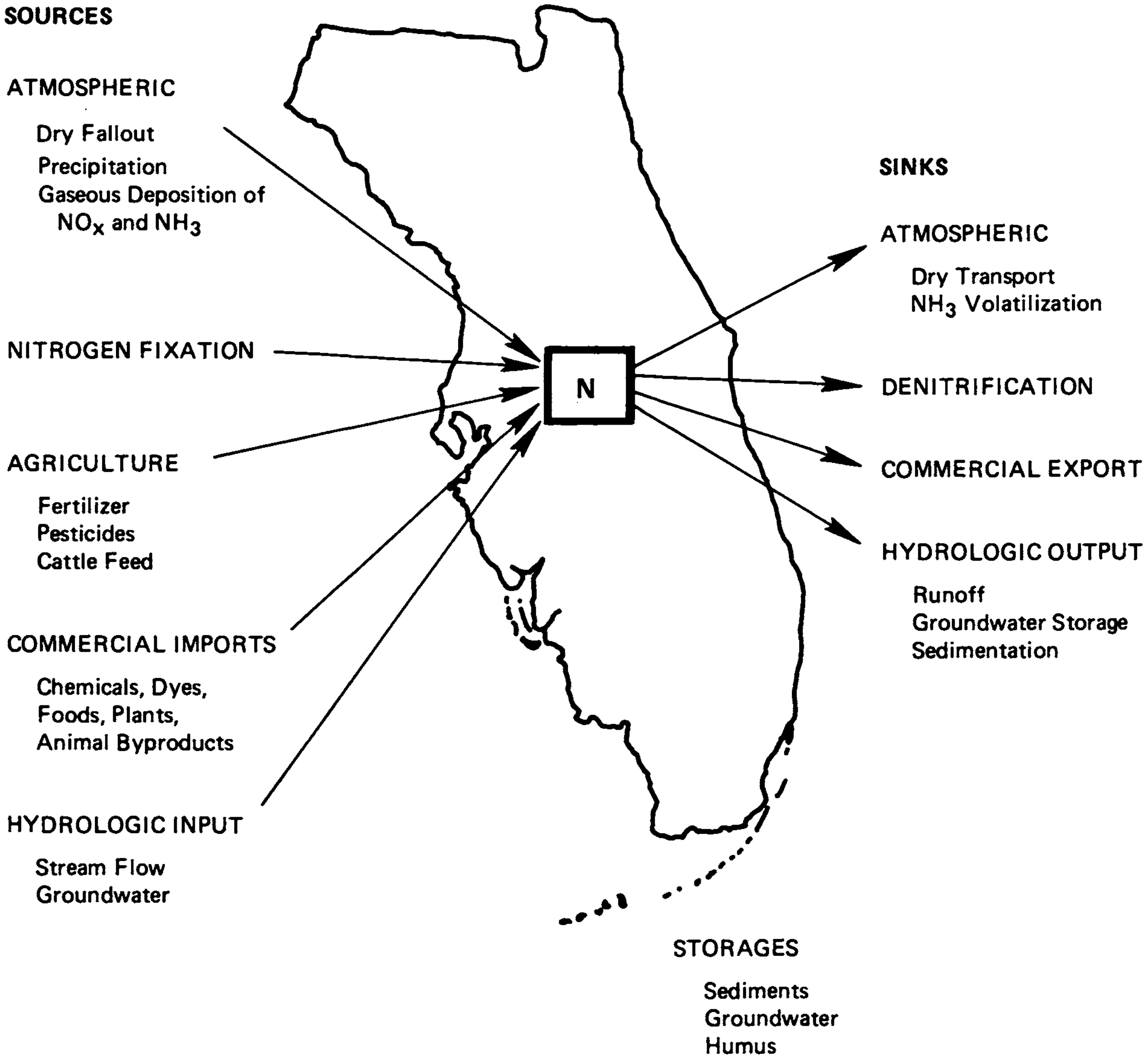


FIGURE A.6 Simplified qualitative nitrogen balance for peninsular Florida.

TABLE A.16 Sources and Sinks for Nitrogen in Peninsular Florida

Flux		10^9 g N/yr
Sources		
Precipitation		120
Nitrogen fixation		39
Agricultural imports		22
Fertilizer applications		105
Gaseous deposition:	Ammonia	32
	Nitrogen oxides	60
Total		378
Sinks		
Runoff		77
Agricultural exports		23
Denitrification		46
Biological production of nitric oxide		21
Volatilization of ammonia		54
Total		221
Unaccounted for inputs		154

TABLE A.17 Hydrologic Nitrogen Budget for Peninsular Florida

Basin	Area (km^2)	Rainfall (m/yr)	N Concentration (g/m^3)	Precipitation N Input (10^{9}g)	Observed[a] Runoff (10^{9}m^3)	Calculated[b] Runoff (10^{9}m^3)	Calculated N Output (10^{9}g)
Altamaha River and St. Mary's River	3,897	1.36	0.718	3.78	1.06	1.87	1.82
St. Johns River	29,282	1.39	0.718	29.02	4.92	14.05	19.03
Suwanee River and Aucilla River	20,739	1.32	.399	10.92	10.65	9.95	7.91
Peace River, Hillsborough River and Withlacoochee River	25,410	1.38	0.779	27.30	2.48	9.91	10.03
South Florida Okeechobee Canals and Everglades	37,410	1.44	0.900	48.49	8.34	13.47	18.95
Total	116,738			119.5			57.7

[a] Calculated from flow data.

[b] Calculated according to the method of Langbein et al. (1949).

Hydrologic Pathways

Hydrological units 1 and 3, which extend beyond the drainage basins shown on Figure A.5 into southern Georgia, receive some nitrogen from rainfall north of the Florida state line. This rainfall nitrogen is included in the data in Table A.17, but no other nitrogen inputs to these units are assumed. Much of the area in these two units is made up of the relatively undisturbed Okefenokee Swamp, and anthropogenic flows of nitrogen are insignificant. Nitrogen fixation in this area also is likely to be insignificant because of low pH, lack of blue-green algae, and a high content of nitrogen in peat sediments. Hydrologic inputs of nitrogen in surface and groundwater for units 1 and 3 are easily disposed of and there apperas to be no north-south flow of water in the Floridan aquifer at the northern system boundary. No streams enter the system because the northern watershed boundaries of the St. Mary's-Altamaha and Suwannee Rivers were selected as the limits of the system.

Hydrologic outputs from the system were calculated from gauged runoff data (U.S. Geological Survey 1975), using annual average flows and published estimates of the areas drained by each stream. Stations were chosen to provide the greatest amount of watershed integration (i.e., the farthest downstream stations), together with the most reliable and complete records of flows. Nitrogen concentrations for these stations from the period 1970 to 1975 were retrieved from the STORET data storage system. Although nitrogen concentration varies considerably with flow in northern temperate streams, it increases by less than 1 percent for each doubling of flow in Florida streams (U.S. EPA 1975b). This observation presumably results from the low water storage which allows less accumulation of nitrate in the well-drained Florida sands, and from the lack of meltwater in the spring. Calculation of transport from a gauged area by simply multiplying average streamflow by average nitrogen concentrations thus appears justified.

Estuaries, downstream reaches, and coastal areas, however, were not gauged. It also was impossible to measure the nitrogen lost in seepage across coastal boundaries. In order to estimate transport by ungauged pathways, the theoretical runoff anticipated in each accounting unit was calculated by a method (Langbein et al. 1949) that relates the evapotranspiration rate (ET) to mean annual air temperature. This method is reasonably accurate when periods of highest rainfall correspond to periods of highest temperature, which is generally the case in Florida. The calculated potential ET then is subtracted from the rainfall to obtain the estimated annual runoff (Table A.17). In the Florida peninsula, this amounts to 25 to 35 percent of the annual precipitation.

The estimated hydrologic nitrogen output is thus calculated according to the equation:

$$\frac{R_c}{\sum^{n} R_o} \times \sum^{n} [R_{o_1} \times C_{N_1} + R_{o_2} \times C_{N_2} . + \cdots R_{o_n} \times C_{N_n}] = \text{output}$$

where R_c is the calculated runoff, and $R_o \bullet C_N$ represents the observed runoff and nitrogen concentration in each of the n streams in the hydrologic unit. The nitrogen concentration in unobserved drainage, including groundwater, was assumed to be the same as that in the gauged streams. Since the mean nitrogen transport per unit of runoff was similar for most surface streams in the same accounting unit, this assumption is reasonable for surface outflows, but its application to groundwater flow is somewhat tenuous. Data on nitrate concentrations in shallow groundwater in coastal areas would be useful in validating of this assumption. The few reported data on nitrate levels in shallow wells exhibit such wide variations in nitrogen concentration that direct calculation of mass transport of nitrogen groundwater seepage is not possible. Observed (gauged) drainage was found to account for only 56 percent of the total calculated drainage; since actual ET may fail to equal potential ET, this calculation is minimum estimate.

The total estimated transport is 57.7 x 10^9 g N annually, or 48 percent of the input from precipitation. This estimate is likely to be low for several reasons. It may not include pulsed fluxes of particulate nitrogen in the form of algae and macrophytic detritus, and sediment transport is also excluded. Furthermore, the large population living along the Florida coasts, conservatively estimated at four million, may be disposing of approximately 19 x 10^9 g N/yr in sewage discharged to the ocean. Urban stormwater runoff also contributes some nitrogen to estuaries and coastal waters. These outflows are difficult to measure directly since incoming tides transport some of the nitrogen released into estuarine waters upstream toward the sampling points during certain parts of the year. The total hydrologic nitrogen output from the peninsula was estimated to be 58 + 19 = 77 x 10^9 g N/yr.

Nitrogen Reservoirs in the System

Storage of nitrogen within the system in soil humus, sediment, and groundwater also is difficult to measure. Generally, soil organic nitrogen is assumed to be in a steady state in mature systems, but experiments to prove this hypothesis have been inconclusive. Salt marshes probably accumulate some organic nitrogen, but most nitrogen is assumed to be exported as detritus. The accretion of detrital nitrogen by mangroves is another undetermined storage.

Because the anaerobic sediments of marshlands provide optimal conditions for such storage, these systems were examined for accumulation of nitrogen. Assuming an age of 5,000 to 10,000 years for Everglades peat (Davis 1946) and a total nitrogen content of the peat within the system boundaries of 5.75×10^{13} g N, the rate of accumulation is 5.8 to 11.5×10^{9} g N/yr, clearly a relatively small sink on an annual basis. Present water and soil management practices produce some mineralization of stored nitrogen, however. A net loss of soil nitrogen to surface water is occurring, but the rate of this loading is unknown. Sediment storage in Lake Okeechobee (see Table A.3) amounts to about 2.6×10^{9} g N/yr. Sedimentation in other Florida lakes collectively could amount to 2 to 4 times this value, for a total storage in lake sediments of 8 to 13×10^{9} g N/yr.

Groundwater storage, particularly in the deep Floridan aquifer, is a sink with important geochemical and public health significance. A review of water quality records published by the Florida Geological Survey (e.g., Healy 1972) indicated that nitrate and nitrite levels do not exceed the 10 ppm standard for nitrate-nitrogen either in the deep limestone Floridan aquifer or in the shallower Biscayne aquifer south of Lake Okeechobee. The few published chemical data on shallow aquifers indicate highly variable concentrations of nitrate, with large variations over short distances. Whether these variations result from errors in sampling or from local influences, (barnyards, soil type, drainage) is not discernible from the data.

Review of Healy's (1972) data on municipal water supplies in Florida indicates mean values of 0.27 mg NO_3^--N/l and 0.03 mg NO_2^--N/l in the Floridan aquifer. A few scattered high concentrations of nitrate showed no discernible spatial pattern. Nitrite concentrations were usually below 0.01 mg N/l. The few data for shallow aquifers (Biscayne, Hawthorne, Gravel) in the southern part of the state indicate a mean of 0.38 mg NO_3^--N/l, and nitrite was usually below 0.01 mg N/l. In order to calculate changes in storage, it is necessary to know changes in nitrogen concentrations over time as well as the amounts of water stored in an aquifer. The data base for the former is inadequate, and the latter apparently are not available for most of the state.

Agricultural exports were calculated to be 15.3×10^{9} g N/yr, from data reported by the Florida Crop and Livestock Reporting Service (Florida Agricultural Statistics [FAS] 1975a-1975f). Based on information in Florida Statistical Abstracts (Thompson 1975, 1976) and Williams and Hopkins

(1968), removal of 7.7×10^{9} g N/yr from forests was calculated. The remaining exports losses of nitrogen, via denitrification and ammonia volatilization, together with system storages, are assumed to make up the annual deficit. These fluxes are considered in the following section on atmospheric processes in the nitrogen cycle.

The important sources for the macro-model appear to be the atmospheric deposition of gases and aerosols, followed by industrial fixation of fertilizer nitrogen. Only 45 percent of the input is lost as runoff and agricultural exports. The remaining 55 percent of the input is poorly accounted for, as a combination of atmospheric sinks and system storage, but uncertainties in source and sink estimates preclude precise apportionment.

Atmospheric Pathways

Nitrogen Fixation. The inputs to peninsular Florida by biological nitrogen fixation for various categories of land use are summarized in Table A.18. Mixed hay grown on pasture land supplies a considerable proportion of this nitrogen; soybeans and lucerne, which are major nitrogen-fixing crops in the midwest are not planted extensively in Florida.

Most values for nitrogen fixation rates in the available literature are for soils in the temperate zone or for allophane-dominated soils in the tropics, and thus are not applicable to Florida soils. The long, subtropical summer in Florida should promote fixation, but soils in the state are low in organic matter and are often well-drained and acidic; these factors decrease the capacity of the natural soil microflora to fix nitrogen. The accuracy of literature values for terrestrial nitrogen fixation also is questionable, even for the sites of the original studies. For example, Jorgensen and Wells (1971) found large areal variations for fixation in a stand of loblolly pine (Pinus taeda L.) in South Carolina, which they attributed to uneven distribution of litter. Extrapolation of in vitro measurements to field conditions is difficult, and short-term fluctuations in soil moisture may alter considerably nitrogen fixation rates in the field. Furthermore, because non-obligatory associations of bacteria in the phylloplane and rhizosphere are only recently becoming understood (see Chapter 2 and Burns and Hardy [1975]), previously published nitrogen fixation rates for non-leguminous systems may be low. Because studies on accumulation of nitrogen in standing crops and in litter in Florida pine forests did not include data on losses by leaching (Smith and Prichett 1976), calculation of nitrogen fixation in the system by mass balance was impossible.

TABLE A.18 Estimated Nitrogen Fixation for Land Use Categories in Peninsular Florida

Land Use	Area (10^9 m^2)	Annual N Fixation Rate (g/m^2)	Annual N Fixation ($10^9 g$ N)	Reference
Soybeans	0.56[a]	4.8	2.69	Burns and Hardy (1975)
Peanuts	0.11[a]	8.6	0.95	Nutman (1965)
Mixed Hay	1.81	11.8	21.0	Nutman (1959)
Other crops[b]	1.1	0.5	0.55	Burns and Hardy (1975)
Forest	51[c]	0.1	5.1	Jorgensen and Wells (1971)
Grassland	26.6[d]	0.2	5.32	Paul et al. (1971), Steyn and Delwiche (1970)
Wetlands and Water	9.8	0.3	2.9	Brezonik (1972)
Total			38.5	

[a] Assuming half the production occurs west of the Suwannee.

[b] Excluding vegetable crops.

[c] Includes woodland pasture, half the forestry land assumed west of Suwannee River.

[d] Includes native range, hay, and improved nonlegume pastures.

The fixation rate that was used for lakes and wetlands in Table A.18 is based on areally weighted fixation rates from 55 Florida lakes (P.L. Brezonik, University of Florida, Gainesville, unpublished data) that may not be typical of all such sites. Approximately 25 percent of the lakes exhibited acetylene-reducing activity on at least one of seven sampling dates during one year.

Denitrification. Denitrification is one of the least quantified processes in the nitrogen cycle. Recent work seems close to producing accurate in situ data by ^{15}N tracer techniques, but most published estimates are based on mass-balance analyses on lysimeters, and did not distinguish between losses by denitrification and by ammonia volatilization. It is difficult to extrapolate from the meager data that exist to estimate rates of denitrification for the Florida peninsula. Coniferous forests are a poor environment for denitrification of soil nitrogen because of the virtual absence of nitrifiers in the acid soil and litter (Smith and Prichett 1976), although nitrate deposited by rainfall may be denitrified. Some preliminary estimates of denitrification in the sediments of Lake Okeechobee, obtained by using a mass-balance approach, indicate denitrification rates of up to 1.45 g N/m_2-yr (see Section 1 of this appendix). If these rates are typical for wetlands, denitrification losses from aquatic systems in Florida could be as high as 14.2 x 10^9 g of N/yr. For the mass balance in Table A.16, it was assumed that half of the Suwannee River drainage basin in Georgia is in the Okefenokee wetlands. The average of the four denitrification estimates for Lake Okeechobee (Table A.3) is 0.82 g N/m_2-yr; multiplying this value by the total wetland area in the system studied yields a loss of 11 x 10^9 g N/yr. The Council for Agricultural Science and Technology (CAST 1976), in constructing a global mass-balance for nitrogen, used a denitrification rate of 1.0 g N/m_2-yr for cropland; applying this figure to Florida cropland results in an additional loss of 35 x 10^9 g N/yr, for a total loss of about 46 x 10^9 g N by denitrification.

Another gaseous nitrogen sink is the biological reduction of nitrate to nitrite, followed by the abiological production (at pH ≤5) of nitric oxide from nitrous acid. While this reaction can occur in anaerobic silage (see Chapter 2), its significance in natural systems is debatable (Robinson and Robbins 1971, Alexander 1965). The only direct measurements of production of nitric oxide in undisturbed systems apparently are those made by Kim (1973). Kim estimated nitrogen dioxide production from nitric oxide at 0.91, 0.52, and 0.83 g N/m_2-day for pine, oak, and grassland, respectively. Applying those rates to peninsular Florida yields an estimated gaseous loss of 21.4 x 10^9 g of N/yr by this pathway.

<u>Ammonia Volatilization</u>. The volatilization of ammonia is a major flux of gaseous nitrogen that has been studied most extensively on feedlots (see Chapter 6), high-density pastureland (Simpson 1968, Denmead et al. 1974), and crop and forest lands that have been fertilized with urea (Volk 1959, Nommik 1966). Rates of ammonia volatilization in less perturbed systems, however, are not well known. Ammonia volatilization from soil surfaces is enhanced by high temperature and by a low cation-exchange capacity of the soil, both of which are characteristic of Florida soils. Although these soils tend to be acidic (pH 5.5 to 6.5), localized increases in pH result from the hydrolysis of urea in manure and urine (Viets 1974). On the other hand, low densities of livestock held in feedlots favor leaching over volatilization, presumably because of limited compaction of surface soils. Cattle in Florida are generally raised at densities of about one animal/ha or less, but two large feedlot operations may account for 10 to 15 percent of the total cattle inventory.

Unfortunately, no measurements of ammonia volatilization have been made in Florida. Furthermore, after ammonia has been volatilized, a considerable proportion may be readily reabsorbed by the plant canopy (Denmead et al. 1976) and thus never leave the system. Based on assumptions given in the next section, losses from the system by ammonia volatilization were calculated at 54 x 10^9 g of N/yr.

<u>Deposition of Atmospheric Nitrogen Forms</u>. Once a gas enters the atmosphere, it can return to earth by dry or wet precipitation, move out of a region by advection, or react chemically to form another gas or an aerosol. An aerosol can then be removed by precipitation, sedimentation, or impaction of dry particles on vegetation. Gases can be absorbed by water or be taken up by plants. While aerosol deposition is at least partially accounted for in samples of bulk precipitation, gaseous absorption is difficult to measure and difficult to estimate, because actual measurements of deposition rates for ammonia and nitrogen oxides have been reported by only a few workers for selected conditions. Gaseous absorption depends on a host of variables, including the wetness and orientation of leaf surfaces, windspeed, solubility, and mass transfer coefficients.

Whelpdale and Munn (1976), Liss (1976), and Kabel (1976) calculated gaseous absorption rates by using deposition velocities (see Chapter 6). Robinson and Robbins (1971) assumed a deposition velocity of 1 cm/sec for ammonia, based on analogy with sulfur dioxide, for which data were available, and Söderlund and Svensson (1976) used a value of 0.8 cm/sec. Kabel (1976) calculated a deposition velocity of 0.5 cm/sec for nitrogen dioxide (NO_2) absorbed at a lake surface. He reported similar deposition velocities for most gases, but noted that gas solubility markedly affected deposition.

Kabel estimated a deposition rate of 87 ng/m^2-sec for NO_2 into water, based on the above deposition velocity and an assumed nitrogen dioxide concentration of 20 μg/m^3. Extrapolating to an annual rate yields a rate of 0.84 g N/m^2-yr. Applying this calculation to the 9.8 x 10^{9}m^2 of wetlands in the study area and reducing the NO_2 concentration to 4 ppb (7.5 μg/m^3), the temperate zone background level of NO_2 reported by Söderlund and Svensson (1976), a deposition of 43.1 x 10^9 g N/yr for NO_2 is obtained. For NO_2 deposition on land surfaces (absorption by plants and soil), a deposition velocity of 0.8 cm/sec was used, based on the high end of the range cited by Söderlund and Svensson (1976). Using the atmospheric ammonia concentration of 2 ppb reported by Robinson and Robbins (1971) and a deposition velocity for ammonia of 0.8 cm/sec, ammonia deposition was calculated to be 32.3 x 10^9 g N/yr in the study area. The total deposition of gaseous nitrogen in the study area thus amounts to about 92 x 10^9 g N/yr.

Combustion Inputs. Production of nitrogen oxides by combustion in peninsular Florida is estimated at 156.5 x 10^9 g N/yr (Table A.19), based on annual fuel consumption data from the Florida Statistical Abstracts (Thompson 1975) and from the Compilation of Air Pollutant Emission Factors (U.S. EPA 1973). A brief inspection of the ranges for the emission factors, and awareness of cautions that must be observed in applying them, suggest that this estimate may be accurate only within an order of magnitude. Furthermore, other sources of nitrogen oxides, such as fires (including controlled burning) and aircraft engines (which are likely to be a comparatively minor source) were not included in this inventory. Assuming that the nitrogen in ammonia emissions from industry and fires is approximately 21.5 percent of the NO_x-N emitted (Robinson and Robbins 1971), combustion sources in Florida also emit 33.7 x 10^9 g N/yr as ammonia.

Discussion. Atmospheric fluxes of nitrogen in the study area are shown in Figure A.7. Industrial and natural production of ammonia and nitrogen oxides totals 266 x 10^9 g N/yr, while only 212 x 10^9 g N/yr is returned to the system by atmospheric scavenging processes. The remaining 54 x 10^9 g/yr is presumed to be transported away from the state by net advection. Although no comprehensive accounting of atmospheric fluxes is possible now, these conclusions seem at least qualitatively correct. Because the study area is surrounded largely by oceans, it is unlikely that air transported into the atmosphere over the state would have a fixed nitrogen content significantly above background levels. The atmosphere over the state thus appears to act

TABLE A.19 Production of Nitrogen Oxides by Combustion of Fossil Fuels in Peninsular Florida

Energy Source	Amount Used	Emission Factor (as NO_2 per unit)[a]	Total N Produced (10^9g)
Coal	5.55×10^6 tons	18 lb/ton	27.6
Petroleum	5.64×10^{10} miles driven	5.4 g/mile	92.3
Natural Gas			
For power production	1.70×10^5 Mcf	600 lb/Mcf	14.1
Other	1.25×10^5 Mcf	100 lb/Mcf	2.3
Fuel Oil			
For power production	2.81×10^9 gallons	105 lb/gallon	40.8
Domestic	4.51×10^5 gallons	12 lb/10^3 gallons	1.2
Distillate	1.67×10^5 gallons	60 lb/10^3 gallons	2.1
Residual	2.90×10^5 gallons	60 lb/10^3 gallons	3.7
Total			184.1
Assuming 85% of production is in the study area			156.5

[a] Derived from U.S. EPA (1973).

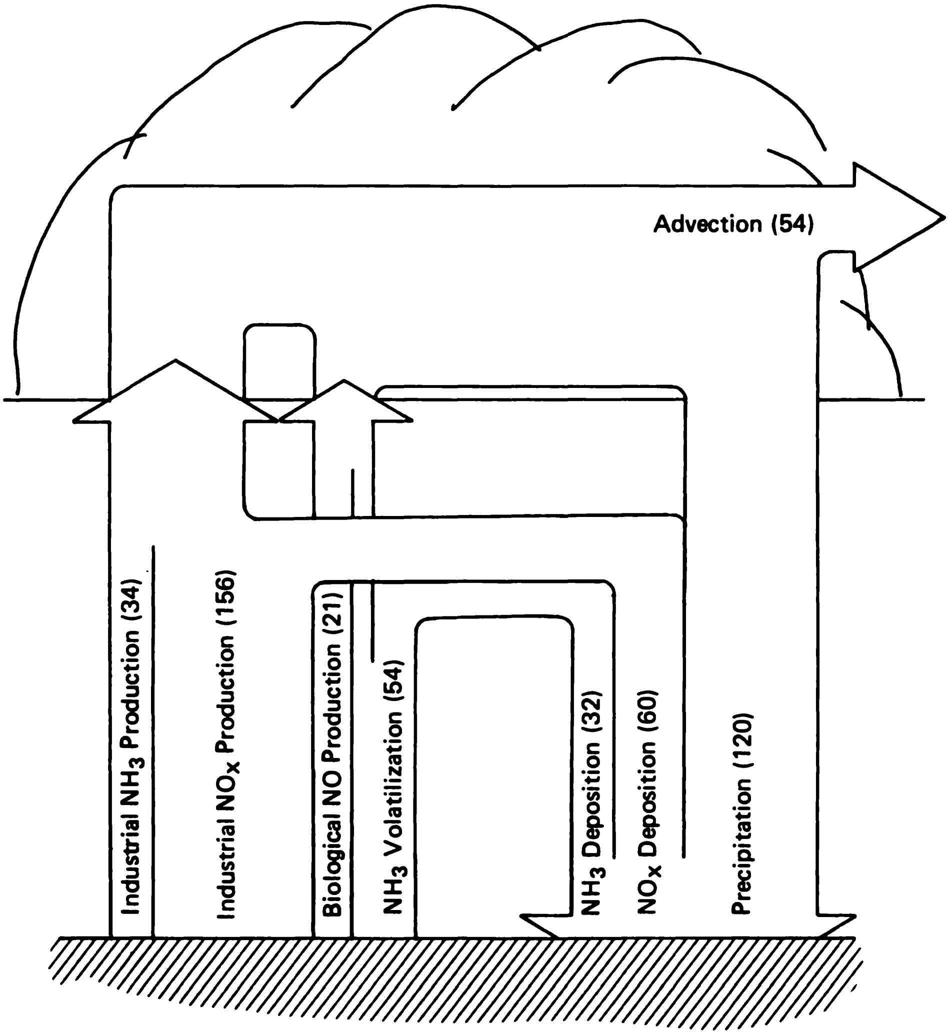


Figure A.7 Atmospheric fluxes of fixed nitrogen over peninsular Florida. Numbers in parentheses are in 10^6 kg N/yr.

as a net source, rather than as a net sink of fixed nitrogen for surrounding air masses.

Livestock and Agricultural Submodels

Construction of regional macromodels requires that certain internal subsystems be modeled separately in order to estimate imports and exports of nitrogen. These submodels may be useful because they elucidate internal processes and serve as checks on the regional model. The agricultural subsystem is expected to represent a significant segment of the anthropogenically-driven portion of the nitrogen cycle. This is especially true of the livestock industry; a livestock submodel, shown in Figure A.8, was used in the construction of the regional macromodel.

Data on animal import and export, production, and inventories shown in Figure A.8 were obtained from the Florida Crop and Livestock Reporting Service (FAS 1975a, 1975d, 1975e). Total waste production by livestock was calculated from the inventories and from per-animal waste rates given in Blanck (1955), Dale (1971), Taiganedes and Stroshine (1971), and Vollenweider (1968). Nitrogen in standing stock and annual meat production was calculated from the protein composition of farm animals (Palmer and Bowers 1972, Lawrie 1974) and inventory and slaughter data. Data on fish production were derived from Jacquot (1961) and Anderson et al. (1975). Per capita consumption of animal products was assumed to be at the national average (FAS 1975a, 1975d, 1975e). In order to calculate imports of feed and meat products, which are not published, a mass balance was calculated for each animal compartment.

The calculations indicate a total import to the Florida peninsula of 21.7 x 10^9 g N/yr in animals and meat products. The total production of animal and dairy products in nitrogen equivalents is 29.5 x 10^9 g/yr, of which 6.5 x 10^9 g are exported in livestock, poultry and fish products, and 23 x 10^9 g are in meat, fish, and dairy products consumed within the state. The production of this food nitrogen requires an input of about 242 x 10^9 g N in animal feed (Figure A.8); some of this feed is obtained from feed grains produced in the state, some from pasturage, and some from imported feeds.

The livestock submodel was then incorporated into an agricultural model shown in Figure A.9. Food crop production was estimated 25.2 x 10^9 g N/yr, field crops at 24.5 x 10^9 g N/yr, and pulp wood production at 7.66 x 10^9 g N/yr based on FAS (1975c, 1975f) and Florida Statistical Abstracts (Thompson 1975). Together with the nitrogen produced in pastureland (P), these inputs comprise the

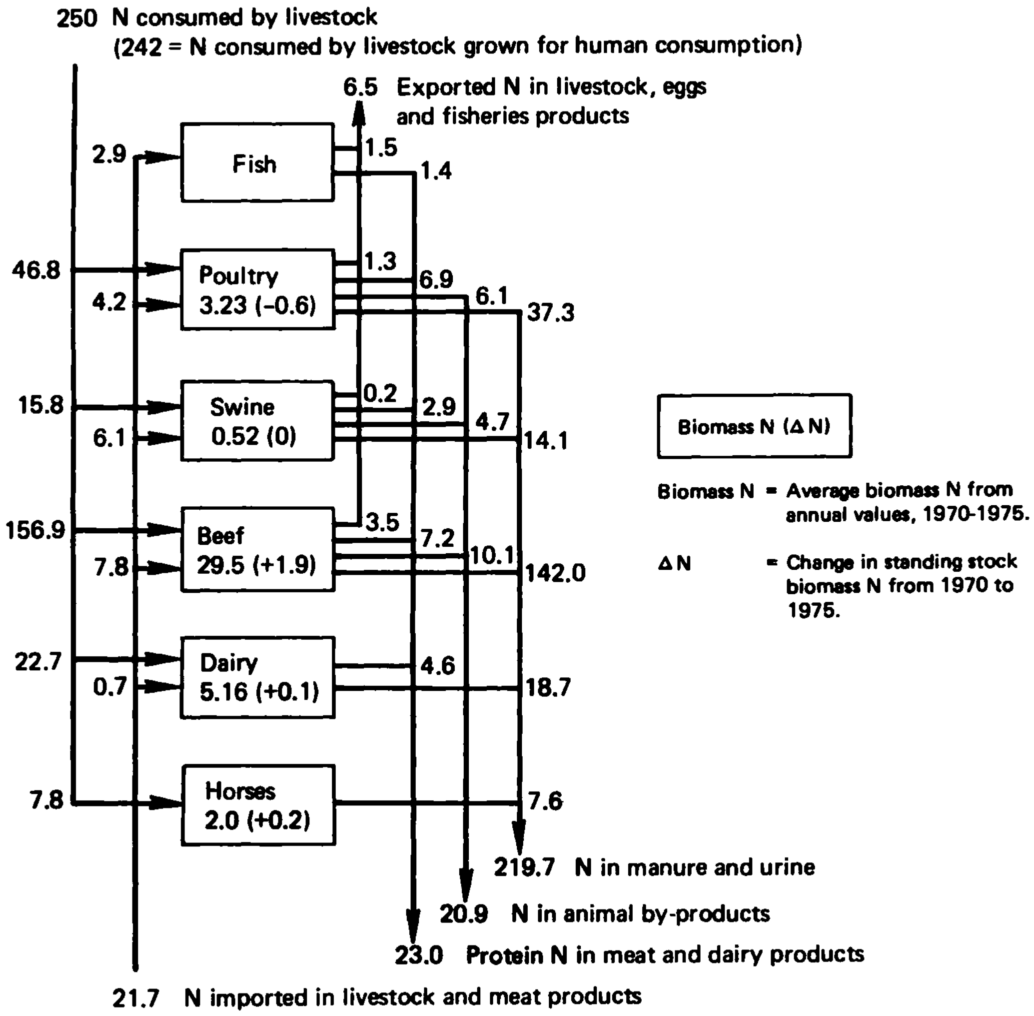


FIGURE A.8 Flows of nitrogen in the livestock, fish and dairy industries in peninsular Florida. Values are averages for the period 1970-1975. All values expressed in 10^6 kg N/yr.

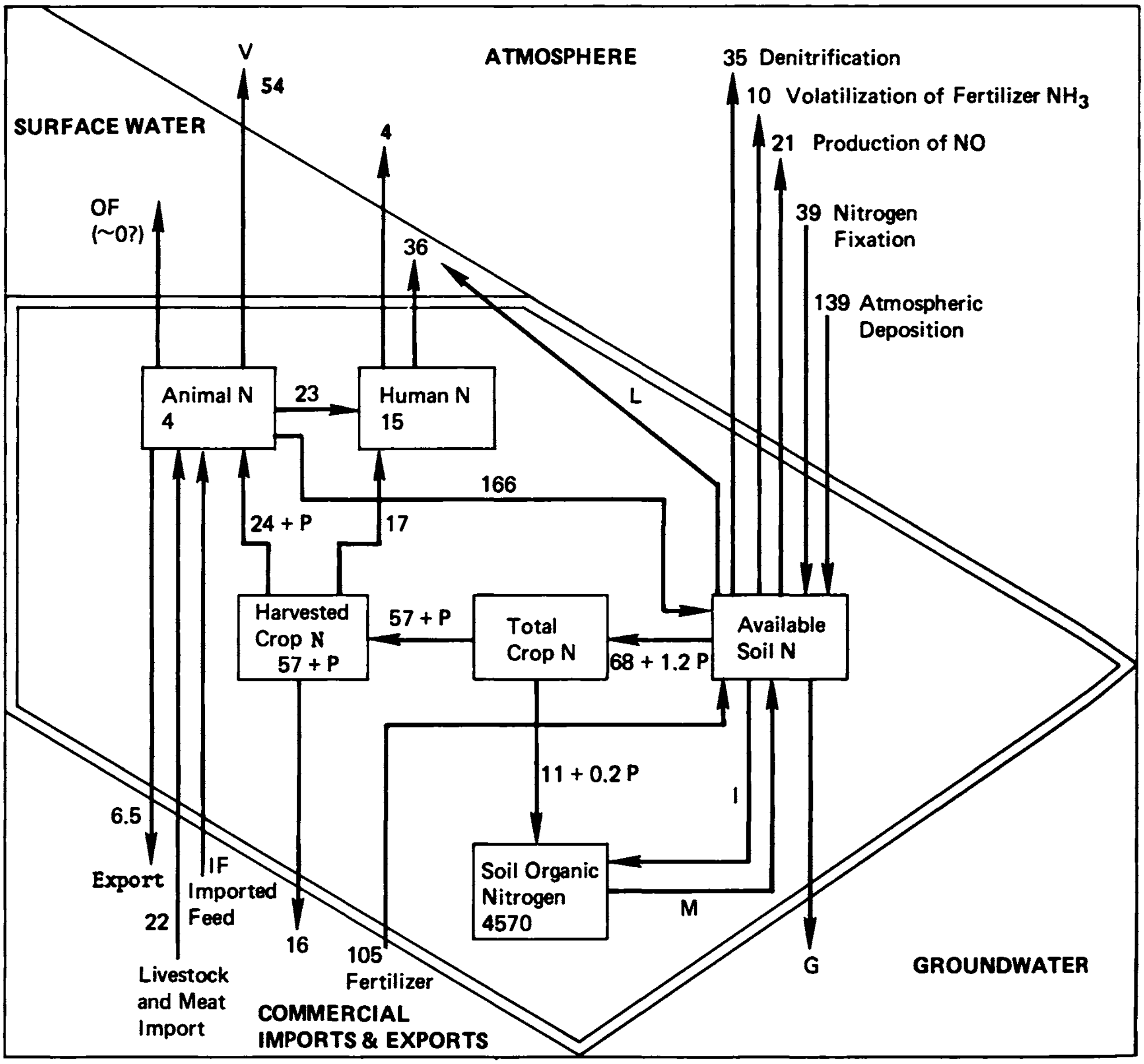


FIGURE A.9 An agricultural mass balance model for peninsular Florida. P = pasture nitrogen; V = volatilized ammonia-nitrogen; I = microbial immobilization of fertilizer nitrogen; L = nitrogen leached to surface water; G = nitrogen leached to groundwater; IF = imported nitrogen in feeds; OF = overland flow; M = mineralization. Flows are expressed in 10^6 kg N/yr; pool sizes are expressed in 10^6 kg N.

harvested N compartment. A value for P is difficult to calculate because of the diversity of the state's pasture land. Crop nitrogen values were obtained from Duckworth (1966), Hulme (1970), Inglett (1972), Kefford and Chandler (1970), Kyle (1955), Pomeranz (1964), Spenser and Meade (1905), Sprague (1955, 1959), Talburt and Smith (1959), Tressler and Joslyn (1954), Tso (1972), White and Silvey (1974), and Woodroof (1973). Production of nitrogen in the forestry industry is based on tree composition data (Smith and Prichett 1976) and wood product data (Thompson 1976) using the conversion factors of Williams and Hopkins (1968).

Exports from the harvested crop reservoir, calculated from the crop statistics referenced above, amounted to 8.6 x 10^9 g N/yr. Most of this crop export is in citrus and vegetables. Human consumption within the state was assumed to account for the remainder of the harvested food crops (16.6 x 10^9 g N/yr). It was assumed that animals within the state consume all of the field crops (24.5 x 10^9 g N/yr) plus an unknown amount of pasture nitrogen production (P). All of the nitrogen in the timber crop (wood only) was assumed to be exported (7.7 x 10^9 g N/yr). Leaves, roots and bark are not included in this figure and are assumed to remain on the land. Probably most of the nitrogen in wood is actually lost from the system in paper mill effluents, which enter estuarine areas downstream from the sampling stations used to calculate surface water export (Table A.17). This flux nevertheless represents a true export across the system boundaries. The total nitrogen in harvested crops is the sum of the figures given here, approximately (57 + P) x 10^9 g N/yr.

The animal nitrogen compartment receives feed and pasturage produced within the system as well as an unmeasured amount of imported feed (IF); the total input to this compartment is (24.5 + P + IF) x 10^9 g N/yr. Outflows of nitrogen are given in Figure A.8: 6.5 x 10^9 g/yr exported, 23 x 10^9 g/yr consumed by humans, 20.9 x 10^9 g/yr in animal by-products, and about 220 x 10^9 g/yr in animal waste, for a total flux of about 270 g N/yr through the animal compartment. Subtracting the 22 g N/yr of imported meat and livestock leaves 248 x 10^9 g N/yr produced from imported and local feed grain plus pasturage nitrogen. Thus, 24.5 + P + IF = 248 x 10^9 g/yr, or the sum of pasturage plus imported feed nitrogen must be 224 x 10^9 g/yr. The magnitude of either figure thus can be calculated if information on the other becomes available.

The 220 x 10^9 g of animal waste cannot be apportioned to various sinks with great accuracy. Overland flow (OF) into surface water from livestock operations is probably not extensive because of Florida's sandy, well-drained soils, but some overland flow may occur where cattle are grazed on floodplains. For purposes of the mass balance, OF was assumed to be zero. Ammonia volatilization (V) was estimated to be 25 percent of the nitrogen in animal waste, or 54×10^9 g N/yr. This figure is subject to great uncertainty and should be either measured or corroborated from a mass balance on the animal nitrogen compartment. The remaining nitrogen (166×10^9 g/yr) is transferred to the available soil nitrogen compartment, which includes the soil inorganic nitrogen plus some soluble and easily decomposable organic nitrogen forms such as urea. Some unknown fraction of the manure probably is refractory and directly enters the slowly-available soil organic nitrogen pool.

Many of the remaining flows are difficult to quantify accurately. Total crop production (as nitrogen) is 1.2 times the harvested crop nitrogen, with 20 percent of the total crop production transferred to the soil organic nitrogen compartment as unharvested roots, litter, and stalks. Because the soil organic nitrogen pool is so large compared to the other compartments, it is not practical to assume that it is at steady-state in order to compute other flows by difference. The available soil nitrogen pool receives atmospheric inputs based on estimates given in the earlier section on atmospheric fluxes. Fertilizer input (105×10^9 g N/yr) to this pool (Table A.16) is based on information from the Florida Department of Agriculture and Consumer Services. Losses from this pool include (1) a 10 percent loss of applied fertilizer nitrogen through volatilization; (2) denitrification, which was calculated according to CAST (1976); (3) leaching losses to runoff (L); and movement to deep groundwater (G). Immobilization (I) transfers some available soil nitrogen to the soil organic nitrogen compartment, but a greater amount of nitrogen must be returned to the available pool by mineralization (M) if no changes occur in the size of the available soil nitrogen pool. Examination of the mass balance for the soil nitrogen compartment indicates that either P or V must be large in order to prevent leaching of nitrogen to groundwater, assuming the estimates of gaseous fluxes are reasonable.

A Citrus Submodel

The Florida citrus industry, made up of more than 15,000 producers and associated dealers, packing houses, and concentrating plants, produces 95 percent of the frozen orange juice concentrate in the United States (IFAS 1975). The value of Florida's 353,000 ha of citrus groves ($550 million in 1973) is one quarter of the value of Florida's agriculture, forest, and fisheries. Citrus groves are found primarily on well-drained sands of the Central Florida Ridge, and nitrogen applied to the surface is may be leached with ease because of the low cation-exchange capacity of the soil. Because the groves are often located close to lakes to protect against frost, the lake waters may be enriched with nutrients in runoff and seepage from the groves. Central Florida is also a principal recharge area for the deep limestone Floridan Aquifer, which supplies most of the peninsula's drinking water. Because nitrate contamination of this aquifer could be a serious problem for Florida's cities, the nutrient balance in the groves was briefly examined.

Most of the citrus acreage in the state is devoted to production of oranges. The sources of nitrogen for orange groves are rainfall, dry fallout, and fertilizer, which is usually applied at the soil surface. Although legumes are occasionally grown as ground cover, groves are usually bare-cultivated. During 1973, the state's orange grove area of 2.60×10^5 ha received 125.8 cm of rain (based on north and south central region averages from March 1972 to February 1973 in U.S. Climatological data). Assuming a mean nitrogen content of 0.75 mg/l, bulk precipitation delivered about 2.5×10^9 g of N to orange groves that year. The rule of thumb for fertilization is 182 g of nitrogen (0.4 lb) per box of oranges expected (Volk 1974). The 1973 yield of 1.76×10^8 boxes thus probably received 32×10^9 g of fertilizer nitrogen, and the total nitrogen input to orange groves was 34.5×10^9 g. Assuming a yield of 6.76×10^{12} g of fruit with 0.16 percent nitrogen, crop harvest removed 10.8×10^9 g of nitrogen from the system. The difference between input and output (23.7×10^9 g) may be lost by seepage below the root zone, by immobilization into soil organic matter, by volatilization of ammonia, or by denitrification. Two-thirds of the nitrogen input is unaccounted for in this model; this is typical of nitrogen losses reported for other citrus-dominated systems (Bingham et al. 1971, Forbes et al. 1974, Avnimelech and Raveh 1976).

The acidic nature of the citrus soil makes ammonia volatilization unlikely, and there is probably insufficient carbon in the soil water to support substantial denitrification. If all of the nitrogen not removed in oranges were immobilized in the soil, the fraction immobilized would be 69 percent, a high figure compared to values from the literature (e.g., Allison 1965, Black 1968). Agricultural soils generally reach a steady state with respect to nitrogen, given a sufficiently long period of time (Stevenson 1965). Subtropical temperatures tend to hasten the approach to steady-state by increasing microbial processes (Stevenson 1965), and steady-state conditions may be reached in as little as twenty years in some Florida agricultural systems (Nathan Gammon, Department of Soil Sciences, University of Florida, personal communication, 1976). Accumulation of nitrogen in the soil of citrus groves in Central Florida apparently has not been studied.

Some fertilizer nitrogen applied to citrus groves is certainly leached to the watertable aquifer, where it may flow into local seepage lakes. However, Brezonik and Messer (1977) found low-to-moderate nitrogen concentrations in a central Florida lake with a large amount of citrus production in its watershed. Some denitrification may occur as groundwater seeps through carbon-rich lake sediments.

Precipitation exceeds evapotranspiration by approximately 30 percent in the Florida peninsula, and about 38 cm of precipitation is not removed by ET. If all of the 23.7×10^9 g of nitrogen not removed in oranges were dissolved in the 9.8×10^8 m^3 of excess rainfall, the resulting concentration of 24 mg N/l would considerably exceed the accepted drinking water standards. Forbes et al. (1974) found an average of only 6 mg N/l below the root zones in the well-drained sands of a central Florida orange grove; the implication therefore is that some denitrification occurs in the root zone. Since many orange groves occupy possible recharge areas for the Floridan Aquifer, further studies are warranted on the fate of fertilizer nitrogen in these areas.

Summary and Conclusions

The model of the nitrogen cycle in peninsular Florida illustrates the importance of gaseous fluxes of ammonia and nitrogen oxides. Aerosols may be formed by reaction of ammonia released by the natural decomposition of organic matter with nitrogen oxides fixed by combustion. Such aerosols return the gaseous nitrogen to earth, through dry deposition or rainfall. However, most of the fixed nitrogen that leaves the system apparently escapes through gaseous pathways, since the hydrologic and agricultural outputs from the state (Tables A.16 and A.17) are estimated to be only 26 percent of the total of inputs listed in Table A.16. If all anthropogenic releases of fixed nitrogen to the atmosphere were returned to earth in bulk precipitation within the boundaries of the system, the nitrogen input would exceed the application of fertilizer nitrogen by 80 percent.

The long-term effects of increased atmospheric fluxes on the evolution and productivity of natural systems warrant consideration. The potential for eutrophication of natural waters because of atmospheric nutrient loading is discussed in Chapter 6. The large inputs of nitrogen oxides and fertilizer-derived nitrogen aerosols may increase productivity in nitrogen-limited systems and lead to increased transfer of organic matter to the forest floor or to wetland sediments, possibly resulting in increasing anaerobiosis. If such anaerobic zones are "patchy" on a macro- or micro-scale, diffusion or advection of nitrate or nitrite into the anaerobic zones from surrounding soil or overlying water may lead to increased denitrification. Some implications of this chain of processes on a global scale are discussed in Chapter 7.

Uncertainties involved in some of the mass balance estimates preclude firm conclusions regarding the potential for groundwater pollution. Although no data on the turnover time of the limestone Floridan aquifer could be found, total flows of artesian springs, which are significant sources of water for Florida rivers, can be used to estimate the minimum flow rate into this aquifer. The total annual flow from Florida springs was estimated to be 6.34 x 10^9 m^3 by Rosenau and Faulkner (1975). Therefore, a minimum of 63.4 x 10^9 g NO_3^--N/yr would be needed to exceed the present 10 mg/l standard for nitrate-nitrogen in the recharge water. This represents 17 percent of the estimated nitrogen input to the state (Table A.16). If there is extensive offshore seepage or outflow through submarine springs, estimated throughflow would be larger and thus the possible groundwater nitrogen concentration would be lower. Knowledge of the capacity of the aquifer would allow calculation of a time frame for the buildup of groundwater nitrogen. The shallow watertable aquifers undoubtedly have smaller volumes and shorter residence times, and nitrate pollution here could be more severe.

The most disturbing aspect of this regional nitrogen balance is its failure to account for about 40 percent of the estimated inputs. In many mass-balance models, denitrification is forced to account for the discrepancy; in the present case, however, it is probably more realistic to assign the unaccounted-for nitrogen to a number of poorly-measured outflows, as well as to some long-term storages. Urban runoff in coastal areas, transport in sediments by wind, and higher rates of volatilization of ammonia would increase exports. Conversely, lower values for deposition of gaseous forms of nitrogen would reduce the amount of excess input.

It is possible that some or all of the input that is unaccounted for could be stored in the system as organic soil nitrogen, but the soil nitrogen pool is so large and heterogeneous that direct measurements of short-term changes in its size are not feasible. The unaccounted-for input of 154 x 10^9 g N/yr represents roughly one percent of the total nitrogen stored in the upper 6 inches of soil and sediment deposits in the study area. An accumulation of one percent per year would not be noticed over short periods of time, but this seems a rather rapid accumulation rate compared to those measured in natural climax systems (e.g., the rate of accumulation of nitrogen in peat soils of the Everglades was 6 to 12 x 10^9 g N/yr). Further information on the long-term rates of natural accumulation of nitrogen in Florida soils based on paleontological methods would be useful in placing this unaccounted-for input into perspective.

Although the data do not permit more precise conclusions, more than half of the estimated present nitrogen loading in peninsular Florida (Table A.16) results from human activities; much of this anthropogenic loading has occurred only in the last 25 to 50 years. Although it is tempting to use this recent increase in loading to explain the imbalance between inputs and outputs, human activities also are a factor in a substantial, but unquantifiable, portion of the outflow values listed in Table A.16.

Although regional models do not appear useful as management tools at this time because of insufficient data for several important fluxes, they are not merely academic exercises. This approach produces several positive results:

(1) Research needs that might be overlooked are discovered as the data collection proceeds (or, more often, as it ceases to proceed).

(2) Priorities can be assigned to these needs based on the estimated importance of particular pathways or processes.

(3) A semi-quantitative analysis of some flows can be performed. For example, use of published deposition velocity figures for nitrogen dioxide and ammonia led to the calculation of atmospheric fluxes that are of the same magnitude as easily measured nitrogen flows, such as fertilizer input.

Some data needs uncovered in preparing this mass balance study for peninsular Florida include:

(1) Deposition velocities, atmospheric concentrations, and factors affecting transport of ammonia and nitrogen oxides to plant and soil surfaces.

(2) Regional advective fluxes of ammonia and nitrogen oxides;

(3) Rates of volatilization of ammonia from low-density pastureland on well-drained, acid sands;

(4) The potential of wetlands and periodically-flooded flatwoods soils for nitrification-denitrification;

(5) The potential of unfertilized acid soils for abiological production of nitric oxide;

(6) Leaching rates of nitrogen and groundwater in orange groves, and the hydrology of these systems with respect to the Floridan Aquifer;

(7) Rates of accumulation of organic nitrogen in soil and wetland systems; and

(8) Hydrologic information (recharge rates and volumes) of the Floridan and Biscayne aquifers.

The model developed in this section has raised a number of questions about a cycle that is often regarded as well understood. The model needs to be refined as new data become available so that eventually it will answer as many questions as it poses.

(7) THE GLOBAL NITROGEN CYCLE

While the thought of a global nitrogen mass balance might initially seem staggering, the high degree of aggregation and simplification of system boundaries and transport vectors make such a balance relatively easy to construct. However, the data base is limited, especially for the Southern Hemisphere, the developing nations, communist-bloc countries, and the oceans. A number of global nitrogen balances have been published; for the most part, each has been a refinement of previous attempts, expanded to consider new knowledge. The first sophisticated budget was developed by Hutchinson (1954), using geochemical data from Clark (1924). Delwiche (1970) modified Hutchinson's balance somewhat, and Burns and Hardy (1975) updated Delwiche's balance by including recent data on biological nitrogen fixation. Robinson and Robbins (1971) emphasized atmospheric fluxes in a controversial global budget that differs from most other analyses (see Chapter 5). Liu et al. (1977) and Sze and Rice (1976) used Burns and Hardy's budget as the basis for discussions of the potential impact of fertilizers on atmospheric N_2O. The mass balance by Söderlund and Svensson (1976) is the most complete and well-documented analysis to date.

A global mass balance should address several questions. One of the most important is to estimate the relative contribution of anthropogenic inputs to global mass flows of fixed nitrogen. This requires as accurate an assessment as possible of biological nitrogen fixation, and accurate differentiation between that occurring naturally and that induced by man. Another question of major interest is the global rate of denitrification, particularly as a source of N_2O. Estimation of residence times of various nitrogen compartments is useful in assessing time frames in which various stresses will cause perturbations in the environment. Finally, as with all educated modeling efforts, gaps in the data base are revealed and directions for future monitoring and research become evident.

The following section summarizes the various global nitrogen budgets and cycles presented to date, supplements findings with new information where appropriate, and attempts to evaluate the accuracy of the various global nitrogen budgets. This summary draws upon Söderlund and Svensson (1976) extensively, and that study should be referred to for in-depth treatment of the subject.

Global Nitrogen Inventories

Geological Reserves

Four major reservoirs--primary rocks, sedimentary rocks, coal, and clay-fixed NH_4^+ in soils--provide the primary geologic reserves of nitrogen (Table A.20). These reserves are largely inert, with only minor amounts reaching the active nitrogen cycle in a year. Stevenson (1965) calculated the nitrogen bound in primary rocks as 1.9×10^{11} Mt (1.9×10^{23} g), based on an average total nitrogen content of about 50 mg/kg. However, Stevenson felt this value might be as much as five times too high. Ancient sedimentary rocks were estimated by Stevenson to contain about 4×10^5 Mt N, while coal deposits were estimated by Donald (1960) to contain about 1.2×10^6 Mt of nitrogen. The latter value was changed by Burns and Hardy (1975) to 1×10^5 without any explanation. Nitrogen that is bound in soil in clay-fixed forms has never been estimated from basic data. Delwiche (1970) proposed 1.4×10^5 Mt of inorganic nitrogen on land, but provided no explanation for the calculation. Burns and Hardy (1975) revised this figure to 10^5 Mt, again without explanation. Most soils contain fixed ammonium ion (Bremner 1967), and while a compilation of average values does not exist, 50 mg N/kg might be a reasonable value for a worldwide average; this would equal 7.3×10^4 Mt for a 10 m deep soil profile. (The world soil area is $1,221 \times 10^8$ km².)

Oceanic Reservoirs

Only limited data are available on nitrogen pools in the ocean. Vaccaro (1965) estimated a soluble inorganic nitrogen content of 6×10^5 Mt, and Emery et al. (1955) reported a nitrate-N content of 5.7×10^5 Mt. Söderlund and Svensson (1976) thought that this value might be correct within a factor of five, and they also estimated the nitrite-N content to be about 500 Mt. From the data of Hahn (1974), they estimated a N_2O content of 200 Mt N to a 3,000-m depth, but they felt that this estimate could be in error by an order of magnitude. Using an ammonia-N concentration of 5 μg N/l for deep areas and 50 μg N/l for near-shore areas, Söderlund and Svensson (1976) estimated an NH_4^+-N inventory of at least 7×10^3 Mt. Martin (1970) estimated

TABLE A.20 Global Nitrogen Inventories

Location and Form	Mt N	Reference
Geological		
Primary rocks	1.9×10^{11}	Stevenson (1965)
Sedimentary rocks	4×10^{5}	"
Coal deposits	1.2×10^{6}	Donald (1960)
Clay-fixed ammonium	7×10^{4}	This Report
Oceans		
NO_3^-	5.7×10^{5}	Emery et al. (1955)
NO_2^-	5×10^{2}	Söderlund and Svensson (1976)
N_2O	2×10^{2}	"
NH_4^+	7×10^{3}	"
N_2	22×10^{6}	Martin (1970)
Plant biomass	3×10^{2}	Söderlund and Svensson (1976)
Animal biomass	1.7×10^{2}	Delwiche (1970)
Dissolved organic matter	5.3×10^{5}	Söderlund and Svensson (1976)
Particulate organic matter	$0.3\text{-}2.4 \times 10^{4}$	"
Terrestrial		
Soil organic matter (humus)	3×10^{5}	Söderlund and Svensson (1976)
Inorganic (NH_4^+ and NO_3^-)	1×10^{3}	Burns and Hardy (1975)
Plant biomass	1.6×10^{4}	Söderlund and Svensson (1976)
Animal biomass	1.7×10^{2}	"
Microbial biomass	5×10^{2}	"
Atmosphere		
NH_3	0.9	Söderlund and Svensson (1976)
NH_4^+	1.8	"
NO_3^-	0.5	"
NO_x	0.9	"
Organic	1.0	"
N_2	3.9×10^{9}	"
N_2O	1.5×10^{3}	This Report

that at least 22 x 10^6 Mt of N_2 are dissolved in the oceans. Using a value of 1.8 x 10^3 Mt of carbon (Whittaker and Likens 1973) in oceanic plant biomass (mainly phytoplankton) and a C:N ratio of 6, Söderlund and Svensson (1976) calculated a pool size of 300 Mt for the nitrogen in oceanic biomass. Delwiche (1970) estimated that 170 Mt of nitrogen exists in marine animals. Dissolved and particulate organic nitrogen in the sea was estimated by Söderlund and Svensson (1976), using Riley's (1973) estimates of dissolved and particulate organic carbon and C:N ratios of 6 for <200 m and 2.7 for >200 m deep waters.

Terrestrial Reservoirs

Bohn (1976) used FAO-UNESCO soil maps to estimate the world's soil organic carbon at 3 x 10^6 Mt. Assuming a C:N ratio of 10:1 for humus gives a value of 3 x 10^5 Mt of nitrogen. Stevenson (1965) used Goldschmidt's (1954) estimate of 1.4 x 10^7 Mt of pedospheric carbon, 60 percent of it in humus, to estimate the soil organic nitrogen pool at 8.2 x 10^5 Mt. The pool of inorganic nitrogen (nitrate and exchangeable ammonium) in soil is highly transient, and cannot be estimated accurately, but generally constitutes less than 2 percent of the total nitrogen in soils (Bremner 1967). If it is assumed (and the assumption should be made with caution) that a 10 m deep soil profile contains a weighted average of 10 mg N/kg of inorganic nitrogen, this pool would be 1.4 x 10^4 Mt of nitrogen. Delwiche (1970) estimated the total inorganic nitrogen pool of soils, including ammonium in clay-fixed form (see above), at 1.4 x 10^5 Mt; Burns and Hardy (1975) revised that estimate to 1 x 10^5 Mt, but neither gave a basis for their estimates. Söderlund and Svensson (1976) chose not to make an estimate of the inorganic soil pool, because of insufficient information.

Garrels et al. (1975) estimated the biomass of carbon at the earth's surface to be 4.8 x 10^5 Mt. At a C:N ratio of 30:1, this would be 1.6 x 10^4 Mt of biomass nitrogen, which is within the range estimated by Söderlund and Svensson (1976) with independent data. Delwiche (1970) estimated 1.7 x 10^2 Mt of nitrogen in animal biomass, while Söderlund and Svensson (1976) estimated 5 x 10^2 Mt of nitrogen in terrestrial microorganisms.

Atmospheric Inventory

Tables A.21 and A.22 summarize estimates of the atmospheric pool sizes and concentrations of various forms of nitrogen. While numerous reports dealing with the ambient concentrations of nitrogen gases are available from the northern hemisphere, almost no data are available for

TABLE A.21 The Inventory of NO, NO_2, and Nitrate in the Atmosphere

Region	Area ($10^{12} m^2$)	NO, NO_2 (ppb [v])	Particulate NO_3^--N ($\mu g/m^3$)	ΣN (Mt)
Polar	8	0.5	0.1	0.01
Temperate	85	4.0	0.25	0.45
Tropics	55	0.8	0.25	0.08
Ocean	361	0.3	0.02	0.15
Upper troposphere	510	0.15	0.15	0.8
Total				1.6

SOURCE: Modified from Söderlund and Svensson (1976).

TABLE A.22 Ranges of Estimates of the Atmospheric Nitrogen Inventory

Form of N	Robinson and Robbins (1975)	Junge (1974)	Söderlund and Svensson (1976)	Burns and Hardy (1975)	Schütz et al. (1970)	This Report
			(Mt N)			
N_2	3.865×10^9	--	3.870×10^9	3.865×10^9	--	--
N_2O	1,361	1,300	1,300	1,400	1,300	1,500
NO	--	--	--	2	--	--
NO_2	--	--	--	4	--	--
NO_x	14	--	1-4	--	--	--
NH_3	27	--	0.9	27	--	--
NO_3^-	0.2	--	0.5	0.2	--	--
NH_4^+	3.7	--	1.8	4	--	--
N_2 in Oceans	--	--	--	22×10^6	--	--
Particulate Organic N	--	--	1.0	--	--	--

the southern hemisphere, making these atmospheric estimates uncertain. Söderlund and Svensson (1976) recently computed an atmospheric inventory (Table A.21) that resulted in much lower estimates for NO_x and ammonia than the widely quoted values of Robinson and Robbins (1971). Söderlund and Svensson (1976) used literature-derived mean values for ammonia-nitrogen of 0.4, 12, and 1.2 ppb(v) for ocean, tropical, and temperate land areas, respectively; the corresponding aerosol ammonium-nitrogen values were 0.4, 2, and 3 μg NH_4^+-N/m^3. Upper troposphere values were 0.1 ppb (v) for NH_3-N and 0.7 $\mu g/m^3$ for particulate NH_4^+-N. The resulting inventory values are 0.9 Mt NH_3-N and 1.8 Mt of NH_4^+-N, for a total of 2.7 Mt of ammonia-nitrogen, which are less than a tenth of the values used by Robinson and Robbins (1971). The NO, NO_2, and particulate NO_3^--N estimates in Table A.21 are also from Söderlund and Svensson (1976).

The wide disparity in literature estimates for the amounts of some of the atmospheric nitrogen components is illustrated in Table A.22. Particularly large differences are noted between the estimates of Robinson and Robbins (1971, 1975) and Söderlund and Svennson (1976) for NH_3 and NO_x, and the estimates of the former authors now appear questionable. Robinson and Robbins used much higher average concentrations of these forms of nitrogen and did not consider the differences in values obtained over various land areas. In the case of NH_3 and NH_4^+, Robinson and Robbins did not consider the characteristic mixing height, whereas Söderlund and Svennson did. The use of a mixing height accounts for the sharply decreasing concentrations of NH_3 and NH_4^+ that are usually observed with increasing height above the ground. (See Chapter 5 for more detailed discussion of these estimates of atmospheric nitrogen pools.)

Nitrogen Sources

Biological Nitrogen Fixation

Burns and Hardy (1975) estimated biological nitrogen fixation on land at 139 Mt/yr (Table A.23). This is considerably higher than earlier estimates (see Chapter 2), and is largely a result of new information. For example, Delwiche (1970) estimated biological fixation at 54 Mt N/yr. The estimate by Burns and Hardy is subject to further revision, however, since the acetylene reduction method was used to obtain much of the new information, and the conversion factors for the ratio of nitrogen fixed/acetylene reduced may need to be revised (see Chapter 4). Furthermore, the rates for sources other than cropped legumes are highly uncertain. Burns and Hardy (1975) estimated marine fixation to be 36 Mt N/yr, but no basis for their calculation was given. Söderlund and Svensson (1976)

TABLE A.23 Global Nitrogen Fixation Rates for Terrestrial Systems

System	kg N_2 Fixed per ha per Year	Mt Fixed N
Agricultural		
Legumes	140	35
Rice	30	4
Other crops	5	5
Grasslands	15	45
Forest	10	40
Other	2	10
Total		139

SOURCE: Adapted from Burns and Hardy (1975).

estimated pelagic fixation in tropical oceans (about one-third of the world's ocean) at 15 to 80 Mt N/yr, and estimated total pelagic fixation at 20 to 120 Mt N/yr. Fixation in shallow water sediments was conservatively estimated at 10 Mt N/yr. Fixation in lakes and lake sediments represents an insignificant contribution to the global cycle.

Industrial Fixation, Combustion and Lightning

The global industrial capacity for fixation of nitrogen as ammonia is currently 78 Mt N/yr (W.C. White, Vice President, The Fertilizer Institute, personal communication 1977). If production rates of 90 percent capacity are assumed, and if 70 percent of this worldwide production is used for fertilizer (CAST 1976), fertilizer input on agricultural land is about 49 Mt N, compared to about 89 Mt currently being fixed on agricultural lands by biological means (Table A.24).

Combustion inputs of NO_x-N were estimated by CAST (1976) at about 20.7 Mt worldwide (Table A.24), and at 19 Mt by Söderlund and Svensson (1976). Global contributions of wood burning to atmospheric fluxes of fixed nitrogen previously have been considered negligible (for instance, see Robinson and Robbins 1971). Recent data suggest, however, that much more wood is being burned, for fuel and as a result of deforestation to clear land for agriculture, than was previously thought (Adams et al. 1977, Woodwell et al. 1978). Crude calculations of the nitrogen emissions from wood and forest burning (see Chapter 6) indicate that this source may contribute from 10 to 200 Mt of fixed nitrogen to the global atmosphere per year. Further studies are needed to verify this potentially large flux.

The significance of lightning in fixing atmospheric nitrogen has long been controversial (see Chapter 6). Söderlund and Svensson (1976) acknowledged the possible significance of this source but did not present numerical estimates. Chameides et al. (1977) recently extrapolated from theoretical calculations and laboratory data to estimate a global rate of fixation by lightning of approximately 30 Mt/yr. Further studies are needed to verify these calculations.

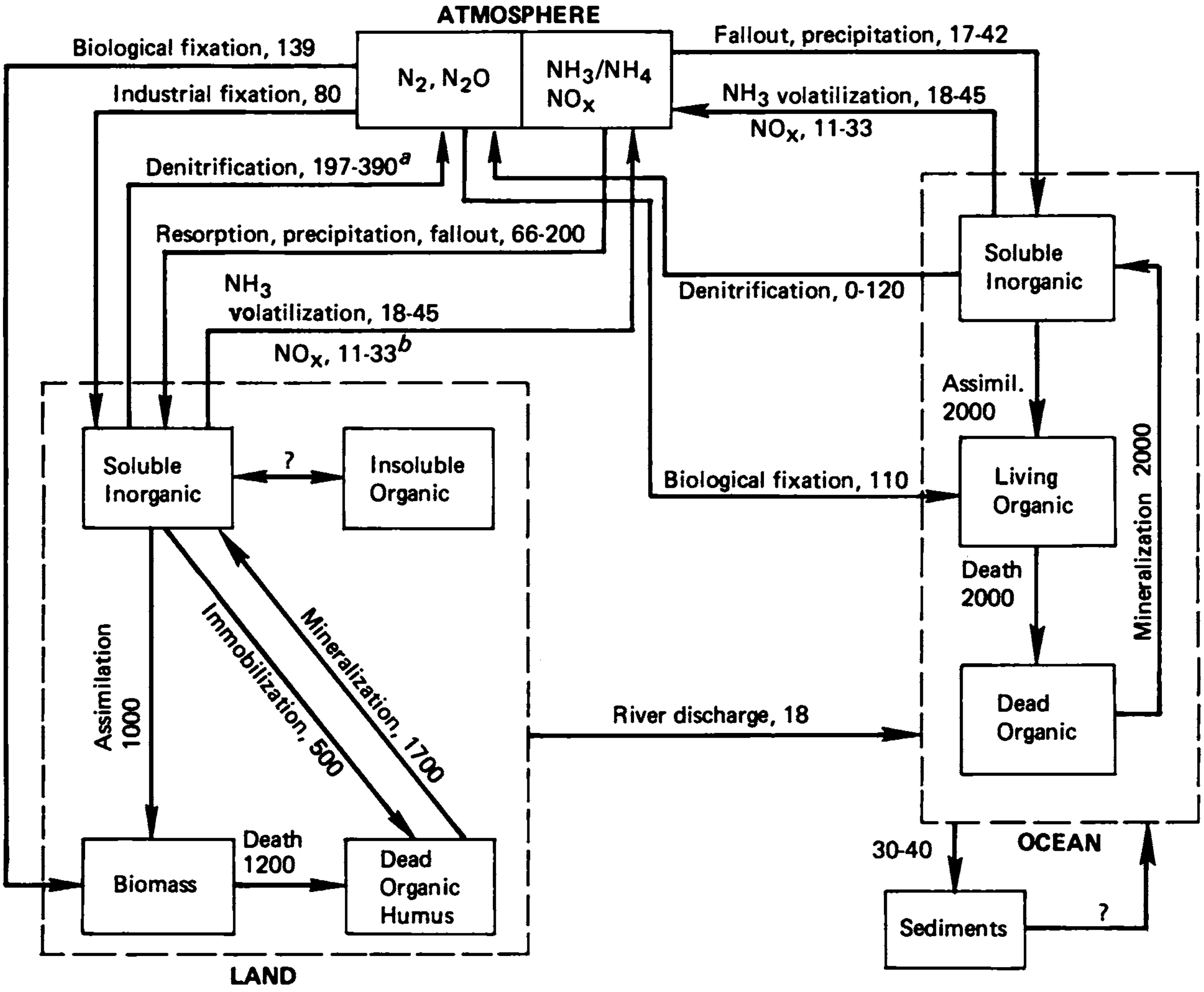
Mass Transfer Rates

Figure A.10 presents a combination of estimates of inputs and outputs to the land and ocean obtained from Söderlund and Svensson (1976) and made in this report. Internal transfer rates (within the land and oceanic compartments) are from Liu et al. (1977). The input-output

TABLE A.24 Global Sources of Fixed Nitrogen, 1976

Source	Amount (Mt N/yr)
Biological fixation	
Agricultural lands[a]	89
Other terrestrial[a]	49
Ocean[b]	
Pelagic	20 to 120
sediments	10
Industrial fixation	
Fertilizer	49
Other industrial NH_3[c]	21
Combustion[d]	21
Wood burning[e]	10 to 200
Lightning[f]	30
TOTAL	299 to 589

[a] Burns and Hardy (1975).
[b] Söderlund and Svensson (1976).
[c] The Fertilizer Institute (1976), information supplied by W. C. White, Vice President. Perhaps 50% of this N is in manufactured products, which do not enter the N cycle for considerable period of time.
[d] Council for Agricultural Science and Technology (1976).
[e] This study; see Chapter 6.
[f] Chameides et al. (1977).



[a] Forced to balance (inputs less outputs = denitrification).

[b] Emissions from wood burning and lightning not included. See text for discussion.

FIGURE A.10 The global nitrogen cycle. Fluxes are in millions of metric tons of nitrogen per year.

data are within the confidence limits established by Söderlund and Svensson (1976), and demonstrate the paucity of information presently available. Of special interest is the estimate of denitrification from land surfaces of 197 to 390 Mt/yr. The forced-balance estimate of denitrification in this report is higher than in others, particularly that of Söderlund and Svensson (1976), largely because of higher estimates of inputs from precipitation and industrial fixation and lower estimates of volatilization of ammonia.

Various estimates of terrestrial denitrification are summarized in Table A.25. The values range from 43 Mt (Delwiche 1970) to 197-390 Mt (this report). Since all the estimates involve numerous unproved assumptions, they all must be treated with caution. Continuous updating will be needed as new information becomes available.

An even wider disparity exists for various estimates of denitrification in the oceans (Table A.25). With the exception of Delwiche's (1970) early estimate, forced balance calculations have estimated the rate at around 120 Mt/yr. Goering (1976) considered data on observed denitrification rates and oceanic properties (depth, oxygen states) and estimated that up to 330 Mt of nitrogen is lost per year. It is noteworthy that Goering's estimate of denitrification on the continental shelf constitutes more than 90 percent of his estimate of the total loss, and that this portion of the estimate was based on a single measurement. In contrast, the forced calculation in Figure A.10 indicates 0 to 120 Mt/yr. Large uncertainties in estimates of the rates of biological fixation in the oceans and rates of mineralization of nitrogen in marine sediments contribute to the insensitivity of this balance.

Conclusions

The mass balance for nitrogen at the global scale involves such a large degree of aggregation and so many assumptions that a high degree of inaccuracy is inevitable. The inaccuracies in transfer rates are even greater than those for pool estimates. Nevertheless, mass balance calculations are useful in examining the extent of human influence on the cycle, and predicting where this influence might be most pronounced.

On the input side, industrial fixation for fertilizer now adds about 35 percent as much nitrogen to terrestrial systems as does biological nitrogen fixation. If leguminous fixation (Table A.23) is considered an anthropogenic source, total anthropogenic fixation (about 126 Mt N/yr, excluding the uncertain estimates for combustion of biomass) contributes from 48 to 77 percent as much nitrogen to the environment as does estimated natural nitrogen fixation, or

TABLE A.25 Summary of Estimates of Global Rates of Denitrification

Source	Denitrification Rate, Mt N/yr[a]		
	Land	Oceans	Global
Delwiche (1970)	43	40	83
Richards (1971)		230	
Burns and Hardy (1975)	140	70	210
CAST (1976)	71.4-100	100	171-200
Söderlund and Svensson (1976)	108-160	25-179	133-339
Sze and Rice (1976)	135	125	260
Liu et al. (1977)	140	130	270
Goering (1976)		330	
This Report	197-390	0-120	197-510

[a] All estimates are by forced balance (total inputs - total of other outputs), except CAST (1976), Richards (1971), and Goering (1976) See text of this Appendix and also Chapter 2 for discussion.

from 32 to 43 percent of total inputs. Other sections of this report discuss in detail the possible implications of this anthropogenic perturbation of the global nitrogen cycle, and Chapter 5 reviews some of the major methodological issues raised by the global balances.

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APPENDIX B

A STATISTICAL ANALYSIS OF SOME FACTORS ASSOCIATED WITH CANCER MORTALITY INCLUDING THE ROLE OF NITRITE IN DIET

To assess accurately the risk of human cancer associated with the occurrence in the environment of a potentially carcinogenic substance, it is necessary to have detailed information on exposures, experimental data from studies on laboratory animals, and epidemiological evidence of the effects of exposures on human populations. Unfortunately, such evidence is almost always incomplete and insufficient. This is the case for an assessment of the risk of cancer associated with nitrosamines, and with exposure to precursors of these carcinogens, i.e., nitrate and nitrite (see Chapter 9 and Appendix A).

When the needed detailed information is not available, statistical studies that seek correlations between environmental variables and the incidence of disease can provide some insights and generate hypotheses. For example, Lave and Seskin (1970) employed a cross sectional regression analysis of data on specific measures of air pollution and the incidence of morbidity and mortality to estimate the impact of air pollution on human health. They attempted further to quantify the economic losses attributable to those effects. Similarly, Kneese and Schulze (1977) used cross-sectional data for sixty cities in the United States in an effort to identify environmental factors that may show correlations with cancer mortality. This appendix extends the results of that study, which showed a correlation between cancer and nitrite-containing foods, to include data on ingestion of nitrite, nitrate, vitamin C (ascorbic acid), and other dietary factors such as protein, fat and cholesterol.

LIMITATIONS OF THE STATISTICAL APPROACH

The usual caveats concerning the validity of statistical analysis of environmental factors in human health apply to these results, but several particular statistical problems also should be noted. First, bias resulting from the simultaneity of many equations is likely to be present.

When such simultaneity is not identified, valid interpretation of many of the commonly employed statistical forms is impossible; not only the magnitude but also the sign of many of the estimated coefficients might be different in the implicit, but unknown, reduced-form equations. Second, heteroskedasticity (nonconstant variance in the data set) is likely to be a serious problem in studies such as this. For example, the variation about some mean level of mortality rates in cities with high pollution levels is often greater than those with lower pollution levels. Since epidemiologic studies tend to use cross sectional data rather than time series data, this problem is likely to be pervasive. Third, multicolinearity is likely, especially in epidemiologic studies where explanatory variables are themselves highly correlated. This may be a serious problem for particular data sets. Thus, unless a known system of simultaneous structural equations can be specified--and our state of knowledge is unlikely to allow us to do so--and unless the data are homoskedastic (of constant variance), and the independent variables are uncorrelated, the meaningfulness of the estimated coefficients in terms of magnitude and even sign will be doubtful. Furthermore, statistical tests relating to the significance of the model are likely to be invalid, and choosing among alternative hypotheses about the impacts of environmental factors on health may be impossible.

In addition to these particular statistical problems, the inadequacy of statistical correlations for establishing causality must also be kept in mind. For example, if heart attacks are actually related to cigarette consumption, but smoking is correlated with coffee consumption for behavioral reasons, a spurious positive correlation might be shown between heart attacks and coffee consumption, especially if cigarette consumption is excluded from an estimated statistical relationship. In other words, correlation does not prove causation, and statistical hypothesis-testing can never confirm, but can only reject, a maintained hypothesis.

Turning to a more relevant example, if most human nitrite ingestion is through consumption of cured pork products and if the largest source of exposure to nitrosamines is through formation in vivo from nitrite and amines, one might suspect that cancer mortality and consumption of cured pork would be correlated. Such a correlation has been shown (Kneese and Schulze 1977); but the only valid conclusion is that we do not reject the hypothesis that pork consumption (and perhaps, in turn, nitrite ingestion) is related to human cancer. If, alternatively, one accepts the maintained hypothesis on *a priori* grounds, and no bias exists in the estimation procedure, regression analysis using ordinary least squares can give a best linear estimate of the actual relationship in the sample population between, for example, cancer mortality and a dietary factor such as nitrite ingestion. However, regression analysis cannot prove that a causal relationship exists.

With these caveats in mind, we now turn to construction of the data used in this analysis.

CONSTRUCTION OF THE DATA SET

The variables used in the regression analysis may be grouped into four categories: (1) cancer mortality, (2) socioeconomic factors, (3) air and water pollutants, including radiation, and (4) nutrients, dietary factors and lifestyle variables, including cigarette smoking. In all, data for 60 cities on some three dozen potential factors in cancer mortality were included. Table B.1 describes a selected set of the variables and indicates the sources of the data.

In this analysis, the index of cancer mortality employed was the aggregate rate for all body sites, although several subcategories also were analyzed, including digestive, respiratory, breast, genital, urinary, leukemia, and other cancers. Socioeconomic factors tested include the change in population from 1960 to 1970, the percent non-white population, and the median age. Not included in Table B.1, but also tested, were median age raised to various powers, median income, employment in primary metals industries, and employment in chemicals and allied industries. Air and water quality variables not shown in Table B.1 included atmospheric nitrates and nitrogen dioxide, and nitrates in drinking water; particulate air pollutants, beta, ultraviolet and cosmic radiation, and water hardness were also tested.

Nutrients and dietary factors tested included nitrite, nitrate, saturated fatty acids (in animal products), protein (animal), cholesterol (animal), fiber, calories, vitamin A, and vitamin C (in fruits and vegetables eaten fresh). In addition, coffee, alcohol, and cigarette consumption patterns were tested. Cigarette consumption was estimated from a cigarette tax revenues for each state in which a sample city was located; the result is thus a state-wide average that includes rural populations. Per capita cigarette consumption was estimated using the total state population, although this might be improved by using the population over 16 years of age.

The procedure used to construct the dietary data sets was somewhat involved. Food consumption estimates were first constructed for each of the 60 cities, using data on a sample of 2832 urban households, distributed among eight income brackets, for four regions of the United States,

TABLE B.1 Variables Used in the Analysis of Environmental Factors in Cancer Mortality in 60 Cities in the United States, and Sources of Data

Variable		Year	Units	Mean	S.D.	Sources
CANC	Cancer Mortality	1972	deaths/1000	1.96	0.42	(1)
DPOP	Change in Population	1960-1970	%	4.71	18.46	(2)
NONW	Non-white Population	1969	fraction	0.23	0.15	(3)
MAGE	Median Age	1969	years	28.82	2.74	(4)
AMMN	Atmos. Ammonium	1966	$\mu g/m^3$	1.15	1.42	(5)
GAMA	Terres. Gamma Rad.	1958-1963	mrem/yr/cap	40.22	10.78	(6)
NTRI	Nitrites in Food	1955	g/yr/cap	1.27	0.14	(7) (8)(10)
NTRA	Nitrates in Food	1955	g/yr/cap	69.86	9.05	(7) (8)(10)
SFAT	Saturated Fatty Acids[a]	1955	g/yr/cap	16220.00	874.65	(8)(9)(10)
PROT	Protein[a]	1955	g/yr/cap	26557.00	1314.00	(8)(9)(10)
CHOL	Cholesterol[a]	1955	g/yr/cap	234.81	6.98	(8)(9)(10)
CVIT	Vitamin C[b]	1955	g/yr/cap	16.96	1.46	(8)(9)(10)
COFF	Coffee	1955	kg/yr/cap	5.82	0.70	(8) (10)
CIGS	Cigarettes	1956	packs/yr/cap	110.23	18.41	(11)

[a] Includes only animal products.

[b] Includes only fruits and vegetables eaten fresh.

SOURCES:

(1) National Center of Health Statistics. Vital Statistics of the U.S.: 1972, vol. II, Mortality, Part B, Tables 7-9.

(2) United States Bureau of the Census, U.S. Census of Population: 1970, Vol. 1-50.

(3) See (2). Tables 23, 27, 31.

(4) See (2). Table 24.

(5) United States Department of Health, Education and Welfare. Air Quality Data from the National Surveillance Network and Contributing State and Local Networks, 1966, Table 16.

(6) United States Environmental Protection Agency. Natural Radiation Exposure in the United States, 1972, Report No. ORP/SID 72-1, Table A-1, 1974 Reprint.

(7) White, Jonathan W., Jr., "Relative Significance of Dietary Sources of Nitrate and Nitrite", Journal of Agricultural and Food Chemistry, vol. 23, No. 5 (1975), Table VI, p. 890.

(8) United States Department of Agriculture. Household Food Consumption Survey, 1955, Reports Nos. 2-5.

(9) Watt, Bernice K., and Annabell L. Merrill. Composition of Foods: Raw, Processed and Prepared, United States Department of Agriculture, Agricultural Handbook No. 8, 1968.

(10) United States Bureau of the Census. U.S. Census of the Population: 1960, vol. I, Tables 140, 148.

(11) Tobacco Tax Council. Cigarette Taxes in the U.S., 1956, Table 15.

collected by the U.S. Department of Agriculture for 1955. The results are regionally-specific weighted averages of consumption of various foods by families in each income bracket, multiplied by the fraction of each city's population in each income bracket. Data for specific dietary factors were then generated by multiplying the consumption rates of 49 foods by their respective concentrations of a given substance, such as nitrite.

Several regional patterns are observable in the data resulting from this procedure. For example, people in Southern cities, at least in 1955, appeared to consume more nitrite and nitrate, but less protein, cigarettes, and alcohol than people of other regions. In the northeast, people consume less nitrite but more cigarettes than people of other regions.

RESULTS OF REGRESSION ANALYSIS

The independent variables chosen for inclusion in a regression analysis with cancer mortality were selected on the basis of several hypotheses that relate them, directly or indirectly, to cancer. The hypotheses of principal interest here, of course, are those concerning nitrite and nitrate in the environment and in the diet (see Chapter 9). The largest sources of direct ingestion of nitrite are lunch meats and cured pork; these products may also contain nitrate and preformed nitrosamines. Ascorbic acid may inhibit the formation of nitrosamines in vivo; if there were a significant negative relationship between ascorbic acid and cancer, therefore, it could lend some additional credence to the nitrite hypothesis. Other variables included on the basis of other hypotheses about factors in cancer mortality include cigarette smoking, and the amounts of protein and fat in the diet.

Table B.2 presents the equation that resulted from the inclusion of the variables listed in Table B.1. The negative coefficients for SFAT and CHOL are significant at the 95 percent level. This outcome was not expected; it may be speculated, however, that these variables contribute to competing causes of death, such as cardiovascular disease, and affect cancer mortality indirectly, by contributing to a lower median age in cities with high rates of cardiovascular mortality. This is an example of possible simultaneous equation bias. If the SFAT and CHOL variables are removed from the equation, COFF and NTRA become insignificant ($t \leq 1.00$). Table B.2(b) presents the equation with all four of these variables removed.

Table B.3 presents a correlation matrix for all variables with correlations ≥ 0.80. The only notable multicolinearity problems are those between dietary

TABLE B.2 Regression Equations Used in the Analysis of Environmental Variables and Cancer Mortality[a]

(A) Regression equation that includes all of the variables listed in Table B.1.

$$\text{CANC} = \underset{(-3.17)}{-8.500} - \underset{(-1.97)}{0.00438}\ \text{DPOP} + \underset{(2.26)}{0.620}\ \text{NONW} + \underset{(7.33)}{0.101}\ \text{MAGE} + \underset{(2.50)}{0.0661}\ \text{AMMN}$$

$$+ \underset{(0.54)}{0.00194}\ \text{GAMA} + \underset{(3.32)}{4.688}\ \text{NTRI} + \underset{(3.05)}{0.000687}\ \text{PROT}$$

$$\underset{(-2.21)}{-\ 0.204}\ \text{CVIT} + \underset{(1.20)}{0.00271}\ \text{CIGS} + \underset{(0.96)}{0.0207}\ \text{NTRA}$$

$$\underset{(-1.57)}{-\ 0.000642}\ \text{SFAT} - \underset{(-1.58)}{0.0380}\ \text{CHOL} + \underset{(2.13)}{0.710}\ \text{COFF}$$

$R^2 = 0.787$ D.F. = 46

(B) Regression equation with factors for saturated fatty acids, cholesterol, coffee, and nitrates in diet excluded.

$$\text{CANC} = \underset{(-4.08)}{-9.593} - \underset{(-2.32)}{0.00470}\ \text{DPOP} + \underset{(1.49)}{0.332}\ \text{NONW}$$

$$+ \underset{(7.23)}{0.0979}\ \text{MAGE} + \underset{(2.63)}{0.0651}\ \text{AMMN} + \underset{(1.26)}{0.00418}\ \text{GAMA} + \underset{(4.07)}{2.69}\ \text{NTRI}$$

$$+ \underset{(3.25)}{0.000338}\ \text{PROT} - \underset{(-3.21)}{0.249}\ \text{CVIT} + \underset{(1.17)}{0.00258}\ \text{CIGS}$$

$R^2 = 0.764$ D. F. = 50

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[a] Numbers in parentheses are correlation coefficients (t values).

TABLE B.3 Correlation Matrix for Variables Having Correlations ≥ 0.80

	NTRI	NTRA	SFAT	PROT	CHOL	FIBR	CALO	VITA	VITC	COFF	ALCO
Nitrite	1.0										
Nitrate	.68	1.0									
Sat. Fat	-.03		1.0								
Protein	-.57	-.76	.82	1.0							
Cholesterol	-.03		.74	.72	1.0						
Fiber			.86	.80	.86	1.0					
Calories	.86						1.0				
Vitamin A	-.75	-.84		.95		.72		1.0			
Vitamin C	.06		.93	.75	.86	.81			1.0		
Coffee	-.40	-.79	.91	.93	.66	.88		.89	.78	1.0	
Alcohol	-.69	-.89	.73	.94		.74		.98			1.0

variables. Of these, the most important are between PROT and each of VITA, COFF, and ALCO, and between VITC and SFAT (see Table B.3). Considered as alternatives, however, these other variables do not test out significantly in the equation. Vitamin C, however, loses its significance if either NTRI or PROT is removed from the equation. This was not surprising, since each of these latter variables explains a substantial portion of the residual variation in cancer mortality.

DISCUSSION

This regression analysis shows strong statistical associations between cancer mortality and both nitrite and protein in the diet. In both regressions, nitrite is the second most significant of the explanatory variables tested, with t values that exceed the 99 percent confidence level; only the median age of the population correlates more strongly with cancer mortality. In addition, the analysis shows a strong negative correlation between vitamin C in the diet and cancer mortality.

It must be emphasized again that correlation does not prove causation, and that spurious results are often found when unknown colinearity exists. Nevertheless, the hypotheses presented in Chapter 9 concerning the possible roles that nitrate, nitrite, and vitamin C in the diet may play in the development or prevention of human cancer cannot be rejected on the basis of this analysis.

If it is accepted as an assumption for further analysis that those hypotheses are valid, and *if* the regressions presented here are not biased, the coefficients specified in Table B.2 can be used to estimate the incremental risk of cancer posed by nitrite in the diet. For instance, an earlier analysis (Kneese and Schulze 1977) showed a strong positive correlation between cancer mortality and consumption of pork products. They calculated that the association with pork consumption was related to a cancer mortality rate of 753 per 100,000 people per year, or nearly 113,000 cancer deaths in the urban population of the United States each year (see discussion in Chapter 11). Such an estimate of risk is almost certain to be erroneous, however, since many variables that affect cancer mortality are unknown or unquantifiable, and the small number of factors that could be included in the analysis is extremely unlikely to include all of the important determinants of variations in cancer risks among cities. On the other hand, the magnitude of the excess mortality correlated with diet is great enough to suggest that further research of this sort could be fruitful, both to develop and test hypotheses and to illuminate more clearly the problems of colinearity.

One result of this analysis that bears further examination is the relatively weak correlation (below the 95 percent confidence level) between nitrate in the diet and cancer mortality. Because dietary nitrate may be a source of nitrite formed in vivo (see Chapter 9 and Appendix C), a stronger correlation might have been expected.

A problem that greatly complicates an analysis of this sort is the long latent period that characteristically occurs between initial exposure to a carcinogenic agent or process and the appearance of human cancer or mortality from cancer. Thus, it is probably most appropriate to examine correlations between dietary (and other) variables as they were in the 1950s, and cancer mortality in the 1970s. For example, Kneese and Schulze (1977) showed a strong correlation (t=2.36) between consumption of pork in 1959 and cancer mortality in 1972; however, when data for pork consumption in 1969 were used, there was no significant correlation. If data appropriate to the time lags that may be involved are not available, the results of regression analysis are likely to be even less certain. Beyond this, however, there is inadequate medical/biological understanding of the basis for the latent period in cancer, and knowledge is not available to suggest what amount of lag time would be appropriate to include when considering particular kinds of cancer or particular carcinogens.

Finally, if the correlations shown here are accepted *a priori* as reflecting valid biological hypotheses of causation, and if the absence of a more complex analysis that could refine the relationships among many more variables is recognized, the coefficients imply that a very large rate of cancer mortality is associated with dietary nitrite. In contrast, Appendix C develops estimates of risk that are based on available biological data and models, and the result, even with a set of assumptions about exposure to nitrosamines that probably are gross overestimates, is a much smaller risk of cancer mortality. It is impossible to resolve this divergence of results at present. The analyses in both of these appendices go beyond the limits of current knowledge and into the realm of educated speculation. While we believe such exercises are useful, it must be left to future research to reduce the uncertainties and determine what role (if any) nitrate and nitrite may in fact play in contributing to human cancer mortality.

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APPENDIX C

QUANTITATIVE ASSESSMENT OF THE RISK OF HUMAN CANCER ASSOCIATED WITH EXPOSURE TO NITRATES, NITRITE, AND NITROSAMINES IN THE ENVIRONMENT

Perhaps the most critical element in policy decisions related to toxic substances in the environment is assessment of the potential hazards to human health related to exposure to ambient levels of the toxic contaminants. Unfortunately, however, the scientific data base is nearly always inadequate to support truly quantitative estimates of risk. In a typical case, there are at least four major areas of uncertainty:

(1) a lack of adequate information about the exposures that occur in human populations at environmental levels of the contaminant;

(2) a lack of dose-response data in humans to support projections of the effects of likely levels of exposure;

(3) a comparable lack of dose-response data, even in laboratory animals, at the very low levels of exposure that commonly occur in the environment; and

(4) a lack of understanding of the interactions and influences that environmental variables and characteristics of the exposed population may have on the effects of the contaminant.

The state of scientific knowledge at present makes it unlikely that these uncertainties can be eliminated. However, it is possible to simplify the analysis by making a numer of (often arbitrary) assumptions. For instance:

(1) "typical" exposure levels can be calculated from limited data, or can be estimated arbitrarily to encompass what appears to be a reasonable range.

(2) dose-response curves derived from animal studies can be used as analogs to estimate human responses.

(3) the dose-response curve can be extrapolated, using best scientific judgment concerning its probable form, from

known responses at high doses to estimated responses at much lower doses.

(4) for lack of any sounder choice, the influence of confounding variables can simply be left out of the calculations.

Estimates of risk based on such an approach have increasingly been attempted: for example, see the recent assessment by the National Research Council of halomethanes in drinking water (NRC 1978). The results, while crude, have some value in decision making, if only to place in perspective the hazards of pollutants whose toxic properties are known qualitatively (e.g., mutagenic, carcinogenic). Quantitative assessments of this sort, however, are no stronger than the structure of assumptions on which they rest. Because many of the assumptions are merely pragmatic and have no convincing scientific basis, risk estimates of this type cannot be accepted as conclusive results. They should instead be viewed as initial attempts that are subject to revision as better information becomes available.

This appendix presents a crude attempt to assess the potential risk of cancer that may result from environmental exposures to nitrates, nitrite, and nitrosamines. The discussion that follows devotes as much attention to the gaps in the data base and to the nature of required assumptions as it does to the projected quantitative estimates of risk.

EXPOSURE LEVELS

A prerequisite to an estimate of the carcinogenic risk related to nitrates is an estimate of human exposure to carcinogenic N-nitroso compounds. Chapter 9 reviewed sources of such exposures, and concluded that the formation of nitrosamines in vivo from ingested or inhaled precursors is probably the largest source of exposure in the general population. In most cases, the major source of nitrate (and of pre-formed or subsequently-formed nitrite) is foods, but a relatively small number of people using high-nitrate water supplies (usually private wells) may comprise an important subset of unusually high exposures. People may also be exposed to preformed nitrosamines in polluted air, drinking water, certain foods, and tobacco smoke (see Chapter 9). Accurate measurements of typical doses of either preformed nitrosamines or of nitrosamines formed in vivo from ingested or inhaled precursors are simply not available.

For this analysis, three different approaches were used to calculate exposures to N-nitroso compounds, particularly to dimethylnitrosamine (DMN). First, actual blood levels of nitrosamines measured by Fine et al. (1977b) in a single human subject were used to estimate exposures from diet and from in vivo formation. Second, available estimates of ingestion of nitrate and nitrite in the United States (see Chapter 9) were combined with some assumptions about rates of nitrite formation and of nitrosation in vivo to produce estimates of possible exposure to DMN. Third, the limited data available on DMN levels in ambient air near an industrial source of DMN emissions (Fine et al. 1977a) were used to estimate exposures of people living near such a source.

Calculation from Measured Blood Levels of DMN

Fine et al. (1977b) measured nitrosamine levels in the blood of one human subject, before and after he ate a lunch consisting of spinach, cooked bacon, tomato, bread, and beer. Before lunch, the subject was estimated to have a total of 2 μg DMN in his blood; the DMN content of the lunch itself was 1.6 μg. After lunch, the estimated DMN in the subject's blood rose to 4.35 μg, implying that about 0.75 μg of DMN was formed in vivo, presumably from nitrate/nitrite in the spinach and bacon and from amines, reacting in the stomach. Diethylnitrosamine (DEN) was also measured before lunch at 0.51 μg in total blood, and after lunch at 2.6 μg, implying in vivo formation of about 2.1 μg. When the subject avoided foods that contained nitrate and nitrite, the DMN content of his blood was below the level of detectability with the instruments used.

For purposes of this analysis, we assume that the subject was typical in terms of his capacity for in vivo formation of nitrosamines, and that the lunch represents a typical (in nitrate, nitrite, and nitrosamine content) meal consumed once a day by the average individual. The resulting estimated daily exposure of about 1.7 μg of preformed nitrosamines (DMN plus DEN) plus about 2.8 μg of nitrosamines formed in the body represents a dose rate of about 0.06 μg/kg of body weight per day in a 70 kg adult; this can also be expressed as an average exposure equivalent to approximately 2.2 parts per billion of total nitrosamines in the diet, assuming 2 kg/day of ingested foods and beverages.

Estimation from Theoretical Calculations

Exposure to nitrosamines can also be calculated from estimates of exposure to nitrate and nitrite. The average daily intake of nitrate for residents of the United States has been estimated at about 100 mg/day, as nitrate (White 1975; see Chapter 9, Table 9.1). A relatively small number of individuals using high-nitrate well waters could ingest considerably greater amounts of nitrate. If it is assumed that 10 percent of the ingested nitrate is converted to salivary nitrite (see Chapter 9), and that an additional 2 mg of nitrite are ingested daily in cured meats by the average person, typical daily nitrite exposure can be estimated at 12 mg (as NO_2^-).

As discussed in Chapter 2, the rate of nitrosation of amines in the gastric juice is proportional to the square of the nitrite concentration. However, the rate of reaction also depends on the pH in the stomach, the amounts of and basicity of the amines involved, and the presence of catalysts, such as thiocyanate, and inhibitors, such as ascorbate. Because the combined influence of these (and possibly other) factors is not reliably known, it is not possible to predict accurately the rate of formation of nitrosamines following exposure to a specific dose of nitrite.

Experimental data on rates of in vivo nitrosation, however, can provide some perspective on this question. Mysliwy et al. (1974) demonstrated that the nitrosation of pyrrolidine occurs in the dog's stomach much more rapidly than is expected from simple kinetic expressions. After intubation of 725 μmoles of sodium nitrite and 10 μmoles of pyrrolidine, the maximum amount of nitrosopyrrolidine detected in the stomach at any one time was approximately 1.4 μmoles. Thus, at least 0.2 percent of the administered nitrate could be accounted for at a single instance as the nitrosamine. Because absorption into the blood is rapid and other losses of the nitrosamine from the stomach may occur, 0.2 percent represents a mimimum estimate for the nitrosation of this particular secondary amine in the dog's stomach.

For this analysis, it is arbitrarily assumed that at typical daily doses the rate of formation of nitrosamines (as DMN) is equal to 5 percent of the amount of nitrite present. At this rate of nitrosation, 13 μmoles (962 μg) of DMN would be formed from a dose of 261 μmoles of nitrite. However, this calculation is likely to be a substantial overestimate, because in actuality the daily dose of nitrite is not present in the stomach at one time, but is spread throughout the day (see Chapter 9).

The daily dose of 962 μg DMN, calculated by this method, can be expressed as a rate of about 14 μg/kg of body weight per day, or as an average dietary content of 481 ppb DMN for a "typical" adult. This estimate is more than 200 times higher than the estimate calculated above from measured blood levels. The first estimate did not account for possible losses of nitrosamines from the blood by excretion, exhalation, or cellular uptake, and may underestimate the actual daily dose; and as discussed above, the second calculation is probably an overestimate. The two estimates probably reflect reasonable boundaries, given the inadequacy of current knowledge, for assumptions about average exposures to nitrosamines.

Estimation of Exposures by Inhalation of Nitrosamines

Fine et al. (1977a) measured DMN levels in the air of Baltimore, Md., in the vicinity of a chemical factory that was manufacturing dimethylhydrazine. Average DMN concentrations in air on the site of the manufacturing plant were 11.6 $\mu g/m^3$; in neighborhoods near (within 800 m of) the factory, DMN levels averaged 1.07 $\mu g/m^3$; and at several sites in downtown Baltimore, average concentrations ranged from 0.03 to 0.10 μg DMN/m^3. An individual breathing 20 m^3 of air per day would be exposed to 21.4 μg DMN/day in the neighborhood of the source, or to from 0.6 to 2.0 μg DMN/day in the city at large. An industrial worker who spent part of the day (and breathed 10 m^3 of air in that period) on the plant property, and spent the remainder of each day at locations outside the immediate vicinity of the plant, would inhale about 117 μg DMN/day. (Workers in some specific sites within the factory might be exposed to much higher doses, however; see Fine et al. [1977a] for more detailed breakdown of DMN levels in air within the plant's boundaries.) Assuming that all of the inhaled nitrosamine is absorbed, the "average" population exposure by this route is below the lower estimate of doses from the diet and in vivo formation. Only a limited number of people, in the neighborhood of or on the site of such an industrial source, would seem likely to derive a larger part of their exposure from inhalation. Furthermore, the "neighborhood" exposures calculated here are substantially smaller than the greater of the estimated exposures from in vivo formation.

Table C.1 summarizes the possible exposures calculated by the three approaches.

DOSE-RESPONSE RELATIONSHIPS

Neither epidemiological nor toxicological data exist to define a dose-response curve for the potential induction of cancer in humans by any of the N-nitroso compounds that are known to be carcinogenic in laboratory animals. Although several experiments on various species of animals are reviewed in Chapter 9, only one study (Terracini et al. 1967) provides sufficient data to derive a dose-response curve. Results of that study, showing the induction of liver cancer in female rats by dietary DMN, are summarized in Table C.2.

TABLE C.1 Calculated Exposures to Nitrosamines in Several Cases[a]

Route of Exposure	Basis of Calculations	Exposures to Nitrosamines		
		Total dose, μg DMN/day	μg DMN/kg of body weight/day	Equivalent dietary concentration, ppb DMN
Diet plus in vivo formation	Measured levels in blood	4.5[b]	0.06[b]	2.2[b]
In vivo formation	Theoretical assumptions	962	14	481
Inhalation: Ambient air	Measured air concentrations in Baltimore, Md.	0.6-2.0	0.01-0.03	--
Neighborhood of Source	"	21.4	0.3	--
On site of Source	"	117	1.7	--

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[a] See text for discussion of the basis of calculations.

[b] Includes both DMN and DEN; see text.

TABLE C.2 Dose-Response Data from Terracini et al. (1967) on the Production of Liver Cancer by Dimethylnitrosamine in the Diet of Female Rats

Lifetime exposure to DMN (ppm in diet)	Percent of rats that developed liver cancer
0	0
2	0
5	7.3
10	40
20	65.2
50	83.3

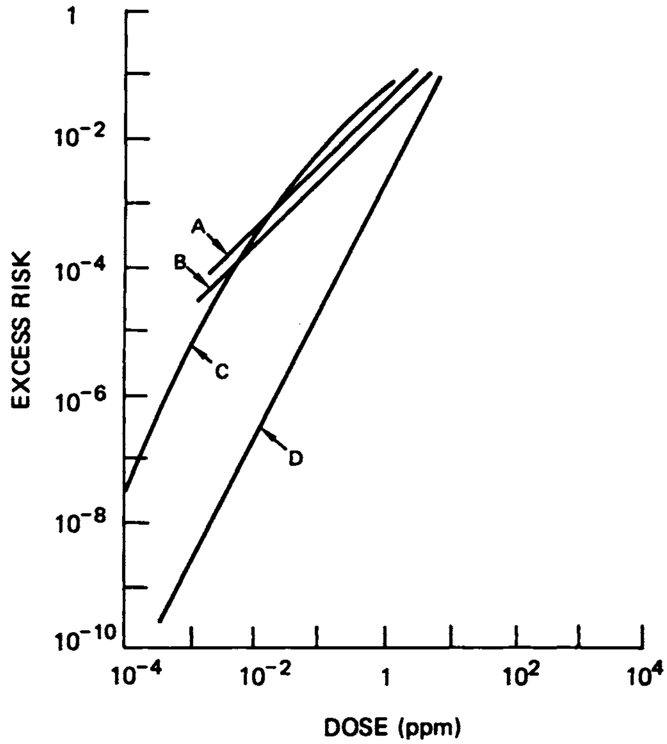
Guess et al. (1977) used the data of Terracini and coworkers to plot dose-response curves for DMN; the results of their plots are shown in Figure C.1. The curves represent actual calculated excess risk or estimated upper limits on excess risk (i.e., risk above the spontaneous incidence) of cancer in test animals, derived by several different statistical models. There are some toxicological data showing that inhaled nitrosamines can produce tumors at a number of sites in test animals (see Chapter 9), but not enough information is available to plot a dose-response curve for inhaled DMN.

ESTIMATION OF RISK OF HUMAN CANCER FROM NITROSAMINES

The dose-response curves in Figure C.1 can be used to estimate the risk of liver cancer posed by the calculated exposures to nitrosamines. The potential for cancer incidence at the doses given in Table C.1 is estimated here by comparing the calculated exposures, expressed as equivalent concentrations of DMN in diet, with the dietary exposures used in the rat studies. The extrapolations were conducted using the multi-stage model described by Guess and Crump (1976), represented by Curve D in Figure C.1.

According to this model, the excess (additional) lifetime risk of liver cancer represented by exposure to an average of 2.2 ppb DMN in the diet is about 1×10^{-8}; that is, roughly one expected case of cancer in 100 million individuals exposed to such doses for their entire lifetimes. On the other hand, the calculated dose rate of 0.481 ppm DMN in the lifetime diet represents an excess risk of about 6×10^{-4}, or 60 cancers per 100,000 exposed population. (Since this dose rate is about one-tenth of the dose that produced tumors in 7.3 percent of the rats exposed [see Table C.2], a risk estimate of this magnitude is not surprising.)

If it is assumed that humans metabolize DMN the same way rats do, and that the two species are equally sensitive to the induction of tumors by this compounds, these calculations can be taken as crude estimates of the risk of liver cancer in humans represented by the exposures to DMN presented in Table C.1. The current incidence of liver cancer in the United States is about two cases per 100,000 people per year, or about 140 cases in 100,000 70-year lifetimes. The calculated risks from estimated exposures to nitrosamines could therefore be expressed as the equivalent of from about 7×10^{-4} to 43 percent of the current rate of liver cancer.



SOURCE: Modified from Guess et al. (1977).

FIGURE C.1 Dose-response relationships for liver cancer in female rats given dimethylnitrosamine in diet, derived by Guess et al. (1977) from data of Terracini et al. (1967). Curves A, B, and C represent upper confidence limits for added risk of cancer, determined by different methods, and curve D is the estimated added risk according to the model described by Guess and Crump (1976).

DISCUSSION

The wide disparity in the two estimates of risk presented here is most directly the result of the wide difference in the estimates of human exposures to nitrosamines in the diet and formed in vivo. While the upper estimate of risk represents a rate of cancer incidence equivalent to nearly half of the current human liver cancer rate, it must be recalled that the estimated exposure on which that risk estimate rests was calculated from some arbitrary theoretical assumptions that are quite tenuous. Furthermore, since the slope of the upper portion of Curve D in Figure C.1 is rather steep, the outcome of this exercise is highly sensitive to the magnitude of the estimated dose. That is, a change of only a factor of three in the dose estimate produces approximately an order-of-magnitude change in the estimate of added cancer risk. As was noted earlier, the smaller estimate of dose, although it is derived from actual measured nitrosamine levels in human blood, may be an underestimate; and the assumptions used to calculate the larger dose make it highly likely that this is an overestimate. Either of the dose estimates used here might easily be in error by a factor of ten; consequently, it is not possible to know whether either calculated risk is accurate even within two orders of magnitude. To determine where between these two extremes a more credible estimate of the risk might lie requires much more information than is available about actual human exposures to nitrosamines.

Several other limitations specific to this analysis also contribute to the uncertainty of the resulting risk estimates. This analysis was limited to an assessment of the risk of a single and relatively uncommon cancer, liver cancer, associated with a single compound, DMN. Experimental results reviewed in Chapter 9 have shown that many different N-nitroso compounds can produce tumors in many different sites, and that DMN can induce cancers at sites other than the liver. However, the inadequacy of dose-response data in those cases precludes comparable estimates of risk for other cancers and other N-nitroso compounds. Nevertheless, several other N-nitroso compounds with varying degrees of potency and with different target organs could also be formed from nitrite in vivo. The possibility exists, therefore, that the estimates of risk of DMN-induced liver cancer represent only a fraction of the actual risk. Also, the risk is assessed here in terms of lifelong exposure to an estimated average daily dose, while real exposures are widely variable, and less-than-lifelong exposure undoubtedly entails some risk. However, the long latent period inherent in the development of most human cancers, and the nature of the data base from animal tests, make it impractical to attempt to estimate risks on a less-than-lifetime basis. Finally, it is worth noting again that scientific support is lacking for some necessary assumptions, such as that the carcinogenic potency of nitrosamines is equivalent in rats and in humans, or that constant high exposures in a controlled laboratory test can be compared with typical intermittent human exposures in a much more variable environment.

In summary, numerous uncertainties inherent in this analysis can be identified, and the likely direction of the influence of some factors not accounted for can be hypothesized, but quantitative adjustments of the risk estimates cannot be made with available knowledge. The absolute estimates of risk made here cannot be accepted as conclusive; they are instead only educated speculations, made primarily to illustrate current methodologies and information gaps. Furthermore, the differences between these estimates and the estimated risks of cancer mortality described in Appendix B, calculated by statistical correlation, cannot be resolved. The chief value of each analysis is its indication of the severity of limitations that the current lack of data imposes on efforts to quantify risks, and of the nature of needed research to support improved risk assessments.

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APPENDIX D

RESEARCH NEEDS

Each chapter of this report identifies areas in which scientific knowledge is incomplete; often the lack of information is an important consideration in the public policy decision making. Although many policy choices will be made before some relevant scientific questions can be resolved, research could help significantly to narrow critical uncertainties.

This Appendix presents a list of critical research topics compiled at the panel's workshop meeting. Most of the topics listed are rather broad information needs. The questions listed are for the most part feasible for study with current knowledge and available techniques. Because of the limited time available and the secondary nature of this task in relation to the principal work of the panel, no attempt has been made to suggest funding levels, institutional arrangements, or specific research approaches that might be required to meet the identified information needs. Also, it has not been possible to note the many instances where current research efforts are directed toward answering questions listed.

SUGGESTED TOPICS FOR RESEARCH

The research topics that follow are grouped according to major problem areas. In most cases, the research needs on a given issue constitute a multidisciplinary package. We believe that an integrated, multidisciplinary approach to research is required, both to support the synthesis of fragmented information and to stimulate a balanced attack on critical issues.

Potential Impacts of Nitrogen Fixation on the Stratospheric Ozone Layer

To assess the threat to the ozone layer represented by human activities that fix nitrogen, information is needed on the following topics:

(1) Production rates and residence time for N_2O in the global atmosphere.

(2) Extent and mechanisms of production and/or removal of N_2O by the oceans.

(3) Production of N_2O in soils: rates, extent, and factors that affect N_2O/N_2 ratios of denitrification in different soils; extent of absorption of N_2O by soils; and significance of nitrification in N_2O production.

(4) Amounts and N_2O/N_2 ratios of denitrification in wetlands and sediments of shallow ocean areas.

(5) Role of combustion of fossil fuels and biomass as a source of fixed nitrogen and, directly and indirectly, of N_2O.

(6) Contributions of nonsymbiotic nitrogen fixation in terrestial systems.

(7) Importance of gaseous fluxes in local, regional, and global cycles, especially the deposition of NO_2, NH_3, and nitrate aerosols as contributions to soil or aquatic systems.

(8) Net effects, especially in terms of production of N_2O, of wastewater treatment systems that emphasize denitrification; and development of methods to minimize N_2O production.

(9) Projections of long-term trends in human activities that fix nitrogen.

(10) Biological and ecological effects of increased uv irradiation, and measures that might be taken to protect sensitive organisms from increased exposure to uv radiation.

The Extent and Damages of NO_x Contributions to Acidity of Precipitation

Future assessments of this issue will require expanded information through research on the following topics:

(1) Basic chemical and physical mechanisms in the generation and transport of NO_x, the formation of acidic aerosols, and the acidification of precipitation.

(2) Relative contributions of sulfur oxides and nitrogen oxides to acidity of precipitation, especially on a regional scale.

(3) More detailed information on the extent and severity of acid precipitation, on a national basis. Needs include both several years of trend data from a nationwide precipitation monitoring system and occasional intensive surveys once baseline trends are known.

(4) More detailed monitoring of acidity of precipitation within areas, seasonally, and within rainstorms.

(5) Role of volatilization of ammonia and other soil-derived bases in neutralizing the acidity of rainfall.

(6) Increased quantification of the relative contributions of stationary combustion sources and regional (i.e., urban mobile combustion) sources to the acidification of rainfall.

(7) Examination of alternative control strategies based on (6), which might include zoning or industrial siting restrictions.

(8) Evaluation of control technologies to determine the effects of control of one kind of emission (e.g., SO_x or NO_x) on other emissions.

(9) Animal studies on the acute and chronic toxicity of inhaled organic and inorganic nitrate aerosols.

(10) Effects of acidic precipitation on the productivity and stability of terrestrial and aquatic ecosystems.

(11) Extent of damages to structures and materials exposed to acidic aerosols and acidic precipitation, and the effectiveness of protective measures to prevent such damages.

(12) Contributions of sources other than combustion, such as oxidation of ammonia, to the acidity of precipitation.

(13) Evaluation of the effectiveness of measures (such as liming of soils or lakes) that could mitigate the effects of acidic precipitation.

Water Quality Impacts of Human Manipulation of the Nitrogen Cycle

Research needs in this problem area include:

(1) Site-specific (as opposed to state or regional) curves for crop yield response to nitrogen fertilizers under varying management conditions and weather patterns.

(2) More precise data on actual rates of nitrogen fertilizer consumption at the watershed level.

(3) Additional studies of the fate of nitrogen fertilizers in soils, based on actual field situations.

(4) Long-term influences of changing land use, tillage, and cropping patterns on the transport of nitrogen into surface, subsurface, and ground waters.

(5) Improved modeling of fluxes, sinks, and reservoirs of fixed nitrogen in managed agricultural ecosystems, on local to regional scales.

(6) Further evaluation of the health hazards posed by nitrate in water, including improved quantification, through laboratory and epidemiological studies, of dose-response functions in the production of methemoglobinemia and possible behavioral effects, both in humans and in livestock. (See also section on the role of nitrates in risks of cancer, below.)

(7) Factors that control eutrophication in marine and estuarine systems, with emphasis on the role played by nitrogen derived from human activities.

(8) Elucidation of the extent to which nitrogen is the limiting nutrient in moderately eutrophic lakes, and of the need for or potential effectiveness of control of nitrogen to improve water quality.

(9) Improved mass-balance models for nitrogen in lakes.

(10) Alternative approaches for the prevention of exposure of sensitive populations to excessive nitrate in drinking water.

(11) Further development of cost-effective wastewater treatment processes that emphasize denitrification to N_2.

(12) Further development of methods to increase the efficiency of use of fertilizer nitrogen, including a total ecosystem management systems approach.

(13) Further evaluation of the effectiveness and the economic and societal impacts of management measures to control potential nitrate pollution from fertilizer use, land disposal of wastes, irrigation return flow, and stormwater runoff from urban lands, livestock areas, and forests.

Potential Carcinogenic Hazards Associated with Nitrates in the Environment

Research needs within this problem area include:

(1) Animal studies to determine quantitatively the relationships between chronic ingestion or inhalation of nitrate, nitrite, and other precursors and the *in vivo* formation of N-nitroso compounds.

(2) Clinical studies of populations of humans exposed to ingestion or inhalation of nitrates, nitrites, and other precursors, to determine the extent to which *in vivo* nitrosation may occur.

(3) Animal studies to provide more quantitative dose-response data for the formation of malignant tumors at low doses of N-nitroso compounds.

(4) Epidemiological studies of the comparative incidence of cancer mortality and morbidity in populations exposed to different levels of preformed N-nitroso compounds in air, water, or foods.

(5) Similar epidemiological studies comparing populations with differing exposures to precursors of N-nitroso compounds, especially nitrate in drinking water and nitrite in foods.

Regional Management Strategies for Nitrate-Related Environmental Problems

Development and implementation of an effective management strategy to control many nitrate-related environmental impacts should most appropriately be carried out on a regional scale. The following kinds of research might be required to support such an approach:

(1) Development of criteria and monitoring systems to provide early warnings of nitrate-related impacts.

(2) Development of educational systems to inform appropriate decision makers of potential hazards.

(3) Design of alternative, regionally specific control strategies that can be implemented on timetables appropriate to the problems.

(4) Exploration of possible mechanisms to finance control measures and distribute costs among those that create the problems.

Other Research Needs

The following topics either apply to each of the problem areas above, or go beyond them:

(1) Further evaluation of the ranges in and significance of variations in the natural abundance of ^{15}N in ecosystems, on a world-wide basis.

(2) Economic assessment of potential damages to human health, ecosystems, and the non-living environment that may result from nitrates or other fixed nitrogen.

(3) General systems analysis to explore the interrelationships among control measures that would (a) reduce the rate of production of N_2O, (b) reduce inputs of nitrogen compounds to surface or ground waters, or (c) reduce the contributions of NO_x to acidity of precipitation. Such an analysis would require systematic study of all scales of the nitrogen cycle, and could rank major sources and transport pathways of fixed nitrogen in terms of priority for and feasibility of controls.