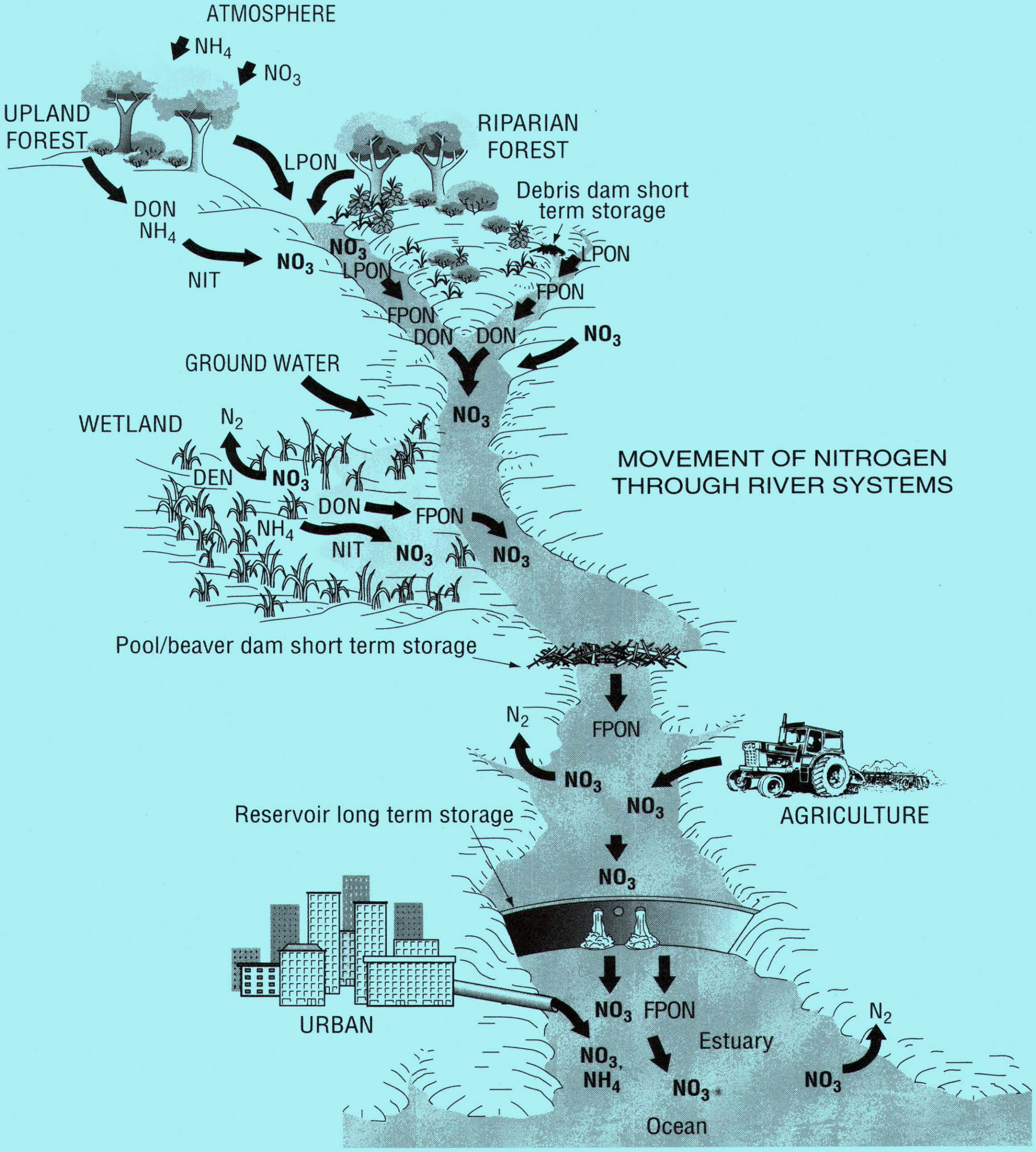
U.S. GEOLOGICAL SURVEY NITROGEN-CYCLING WORKSHOP
Denver, Colorado
October 30-November 2, 1995

U.S. Geological Survey
Open-File Report 96-477



U.S. GEOLOGICAL SURVEY NITROGEN-CYCLING WORKSHOP
Denver, Colorado
October 30 - November 2, 1995

Edited by Larry J. Puckett and Frank J. Triska

U.S. Geological Survey

Open-File Report 96-477

Reston, Virginia

1996

U.S. DEPARTMENT OF THE INTERIOR

BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY
Gordon P. Eaton, Director

MARCH 3, 1849

For additional information, write to:

Chief, National Water-Quality
Assessment Program
U.S. Geological Survey
Mail Stop 413
12201 Sunrise Valley Drive
Reston, VA 20192

Copies of this report can be purchased from:

U.S. Geological Survey
Branch of Information Services
Box 25286
Denver, Colorado 80225-0286

CONTENTS

APPENDIX

CONVERSION FACTORS AND ABBREVIATIONS

Divide	**By**	**To obtain**
	Length	
millimeter (mm)	25.4	inch (in.)
centimeter (cm)	2.54	
meter (m)	0.3048	foot (ft)
kilometer (km)	1.609	mile (mi)
	Area	
square meter (m^2)	0.0929	square foot (ft^2)
square kilometer (km^2)	2.590	square mile (mi^2)
	Volume	
liter	3.785	gallon (gal)
milliliter	3785	
	Flow	
cubic meter per second (m^3/s)	0.02832	cubic foot per second (ft^3/s)
liter per second per square kilometer[$(L/s)/km^2$]	10.93	cubic foot per second per square mile [$(ft^3/s)/mi^2$]
meter per kilometer (m/km)	0.1894	foot per mile (ft/mi)
liter per second (L/s)	0.06308	gallon per minute (gal/min)
cubic meter per second (ml/s)	0.04381	million gallons per day (Mgal/d)
	Hydraulic Conductivity	
meter per day (m/d)	0.3048	foot per day (ft/d)
	Transmissivity	
square meter per day (m^2/d)	0.09290	square foot per day (ft^2/d)

CONVERSION FACTORS AND ABBREVIATIONS--Continued

Physical and Chemical Water-Quality Units

Temperature: Water and air temperature are given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by use of the following equation:

$$°F = 1.8(°C) + 32$$

Specific electrical conductance of water is expressed in microsiemens per centimeter at 25 degrees Celsius (µS/cm). This unit is equivalent to micromhos per centimeter at 25 degrees Celsius.

milligrams per liter (mg/L) or micrograms per liter (µg/L): Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as weight (milligrams) of solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to one milligram per liter. For concentrations less than 7,000 mg/L, the numerical value is the same as for concentrations in parts per million.

millivolt (mv): A unit of electromotive force equal to one thousandth of a volt.

nephelometric turbidity unit (NTU): A measure of turbidity in a water sample, roughly equivalent to Formazin turbidity unit (FTU) and Jackson turbidity unit (JTU).

Other

Sea level: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)--a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called "Sea Level Datum of 1929."

U.S. Geological Survey Nitrogen-Cycling Workshop: Overview of Major Issues and Recommendations

By Larry J. Puckett and Frank J. Triska

Introduction

The global nitrogen cycle has been severely altered by mankind, and the long-term consequences of this alteration remain largely unknown. Annual amounts of nitrogen fixed industrially for fertilizer, emitted by fossil-fuel combustion and fixed agriculturally by leguminous crops, already exceed fixation by all natural processes combined (Vitousek, 1994). In parts of Europe, nitrate contamination is already severe, especially in low-lying, agriculturally dominated regions. These regions have been farmed for centuries using manure and for decades using high applications of inorganic fertilizer. As a result, nitrate concentrations in European surface waters commonly exceed 10 mg/L as N, the level considered safe by the U.S. Environmental Protection Agency (EPA) for drinking water. In 1987, the Danish government passed the "Action Plan on the Aquatic Environment" to reduce nitrogen discharge to the aquatic environment by 50 percent by 1994 (Kronvang et al., 1993). Similar programs have also been contemplated in Sweden and Germany.

Although nitrogen contamination is not as acute in the United States, nitrate contamination is common in rural ground water, and it is also increasing in surface waters. Smith, Alexander and Wolman (1987), using a 7-year data set from 300 surface-water locations, found a significant increase in the concentrations of nitrate at 116 stations and a decrease at only 27 stations. Nitrate increase was more widespread than any of 22 other water-quality parameters analyzed in their study. Nitrate concentration has increased 2.5-fold since 1960 at the mouth of our largest drainage, the Mississippi River Basin (Turner and Rabelais, 1991). Since 1945, fertilizer use, the most important source of nitrogen, has increased 20-fold to more than 11 million tons per year (Puckett, 1995). Recent projections suggest it will increase by 7 to 8 percent in 1996 and continue to increase in response to changes in the Farm Bill (Farm Chemicals, 1996). Because the inherent capacity for landscapes to assimilate massive nitrogen loading is unknown, the potential for future negative environmental consequences on the scale of those experienced in Europe is high.

Even at concentrations less than the EPA drinking water standard, nitrate contamination can be an important environmental concern due to its interaction with biota and other element cycles. Nitrate enhancement at one-tenth to one-half of the EPA standard can result in massive nuisance algal blooms with associated fluctuations of pH and dissolved oxygen. Diurnal fluctuations of pH may violate EPA or state standards due to these effects. Sloughing of algal mats and associated decomposition can deplete dissolved oxygen and promote fish kills. Taste and odor problems are other common factors affecting the recreational and consumptive use of nitrate-contaminated waters.

The U.S. Geological Survey (USGS), through its various water-quality programs, currently monitors nitrogen in the nation's surface and ground waters. For example, early nationwide reports from the National Water-Quality Assessment (NAWQA) Program may prove an important bellwether as application rates eventually exceed the landscape's capacity to assimilate nitrogen. This report summarizes the results of a workshop convened at the request of the Chief Hydrologist, to examine nitrogen-cycling research within the U.S. Geological Survey. The workshop was held October 30-November 2, 1995 in Denver, Colorado, and was designed to provide a forum for sharing of information, results, and knowledge among USGS scientists conducting investigations on any aspect of the nitrogen cycle. The goals of the workshop were to assess the state of our knowledge, the depth and breadth of our research on nitrogen cycling, and to develop recommendations and strategies to address nitrogen contamination as an emerging environmental problem.

Format

Workshop participants were solicited from all programs within the USGS--most attendees were scientists of the National Research Program (NRP) and District offices of the Water Resources Division (WRD). A total of 43 talks in 8 topical sessions were presented. Each session consisted of oral presentations of 20 minutes each, and ended with a 30-minute panel discussion. The panels defined the major points covered during the session and identified gaps in the state of the science. At the end of the workshop, participants from each session met in work groups to summarize the results of their session and to formulate recommendations for addressing important issues. The participants were requested to consider several specific questions that were designed to focus their discussions. The most important of these were:

1. What major issues concerning nitrogen-cycling processes remain unanswered?
2. What issues are likely to become important in the next five to ten years?
3. Among the issues identified in 1 and 2 above, where does the USGS stand with respect to our ability to address them, with respect both to resources and agency mission?

In addition to identifying issues, the participants were asked to make recommendations on USGS options for addressing these issues. The recommendations cover three topics:

1. Low-cost options that would consist primarily of increased cooperation and joint efforts among studies currently being conducted. This might also include plans for a series of publications (both technical and lay reader reports) on the state of our knowledge of nitrogen cycling and human influences on it.
2. Moderate-cost options to include recommendations for new personnel, equipment, or methods development. They might also include recommendations for joint studies among groups of scientists or as a part of existing programs.
3. Major-cost options to include new studies in fields not currently being investigated by the USGS. These might also include major task groups, or new programs and data collection efforts or strategies aimed at making new regional- or continental-scale statements about nitrogen cycling.

Major Issues

Integration Across Scales

Our lack of understanding of the linkages among the various controlling processes as we proceed from small-scale study areas to successively larger watersheds is one of the most poorly developed aspects of nitrogen-cycling theory (and most other water quality issues). This seemingly basic issue limits our ability to apply what we learn in small, relatively homogeneous research settings to the larger and more complex settings representing scales that affect human communities. Although there are numerous limitations due to gaps in our knowledge, there is also a wealth of data collected in years of monitoring and assessment studies, as well as specific research projects. All of these resources are underutilized from a system perspective. One important factor contributing to our inability to integrate across scales is that scientists working at small scales rarely have the opportunity to interact with those working at larger scales. Sampling methods and approaches often differ by scale even when analytical techniques are identical. Scientists interested in theoretical aspects are rarely interested in accessing and using large data bases to generalize their findings. Finding data in a usable format may be difficult and cumbersome.

Development of a simple, consistent, conceptual framework is a critical prerequisite for developing a watershed perspective in nitrogen cycling, identifying information gaps, synthesizing existing data, and proposing future programs. Such a framework must be able to cross spatial and temporal scales and serve as a guide wherein investigators can rapidly chart their position on the continuum, identify their research contribution, and determine gaps in nitrogen-cycling data at their site. A simple model based on the river continuum concept (Vannote and others, 1980) is shown in Figure 1. Although simplistic, this type of device can help develop an ecosystem-watershed approach, because it emphasizes linkages between the terrestrial and aquatic environment, upstream to downstream reaches, and freshwater to marine systems. Within this spatial continuum it also links hydrologic transport, retention (biological and physical), and biogeochemical transformation of contaminants.

The continuum begins in upland and riparian areas. Direct inputs are limited to large particulate organic nitrogen (LPON) such as leaf litter, interception of dissolved organic nitrogen (DON) as throughfall, and dissolved inorganic nitrogen (DIN) as ammonium and nitrate in precipitation. Hydrologic sources include subsurface transport of nitrogen via ground water to the river channel. In well-drained riparian zones nitrogen input is primarily in the form of DON and (or) nitrate. In wetland riparian areas nitrogen input is primarily as DON or ammonium. Retention in the upland includes biotic uptake into biomass and abiotic sorption to soils. Various forms of nitrogen may also be transformed microbially by nitrification (ammonium oxidation to nitrate in aerobic ground water), denitrification (nitrate reduction to nitrogen gas in anoxic ground water), and ammonification (ammonia production from decomposing organic matter). The above processes may alter the relative composition and concentration of various nitrogen forms during subsurface and surface-water transport along the river corridor.

In low order streams (1-2), important processes (as indicated by the pie diagrams) includes breakdown of LPON to fine particulate organic matter (FPON), nitrification (NIT), and a small amount of uptake by mosses and shade-adapted algae for benthic primary production (BPP). Nitrogen loads and concentrations are typically small in these environments. As stream order increases (3-5), large particulate sources gradually become less significant. Breakdown and recycling of particulates continue throughout the network as FPON directly enters the food web through invertebrate consumption. BPP by algae and macrophytes are an important sink for dissolved nitrogen. Ammonium formed from decomposition of particulate organic nitrogen (PON) is readily nitrified.

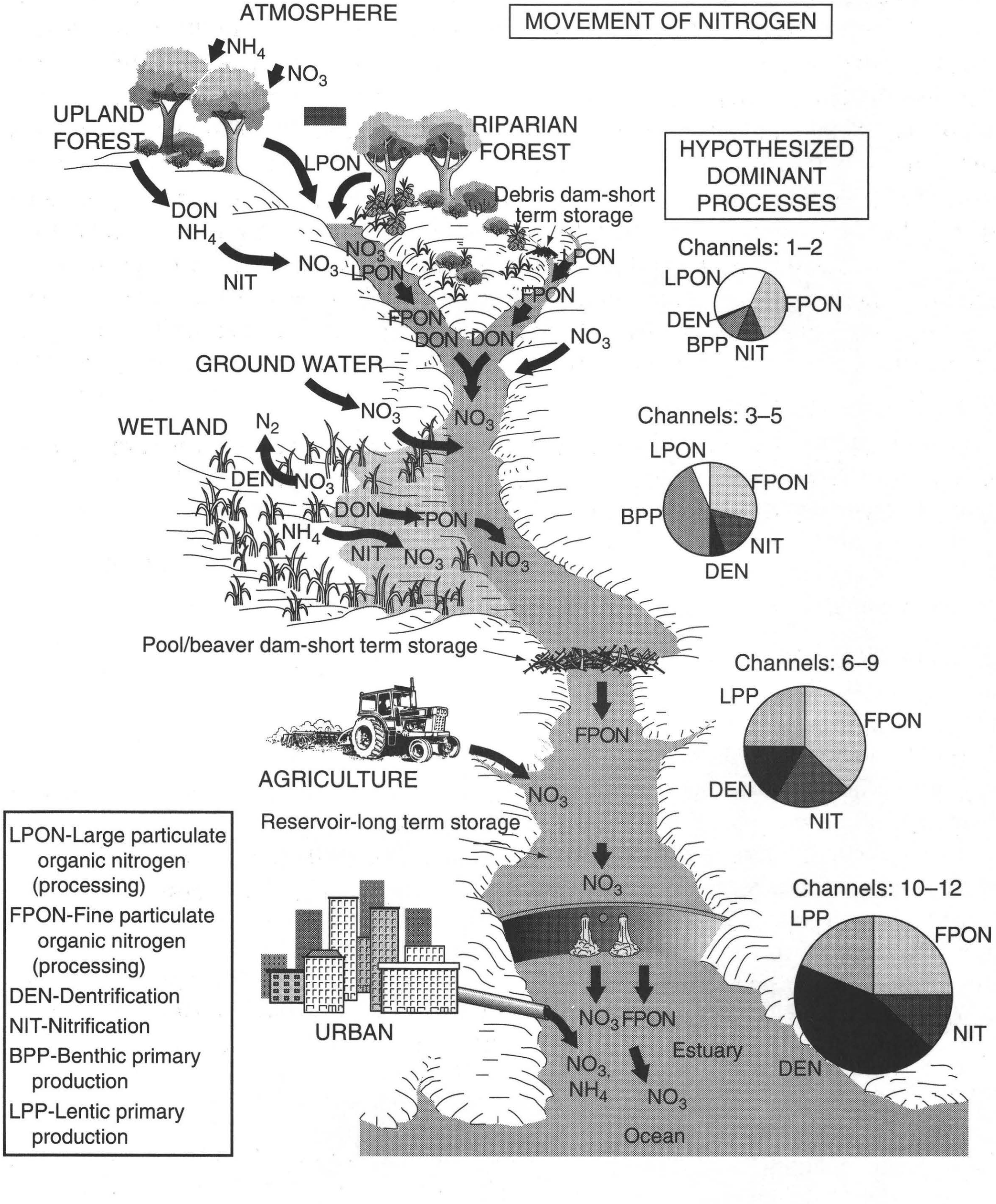


Figure 1. A simple model of nitrogen movement from forested upland watershed to larger streams and ultimately to the ocean, showing the various dominant processes responsible for nitrogen transformations in each segment of the hydrologic system. The diameters of the pie diagram are proportional to the size of the nitrogen fluxes in the channel orders.

Denitrification occurs primarily in pockets where PON accumulates if dissolved oxygen becomes depleted, especially in retention structures such as pools or beaver dams. As tributaries connect to form larger order streams (6-9), both intensive agriculture and urbanization become significant nitrate sources. By this point, nitrogen loads and often concentration have dramatically increased and FPON and NO_3- are the primary nitrogenous constituents in surface water. Where sediment loads prevent light penetration to the bottom, lentic primary production (LPP) is dominant. As channel gradient decreases and sediment grain size becomes smaller, exchange between the bed and surface water gradually decreases and denitrification is an increasingly important sink for nitrogen. Thus atmospheric flux of denitrification products, N_2 and N_2O increase throughout the river corridor. Dams along large rivers can provide in long-term nitrogen storage by sedimentation and alter the nitrogenous composition of input and output waters. As rivers continue to increase in size there is a shift from benthic to water column uptake associated with primary production and nitrification associated with ammonium sources such as sewage treatment facilities. Benthic processes are primarily associated with ammonification through decomposition of organic matter and denitrification. The total river continuum extends from headwater to estuary including coastal and marine environments.

Even a simple conceptualization at the watershed level can serve as a framework to organize data previously collected, to plan future research, and to illustrate a regional or even national perspective on nitrogen cycling. Such a framework can also:

1. Identify positions along the continuum emphasized by past work and parts of the river network that may have been neglected,
2. Serve as a guide to synthesize data and concepts,
3. Identify gaps in our knowledge,
4. Be used to test hypotheses.

For example, we might propose the hypothesis that nitrification in riparian zones and channels is the dominant nitrogen-cycling process in low-order streams (1-3 order), biomass production is dominant in mid-order streams (4-6 order), and denitrification is the dominant nitrogen-cycling process in higher (6-7) order rivers. Is our agency positioned to test such hypotheses? In fact is there a complete data set anywhere in the country for a single river network?

Future development of a suitable conceptual framework is an essential prerequisite for planning any new large-scale nitrogen-cycling study program. It would also be a valuable planning and organizing tool in data syntheses for existing monitoring and assessment programs.

Surface-Water Contamination

While the USGS has a strong history of leadership in the scientific community in identifying contamination of surface waters, there is still much we need to know. In particular, additional research is needed on sources of contamination, interactions with ground water, transport and transformation of nitrogen, and interactions with biota.

The USGS should play a major role in process research relating nitrogen transport and transformation to regional land-use factors that result in surface-water contamination. Although the USGS has a well-developed program in small forested watershed studies, much could be done to improve our understanding and abilities to compile mass budgets for large watersheds. Using our GIS capabilities, we can develop better methods for estimating the contributions of fertilizer, manure, atmospheric deposition, and point sources to the nitrogen budget of watersheds. In addition, we need to be able to provide better estimates of the potential sinks for nitrogen in these watershed budgets. Part of these improvements should be in refining our estimates of natural sources of nitrogen, denitrification and volatilization at large scales, removal of nitrogen in harvested crops, and retention and storage in biomass and soil organic matter. These studies could be integrated with process-oriented research being conducted in cooperation with the Department of Agriculture to take advantage of their resources and expertise with respect to fertilizer and manure sources of nitrogen.

Ground-water surface-water interactions and the potential for contaminated ground water to affect on surface-water quality are areas of growing scientific interest but little awareness on the part of the general public, water-resources managers, or politicians. Basic questions concerning ground-water surface-water interactions include:

1. How important is ground water as a source of surface water contamination?
2. What is the spatial scale of the problem?
3. What regional generalizations can be made?
4. Are ground-water-nitrate plumes near streams stable or transient features and are they generally expanding or contracting?
5. What is the role of the riparian zone in attenuating nitrate concentrations in ground water before it enters streams?
6. What routine measurements can be made to quantify the effects and processes involved?

We need to know more about processes that control the transport and associated transformations of nitrogen along the river continuum. In particular, we need to understand variability in various nitrogen transformations along the river network with greater focus on transformation rates between inorganic and organic forms. The role of hyporheic zone processes in nitrogen transformations has been studied only recently, and only in small streams. We can only speculate about the importance of various hyporheic processes along a complete river continuum. Reservoirs represent another important site of nitrogen transformation, especially conversion of DIN to organic forms, sedimentation, and denitrification. Throughout the river continuum there is the potential for large fluxes of N_2 and N_2O to the atmosphere as products of denitrification; however, little is known about this pathway at any point along the river corridor.

Nitrogen contamination is recognized primarily as a drinking-water issue, but it is especially important with respect to ecosystem health. The USGS could make a major contribution by answering questions not only on the distribution of nitrogen in surface waters throughout the Nation but also on where nitrogen limits biological productivity. For many years scientists have relied on the Redfield ratio of nitrogen to phosphorus of 16:1 as a barometer of nutrient limitation. However, is this the best indicator, or should we also be examining carbon, silica, and other constituent relations? Generally, more research in both the NRP and other operational programs should be focused on eutrophication as an interaction of many element cycles.

We need to consider whether chronic effects are occurring in both terrestrial and aquatic systems due to increased nitrogen loading over long periods. Without long-term information it may be impossible to detect subtle shifts in terrestrial and aquatic populations before they reach catastrophic proportions. Long-term information is also very important for evaluating the possible impacts of episodic events on both water quality and biota. Episodic events include extended droughts, floods, forest fires, spills of toxic or hazardous substances, hurricanes, other high wind and rain events, and volcanic eruptions. Floods enormously enhance sediment transport and can restructure channels to the point of changing river courses. Episodic events are known to reset biological communities, and are considered critical to riverine ecology. However, nor thewe know little about the impact of episodic events on either short-term or long-term water quality.

Fluxes to Coastal Waters

Nutrient flux, especially nitrogen, to estuarine and coastal waters is an issue likely to become increasingly important over the next five to ten years. Unlike freshwaters that are commonly phosphorus limited, shallow marine waters are more likely to be nitrogen limited, and therefore more sensitive to nitrogen inputs. Problems associated with nutrient inputs to these areas have been highlighted recently as a result of problems in the Chesapeake Bay, the Gulf of Mexico, Albemarle and Pamlico sounds.

The USGS has a traditional role in this issue through the National Stream Quality Accounting Network (NASQAN) and NAWQA. We should exploit our strengths in monitoring flow and water quality to expand existing programs and develop new ones to focus on the factors controlling nutrient fluxes to potentially sensitive areas. In addition to streamflow and water-quality monitoring, we should build on our strong GIS capabilities to include determination of nutrient sources to streams and the impacts of land-use change and the importance of differences in land use. Concurrent research on nitrogen transformations throughout the river continuum is critical to a better understanding of the magnitudes of fluxes to estuaries and other coastal waters.

There is little information on the relative magnitudes of fluxes of the different dissolved forms of nitrogen (NO_3-, NH_4^+, Organic-N) and on the relative sensitivity of coastal waters to the form of nitrogen that is delivered. New initiatives in this direction might be developed in cooperation with EPA or National Oceanic and Atmospheric Administration (NOAA), as part of their ongoing investigations focused on environmental problems in receiving waters.

Long-Term Monitoring

The USGS should stress a program-wide emphasis on long-term monitoring of both surface water and ground water and maintain continuity in our long-term monitoring networks instead of finding an "issue" to justify their continuation. NAWQA and NASQAN II will do some of the necessary monitoring but not enough to adequately address the issue Nationwide. This emphasis should extend beyond the usual monitoring parameters to some that reflect biological conditions and ecosystem health. We need to do a better job of explaining the importance of long-term data, particularly indicators of environmental health. Environmental indicators are like economic indicators--they serve as an "early-warning system" to detect environmental degradation before it becomes severe enough to affect human health. In addition, long-term data are necessary in order to separate small-scale perturbations from long-term cycles.

Nitrogen Contamination of Ground water

In many areas of the Nation concentrations of nitrate in shallow ground water exceed the EPA maximum contaminant level for drinking water (10 mg/L as N). As nitrogen fertilizer use continues to increase for both agricultural and residential purposes, there is concern that concentrations of nitrate in ground water will increase accordingly. Additional study is needed on residential use of fertilizer for lawns, golf courses, and other "green" areas. These studies are particularly challenging because we have little experience in determining the scale of the impact, and its potential relation to ecosystem health.

One area in which the USGS clearly leads the world scientific community is age dating of ground water, particularly through the use of chlorofluorocarbons. This technique allows scientists not only to assign a recharge date to ground water but, by sampling along a flow path or depth gradient, to reconstruct a history of change in ground-water chemistry over time. Widespread use of this approach in concert with information on land-use change in an area can provide a form of trend analysis. It is also very important to have accurate age data when selecting wells that are to be monitored as part of a trend-analysis study since it allows some reasonable estimate of how long it might take a contaminant plume to reach the sampling depth. Otherwise we could be waiting for years or decades to observe a predicted change in chemistry.

Another area in which the USGS has considerable potential for a leadership role is in developing methods for identifying sources of nitrogen contamination. Methods currently being used include isotopic techniques that directly indicate the source of the nitrogen, and geochemical techniques that use various conservative constituents as tracers. More research is needed to test the accuracy of the double isotope method, which is based on measurements of both nitrogen and oxygen isotopes in nitrate, in a variety of agricultural and urban settings. There is also the potential that various biological markers, specific to certain animals, could be useful as tracers.

At larger scales, the USGS should play a major role in process research relating nitrogen transport and transformation to regional hydrogeology and land-use factors that result in ground-water contamination. Using GIS methods, we can correlate ground-water contamination with ancillary variables such as land use, soil type, hydrogeology, and geomorphology for risk analysis of contamination potential. As with surface-water studies, these could be integrated with process-oriented research being conducted in cooperation with the Department of Agriculture to take advantage of their resources and expertise with respect to fertilizer and manure sources of nitrogen.

The USGS currently has only a small role in bioremediation research. Should the USGS desire to initiate a more comprehensive bioremediation program it would probably be necessary to hire more microbiologists to adequately address the topic. Without these new personnel our strongest expertise in this area would probably be in investigating the hydrogeochemical aspects of bioremediation processes.

Recommendations

Low-Cost Options

1. Create a nitrogen or nutrients special interest group (SIG) with its own home page that should include:

- A copy of this report,
- A bibliography of selected references,
- Descriptions of new and current studies and important results,
- Suggestions for new studies based on hypotheses that need testing,
- A list of available expertise in the USGS for consulting on projects and proposals.

2. Develop a training course focused on designing studies that will provide an integrated approach to monitoring, assessment, and process-oriented interpretations.
3. Increase technology transfer between the NRP and District scientists through the Regional Water-Quality Specialists.
4. Encourage special sessions on different aspects of the nitrogen cycle every few years at meetings of the American Geophysical Union (AGU), Geological Society of America (GSA), and other professional societys.
5. Prepare a fact sheet on nitrogen contamination of ground water under urban and agricultural land use settings.
6. Prepare a fact sheet on spatial and temporal trends in nitrogen contamination. Emphasize the importance of long-term monitoring in determining trends and for evaluating the success of major programs under the Clean Water Act.
7. Prepare a fact sheet on the importance of fluxes to major estuaries and shallow coastal marine waters.
8. Prepare a fact sheet or a report to Congress on needed research directions, emphasizing the relation of nutrients to both human and ecosystem health. This report could be prepared in collaboration with other Federal agencies and cooperators.

Moderate-Cost Options

1. Organize a workshop to consider a simple, consistent, conceptual framework for developing a watershed perspective in nitrogen (element) cycling that could in turn be used as a basis for identifying gaps, synthesizing existing data, and proposing and coordinating future programs. Such a framework should cross spatial and temporal scales, and serve as guide wherein each site/watershed study could be rapidly charted in terms of spatial position, identify its research and/or) monitoring contribution, and determine gaps in nitrogen- and other element-cycling data in the study.
2. Fund an initiative to investigate processes controlling fluxes of nitrogen gases (especially N_2O) in several large river systems throughout the Nation.
3. Fund a regional or national synthesis team to focus on issues related to nitrogen cycling at different scales.
4. Fund a regional or national synthesis team to develop relatively low-cost products such as maps of denitrification potential, leaching potential, sensitivity to nitrate contamination.

5. Expand ground-water and surface-water transport modeling to include an interface between them.

6. Fund the National Water-Quality Laboratory to develop and implement new methods for low-level determinations of organic nitrogen in surface waters.

7. Develop guidelines for interpreting relations between biological indicators and various water-quality conditions, especially for macrophytes and algae.

8. Establish an episodic response fund to investigate impacts of short-term anomalous events that might affect water quality and biota.

9. Encourage monitoring programs to analyze water samples for potentially important indicators such as chloride, chlorophyll-A, dissolved oxygen, dissolved and suspended organic carbon, dissolved and suspended organic nitrogen, and silica at long-term monitoring sites as well as intensive study sites. Encourage the use of age dating in ground-water studies.

10. Organize a workshop on nitrogen cycling and biota, and interactions with other element cycles.

11. Establish a merit based proposal fund for small awards (<$10,000) to enhance cooperation between research and operations programs. Possible awards might include:
    - Support for writing of a synthesis paper authored by NRP and District scientists using data from programs whose funding ended or a synthesis data set of national interest,
    - Support visits by District scientists to learn "hands on" techniques at NRP laboratories, or vice versa,
    - Fund small collaborative efforts between District and NRP scientists, that could not be accomplished by either alone.

12. Continue funding to develop and improve techniques (isotopic, geochemical, biological) for identifying sources of nitrogen in ground water and surface water.

High-Cost Options

1. Establish a core watershed network to cover a broad range of spatial scales and land-use characteristics to investigate the linkages among various nitrogen- and other element-cycling processes. Incorporate existing research watersheds, NAWQA land use, flow path and surface water monitoring watersheds, WEBB sites, Benchmark watersheds, and NASQAN watersheds in this network.

2. Develop an initiative on fluxes and sources of nutrients to estuaries and coastal waters, emphasizing the potential impacts to these important natural resources, possibly in cooperation with EPA and (or) NOAA.

3. Develop an initiative to determine where nitrogen is the limiting nutrient in fresh waters, possibly in cooperation with EPA.

4. Develop an initiative to focus on agricultural impacts on ground and surface waters, possibly in cooperation with the Department of Agriculture.

5. Develop an initiative on the transport and fate of nitrate in ground water.

6. Develop an initiative on bioremediation of contaminated ground water.
7. Develop an initiative to investigate linkages between various element cycles and nitrogen cycles such as:
    - Carbon and nitrogen, which is often used as an indicator of organic matter quality as a food source for biota,
    - Nitrogen and phosphorus, which is a common indicator of nutrient limitations for algae,
    - Nitrogen and silica, which may indicate the potential for silica depletion leading to downstream changes in algal community composition.

The USGS is unique among Federal agencies in having the broad national perspective, highly skilled work force, and reputation for scientific excellence respected around the world that are required in order to undertake many of these tasks. Some of the recommended activities may already be partially in progress and therefore would require only a greater degree of coordination to implement. Other activities represent new data-gathering efforts or programs that would require development of new initiatives in the USGS, some in coordination with other Federal agencies.

Acknowledgments

We would like to thank the office of the Chief Hydrologist for the opportunity to organize and his support of this workshop, and the Office of Water Quality, Office of Hydrologic Research, and the NAWQA Program for their support. This final report is a highly condensed summary of ideas contributed by all workshop participants and a synthesis by focus session leaders. The full report submitted by each working group chairman, and the membership of each working group is presented as Appendix I. We thank all workshop participants for the generous contribution of their time and ideas.

Bibliography

1. Farm Chemicals, 1996, Changes in store: Farm Chemicals v. 159, no. 1, p. 20-21.
2. Kronvang, B., Aertebjerg, G., Grant, G., Kristensen, P., Hovmand, M., and Kirkegaard, 1993, Nationwide monitoring of nutrients and their ecological effects: State of the Danish aquatic environment: Ambio v. 22, p. 176-187.
3. Puckett, L.J., 1995. Identifying sources of nutrient contamination in watersheds: Environmental Science and Technology v. 29, p. 408A-414A.
4. Smith, R.A., Alexander, R.B., and Wolman, M.G., 1987, Water quality trends in the nation's rivers: Science v. 235, p. 1607-1615.
5. Turner, R.E., and Rabelais, N.N., 1991, Changes in Mississippi River water quality in this century: Bioscience v. 41, p. 140-147.
6. Vannote, R.L., Minshall, G.W., Cummins, K.W., Sedell, J.R., and Cushing, C.E., 1980, The river continuum concept: Canadian Journal of Fisheries and Aquatic Sciences 37, p. 130-137.
7. Vitousek, P.M, 1994, Beyond global warming: Ecology and global change: Ecology, v. 75, p. 1861-1876.

Group 1: Scope of the Problem--Ground-Water

Chairperson--Dennis R. Helsel

Abstract	Presenter
National Synthesis of Retrospective Nutrient Data from the NAWQA Study Units	David K. Mueller
Relation Between Land Use and Distributions of Dissolved Nitrogen Species in Shallow Water in Two New Jersey Coastal Plain Aquifer Systems	Eric F. Vowinkel
Overview of Nitrate Concentrations in Ground Water of the Upper Snake River Basin, Idaho and Western Wyoming	Michael G. Rupert
Ground-Water and Sediment-Quality Monitoring of the Superior-Hardy Special Protection Area, Nuckolls County, Nebraska	Abraham H. Chen
Influence of Dairy and Poultry Operations on Nitrate Concentrations in the Upper Floridian Aquifer in North-Central Florida	Hilda H. Hatzell
The Relation Between Nitrate in Drinking Water and Stomach Cancer in the Semi-Arid Plains of Hungary and the USA	Gerald L. Feder

National Synthesis of Retrospective Nutrient Data from the NAWQA Study Units

David K. Mueller[1], Pixie A. Hamilton[2], and Dennis R. Helsel[3]

Historical data on nutrient (nitrogen and phosphorus species) concentrations in ground- and surface-water samples were compiled from 20 study units of the National Water-Quality Assessment (NAWQA) Program and 5 supplemental study areas. The resultant national retrospective data sets contained analyses of about 12,000 ground-water and more than 22,000 surface-water samples.

Nitrate was the nutrient of greatest concern in the historical ground-water data. It is the only nutrient that is regulated by a national drinking-water standard. Nitrate concentrations were significantly different in ground water affected by various land uses. Concentrations in about 21 percent of the samples collected in agricultural areas exceeded the drinking-water standard. However, the standard was exceeded in only 1 percent of samples collected from public-supply wells. A variety of ancillary factors had significant relations to nitrate concentrations in ground water beneath agricultural areas. Concentrations generally were highest within 100 feet of the land surface. They were also higher in areas where soil and geologic characteristics promoted rapid movement of water to the aquifer. Elevated concentrations commonly occurred in areas underlain by permeable materials, such as carbonate bedrock or unconsolidated sand and gravel, and where soils are generally well drained. In areas where water movement is impeded, denitrification might lead to low concentrations of nitrate in the ground water. Low concentrations also were related to interspersion of pasture and woodland with cropland in agricultural areas. Elevated nitrate concentrations in areas of more homogeneous cropland probably were a result of intensive nitrogen fertilizer application on large tracts of land.

Certain regions of the United States seemed more vulnerable to nitrate contamination of ground water in agricultural areas. Regions of greater vulnerability included parts of the Northeast, Midwest, and West Coast. The well-drained soils, typical in these regions, have little capacity to hold water and nutrients; therefore, these soils receive some of the largest applications of fertilizer and irrigation in the Nation. The agricultural land is intensively cultivated for row crops, with little interspersion of pasture and woodland.

Nutrient concentrations in surface water also were generally related to land use. Nitrate concentrations were highest in samples from sites downstream from agricultural or urban areas. However, concentrations were not as high as in ground water and rarely exceeded the drinking-water standard. Elevated concentrations of nitrate in surface water of the Northeastern United States might be related to large amounts of atmospheric deposition (acid rain). High concentrations in parts of the Midwest might be related to tile drainage of agricultural fields. Ammonia concentrations were highest downstream from urban areas. These concentrations generally were high enough to warrant concerns about toxicity to fish. Recent improvements in wastewater treatment have decreased ammonia concentrations downstream from some urban areas, but the result has been an increase in nitrate concentrations.

[1] U.S. Geological Survey, MS 415, Lakewood, CO 80225
[2] U.S. Geological Survey, 3600 Broad St., Richmond, VA 23230
[3] U.S. Geological Survey, MS 413, Reston, VA 20192

Relation Between Land Use and Distributions of Dissolved Nitrogen Species in Shallow Water in Two New Jersey Coastal Plain Aquifer Systems

Eric F. Vowinkel[1] and Zoltan Szabo[1]

Application of nitrogen fertilizers to soil in agricultural and residential areas of the New Jersey Coastal Plain in the past 50 years has significantly affected the concentrations of N (nitrogen) species (nitrate, nitrite, ammonium, and organic N) in shallow water from the outcrop areas of two aquifers having similar hydrogeologic characteristics--the Kirkwood-Cohansey and Potomac-Raritan-Magothy aquifer systems. The relation between land use and distributions of N species in shallow ground water were evaluated at two scales--regional and local. At the regional scale, concentrations of N species in water samples collected from 220 wells in predominantly undeveloped, agricultural, or residential areas with screened intervals less than 30.5 m (meters) below land surface were used to compare the distributions of N species by land-use area. At the local scale, concentrations of N species in water samples collected from five sets of nested wells near ground-water divides in agricultural areas overlying the Kirkwood-Cohansey aquifer system were used to compare distributions of N species along ground-water flow paths.

Concentrations of total N in water from the 220 wells ranged from 0.1 to 33 mg/L (milligrams per liter) as N. Results of nonparametric statistical analyses indicate that distributions of concentrations of nitrate, ammonium, and organic nitrogen and the ratios of their concentrations to total N differed significantly ($p = 0.05$) among the three land-use areas in both aquifer systems. For example, the median concentrations of nitrate as N were 7.2 and 8.5 mg/L in agricultural areas, 1.8 and 3.6 mg/L in residential areas, and less than 0.1 mg/L in undeveloped areas of the Kirkwood-Cohansey and Potomac-Raritan-Magothy aquifer systems, respectively. The concentrations and relative proportions of N species were similar between aquifer systems for all of the N species for the same land-use types. The similar results between land-use areas in the two aquifer systems indicate that the observed relations between land use and shallow-ground-water quality are transferable to other areas of similar hydrogeology and land use.

In undeveloped areas, concentrations of total N in shallow ground water rarely exceeded 1 mg/L; organic N and ammonium commonly are the dominant forms of N. Ammonium and nitrite typically are present in water where DO (dissolved oxygen) is absent--usually in wetland areas where denitrification can occur. In agricultural and residential areas, nitrate comprises greater than 85 percent of the total N concentration in ground water, probably because the water in these areas typically contains DO. Although N is generally applied to soils as ammonium salts in agricultural areas, ammonium rarely is present in ground water in concentrations above 0.1 mg/L as N because the ammonium is nitrified in the oxygenated soil and ground water. Partly because hydrogen ions are released during nitrification, the pH of the ground water in both aquifer systems in agricultural areas (medians of 4.9 and 5.3) is generally lower than that in undeveloped areas (medians of 5.3 and 6.1). At the local scale, The median N^{15} isotope value in water from12 domestic wells in agricultural areas is about 4 per mil, indicating that the source of nitrate probably is inorganic fertilizers. Molar ratios of concentrations of N_2 gas to argon gas were about 39 in water samples from two sets of nested wells along vertical flow paths beneath agricultural land; these ratios are similar to that of air-saturated water and indicate that denitrification was not occurring.

[1] U.S. Geological Survey, 810 Bear Tavern Road, West Trenton, NJ 08628

Overview of Nitrate Concentrations in Ground Water of the Upper Snake River Basin, Idaho and Western Wyoming

Michael G. Rupert[1]

Nitrite plus nitrate (nitrate) concentrations in ground water of the upper Snake River Basin were evaluated as part of the U.S. Geological Survey National Water-Quality Assessment (NAWQA) Program. Nitrate concentrations exceeded the Federal and State drinking-water standard of 10 milligrams per liter in three areas in Idaho: the Idaho National Engineering Laboratory; the Fort Hall area north of Pocatello; and the area north of Burley. Nitrate concentrations were highest in water from domestic wells and lowest in water from industrial and public supply wells. Concentrations statistically decreased with increasing depth of well, depth to water, and depth below water table. Nitrate concentrations were correlated with land use using a geographic information system. Nitrate concentrations in irrigated agricultural areas were statistically higher than in rangeland or dryland agricultural areas. Concentrations increased downgradient in the A&B Irrigation District (north of Burley) due to loading from agricultural sources. County estimates of total nitrogen loading for the entire basin suggest that septic tanks provide minimal nitrogen loading compared with that from cattle and fertilizers.

[1] U.S. Geological Survey, WRD Boise, Idaho

Ground-Water and Sediment-Quality Monitoring of the Superior-Hardy Special Protection Area, Nuckolls County, Nebraska

Abraham H. Chen[1]

In 1991, the U.S. Geological Survey Water Resources Division, Lincoln, Nebraska, in cooperation with the Nebraska Department of Environmental Quality and the Lower Republican and Little Blue Natural Resources Districts, completed the ground-water-quality monitoring network at a 32-square mile designated Special Protection Area, Nuckolls County, Nebraska. Due to continued occurrences of ground-water concentrations of nitrate in excess of the U.S. Environmental Protection Agency's Maximum Contaminant Level of 10 milligrams per liter in the area, the Department of Environmental Quality designated the area as a Special Protection Area, which was the first such area declared in the State. A continuous long-term monitoring to detect nitrate trends in the ground water and sediment after implementing of Best Management Practices (BMPs) by farm operators of the area was established. A total of 20 monitoring wells were drilled on 16 sites and two sites were also selected for deep coring in the unsaturated zone. Bimonthly ground-water sampling schedule was established, and three sediment sampling times were performed during spring 1991-93.

Ground-water and sediment samples were collected and analyzed for nitrate in 1991 as background information. A mean nitrate concentration for the SPA as a whole was 9 milligrams per liter ranging from 0.1 to 30 milligrams per liter with about 30 percent of the area nitrate levels exceeded 10 milligrams per liter. Because of slow ground-water movement and time lag between the adoption of the BMPs and water-quality improvement, nitrate-level changes in the ground water were not detected on year after implementing of the BMPs. However, the effects of the BMPs on vadose zone can be measured immediately by deep sediment coring 1 year following implementation of the BMPs.

[1] U.S. Geological Survey, 100 Centennial Mall North, 406 Federal Building, Lincoln, NE 68508

Influence of Dairy and Poultry Operations on Nitrate Concentrations in the Upper Floridian Aquifer in North-Central Florida

Hilda H. Hatzell[1]

The number of poultry and dairy operations in north-central Florida has increased during the past 10 to 15 years. These land-use activities could be increasing nitrate concentrations in ground water in the Upper Floridian aquifer. In water from 148 background monitoring wells that were selected to avoid known areas of ground-water contamination, the median nitrate-as-nitrogen concentration in the mid 1980's was 0.05 milligrams per liter (mg/L) which is equal to the method detection limit. The median nitrate concentration of water in 83 private drinking water wells in the same area and time period was 0.96 mg/L. To determine whether poultry and dairy farms in Suwannee and Lafayette Counties are affecting nitrate concentrations in the Upper Floridian aquifer, one hundred private drinking-water wells in north central Florida were sampled for nitrate concentrations and nitrogen isotope ratios from July through September 1991. The nitrate-as-nitrogen concentrations and the delta values of the nitrogen isotope ratio ($\delta^{15}N$) for nitrate were kriged to produce grids of predicted concentrations and delta values. In addition, $\delta^{15}N$ values less than or equal to +2 per mil were classified as derived from fertilizer sources. The $\delta^{15}N$ values less than or equal to +2 per mil were classified as derived from non-fertilizer sources, such as animal manure, or from a mixture of fertilizer and non-fertilizer sources. Indicator kriging was then used to produce a grid of predicted probabilities that the $\delta^{15}N$ was less than or equal to +2 per mil.

Dairy and poultry operations appear to be influencing nitrate concentrations more in Lafayette County than in Suwannee County. The median of predicted nitrate concentrations of 388 grid locations for the overall study area is 1.04 mg/L with a range of 0.35 - 3.57 mg/L. The median of predicted nitrate concentrations of 195 actual poultry and dairy locations in Suwannee and Lafayette Counties is 1.81 mg/L with a range of 0.54 - 3.56 mg/L. A contour map made from the 388 predicted nitrate concentrations indicates that the highest nitrate concentrations occur in western Suwannee County and north-central Lafayette County. A contour map made from the 388 predicted probabilities indicates that the probability that the $\delta^{15}N$ is less than or equal to +2 per mill is greater than 60 percent in western Suwannee County but is less than 40 percent in north-central Lafayette County. The higher percentage implies that nitrates in the ground water in western Suwannee County are more likely to be derived from fertilizer sources than non-fertilizer sources. Conversely, the smaller percentage implies that nitrates in ground water in north-central Lafayette County are more likely to be derived from mixed or non-fertilizer sources. Differences in the nitrate sources between Suwannee and Lafayette Counties could be attributed to such factors as different hydrogeological conditions, the shift from row-crop agriculture to animal operations, and the density of dairy and poultry operations per unit area.

[1] U.S. Geological Survey, 227 N. Bronough Street, Suite 3015, Tallahassee, FL 32301

The Relation Between Nitrate in Drinking Water and Stomach Cancer in the Semi-arid Plains of Hungary and the USA

Gerald L. Feder[1] and Gyorgy Toth[2]

The basis for the present EPA maximum contaminant level (MCL) for nitrate in drinking water of 45 mg/L (as NO_3) is the infant disease methemoglobinemia. However, many medical researchers believe that nitrate in drinking water may be implicated in cancers, especially cancers of the digestive tract. In order to test this hypothesis two hydrologically similar agricultural areas were chosen for study. One area, Szabolcs-Szatmar County on the Great Hungarian Plain is reported to have a high mortality from stomach cancer (33/100,000). This county is a rural agricultural area where corn and sunflowers are the main crops. In the USA an area was chosen that includes 22 rural counties in northwest Kansas and northeast Colorado where corn, sunflowers, and wheat are the main crops. This area has an average mortality rate for stomach cancer of 8/100,000 (USA average mortality rate for the period 1970-79 is 8/100,000). Both areas are semi-arid plains underlain by Cretaceous-Tertiary age sediments.

The shallow individual water wells supplying drinking water for most of the farmers in Szabolcs-Szatmar county are usually polluted and contain high concentrations of nitrate. The median value of the nitrate concentration for 250 wells sampled in this county is 200 mg/L (as NO_3). The drinking water supplies in the Kansas-Colorado study area are a combination of shallow farm wells that are sometimes polluted and municipal wells that supply drinking water that must meet USEPA standards. The median nitrate concentration for 870 wells sampled in this area is 14 mg/L (as NO_3).

These data indicate that there may be a relation between nitrate content of drinking water and stomach cancer, but the relation is not linear and may involve a threshold effect. That is, at slightly elevated levels of nitrate intake there does not appear to be any increase in the mortality rate. Of course, there may be many unknown variables influencing the data. For example, diet, especially vitamin C intake has been shown to have an important effect on susceptibility to developing stomach cancer.

[1] U.S. Geological Survey, MS 431, Reston, VA 20192
[2] Hungarian Geological Institute, 14 Stefania Ut, Budapest, Hungary H-1442

Group 2: Scope of the Problem--Surface Water Session

Chairperson--Charles R. Demas

Abstract	Presenter
An Overview of Nitrogen from Agricultural Nonpoint Sources in Water Resources of the Lower Susquehanna River Basin	Patricia L. Lietman
Estimated Nutrient Loading for Major Tributaries of the Upper Tennessee River Basin	Gregory C. Johnson
Trends in Nitrogen in Connecticut Streams, 1975-88	Elaine C. Todd Trench
Variability of Fluxes and Relative Abundance of Nitrogen Forms to Coastal Waters: A Watershed Based Analysis	Larry J. Puckett
Nitrate, Organic Nitrogen, and Total Nitrogen Transport in Surface Waters of the Hudson River Basin, New York	Patrick J. Phillips
Determination of Total Nitrogen in Filtered and Whole-Water Samples: Analytical Capabilities of the Current NWQL Kjeldahl Method and Potential for Development of New Laboratory Methods with Lower Detection Limits and Improved Precision	Charles J. Patton

An Overview of Nitrogen from Agricultural Nonpoint Sources in Water Resources of the Lower Susquehanna River Basin

Edward H. Koerkle[1] and Patricia L. Lietman[1]

Numerous water-quality investigations of nonpoint sources of nitrogen in the Lower Susquehanna River Basin have shown that nitrogen in surface water and ground water is strongly linked to agriculture. Since 1977, this work has included 13 studies of surface and ground water at both field scale and in watersheds ranging from 0.2 to 500 mi^2. Synoptic and periodic studies 2 to 8 years long have documented concentrations and loadings of nitrogen species, the effects of land use and geology on transport and distribution of nitrogen, and the effects of agricultural-management practices on the fate of agricultural nitrogen inputs. These studies have shown that areas with high densities of livestock routinely have median concentrations of NO_3^- approaching 10 mg/L in surface water and two to three times that concentration in ground water. Carbonate-rock aquifers with shallow water tables contained the highest nitrogen concentrations. Maximum NO_3^- concentrations in carbonate terrane were as high as 20 mg/L in surface water and 80 mg/L in ground water. Ground-water nitrogen accounts for 60 to 80 percent of the annual nitrogen load being transported in streamflow in carbonate-rock aquifers.

Efforts to link agricultural-management practices to water quality has been complicated by many natural and anthropogenic factors. Large observed variability in NO_3^- concentrations in surface-water, from 100 to 400 percent per year, probably masked statistical detection of changes expected from management practices. Lag times may require sampling periods longer than allowed in these studies. In one field study lag times of up to 2 years were noted between surface applications and changes in NO_3^- concentrations in ground water. In watershed studies longer lag times are likely. Anthropogenic factors included large variations in nitrogen input. Nitrogen inputs generally occurred as large pulses once or more annually. Also, compliance with land-treatment guidelines for nitrogen applications was often erratic. Measurements of soluble NO_3^- in the soil showed a median variance of 350 percent among samples from one field site. The upper 4 ft. of soil contained up to 400 lbs. of soluble NO_3^- per acre. Management practices may have unintended effects on water quality. Use of pipe-outlet terraces, a surface-water management practice, did not cause a significant change in nitrogen in surface-runoff after 5 years but an apparent increase in NO_3^- concentrations in ground-water beneath the terraced fields. Statistical analyses were generally limited to trend testing. The large variations in nitrogen input from agricultural activities combined with multiple transformation pathways between inputs and streamflow output precluded using a mass-balance approach except in the smallest and most controlled study areas. To address these problems, a post-implementation period up to 7 years, a paired-basins design, and near-stream ground-water sampling are combined in a current study of the effects of streambank fencing, a surface-water-management practice, on water quality.

[1] U.S. Geological Survey, 840 Market St., Lemoyne, PA 17043

Estimated Nutrient Loading for Major Tributaries of the Upper Tennessee River Basin

Gregory C. Johnson[1] and Maurice W. Treece[1] Jr.

The U.S. Geological Survey is conducting an assessment of water quality in the upper Tennessee River Basin as part of the National Water-Quality Assessment Program. The upper Tennessee River study area encompasses a total of about 21,400 square miles and includes the entire drainage of the Tennessee River and its tributaries upstream of Chickamauga Dam near Chattanooga, Tennessee. During the planning phase of this study, existing streamflow and water-quality data were compiled from local, State, and Federal sources. Nutrient loads for 23 monitoring sites in the basin were estimated for water years 1970 through 1994. Data from point sources (such as effluent from industries and sewage treatment plants) and nonpoint sources (such as fertilizer application, animal waste, and atmospheric deposition) are planned to be analyzed to determine a general nutrient budget for the study area.

Estimated annual nitrogen loads for the Tennessee River at Chattanooga, Tennessee, ranged from 86,500 kg/d in 1979 to 20,000 kilograms per day (kg/d) in 1988, with a mean annual load of 57,200 kg/d. Phosphorus loads at this site ranged from 9,670 to 1,600 kg/d in 1979 and 1988, respectively, and the mean annual load was 5,300 kg/d. The French Broad River near Knoxville, Tennessee, contributed the highest mean annual nitrogen load (23,300 kg/d), and the highest mean annual phosphorus load (1,700 kg/d).

The highest annual yields (load per unit area) were from the French Broad River watershed above Marshell, North Carolina, which averaged 2.18 kilograms per square kilometer per day (kg/km^2/d) for nitrogen, and 0.36 kg/km^2/d for phosphorus. The French Broad River Basin was about 11 percent urban and 23 percent agricultural in 1976, additionally there are numerous industries in the Ashville area. The lowest mean annual yields were in the Ocoee, Little Tennessee, and Emory River Basins for nitrogen (about 0.7 kg/km^2/d), and in the Ocoee, Little Tennessee, and the Clinch River Basins for phosphorus (0.03, 0.03, and 0.02 kg/km^2/d, respectively).

[1] U.S. Geological Survey, 1013 N. Broadway, Knoxville, TN 37917

Trends in Nitrogen in Connecticut Streams, 1975-88

Elaine C. Todd Trench[1]

The U.S. Geological Survey has analyzed water-quality data nationally and in several States to identify long-term changes in the quality of streams in the United States. Trend analysis was performed for total nitrogen, total organic nitrogen, total nitrite-plus-nitrate, and dissolved ammonia nitrogen concentrations at 32 water-quality stations for water years 1975-88, as part of an examination of overall water-quality trends in Connecticut.

Increasing concentrations of total nitrogen, total organic nitrogen, and total nitrite-plus-nitrate were detected in all major drainage basins. Concentrations of total nitrogen increased at 27 of 30 stations during the study period; concentrations did not decrease at any stations. Increases in total nitrogen ranged from 0.01 to 0.26 mg/L (milligrams per liter) per year, with a median increase of 0.03 mg/L per year. Concentrations of total organic nitrogen increased at 23 of 32 stations and decreased at 1 station. Increasing concentrations of total nitrite-plus-nitrate were detected at 17 of 32 stations and decreasing concentrations were detected at 3 stations. Dissolved ammonia data were adequate for trend analysis for only five stations, all of which are located in major drainage basins. Very small increasing trends in dissolved ammonia were detected at two stations— the Connecticut River at Thompsonville and the Quinebaug River at Jewett City.

Decreasing trends in streamflow during 1975-88 were detected at 12 of 20 stations. Increasing trends in the concentrations of total nitrogen and total nitrite-plus-nitrate may be related to decreasing trends in streamflow; however, the concentration of total nitrogen increased at each of the eight stations for which no trend in streamflow was found. Increasing trends in total nitrite-plus-nitrate were observed at six of these eight stations, indicating that increases in total nitrogen and total nitrite-plus-nitrate during the study period were not exclusively caused by discharge variations.

Natural organic material, domestic and industrial wastewater, agricultural and residential fertilizer, animal wastes, and combustion by-products in the atmosphere all contribute nitrogen compounds to freshwater in Connecticut. Statewide increases in total nitrogen reflect inputs from point sources in urbanized basins and nonpoint sources in less developed basins. The five stations where increases in total nitrogen concentrations were largest are located on the Quinnipiac River, the Still River at Brookfield Center, and the Naugatuck River, all of which receive major point discharges. Four of the five stations where the largest percentage increases in total nitrogen have occurred are located on the Saugatuck River, the Salmon River, Burlington Brook, and the Willimantic River at Merrow—streams that drain rural or less developed areas of 100 square miles or less. These results demonstrate the vulnerability of small streams in Connecticut to contamination from nonpoint sources in rural and less developed areas.

[1] U.S. Geological Survey, Hartford, CT

Variability of Fluxes and Relative Abundance of Nitrogen Forms to Coastal Waters: A Watershed Based Analysis

Larry J. Puckett[1] and Lynn A. Malacane[1]

In recent years there has been increasing recognition of the potentially important role of nutrients from terrestrial sources in the eutrophication of coastal waters. This concern has been greater for nitrogen than phosphorus because unlike rivers, lakes, and reservoirs where phosphorus is the limiting nutrient, estuaries and shallow marine waters are more often nitrogen limited. When interpreting the potential impact of nitrogen loads to coastal waters it is important to examine more than just the total flux of nitrogen; understanding the temporal variability of fluxes and the relative abundance of the different forms of nitrogen can be especially important because they may affect how organisms respond to nutrient inputs.

We examined seasonal variability and relative abundance of nitrogen forms (NH_4^+, NO_3^-, organic-N) in nitrogen loads to seven major estuaries and shallow marine environments: Long Island Sound, the Hudson River estuary, the Upper Chesapeake Bay, the Potomac River estuary, Albemarle and Pamlico Sounds, Apalachicola Bay, and Trinity Bay. Loads were also related to the various nonpoint and point sources of nitrogen within the contributing watersheds using a mass-budget approach. In general, larger proportions of organic-N appeared to be associated with longer residence times of water in reservoirs which would allow more time for biological transformations of DIN to organic-N. For example, the Trinity River receives a major portion of its nitrogen from point-source discharges whereas the Susquehanna is primarily an agricultural nonpoint-source dominated river. These rivers pass through large reservoirs before discharging to their estuaries. However, these reservoirs have considerably different influences on nitrogen loads. After passing through Livingston Reservoir (120-day residence time), nitrogen loads in the Trinity River were 47 percent less than above the reservoir and had changed from DIN dominance to organic-N dominance. In the Susquehanna River nitrogen loads were reduced only five percent after passing through the reservoirs (10-day residence time) and there were only minor changes in the different forms of nitrogen. Seasonal variability was similar among most of the rivers, with the majority of loads being transported during the winter and spring months at the time of greatest streamflow.

The fact that much of the nitrogen entering these coastal waters was organically bound is important because it means that it is not immediately available to support algal and macrophyte growth. However, it also suggests that a major pool of organic nitrogen is delivered to coastal waters each year that may become biologically available throughout the year as the organic compounds degrade.

[1] U.S. Geological Survey, National Center, MS 413, Reston, Virginia 20192

Nitrate, Organic Nitrogen, and Total Nitrogen Transport in Surface Waters of the Hudson River Basin, New York

Patrick J. Phillips[1]

Patterns of nitrogen transport in streams tributary to the Hudson River basin indicate that transport of dissolved nitrate, dissolved ammonia, and total organic nitrogen (computed as the mass of total nitrogen minus the mass of dissolved nitrate and dissolved ammonia) fluctuates seasonally and with streamflow. Nitrogen-transport data during 1970-90 from three large Hudson River watersheds with drainage areas exceeding 2,800 square miles (Hudson River at Fort Edward, Hudson River at Green Island, and Mohawk River at Cohoes) and one small watershed with a drainage area of less than 65 square miles (Esopus Creek at Shandaken) indicate the following: most of the nitrogen load at these four sites is in the form of dissolved nitrate and most of the remainder consists of total organic nitrogen. The dissolved nitrate component of annual total nitrogen load ranges from 56 percent at the Mohawk River and Esopus Creek sites to 34 percent at the Hudson River at Ft. Edward; the corresponding ammonia component at all four sites ranges from 2 to 35 percent, and the total nitrogen component ranges from 26 to 41 percent. Although much of the organic nitrogen was transported during high flows, the ratio of organic nitrogen to total nitrogen generally did not increase with increasing flow at these four sites.

On a monthly basis, the dissolved nitrate component (as a percentage of total nitrogen) tends to be inversely related to total organic nitrogen component. In the three large watersheds, the dissolved nitrate component peaks during February through May, and in the small basin, it peaks during November through January, whereas the total organic nitrogen component in all four watersheds peaks during July through September. The largest seasonal change in total organic nitrogen component occurs in the Mohawk River basin, where the dissolved nitrate component constitutes greater than 60 percent of the total nitrogen from February through April, and less than 56 percent from July through September; the organic nitrogen component is less than 15 percent of the total nitrogen load in January and February, but greater than 40 percent of the total nitrogen load from June through September. In general, much of the summertime increase in the total organic nitrogen component at the four watersheds is balanced by a decrease in dissolved nitrate.

The seasonal fluctuations among the three nitrogen species are likely related to biological processes. During summer, nitrate in the streams is taken up by algae and converted to organic nitrogen, whereas during the late winter and early spring, nitrate is not taken up by algae and so constitutes a larger proportion of the total nitrogen load.

[1] U.S. Geological Survey, Troy, NY

Determination of Total Nitrogen in Filtered and Whole-Water Samples: Analytical Capabilities of the Current NWQL Kjeldahl Method and Potential for Development of New Laboratory Methods with Lower Detection Limits and Improved Precision

Charles J. Patton[1]

The Kjeldahl methods for nitrogen (parameter codes 623 and 625) and phosphorus (parameter codes 666 and 665) determinations in filtered and whole-water samples that were developed and validated by the Methods Research and Development Program (Patton and Truitt, 1992) have been in routine operation at the National Water Quality Laboratory since October 1991. The methods were developed and validated by the Methods Research and Development Program. These methods—although rapid and robust—have drawbacks common to other Kjeldahl digestion methods, such as:

- Potential health and safety risks—sulfuric acid, mercury (II), high temperatures;
- Environmental impact and costs associated with waste mercury (II) disposal;
- Propensity of acidic digests to become contaminated by ambient ammonia vapors; and
- Relatively high method-detection limits (0.1 milligram per liter) for nitrogen.

Alkaline persulfate digestion methods, which oxidize organic nitrogen and phosphorus compounds to nitrate and orthophosphate at elevated temperature and pressure—sometimes assisted by ultraviolet radiation—overcome most of the inherent limitations of Kjeldahl digestion methods. In terms of data quality, the lower blanks typical of oxidative digestion methods improve method-detection limits and precision of analytical results by as much as an order of magnitude relative to Kjeldahl digestion methods. In this presentation, Kjeldahl and alkaline persulfate digestion methods for nitrogen and phosphorus determinations are discussed and compared. Arguments are presented in favor of adopting oxidative digestion methods for nitrogen and phosphorus determinations within the U.S. Geological Survey despite the fact that at present (September 1995) they are not accepted for monitoring under the Safe Drinking Water Act or National Pollution Discharge Elimination System.

Patton, C.J., and Truitt, E.P., 1992, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of total phosphorus by a Kjeldahl digestion method and an automated colorimetric finish that includes dialysis: U.S. Geological Survey Open-File Report 92-146, 39 p.U.S.

[1] U.S.Geological Survey, Water Resources Division, National Water Quality Laboratory, 5293 Ward Road, Arvada, CO 80002

Group 3: Atmospheric Deposition and Nitrogen Cycling Processes in Soil Session

Chairperson--Scott Phillips

Abstract	Presenter
Relation of Stream Nitrate Concentrations to N Deposition in Watersheds of the Catskill Mountains, New York Since 1983	Peter S. Murdoch
Processes that Affect the Transformation of Atmospherically Deposited Nitrogen in Catskill Mountain (New York) Watersheds	Douglas A. Burns
Effects of Atmospheric Nitrogen Deposition on the Availability of Nitrogen, Organic Carbon, and Calcium in Forest Soils of the Northeast	Gregory B. Lawrence
Nitrogen Cycling in Alpine Catchments: Loch Vale, Colorado	Donald H. Campbell
Contributions of Mn and Fe Species to Biologically-Mediated Nitrogen Redox Reactions	Carol J. Lind
Nitrogen Transformations and Transport in Acidic Coal-Mine Spoil	Charles A. Cravotta, III

Relation of Stream Nitrate Concentrations to N Deposition in Watersheds of the Catskill Mountains, New York, Since 1983

Peter S. Murdoch[1] and Douglas A. Burns[1]

The Catskill Mountains of New York receive the highest rates of nitrate deposition in the Northeastern United States. Concentrations of nitrate in several Catskill Mountain streams increased at a rate of 2 M/L (micromoles per liter per year) during 1983-90. Generally , the highest concentrations were during spring snowmelt, and the lowest were during the leaf-fall period of early October. Nitrate concentrations during the spring of 1992 decreased to one-quarter the values observed in 1990, however, and have remained low since then. The abrupt increases and decreases in nitrate concentrations have provided an opportunity to study the biogeochemical processes that control nitrate movement through Catskill watersheds.

The observed changes in nitrate concentrations were associated with changes in climatic conditions. A drought during water year (WY) 85 preceded a 4-year period of rapidly increasing stream nitrate concentrations (WY86-90). Winter nitrate deposition (December 15 through March 30) was greater during WY89-90 (the period of highest stream nitrate concentrations) than in the other years of record, and record-low December temperatures combined with a thin snow cover may have allowed soils to freeze. Freezing of fine roots in the soil during December, followed by thawing temperatures in January 1990, may have enhanced nitrification during that winter period. In contrast, winter precipitation during WY91-92 fell mostly as rain. Minimal recharge from snowmelt and scant precipitation during the late spring and early summer of 1991 resulted in the drying up of typically perennial springs and extremely low summer streamflow.

Seasonally averaged, volume-weighted stream nitrate concentrations were poorly correlated with nitrogen deposition in the summer but positively correlated during the dormant season. Stream nitrate concentrations in the spring, and in base flow during the summer, are derived primarily from the spring recharge of ground water by snowmelt. Stream nitrate concentrations are also positively correlated with annual average air temperature; this suggests that microbial processing and subsequent leaching of nitrogen are sensitive to changes in temperature. These correlations indicate that nitrogen cycling in the Catskill watersheds is affected by both seasonal and annual variability in climatic conditions.

[1] U.S. Geological Survey, 425 Jordan Road, Troy, New York 12180

Processes that Affect the Transformation of Atmospherically Deposited Nitrogen in Catskill Mountain (New York) Watersheds

Douglas A. Burns[1], Peter S. Murdoch[1], Gregory B. Lawrence[1],
Carol Kendall[2], and Gary M. Lovett[3]

The rate of atmospheric-N deposition in the Catskill Mountains of New York is about 10 kg ha^{-1} yr^{-1}, among the highest in the United States. Concentrations of NO_3^- in Catskill streams range from less than 5 µmol L^{-1} in early fall to more than 100 µmol L^{-1} during snowmelt. Nitrate is a major factor in Catskill stream acidification and also contributes to downstream nutrient loads. Ammonium and dissolved organic N together constitute less than 20 percent of total dissolved N concentrations in Catskill streams. Studies by the U.S. Geological Survey in the region to date have focused on how the processes that affect the transport and transformation of atmospherically deposited N in watersheds that contain no other significant N sources affect both the temporal and spatial variability of stream NO_3^- concentrations. These studies have addressed three objectives: (1) whether nitrification in watershed soils is a significant source of stream NO_3^-, (2) why stream NO_3^- concentrations remain elevated during the growing season, and (3) whether riparian processes affect stream NO_3^- concentrations.

Results from buried soil-bag incubations indicate that soils in deciduous forest have the potential to nitrify and that potential nitrification rates change in response to soil-temperature changes. Rates of nitrification vary locally with stand type, and decrease in the following order: sugar maple = yellow birch > beech > hemlock. Soil bags removed during winter for analysis indicate that nitrification continues under the snowpack, although at lower rates than during the growing season. The $\delta^{18}O$ and $\delta^{15}N$ content of NO_3^- during spring snowmelt suggest that streamwater is a mixture of atmospherically derived and soil-generated NO_3^-. Current work seeks to measure the relative amounts of atmosphere- and soil-derived NO_3^- in streamwater throughout the year and to determine the fate of atmospherically deposited NH_4^+. Elevated concentrations of NO_3^- in streams during summer result largely from NO_3^- that recharges ground water during fall and early spring, then flows below the root zone before discharging to stream channels. Thus, concentrations of NO_3- in streams at base flow during summer are not directly affected by nitrogen uptake by vegetation during the growing season.

Mass balances were calculated for two stream reaches during four 48-hour periods in the spring, summer, and fall of 1992 to determine the importance of riparian processes in stream NO_3^- transport. Both stream reaches showed significant losses of NO_3^- in all four periods, and NO_3^- losses in one of the reaches exceeded the watershed contribution of NO_3^- from tributaries and ground water. Because ground-water flow rates are high, and dissolved organic carbon concentrations are low (< 200 µmol L^{-1}), riparian waters generally remain well oxygenated, preventing significant downstream losses of NO_3^- through denitrification. Most of the stream losses of NO_3^- are attributed to uptake by the periphytic community. Work to date has shown that, despite a general correlation between the atmospheric input of N and stream export of NO_3^-, hydrologic, biologic, and climatic factors affect N-transformation and transport processes that, in turn, determine the spatial and seasonal patterns of NO_3^- concentrations in streams.

[1] U.S. Geological Survey, 425 Jordan Road, Troy, NY 12180

[2] U.S. Geological Survey, 345 Middlefield Road, MS 434, Menlo Park, CA 94025

[3] Institute of Ecosystem Studies, The New York Botanical Garden, Mary Flagler Cary Arboretum, Route 44A, Millbrook, NY 12545

Effects of Atmospheric Nitrogen Deposition on the Availability of Nitrogen, Organic Carbon, and Calcium in Forest Soils of the Northeast

Gregory B. Lawrence[1] and Mark B. David[2]

Tree growth in forest ecosystems has traditionally been considered a function of N availability, but continued atmospheric deposition of N in the northeastern United States has increased N availability to the extent that, in some forests, it may no longer be growth limiting. Excess N within forest soils can stimulate nitrification, which in turn results in leaching of nutrient cations and subsequent acidification of surface water.

Through support of the U.S. Forest Service Global Change Research Program, relations among N, C, and Ca in soils of red spruce (*Picea rubens*) forests of the Northeast were recently evaluated. Soil and soil solutions were collected in Oa horizons and the upper 10 cm of B horizons at 12 sites in New York, Vermont, New Hampshire, and Maine. Atmospheric deposition at these sites was measured on-site or estimated by a spatial model of N deposition for the Northeast. These sites were selected to encompass the range of environmental conditions to which red spruce in the Northeast are exposed. Average stand age ranged from 90 to 175 years, and apparent stand condition ranged from no visible signs of stress to extensive dieback.

Atmospheric wet deposition of N was positively correlated with elevation ($p < 0.01$; $R^2 = 0.82$) and total N concentrations of Oa horizons ($p < 0.01$; $R^2 = 0.53$), and negatively correlated with Oa horizon C:N ratios ($p < 0.05$; $R^2 = 0.48$). Ratios of C:N were also negatively correlated with elevation ($p < 0.01$; $R^2 = 0.70$), suggesting that climate, as well as deposition, could affect C:N ratios. Although decreasing C:N ratios are commonly associated with increasing microbial activity and carbon mobilization, C:N ratios for these sites were positively correlated with dissolved organic carbon concentrations ($P < 0.01$; $R^2 = 0.82$). This relation could be an indication of varying degrees of humification because less humified organic matter tends to be more easily degraded and has higher C:N ratios than more decomposed organic matter.

At five of the twelve sites, soil solution NO_3^- concentrations in the Oa horizon indicated that nitrification was occurring. As would be expected, these five sites tended to have lower C to N ratios than the other sites, although soils at two sites with low C to N ratios were not nitrifying. Despite the acidifying effect of nitrification, however, those soils that were nitrifying tended to have the highest values for soil-solution pH. Also C to N ratios were negatively correlated with soil-solution pH ($p < 0.01$; $R^2 = 0.70$), which ranged from 3.3 to 3.8. These relations may have been caused by an limitation of nitrification in soils with the lowest solution-pH values. An inverse relation was found between soil solution concentrations of NO_3^- and Ca, suggesting that enhanced N availability may be related to a reduction in the forest-floor pool of available Ca that has likely occurred at these sites.

[1] U.S. Geological Survey, 425 Jordon Road, Troy, NY 12189
[2] University of Illinois, Dept. of Forestry, 1102 S. Goodwin Ave., Urbana, IL 61801

Nitrogen Cycling in Alpine Catchments: Loch Vale, Colorado

Donald H. Campbell[1], Carol Kendall[2], Steve Austin[3], Jeffrey G. Fetkenhour[1], and Justin Stockwell[1]

Nitrate and ammonium concentrations and fluxes in precipitation, snowpack, snowmelt, subsurface water, and two alpine streams were evaluated to investigate nitrogen saturation and cycling. Atmospheric deposition of nitrogen in Loch Vale and nearby areas of northern Colorado is high compared to other parts of the Rocky Mountain region. Volume-weighted mean (VWM) annual concentrations of precipitation during 1992 were 11 μmol L^{-1} NO_3 and 7 μmol L^{-1} NH_4. Nitrate concentrations in two alpine streams in the Loch Vale Watershed had VWM annual concentrations of 21 and 23 μmol L^{-1} NO_3, and less than 1 μmol L^{-1} NH_4. Streamwater NO_3 concentrations ranged from 10 μmol L^{-1} in late summer to greater than 40 μmol L^{-1} during snowmelt. Export of NO_3 in streamflow is approximately equivalent to atmospheric deposition of NH_4 plus NO_3, indicating that inorganic nitrogen is not retained in these catchments.

Concentrations of nitrogen species and other major ions were preserved in individual strata of the snowpack throughout the winter. Also, volume-weighted mean concentrations of NH_4 and NO_3 of snowmelt were equivalent to concentrations of the bulk snowpack at maximum accumulation, suggesting little uptake or conversion of inorganic nitrogen species in the snowpack, during either the cold season or the melt period.

Samples of soil solutions from wetlands and forested areas (which make up a small percentage of the watershed) contained little or no NO_3 throughout the snow-free season, but samples collected at the base of talus generally had NO_3 concentrations of 30-70 μmol L^{-1}, with some greater than 150 μmol L^{-1}. NH_4 concentrations in most soil solutions were 0-3 μmol L^{-1}.

To evaluate sources of NO_3, the dual-isotope (^{15}N and ^{18}O) signature of NO_3 was examined. The streamwater NO_3 is intermediate between that of NO_3 from snowmelt and that expected from nitrification of NH_4. Increased NO_3 in streams during snowmelt probably is caused by a combination of elution from the melting snowpack and flushing of subsurface water, especially from talus. Although little opportunity for uptake of nitrogen is expected in a terrestrial ecosystem that lacks well-developed soil and is limited by a short growing season and cold temperatures, the NH_4 from atmospheric deposition is nitrified. Nitrogen appears to be cycled along subsurface hydrologic flowpaths, even during the period of rapid snowmelt flushing.

[1] U.S. Geological Survey, MS 415, Denver CO 80225
[2] U.S. Geological Survey, MS 434, Menlo Park, CA 94025,
[3] Dept. Earth Resources, Colorado State University, Ft. Collins CO 80523

Contributions of Mn and Fe Species to Biologically-Mediated Nitrogen Redox Reactions

Carol J. Lind[1]

International concern for the anthropogenically-caused increases in the concentration of nitrogen species in the environment has stimulated research concerning biologically-mediated nitrogen redox reactions. Thermodynamic calculations predict the potentials for these biologically-mediated reactions to occur at specific values of pH, pe, concentrations of reactants, etc.

Comparison of the pe value for one redox-pair half-reaction with the pe value for another redox-pair half-reaction will determine the possible path of the coupled half-reactions. In other words, potentially, at a specific pH and specific activities of the half-reaction components, the higher pe value indicates the oxidizing half-reaction and the lower pe value indicates the reducing half-reaction. Frequently reported, biologically-mediated half-reactions that oxidize nitrogen species are NH_4^+ to N_2O, NH_4^+ to NO_2^-, and NO_2^- to NO_3^- and those that reduce nitrogen species are NO_3^- to N_2O, NO_3^- to N_2, NO_3^- to NH_4^+, and N_2 to NH_4^+. The oxidations of nitrogen species were coupled with birnessite reduction to Mn^{2+} and with $Fe(OH)_3$ reduction to Fe^{2+}. Birnessite, a highly-oxidized manganese oxide, and $Fe(OH)_3$ are commonly found in ground and surface waters and in soils. The reductions of nitrogen species were coupled with Mn^{2+} oxidation to Mn_3O_4, to $\gamma MnOOH$, and to $\beta MnOOH$ and with Fe^{2+} oxidation to $Fe(OH)_3$. The initial oxidation product of Fe^{2+} is $Fe(OH)_3$ and, depending on solution conditions, the initial oxidation product of Mn^{2+} is Mn_3O_4, $\gamma MnOOH$, or $\beta MnOOH$. The pH values, activities, and partial pressures applied have been measured in ground and surface waters and in soils. Pe and pH values were compared at pH values of 4, 6, and 8 and $[Mn^{2+}]$ and $[Fe^{2+}] = 10^{-8}$ and $10^{-4}\ ML^{-1}$.

Comparisons of pe values indicate that the potential directions of the coupled half-reactions are as follows: 1) birnessite reduction to Mn^{2+} by all three nitrogen oxidation reactions, with the potential for the birnessite reduction involving the NO_2^- to NO_3^- oxidation decreasing to little or nothing as the $[Mn^{2+}]$ of $10^{-4}\ ML^{-1}$ and pH 8 are approached; 2) potential $Fe(OH)_3$ reduction to Fe^{2+} by the three nitrogen oxidation reactions changes from impossible to possible as solution composition decreases towards $[Fe^{2+}] = 10^{-8}\ ML^{-1}$ and pH 4; 3) Mn^{2+} oxidation to Mn_3O_4, to $\beta MnOOH$, or to $\gamma MnOOH$ by reductions of NO_3^- to N_2O or NO_3^- to N_2, the potential for reactions changing from impossible to possible as $[Mn^{2+}]$ increases towards $10^{-4}\ ML^{-1}$ and pH towards 8; 4) Fe^{2+} oxidation to $Fe(OH)_3$ by reductions of NO_3^- to N_2O, NO_3^- to N_2, and NO_3^- to NH_4^+, oxidation by the NO_3^- reduction to NH_4^+ becoming less likely near $[Fe^{2+}] = 10^{-8}\ ML^{-1}$ and pH = 4; 5) no Mn^{2+} oxidation to Mn_3O_4 nor to $\gamma MnOOH$ by NO_3^- reduction to NH_4^+ except as $[Mn^{2+}]$ increases to near $10^{-4}\ ML^{-1}$ and pH 8; 6) no Mn^{2+} oxidation to $\beta MnOOH$ by NO_3^- reduction to NH_4^+; 7) No Mn^{2+} oxidation to Mn_3O_4, to $\gamma MnOOH$, nor to $\beta MnOOH$ nor Fe^{2+} oxidation to $Fe(OH)_3$ by N_2 reduction to NH_4^+. Dependence of redox couples on solution conditions will be illustrated in pe-pH plots at the workshop.

[1] U.S. Geological Survey, MS 427, Menlo Park, CA

Nitrogen Transformations and Transport in Acidic Coal-Mine Spoil

Charles A. Cravotta, III[1]

Transformations and transport of nitrogen at surface coal mines can have an important effect on the acidification of coal-mine spoil and associated ground water. Ground water and drainage from coal mines commonly are acidic and contain elevated concentrations of dissolved metals and SO_4^{2-} because of the oxidation of pyrite (FeS_2). The iron-oxidizing bacterium, *Thiobacillus ferrooxidans*, which catalyzes the oxidation of FeS_2, requires primarily NH_4^+ or, secondarily, NO_3^- as a nutrient. Furthermore, coupled oxidation of FeS_2 and reduction of NO_3^- to N_2 or NH_4^+ can be an important acid-forming reaction, particularly where the supply of O_2 is limited. Sources of NH_4^+ and NO_3^- at coal mines include clay minerals and blasting-agent residues, which can be mixed throughout the spoil; and sewage sludge or fertilizer, which may be added to the surface of the spoil to promote revegetation. In typical, well-drained agricultural soils ($pH > 5$), the mobilities of NH_4^+ and NH_3 are controlled by sorption, and these reduced nitrogen compounds tend to be oxidized by nitrifying bacteria to NO_3^-, which generally is stable and mobile. However, in acidic systems ($pH < 5$), bacterial oxidation of NH_4^+ to NO_3^- is inhibited, and NH_4^+ ions can be mobilized if clay-mineral sorbents become protonated and unstable.

Ground-water-quality data, which were collected for two years after sewage sludge was applied at a reclaimed surface coal mine in Pennsylvania, indicate that concentrations of acidity, metals, SO_4^{2-}, and NO_3^- and densities of iron-oxidizing bacteria were greater in sludge-treated mine spoil than in untreated spoil having a similar composition. Concentrations of NO_3-N frequently exceeded 20 mg/L in shallow (<2 m), vadose-water samples from sludge-treated spoil, but were always less than 3 mg/L in vadose-water samples from untreated spoil and in ground-water samples from sludge-treated and untreated spoil. Concentrations of NH_4^+ in the ground water beneath sludge-treated and untreated spoil generally exceeded those of NO_3^-, despite abundant supplies of gaseous and dissolved O_2 in the subsurface. These differences in ground-water quality and positive linear correlations between densities of iron-oxidizing bacteria and concentrations of acidity, metals, SO_4^{2-}, NH_4^+, NO_3^- in ground-water samples from the mine suggest that nitrogen-rich materials added to pyritic coal-mine spoil can encourage the subsurface growth of iron-oxidizing bacteria and the formation of acidic mine drainage. Mass-balance computations indicate that elevated concentrations of SO_4^{2-} in ground water from sludge-treated spoil also could have been produced by coupled FeS_2 oxidation and NO_3^- reduction to N_2 or NH_4^+. Hence, the combined effects of direct chemical oxidation of FeS_2 by NO_3^- and indirect effects of NH_4^+ on microbial catalysis of FeS_2 oxidation could be significant.

[1] U.S. Geological Survey, 840 Market Street, Lemoyne, PA 17043

Group 4: Uses of Isotopes for Determining Sources

Chairperson--J.K. Böhlke

Abstract	Presenter
Uses of Oxygen and Nitrogen Isotopes to Trace Sources and Cycling of Nitrate in Hydrologic Systems	Carol Kendal
A New Technique for Collection and Preparation of Dissolved NO_3 for $\delta^{15}N$ and $\delta^{18}O$ Analyses and Preliminary Applications	Steven R. Silva
Tracing Sources of Nitrate in Snowmelt Runoff Using the Oxygen and Nitrogen Isotopic Composition of Nitrate	Carol Kendall
Water Quality and Potential Sources of Nitrate in Shoal Creek and Waller Creek Watersheds, Austin, Texas, September 1994–April 1995	Patricia B. Ging
Movement of ^{15}N-Labeled Nitrogen Fertilizer and Bromide Tracers in Glacial Till and a Claypan Soil	Donald H. Wilkison

Use of Oxygen and Nitrogen Isotopes to Trace Sources and Cycling of Nitrate in Hydrologic Systems

Carol Kendall[1], Steven R. Silva[1], and Cecily C. Chang[1]

Attempts to use $\delta^{15}N$ for tracing the source and fate of nitrate in ground and surface waters often have only limited success because: (1) potential sources commonly have overlapping $\delta^{15}N$ values, (2) denitrification and other reactions can alter the $\delta^{15}N$ values so that only qualitative estimates of relative contributions are possible, and (3) mixing of point and non-point sources along flowpaths makes determination of sources and extent of denitrification very difficult. Workers have speculated that analysis of the $\delta^{18}O$ of nitrate in conjunction with $\delta^{15}N$ would significantly improve our ability to trace nitrate sources and cycling.

This dual-isotope approach has two main potential benefits: (1) nitrate sources that are presently indistinguishable with $\delta^{15}N$ alone (eg., fertilizer vs soil nitrate, or atmospheric vs soil nitrate) may be distinguished when the $\delta^{18}O$ of nitrate is also analyzed; and, (2) the relative contributions from point and non-point sources may be determined regardless of the extent of denitrification that has occurred. However, from the few dual-isotope studies that have been conducted thus far, it is not yet clear whether $\delta^{18}O$ will be the panacea hoped. Recently developed methods for the collection, preparation, and analysis of nitrate for both $\delta^{15}N$ and $\delta^{18}O$ (see presentation by Silva and others) will facilitate more investigations of the utility of the dual-isotope method for tracing sources and cycling of nitrate.

To test the applicability of a multi-isotope approach for tracing nitrate sources in situations where the $\delta^{15}N$ values of the potential sources are generally indistinguishable, we have conducted several recent studies. Most of our work has been aimed at determining the sources of large concentrations of nitrate in streamflow during snowmelt. The two likely sources of the nitrate in these streams are atmospherically-derived nitrate and ammonium in the snowpack, and soil-derived nitrate resulting from nitrification. We use this and other examples to illustrate some of the benefits and pitfalls of the dual-isotope method, and to provide guidelines for its application to future full-scale investigations of nitrate sources.

[1] U.S. Geological Survey, MS 434, 345 Middlefield Rd., Menlo Park, CA 94025

A New Technique for Collection and Preparation of Dissolved NO_3 for $\delta^{15}N$ and $\delta^{18}O$ Analyses and Preliminary Applications

Steven R. Silva[1], Cecily C. Chang[1], Carol Kendall[1], P.B. Ging[2],
and Donald H. Wilkison[3]

A new method for concentrating nitrate from fresh waters for $\delta^{15}N$ and $\delta^{18}O$ analysis has been developed. Nitrate is collected by passing sample water through a disposable, anion exchange resin column in the field which is then transported to the laboratory for extraction and analysis. The benefits of the method are: (1) elimination of the need to transport large volumes of water to the laboratory for processing, (2) elimination of the need for hazardous preservatives, and (3) ability to concentrate nitrate from dilute waters.

Nitrate is stripped from the columns with HCl. The nitrate-bearing eluant is neutralized with Ag_2O, filtered to remove the resulting AgCl precipitate, and the resultant solutions split for separate $\delta^{15}N$ and $\delta^{18}O$ preparations. The portion for $\delta^{15}N$ is freeze-dried and combusted with Cu, CuO, and CaO in sealed quartz tubes to form N_2. The 1σ analytical precision for $\delta^{15}N$ is $\pm 0.05‰$. For the $\delta^{18}O$ portion, oxygen-bearing anions are precipitated with $BaCl_2$ and residual DOC is removed with activated carbon. The solution is filtered, freeze-dried, and combusted with graphite in sealed quartz tubes to form CO_2. The 1σ analytical precision for $\delta^{18}O$ is about $\pm 0.5‰$.

Seven preliminary studies using the new technique indicate that the combination of $\delta^{15}N$ and $\delta^{18}O$ compositions can distinguish between nitrates derived from precipitation, animal waste/sewage, nitrate fertilizers, and natural terrestrial sources. A particularly promising application of the dual isotope technique is to studies of the relative contribution of nitrate from atmospheric and terrestrial sources. Source determinations in agricultural areas are complicated by multiple nitrate sources with overlapping compositions and by the fact that much of the agricultural nitrate is derived through oxidation of ammonium, which tends to yield a narrow range of $\delta^{18}O$ values. In one urban study, the dual isotope approach was particularly successful in identifying surface and sub-surface nitrate sources collected from streams during stormflow and baseflow respectively. In addition to sources separation studies, the dual isotope approach may be useful in documenting denitrification, and applicable to questions of timing and depth of nitrate production.

[1]U.S. Geological Survey, MS 434, Menlo Park, CA 34025
[2]U.S. Geological Survey, 8011 Cameron Rd., Bldg. A, Austin, TX 78754
[3]U.S. Geological Survey, 301 W. Lexington, Independence, MO 64050

Tracing Sources of Nitrate in Snowmelt Runoff Using the Oxygen and Nitrogen Isotopic Composition of Nitrate

Carol Kendall[1], James B. Shanley[2], Douglas A. Burns[3], Donald H. Campbell[4],
Steven R. Silva[1], and Cecily C. Chang[1]

During early spring melt, many small catchments experience episodic acidification of sensitive surface waters. This is sometimes due to large pulses of nitrate and hydrogen ions being flushed into the streams when discharge is low. There has been some controversy over the source of this nitrate. The two likely sources are: (1) atmospherically derived nitrate in the snowpack that is eluted during early melt or (2) nitrate developed in the organic horizons of the soil under the insulating snowpack that is flushed into the stream by percolating meltwater. These two sources of nitrate cannot be distinguished using nitrogen isotopes alone because atmospheric and soil-derived sources of nitrogen generally have overlapping isotopic compositions. We hypothesized that these two sources would have distinctive nitrate-$\delta^{18}O$ values and that the relative contributions of these two sources of nitrogen to streamflow over the melt period could be quantified by the combined use of $\delta^{18}O$ and $\delta^{15}N$ of nitrate.

To test the applicability of this dual-approach for tracing nitrate sources, pilot studies were initiated in three catchments during the 1994 snowmelt season: Biscuit Brook, Catskills Mountains, New York; Andrews Creek, Rocky Mountains, Colorado; and Sleepers River, Vermont. Atmospheric deposition was sampled by collecting snow profiles and cores at several locations prior to melt and by collecting snowmelt lysimeter samples throughout the melt period. Soil was sampled by augering samples from beneath the snowpack and leaching the nitrate and ammonium from them, and by collecting shallow soil-water samples. Ground water and stream samples were collected throughout the melt as well.

Almost all stream samples have nitrate $\delta^{18}O$ and $\delta^{15}N$ values within the range of the pre-melt waters, indicating that atmospheric nitrate is an insignificant source of nitrate in early runoff. Therefore, the nitrate eluted from the 1994 snowpack appeared to go into storage, and most of the nitrate in streamflow during the period of potential acidification was derived from soil sources. The main sources of uncertainty in calculating the relative contributions from the two nitrate sources are the ranges in the end-member compositions and uncertainty about whether snow ammonium is retained in the soil or is nitrified to nitrate.

The $\delta^{18}O$ of nitrate in pre-melt waters is 10 to 20‰ heavier than expected. Given the range of $\delta^{18}O$ values of catchment waters, the $\delta^{18}O$ of nitrate was expected to be in the range of -5 to +5‰. The more positive values probably indicate that atmospheric nitrate is a major source of nitrate to the catchment on a yearly basis, and that the nitrate pulse flushed from storage during early melt is partly derived from precipitation from previous months or years.

[1] U.S. Geological Survey, 345 Middlefield Rd., MS 434, Menlo Park, CA 94025
[2] U.S. Geological Survey, P.O. Box 628, Montpelier, VT 05601
[3] U.S. Geological Survey, Box 25046, Denver Federal Center, Lakewood, CO 80225
[4] U.S. Geological Survey, P.O. Box 1397, Albany, NY 12201

Water Quality and Potential Sources of Nitrate in Shoal Creek and Waller Creek Watersheds, Austin, Texas, September 1994–April 1995

Patricia B. Ging[1], Roger W. Lee[1], and Steven R. Silva[2]

Land use within the Shoal Creek and Waller Creek watersheds, Austin, Texas, is primarily residential (single-family and multifamily dwellings). Impervious cover for both watersheds is approximately 55 percent. The older residential areas might have septic tanks and (or) sewer lines that can deteriorate, which would allow sewage effluent to enter the watersheds. Steep limestone slopes, thin soils, sparse vegetation, and impervious cover contribute to rapid runoff rates in these watersheds that can quickly carry contaminants, such as nitrate, into Shoal Creek and Waller Creek. Nitrogen and oxygen isotopes in nitrate can be used to determine the source(s) of nitrate in surface water.

Water-quality samples were collected for chemical analysis at seven sites in the two watersheds from September 1994 to April 1995. Samples were collected three times during base flow and four times during stormflow. Water-quality samples were analyzed for major ions and nutrients as well as for nitrogen and oxygen isotopes in nitrate. Concentrations of dissolved constituents, including nitrate, are greater in base-flow samples than in stormflow samples, and concentrations are typical of highly urbanized areas. Calculated total dissolved solids range from 214 to 499 milligrams per liter for base-flow samples and from 16 to 187 milligrams per liter for stormflow samples. Isotopic ratios for base-flow samples ($\delta^{15}N$ from +8.4 to +13.1 and $\delta^{18}O$ from -0.08 to +19.0) along with the environmental setting indicate that the possible nitrate source could be sewage or animal waste during low-flow periods; whereas isotopic ratios for stormflow samples ($\delta^{15}N$ from +1.9 to +10.6 and $\delta^{18}O$ from +8.7 to +39.5) along with the environmental setting indicate that the possible nitrate source could be synthetic nitrate fertilizers during high-flow periods. Atmospheric nitrate is not a likely contributor to the nitrate concentrations in Shoal Creek and Waller Creek due to small nitrate concentrations in rainfall for this region.

[1]U.S. Geological Survey, 8011 Cameron Road, Austin, Texas, 78754
[2]U.S. Geological Survey, 345 Middlefield Road, MS 434, Menlo Park, CA 94025

Movement of ^{15}N-Labeled Nitrogen Fertilizer and Bromide Tracers in Glacial Till and a Claypan Soil

Donald H. Wilkison[1], Dale W. Blevins[1], and Michael L. Pomes[1]

Water samples from 59 of 273 rural domestic wells (22%) sampled in northern Missouri in 1991-92 had concentrations of nitrate (NO_3) greater than the Missouri drinking-water standard of 10 mg L^{-1}. As a result, a field experiment was conducted to evaluate the transport of nitrogen (N) fertilizer through the hydrologic regime at the Management Systems Evaluation Area (MSEA) near Centralia, Missouri. Soil at the MSEA site is characterized by a 50% argillic horizon (claypan) located 0.41 to 0.43 m below the soil surface. The claypan is underlain by 17 m of loess and glacial till that comprise the surficial aquifer.

A isotopically labeled ($^{15}NO_3$) fertilizer was applied at a rate of 94 kg of N per hectare in May 1992 to a 400 m^2 test plot. The plot was planted to corn (*zea mays* L.) using conventional farming practices. Bromide was applied concurrently with the ^{15}N-labeled fertilizer. The fertilizer and bromide were then traced through surface runoff, and the unsaturated and saturated zones.

The site is instrumented with a continuous-recording flume, 14 monitoring wells, 18 suction and 10 gravity lysimeters, and 2 neutron-probe access tubes. Samples from runoff, unsaturated-zone water, and ground water were analyzed for nitrogen species, $\delta^{15}N^-NO_3$ (ratio of ^{15}N to ^{14}N in NO_3, relative to atmospheric N, expressed in per mil), and bromide. Anion-exchange resins were used for the collection and preparation of NO_3 from natural waters for the determination of $\delta^{15}N^-NO_3$. Soil, grain, and stover samples were collected annually and analyzed for nitrogen species, δ^{15}N, and bromide.

Less than 2% of the ^{15}N-labeled fertilizer had been lost to runoff in two growing seasons, even though ^{15}N-labeled fertilizer in water samples from the first runoff event after application accounted for 36% of NO_3 in the sample. The ^{15}N-labeled fertilizer accounted for only 5% of NO_3 in runoff three growing seasons (28 months) after application. Concentrations of bromide were at background levels thirty months after application of the ^{15}N-labeled.

Two growing seasons after application, 27.3% of the ^{15}N-labeled fertilizer had been removed with grain harvest, with more than 80% of that being removed the first year. Grain harvest from the third growing season, 1994, removed less than 2% of the original fertilizer, using estimates based on bromide analyses.

At the end of two growing seasons, 5% of the ^{15}N-labeled fertilizer remained in the soil and 30% was in the saturated zone. The NO_3 transport to the saturated zone was limited by evapotranspiration during the growing season. The claypan did not inhibit recharge or NO_3 transport due to the presence of preferential flow paths associated with cracks, worm and rootlet holes, and abrupt grain-size changes.

Interflow, horizontal transport on top of the claypan, accounted for 2% of the ^{15}N-labeled. One-third of the ^{15}N-labeled was not accounted for after two growing seasons and was presumably lost from denitrification and volatilization of ammonia (NH_3) from corn leaves. Additional research is currently underway to model N-transport and to characterize and quantify gaseous N losses through denitrification and NH_3 volatilization.

[1] U.S. Geological Survey, 301 W. Lexington, Independence, Missouri 64050

Group 5: Nitrogen Transport and Fate in Riparian Areas

Chairperson--Richard L. Smith

Abstract	Presenter
Measuring Denitrification Rates in Nitrate-Contaminated Ground Water	Richard L. Smith
Modeling Denitrification Experiments Conducted with ^{15}N Labelled Nitrate in a Sandy Aquifer, Cape Cod, Massachusetts	Stephen P. Garabedian
In-situ Remediation of Nitrate in Ground Water Using Formate Stimulated Denitrification	Brigid Rea Kumler

Measuring Denitrification Rates in Nitrate-Contaminated Ground Water

Richard L. Smith[1], Stephen P. Garabedian[2], and
Myron H. Brooks[3]

Denitrification is a microbial process capable of significantly affecting nitrate contamination in ground water. However, little is known about the rates of the process in situ, especially relative to the rates of nitrate transport. Denitrifying activity was assayed in a nitrate- contaminated, unconfined sand and gravel aquifer located on Cape Cod, Massachusetts using small-scale (10 m), natural gradient tracer tests. Field results were compared to laboratory incubations with aquifer core material from the site. Coinjection of bromide (as a conservative tracer) and acetylene (6.2 and 1.0 millimolar, respectively) into the aquifer produced nitrous oxide within the tracer cloud, peak concentrations, which were 30 micromolar above background, occurred 2 days after the maximum bromide concentrations. A one dimensional advection-dispersion transport model was modified to include an acetylene-dependent nitrous oxide production term, then tested, and used to determine in situ denitrification rates by selecting best-fit simulations of the tracer test breakthrough curves. Included in the model were a 4 day lag period for the acetylene inhibition to become effective and a relatively low sensitivity to acetylene (as compared to pure cultures) to simulate the nitrous oxide breakthrough curves, which were narrow relative to the bromide. In-situ denitrification rates were determined to be 0.60 and 1.51 micromolar N_2O produced day $^{-1}$ for 2 successive tests. Corresponding acetylene block assays with core material collected from the tracer test site and incubated in flasks as mixed slurries and as intact cores resulted in rate estimates that were up to 10-fold higher than the in-situ rates. Results with the coring-dependent techniques were more variable than those from the racer test. The tracer tests integrated the small-scale heterogeneity along a flow path, giving a rate estimate that is more pertinent to the scale of the aquifer. These results demonstrate that denitrification is a major factor in controlling nitrogen speciation within this aquifer, but that the rates of the process are slow relative to bulk ground water flow.

[1] U.S. Geological Survey, 3215 Marine Street, Boulder, CO 80303
[2] U.S. Geological Survey, 28 Lord Street, Marlborough, MA 01752
[3] U.S. Geological Survey, P.O. Box 25406, MS 418, Denver Federal Center, Lakewood, CO 80225

Modeling Denitrification Experiments Conducted with ^{15}N Labelled Nitrate in a Sandy Aquifer, Cape Cod, Massachusetts

Stephen P. Garabedian[1], Richard L. Smith[2], J.K. Böhlke[3],
Tadashi Yoshinari[4], and Kinga M. Revesz[3]

Tracer experiments have been conducted over the last decade at the U.S. Geological Survey's Cape Cod Toxic Substances Hydrology research site in Falmouth, Massachusetts, to investigate denitrification in a sewage-contaminated sandy aquifer. Since 1992, these denitrification experiments have been conducted using ^{15}N labelled nitrate to measure the production rates of individual steps that occur during the degradation process. Breakthrough curves of bromide (a conservative solute used to observe solute velocity and dispersion during the experiments), nitrate, nitrite, nitrous oxide, and nitrogen gas were measured in experiments conducted over 10-m travel distances. Results indicated that ^{15}N was incorporated into all of the intermediate denitrification products. There was a sequential decrease in the ^{15}N content of each intermediate, although there appeared to be a relatively greater accumulation of ^{15}N in nitrite than was expected.

Ongoing numerical experiments indicate that in situ denitrification experiments are often difficult to interpret using mathematical modeling approaches. These difficulties arise due to variability in the subsurface physical, chemical, and microbiological conditions and because the factors controlling the rates of the transport processes (including microscale and averaged pore-scale concentrations) are not well understood. Thus, it appears that linked, first-order, kinetic reactions explain some, but not all, of the observed transport and fate of nitrogen species during these field tracer tests. Results to date indicate that the denitrification rates calculated using the first-order model for the ^{15}N experiments are lower than those calculated from the acetylene block tests conducted at the same site.

[1]U.S. Geological Survey, 28 Lord Road, Marlborough, MA
[2]U.S. Geological Survey, 3215 Marine Street, Boulder, CO
[3]U.S. Geological Survey, 431 National Center, Reston, VA
[4]NY State Dept. Health & School of Public Health, Empire State Plaza, Albany, NY

In-situ Remediation of Nitrate in Ground Water Using Formate Stimulated Denitrification

Brigid Rea Kumler[1], Richard L. Smith[1], and Myron H. Brooks[2]

Nitrate is the most prevalent ground-water contaminant in the United States and worldwide. Effective treatment strategies are needed to help reduce the risk associated with nitrate in drinking water supplies. In-situ stimulation of denitrification to remediate nitrate contaminated ground water was investigated at a study site on Cape Cod, Mass. Other investigations at this site have identified denitrification as an active process within the anaerobic core of a plume of ground water contaminated with sewage effluent. In laboratory experiments, denitrifying activity could be enhanced when either hydrogen or formate were added as electron donors; nitrate was reduced completely to nitrogen gas. Field experiments designed to test small-scale remediation of nitrate contamination through addition of formate were conducted at the same site in 1993 and 1994. Nitrate-contaminated ground water was withdrawn from a previously identified zone of active denitrification, amended with sodium bromide and sodium formate, and injected continuously at 6-8 liter per hour back into the same geochemical zone. Breakthrough of the conservative tracer (bromide) and concentrations of the reactive species (nitrate, nitrite, nitrous oxide and formate) were measured at multilevel samplers 7, 10 and 15 meters (m) downgradient of the injection point. In 1993 formate was added for 16 days. Nitrate concentrations decreased from 23 to 7 milligrams per liter (mg/L) N while nitrite concentrations increased from 0.6 to 14 mg/L N, but only at the end of the experiment after a 46 day delay and 10 m of travel. In 1994 formate was added for 25 days. Nitrate concentrations were observed to decrease immediately upon arrival of the added formate. At 15 m downgradient, nitrate was completely removed, while nitrite concentrations increased from 0.3 to 10 mg/L. No evidence of further reduction of nitrate was found despite the presence of more than 100 mg/L formate. In laboratory experiments conducted after the 1994 injection, core material from the injection zone consumed formate 7-fold faster than control material collected from a location not exposed to formate, demonstrating an in-situ adaptation by the indigenous microbial populations. Results of these experiments demonstrate that the potential exists for using formate-stimulated denitrification at this site, but also indicate the need for more understanding of the factors that influence the ultimate products of nitrate reduction. The differences between laboratory and field results emphasize the need for thorough field testing of bioremediation approaches.

[1]U.S. Geological Survey, 3215 Marine St., Boulder, CO 80303
[2]U.S. Geological Survey, P.O. Box 25406, MS 418, Denver Federal Center, Lakewood, CO 80225

Group 6: Nitrogen Transport and Fate in Riparian Areas

Chairperson--Richard L. Smith

Abstract	Presenter
Chronology and Isotope Geochemistry of Nitrate Contamination in Agricultural Watersheds	J.K. Böhlke
Variations in Nitrate Nitrogen Concentrations Beneath a Riparian Wetland in Minnesota	Lan H. Tornes
The Role of Wetlands in Reducing Nitrogen Loadings to the Otter Tail River in Minnesota	Larry J. Puckett
Ground-Water/Surface-Water Interactions on the Konkapot River, Massachusetts and Connecticut	John R. Mullaney

Chronology and Isotope Geochemistry of Nitrate Contamination in Agricultural Watersheds

J.K. Böhlke[1], Judy M. Denver[2], Richard B. Wanty[3], and Peter B. McMahon[4]

Ground waters underlying agricultural watersheds commonly have large vertical and (or) horizontal gradients in nitrate concentrations. As a result, current fluxes of nitrate into ground water at the water table commonly are different from fluxes of nitrate to surface waters from ground-water discharge. To understand and predict the effects of ground-water discharge on the nitrate contents of surface waters, we need to know whether the ground-water nitrate gradients are transient or steady-state features. We have applied a combination of chronologic, isotopic, and geochemical analytical approaches in several agricultural watersheds in the U.S. to address the following questions: (1) To what extent are nitrate gradients in ground water related to the history of nitrogen input (transient features), or maintained by fluid-aquifer interactions (steady-state features)? (2) What controls the distribution and effectiveness of natural remediation? (3) What are the implications of nitrate gradients in ground water with respect to nitrate loads in surface water?

Samples of ground water were collected in 2-dimensional transects parallel to the directions of flow from recharge areas under fertilized fields to discharge areas beneath streams in 3 study areas, located in Maryland (Delmarva NAWQA), Minnesota (Princeton, MSEA), and Colorado (S. Platte NAWQA). At each of the sites, nitrate concentrations were higher in shallow recharging ground waters than in discharging ground waters and surface waters. Chlorofluorocarbon concentrations were used to determine the time since recharge of the different parcels of ground water; dissolved-gas concentrations were used to estimate the amount of nitrate lost by denitrification in each parcel; nitrogen stable isotope ratios were used to determine the sources of nitrate and to help quantify nitrate-consuming reactions. Those transect data, combined with the major-element chemistry of the waters and with limited time-series data, indicate that vertical and horizontal nitrate gradients in ground water were the result of both transient and steady-state features. Much of the variation of nitrate in recharging ground waters beneath cultivated fields was related to changing agricultural practices over the last 10 to 40 years, while relatively low nitrate concentrations in ground waters discharging to streams were the result of at least three different processes that could be quantified: (1) discharge of relatively old ground waters with low original nitrate contents; (2) denitrification along some ground-water flow paths; and (3) mixing of ground waters with surface waters beneath some discharge sites. Past and future trends in surface-water nitrate loads are likely to depend largely on the historical and hydrogeochemical variables controlling those processes in each watershed.

[1] U.S. Geological Survey, 431 National Center, Reston, VA 20192
[2] U.S. Geological Survey, Federal Bldg., Rm 1201, Dover, DE 19904
[3] U.S. Geological Survey, MS 916, Denver Federal Center, Denver, CO 80225
[4] U.S. Geological Survey, MS 415, Denver Federal Center, Denver, CO 80225

Variations in Nitrate Nitrogen Concentrations Beneath a Riparian Wetland in Minnesota

Lan H. Tornes[1], Larry J. Puckett[2], and Jeffrey D. Stoner[1]

Nitrate-nitrogen (nitrate) concentrations were measured in water from an alluvial aquifer beneath a riparian wetland during August 1994 and August 1995. A grid of sites near the surface of the aquifer was sampled through a mini-piezometer. The wetland is in a ground-water discharge area in northwestern Minnesota at a research site established for the Red River of the North study unit of the National Water-Quality Assessment Program. Mapping the areal distribution of nitrate concentrations in 1994 revealed a laterally variable distribution beneath the wetland. Concentrations ranged from less than 0.1 milligrams per liter (mg/L), the detection limit, to more than 22 mg/L. In 1995, the distribution of nitrate was generally similar, but differences from the previous sampling were evident. Measurable nitrate was found in areas where previously it had not been detected, and in other areas nitrate concentrations had declined. Nitrate concentrations and results of ground-water-flow models suggest that agricultural applications upgradient from the wetland are the primary source of nitrate. Measurements of unstable constituents (dissolved oxygen and various oxidation-reduction couples) indicated that denitrification was occurring beneath the wetland. Variations in nitrate concentration could result from (1) ground water moving rapidly beneath parts of the wetland not having time to denitrify as completely as slower moving water; (2) localized upward movement of older ground water without nitrate mixing with younger shallow ground water having relatively high nitrate concentrations; or (3) local variations in nitrate inputs upgradient.

[1]U.S. Geological Survey, 2280 Woodale Drive, Mounds View, MN 55112
[2]U.S. Geological Survey, National Center, MS 413, Reston, VA 20192

The Role of Wetlands in Reducing Nitrogen Loadings to the Otter Tail River in Minnesota

Larry J. Puckett[1], Lan H. Tornes[2], Timothy K. Cowdery[2], Mark E. Brigham[2], and
Jeffrey D. Stoner[2]

An 8.3 km reach of the Otter Tail River in west-central Minnesota was studied to determine the role of wetlands in reducing nitrogen loadings to the river. The study reach receives water from a 37.6 km^2 agricultural area, consisting of about 27 km^2 of cropland, underlain by a surficial aquifer of glacial sand and gravel. The study reach gains a flow of about 0.4 $m^3\ s^{-1}$ during late summer and winter months as the result of ground water discharge. Mass-input estimates indicate that the area receives more than 200 metric tons of nitrogen yr^{-1}, 72% of which is applied as commercial fertilizer. Wells were installed along a 5-km transect that roughly parallels the direction of ground-water flow through the agricultural area and terminates at a 45-m wide wetland adjacent to the Otter Tail River. Additional wells were installed at other locations throughout the study area. Mini-piezometers were used to sample shallow ground water beneath the wetland. Nitrate concentrations in ground water sampled during the summer of 1994 ranged from below detection (0.05 mg L^{-1}) to 46 mg L^{-1}, with concentrations exceeding 10 mg L^{-1} in 38 percent and 3 mg L^{-1} in 58 percent of the wells sampled in the agricultural area--the median concentration was 4.1 mg L^{-1}. Nitrate concentrations were greater than 10 mg L^{-1} in shallow ground water beneath the edge of the wetland, but NO_3^- concentrations in the Otter Tail River are commonly near or below detection. Assuming conservative transport and mixing of ground water having an average NO_3^- concentration of 3 to 10 mg L^{-1}, the 0.4 $m^3\ s^{-1}$ increase in streamflow should have resulted in a stream concentration of 0.4 to 1.3 mg L^{-1}, whereas in late August 1994 the concentration was only 0.072 mg L^{-1} suggesting losses of nitrogen through denitrification or biological uptake. Ground water sampled below the wetland revealed a trend of decreasing NO_3^- and increasing N_2 gas concentrations proceeding from the edge of the wetland to the edge of the river--most NO_3^- was removed within the first 30 m. Estimates of redox state based on measurements of pairs of dissolved constituents (NO_3-NO_2^-, $Fe_3^-Fe_2^+$, $SO_4^{2-}S_2^-$) indicated that ground water flowing under the wetland passed progressively through zones of more negative redox potential resulting in the sequential reduction of NO_3^-, Fe_3^+, and SO_4^{2-}. Although these results strongly suggest that denitrification along the ground-water flow path immediately beneath the wetland is responsible for NO_3^- removal, further ground water flow modeling and sampling at the wetland edge is planned to rule out the possibility that deeper ground water with low NO_3^- concentrations is effectively diluting the surficial aquifer.

[1] U.S. Geological Survey, National Center, MS 413, Reston, VA 20192
[2] U.S. Geological Survey, 2280 Woodale Dr., Mounds View, MN 55112

Ground-Water/Surface-Water Interactions on the Konkapot River, Massachusetts and Connecticut

John R. Mullaney[1]

A water-quality study of the Konkapot River in western Massachusetts and northwestern Connecticut was conducted in September 1994 in the Connecticut, Housatonic and Thames River Basins as part of the National Water Quality Assessment (NAWQA) program. The objectives of this study were to compare ground-water quality in forested and agricultural areas at the points of discharge to surface water and to see if differences in ground-water quality and land use in the basin could be observed in downstream surface-water quality.

The Konkapot River, a tributary of the Housatonic River, is underlain by a stratified-drift aquifer. The drainage area at the downstream end of the study area is 61.1 square miles. Although land use in the study area is primarily forested (84 percent), land use in areas adjacent to the river changes from primarily forested in the upper basin to predominantly agricultural in the lower basin.

Wells were installed in streambeds at four locations adjacent to forested land and at three locations adjacent to corn fields. Three of the four forested locations were in the upper reaches of the Konkapot River. During September 6-8, 1994, a period of low streamflow, water samples were simultaneously collected from the wells and from the adjacent stream locations. All samples were analyzed for concentrations of nutrients, major ions, dissolved organic carbon, and pesticides. Ground-water samples collected in forested areas had much smaller concentrations of nitrite-plus-nitrate nitrogen (less than 0.05 to 0.18 mg/L (milligrams per liter)) than those collected from wells in agricultural areas (less than 0.05 to 5.1 mg/L). The instantaneous load of dissolved nitrite-plus-nitrate nitrogen in the Konkapot River increased from 0.47 to 28.8 kilograms per day in a downstream direction. The largest increases in nitrogen load and concentration were measured where land use adjacent to the stream changed from mostly forested to mostly agricultural. Because the sampling was done during a low-flow period, most of the increases in concentration and load of nitrite-plus-nitrate nitrogen can probably be attributed to inflow of ground water from beneath agricultural areas in the basin.

---

[1] U.S. Geological Survey, Hartford, CT

Group 7: Nitrogen-Cycling Processes at the Sediment-Water Interface

Chairperson--Frank J. Triska

Abstract	Presenter
Hydrologic Exchange Between a Stream and its Hyporheic Zone: Implications for Nitrogen Cycling in Four Fluvial Environments	Frank J. Triska
Inorganic Nitrogen Transformation Rates at the Sediment-Stream Water Interface in the Shingobee River, North Central Minnesota	John H. Duff
Potential Enhancements to the Stream Water Quality Model, QUAL2E	Robert L. Runkel
Effect of Nitrate, Organic Carbon, and Temperature on Denitrification Potential in Riverbed Sediments	Karla S. Pfenning
Fluxes of Nitrous Oxide to the Atmosphere from the Platte River System, Colorado, and Nebraska	Keven F. Dennehy
Input-Output Nitrogen Losses and Possible Denitrification in Lake Livingston, Texas	Edward Callender
Modeling Nutrient Cycling in Tampa Bay Tampa, Florida	P.F. Wang
A New Approach for Calculating Algal Growth Rate as a Function of Light and Nutrient (N) Availability	James E. Cloern

Hydrologic Exchange Between a Stream and its Hyporheic Zone: Implications for Nitrogen Cycling in Four Fluvial Environments

Frank J. Triska[1], John H. Duff[1], Alan P. Jackman[2],
and Ronald J. Avanzino[1]

The extent of exchange between surface water and both adjacent subchannel and subriparian environments is related to channel morphology and sediment grain size (hydraulic conductivity). In high-gradient, gravel-cobble channels, exchange can extend over a meter in depth and many meters laterally. Exchange can extend to approximately 50 cm in sand-gravel streams, to approximately 10 cm in fine sand bottom streams, and to <1 cm in sand-silt streams. In this presentation, hyporheic exchange is summarized in relation to its depth and its impact on three nitrogen transformation processes (uptake for primary production, nitrification, and denitrification). In Little Lost Man Creek, a gravel-cobble stream in California, exchange extends to 18 m laterally and to >1 m vertically. In a coarse sand-gravel stream (Sycamore Creek, AZ), exchange is reduced to a depth of approximately 50 cm and does not extend laterally into riparian areas. In these streams, nitrification is an important nitrogen transformation process in the hyporheic zone. At the Shingobee River, MN, exchange into the bed's fine sands is approximately 10 cm, and at a sand-silt bottom stream (Gelbaek Stream, Denmark), exchange does not exceed 5 mm if it occurs at all. In these latter streams, denitrification is an important sink for ground water and surface water nitrate. While hyporheic exchange is only a small component of instantaneous discharge, it can constitute a significant source of solutes, especially dissolved oxygen which sustains subsurface metabolism and determines the depth of redox-related nutrient transformations. Nutrient flux through the bed can, in turn, impact rates of primary production. Understanding biotic function in fluvial environments requires knowledge of underlying linkages between nutrient cycling processes and hydrologic properties of the ground-water-stream water interface.

[1]U.S. Geological Survey, MS 496, Menlo Park, CA 94025
[2]University of California, Davis, CA 95616

Inorganic Nitrogen Transformation Rates at the Sediment-Stream Water Interface in the Shingobee River, North Central Minnesota

John H. Duff[1], Frank J. Triska[1], and Alan P. Jackman[2]

The sand-bottom streambed of the Shingobee River has a zone 10-20 cm thick below the sediment-stream water interface where NH_4^+ disappears before ground-water discharges to the stream. Profiles of specific conductance and reduced ions suggest that this thin zone of the streambed is a region of hydrologic exchange between the ground water and channel surface water. An inverse relationship between annual stream water temperatures and NH_4^+ concentrations suggests that temperature- and redox-dependent biotic processes control NH_4^+ transport through this zone during summer whereas hydrologic processes control transport during winter. Depth-integrated inorganic N transformation rates measured under optimal conditions in sediment slurry assays in summer indicated little potential for net NH_4^+ formation in the top 12.5 cm of streambed, and nitrification rates exceeded NH_4^+ formation rates in the top 2.5 cm where O_2 from stream water and NH_4^+ in ground-water discharge were rapidly consumed. Although sediment assays indicated ammonification and nitrification rates were equivalent (5.1 vs. 4.7 mg N m^{-2} h^{-1}), NH_4^+ accumulated in the streambed. Presumably, interstitial O_2 levels inhibited nitrification. The average flux of NH_4^+ in ground-water discharge entering the active streambed zone was calculated to be about 9.4 mg N m^{-2} h^{-1}. Nitrification rates in the top 5 cm of streambed were equivalent to 33% (3.2 mg N m^{-2} h^{-1}) of the NH_4^+ flux to the active zone below. Denitrification potentials were sufficient to reduce up to 11.4 mg N m^{-2} h^{-1} in the top 5 cm of streambed and 22.8 mg N m^{-2} h^{-1} in the top 12.5 cm of streambed. These results suggest both hydrologic advective processes and coupled microbial processes influence inorganic N flux across the sediment-stream water interface.

[1]U.S. Geological Survey, Menlo Park, CA
[2]University of California, Davis, CA

Potential Enhancements to the Stream Water Quality Model, QUAL2E

Robert L. Runkel[1]

QUAL2E is a stream water quality model distributed by the U.S. Environmental Protection Agency. The model is used extensively by many engineers and scientists to study the complex interactions between dissolved oxygen, temperature, algal growth, biochemical oxygen demand, and nutrient cycling. The model simulates the effects of point sources (for example, wastewater treatment plants) and nonpoint sources (agricultural runoff) on instream water quality.

As with many environmental software packages, QUAL2E is the product of many years of development, testing and revision. Over the years, numerous programmers have added their revisions and enhancements to QUAL2E, resulting in a variety of conventions and programming styles. A programming effort consisting of two phases is currently under consideration. During Phase I (Cleanup), the code will be restructured to make it easier to understand and maintain. This will facilitate the addition of new process knowledge and advanced solution techniques (Phase II, Enhancements).

Phase I would include the following tasks:

- Provide a more consistent input format.
- Eliminate existing logic errors and program bugs (if any).
- Eliminate obsolete FORTRAN IV conventions, ‘dead’ code, and unneeded common blocks.

Phase II would potentially include the following enhancements:

- Consideration of the physical process of transient storage, as well as nutrient dynamics within the storage zone.
- Consideration of unsteady flow regimes. At present, QUAL2E assumes a steady flow regime. Modifications would allow for a coupling between QUAL2E and unsteady flow routing models.
- Consideration of immobile plant biomass (for example, periphyton). At present, all plant biomass (chlorophyll a) is suspended in the water column and transported downstream.
- Incorporation of efficient, flexible, and accurate numerical techniques.
- Development of a QUAL2E module for use within the USGS Modular Modeling System.

[1] U.S. Geological Survey, WRD, MS 415, Denver Federal Center, Lakewood, CO 80225
Internet: runkel@otis.cr.usgs.gov

Effect of Nitrate, Organic Carbon, and Temperature on Denitrification Potential in Riverbed Sediments

Karla S. Pfenning[1] and Peter B. McMahon[1]

A study conducted in 1994 as part of the National Water-Quality Assessment's South Platte River Basin investigation, examined the effect of certain environmental factors on denitrification potential in nitrate-rich riverbed sediments. Nitrous oxide (N_2O) production rates were measured in laboratory incubations of riverbed sediments to evaluate the effect of varying concentrations of nitrate and of organic carbon and temperature on denitrification potential. Incubating sediments over a range of nitrate concentrations measured in the field (357 to 2,142 μmol/L) produced no significant increase ($p>0.05$) in N_2O production rates, indicating that the denitrification potential in these sediments was not nitrate limited. In contrast, incubations amended with acetate, as a source of organic carbon, at concentrations ranging from 0 to 625 μmol/L produced significant increases ($p<0.05$) in N_2O production rates, indicating that the denitrification potential in these sediments was organic carbon limited. Furthermore, N_2O production rates also were affected by the type of organic carbon available as an electron donor. Acetate and surface-water-derived fulvic acid resulted in higher N_2O production rates than ground-water-derived fulvic acid or sedimentary organic carbon. Decreasing incubation temperatures from 22° to 4° C resulted in about a 77-percent decrease in N_2O production rates. These results help to explain results from previous studies that indicated only 15 to 30 percent of nitrate in ground water was denitrified prior to discharging to the South Platte River, and that nitrate concentrations in the river generally were higher in winter than in summer.

[1] U.S. Geological Survey, MS 415, Denver, Colorado 80225

Fluxes of Nitrous Oxide to the Atmosphere from the Platte River System, Colorado, and Nebraska

Kevin F. Dennehy[1] and Peter B. McMahon[1]

Fluxes of nitrous oxide to the atmosphere were measured at 15 sites along the Platte River system from upstream of Denver, Colorado, to its confluence with the Missouri River near Omaha, Nebraska, in October 1994, February 1995, and August 1995. Fluxes of nitrous oxide varied with land use. The highest fluxes occurred downstream from Denver's largest wastewater-treatment plant (21,820 to 36,900 μg-N m^{-2} d^{-1}), intermediate fluxes were in areas of irrigated agriculture (less than 55 to 3,481 μg-N m^{-2} d^{-1}), and the lowest fluxes were in undeveloped or nonirrigated areas (less than 55 μg-N m^{-2} d^{-1}). Nitrous oxide fluxes were positively correlated with water temperature and nitrate concentrations in surface water. Denitrification in riverbed sediments is a probable mechanism for nitrous-oxide production. Fluxes of nitrous oxide to the atmosphere from the Platte River system were similar to, or greater than, published fluxes measured at the air-water interface from nitrogen-rich lakes and from soils associated with grasslands and with temperate and tropical forests. Results from this study indicate that large river systems affected by urban and agricultural land uses could be an important terrestrial source of nitrous oxide to the atmosphere.

[1] U.S. Geological Survey, National Water-Quality Assessment Program, South Platte River Basin, Denver Federal Center, MS 415, Denver, Colorado 80225

Input-Output Nitrogen Losses and Possible Denitrification in Lake Livingston, Texas

Edward Callender[1] and Peter Van Metre[2]

Lake Livingston is a relatively large reservoir in southeastern Texas located near the downstream boundary of the Trinity River Basin, one of the U.S. Geological Survey's National Water Quality Assessment (NAWQA) Study Units. As part of the nutrient studies within the basin and the use of sediment cores from Lake Livingston to assess past water-quality trends, nitrogen loads have been computed and compared to storage within the lake sediments. The calculated difference between total nitrogen inputs to the reservoir from the Trinity River and outputs from the reservoir for the period 1970 to 1989 is a minimum of 95×10^6 kg N while the quantity of total nitrogen (mostly organic) accumulated in reservoir sediments is estimated to be 63×10^6 kg N. The difference between the two estimates for nitrogen loss appears larger than experimental error, suggesting that some other process in addition to sediment deposition may be responsible for this loss.

Water-column nutrient data for Lake Livingston suggest that during the late 1970's, nitrogen was "limiting" primary production and that in the late 1980's, phosphorus was controlling primary production due to pronounced increases in nitrogen loading (NO_3) from the Dallas metropolitan area. Such a change in limiting nutrient availability would coincide with the distribution of organic nitrogen in sediment cores, reflecting productivity in the reservoir, decreased phosphorus loading, increased nitrogen (NO_3) loading, and denitrification in the lake water and at the sediment-water interface.

[1] U.S. Geological Survey, MS 432, Reston, VA 20192
[2] U.S. Geological Survey, 8011 Cameron Rd., Austin, TX 78754

Modeling Nutrient Cycling in Tampa Bay, Tampa, Florida

P.F. Wang[1], James Martin[2], and Gerold Morrison[3]

As part of an investigation of water quality and eutrophication conditions for Tampa Bay, Florida, a water-quality model, EUTRO5, was used to simulate and understand the mechanistic relations between external and internal loadings and nutrient cycling in the Bay. Eight water quality variables, which involved four interlocking cycles associated with dissolved oxygen, phytoplankton, nitrogen, and phosphorus concentrations, were simulated simultaneously. Model results were compared with monthly field measurements for the period of 1985-1994. Model results and field data suggest that nitrogen was the limiting nutrient for the growth of the phytoplankton population. Phytoplankton biomass varied seasonally and was the major sink for ammonium in the water column. The ratios of ammonium-nitrogen to nitrate-nitrogen for Tampa Bay were high, compared with those of some other inland and coastal waters. Field data showed that nitrate concentrations in the Bay were below the detection limit (0.01 ppm-N), a condition simulated by the model, whereas average ammonium concentrations were above 0.1 ppm-N. Model results suggest that the high ammonium-to-nitrate ratios can be attributed in part to the relatively low first-order nitrification rate (0.08 day^{-1}) and short retention time (a few days) for the Bay. Results of model-sensitivity runs revealed information governing the cycling of nutrients in the Bay. The major sources of ammonium in the water column included releases from the sediments and mineralization of organic nitrogen. Cycling of nitrogen in the Bay was governed primarily by the biochemical processes associated with phytoplankton population, including growth and death of phytoplankton and mineralization of organic nitrogen. Predicted water-quality variables in response to several designed scenarios for future nitrogen-loading reductions were also analyzed using the model. This analysis suggests that, even with a reduction in the external nitrogen input, release of ammonium from the sediment would remain a significant source of inorganic nitrogen to the water column. Reduction of point- and non-point-source loads may not result in immediate decreases of nitrogen in most segments of the Bay. Further study would better quantify and explain the behavior of sediment nutrient fluxes.

[1] San Diego State University Foundation/Visiting Scientist at U.S. Geological Survey, WRD, 345 Middlefield Road, MS 496, Menlo Park, CA 94025. (Formerly with AScI Corporation)

[2] AScI Corporation, 987 Gaines School Road, Athens, GA 30605

[3] Southwest Florida Water Management District, 7601 Highway 301 North, Tampa, FL 33637

A New Approach for Calculating Algal Growth Rate as a Function of Light and Nutrient (N) Availability

James E. Cloern[1]

The coastal zone has always attracted human settlement, and our population is highly concentrated around the continental margins. By the year 2010, seventy-five percent of the U.S. population will live within 75 km of a coastline. One consequence of this uneven population distribution is that coastal ecosystems (including estuaries, bays, tidal rivers) are among the most intensively fertilized environments on Earth. For example, the San Francisco Bay estuary receives over 60 tons of nitrogen each day from municipal wastewater. Enrichment (eutrophication) of coastal waters is a growing worldwide concern because the frequency and extent of harmful algal blooms appear to be increasing in parallel with increased nitrogen loadings associated with human activities on the land surface. Episodes of fish, shellfish, and waterfowl mortalities have recently been observed in coastal waters of New York, North Carolina, Florida, Texas, and California; each of these episodes was associated with an algal bloom.

Our ability to understand (and ultimately remediate) the effects of coastal eutrophication is limited in part by our very rudimentary understanding of how phytoplankton populations respond to environmental change. No satisfactory method exists for measuring the growth rate of phytoplankton populations in their natural habitat; and no universally-accepted equation set has been developed to describe phytoplankton growth as a function of limiting resources -- light and nutrients (usually nitrogen in the coastal zone). Many traditional modeling approaches describe phytoplankton growth as a response to either light or nutrient limitation (a binary switch). Laboratory experiments with cultures, however, show that algal growth is controlled by interactions between light and nutrient availability. As a step in the development of an ecosystem model of coupled phytoplankton-nutrient dynamics, I found an approach for describing phytoplankton population growth rate in response to these interactions. The model is based on the results of 219 published measurements of growth rate under defined laboratory conditions of light and nitrogen delivery. Simulations with this model suggest that phytoplankton growth efficiency (incremental change in growth rate with an incremental change in light) is much more sensitive to nitrogen enrichment than previously thought, especially under low-light conditions typical of turbid estuaries (or reservoirs). One interpretation of eutrophication is that enhanced nitrogen loadings lead to an enhanced carrying capacity of coastal waters to support phytoplankton populations. Simulations with this new modeling approach suggest a second mechanism might also be stimulation of phytoplankton growth efficiency in turbid waters.

[1] U.S. Geological Survey, MS 496, Menlo Park, CA 94025

Group 8: Role of Special Events

Chairperson--Douglas A. Burns

Abstract	Presenter
Solute Concentration Variations and Mass Balance of Nitrogen Species in a Colorado Subalpine Watershed	Norman E. Peters
Snow Accumulation and Snowmelt Effects on Nitrogen Cycling in the Boreal Forest	Norman E. Peters
Nitrogen and Pesticide Concentrations in an Agricultural Basin in North-Central Connecticut	John R. Mullaney
Nitrogen and Sediment Loadings and Streamflow Variation Due to Thunderstorm Runoff into Lake Tahoe from Incline Creek Basin in Nevada, September 1994	Timothy G. Rowe
Water Quality of Springs and Their Effects on Nitrogen Loads in the Snake River, South-Central Idaho	Gregory M. Clark

Solute Concentration Variations and Mass Balance of Nitrogen Species in a Colorado Subalpine Watershed

Norman E. Peters[1] and Larry D. Beaver[2]

Chemical composition of meltwater from a seasonal snowpack, and ground and stream water was monitored during a one-month snowmelt period for each year from 1992 to 1994 in a 200-hectare sub-alpine watershed in the Rocky Mountains near Steamboat Springs, Colorado. Major ions in meltwater were differentially eluted from the snowpack, and the dominant solutes in meltwater were calcium, sulfate, and nitrate. Concentrations were greater than 40 microequivalents per liter for each of these solutes at the onset of each snowmelt period and decreased to less than 10 microequivalents per liter after a few days of intense melt. In meltwater, ammonium concentrations decreased from 20 to 30 microequivalents per liter at the onset of snowmelt to less than 5 microequivalents per liter.Nitrate concentrations in ground water, although more highly variable than in meltwater, typically were higher than in meltwater; median nitrate concentrations were 14 and 11 microequivalents per liter for ground water and meltwater, respectively. In contrast, ammonium concentrations were lower in ground water than in meltwater; median ammonium concentrations were 1 and 6.5 microequivalents per liter for ground water and meltwater, respectively.

Highest observed nitrate concentrations (maximum of 350 microequivalents per liter in 1992) were detected in ground water sampled from a well in a mid-slope position. High nitrate concentrations were balanced by calcium concentrations. In this mid-slope well, calcium, magnesium, and nitrate increased and then decreased, and alkalinity decreased and then increased. This pattern suggests that hydrogen ions were generated from biotic processes, such as nitrification in overlying soils, which caused the alkalinity decrease. The alkalinity decrease was not sufficient to account for all hydrogen ions that would have been generated, and perhaps most hydrogen ions exchanged with other cations in the soils, particularly calcium. The watershed is sparsely forested, and throughout upland areas, considerable bioturbation of the soils occurs due to small mammal activity under the snowpack. These fauna may also be the source of the nitrate in the mid-slope well. In contrast to concentration variations for nitrate and balancing cations in the mid-slope well, most ground-water solute concentrations for this and other wells decrease as snowmelt progresses, consistent with dilution by meltwater from the snowpack.

Solute concentrations in streamwater also decreased as snowmelt progressed except for ammonium. Highest streamwater ammonium concentrations (8 microequivalents per liter) were observed at the end of the snowmelt period and are attributed to in-stream processes related to a series of beaver dams along the stream channel. A mass balance (stream export minus meltwater and precipitation inputs) for each of the three years indicates that nitrogen species are retained by the watershed. On average, 50% of the atmospheric inputs of nitrate were retained in the watershed and 86% of the atmospheric inputs of ammonium were retained.

[1] U.S. Geological Survey, WRD, 3039 Amwiler Rd., Suite 130, Atlanta, GA 30360;
email: nepeters@usgs.gov
[2] U.S. Geological Survey, MS 412, Denver Federal Center, Lakewood, CO 80225

Snow Accumulation and Snowmelt Effects on Nitrogen Cycling in the Boreal Forest

N.E. Peters[1], T.D. Davies[2], H.G. Jones[3], P. Marsh[4],
J.W. Pomeroy[4], and M. Tranter[5]

Nitrogen (N) availability limits the primary productivity of boreal forests throughout much of their geographical range. Because boreal forests are snowcovered as much as eight months of the year and receive a substantial amount of N during this time, winter cycling of N and its sensitivity to climate change may be an important control on the evolution of boreal forests and related carbon storage. This paper examines N dynamics during winter in the boreal forest and evaluates potential changes in N dynamics with changing climate.

Through dry deposition and episodic wet deposition, N is incorporated in intercepted snow and surface snow as nitrate and ammonium. However, N is not well conserved by snow during the winter. Evidence from western Canada indicates substantial nitrate loss from snow that has been physically transformed through sublimation (intercepted snow) and "kinetic" metamorphism (surface snow). As the snowpack ripens during melt, rapid within-snowpack N transformations occur due to concomitant biological, chemical and physical processes. Biological consumption (by micro-organisms) can substantially reduce the presence and availability of N in melting snow. Most remaining nitrate is eluted with the first components of meltwater and flushes from the snowpack along preferential flowpaths. Upon reaching the soil, nitrate may be incorporated in refreezing ice layers at the soil surface, infiltrate to the soil or runoff to streams. The transport mechanism is determined primarily by the soil texture, snowmelt rate, soil-ice content and soil temperature.

Climate strongly affects most of the factors important to winter cycling of N. Hence, several scenarios of nitrate transport and storage under possible future climates were examined. For instance, in warmer winters intercepted snow sublimation will increase slightly while kinetic metamorphism will decrease substantially, reducing the net exclusion of N from snow crystals. However, an increased frequency of mid-winter melts may promote enhanced within-snowpack biological activity, resulting in increased N consumption and transformation from nitrate to ammonium. Warmer soils will increase the forest uptake of the remaining N.

[1] U.S. Geological Survey, 3039 Amwiler Rd., Atlanta, Georgia, 30360-2824, USA

[2] Climate Research Unit, University of East Anglia, Norwich, NR4 7TJ, UK

[3] INRS-Eau, Université du Québec, Sainte-Foy, Québec, G1V 4C7, Canada

[4] National Hydrology Research Institute, Environment Canada, 11 Innovation Boulevard., Saskatoon, Saskatchewan, S7N 3H5, Canada

[5] Department of Geography, University of Bristol, Bristol, BS8 1SS, UK

Nitrogen and Pesticide Concentrations in an Agricultural Basin in North-Central Connecticut

John R. Mullaney[1] and Marc J. Zimmerman[2]

As part of the National Water Quality Assessment (NAWQA) Program, water samples were collected from streams in three subbasins of the Scantic River in north-central Connecticut during 1992-94. The purpose of the these investigations was to study the effects of land use on water quality in an agricultural basin. The Scantic River and two smaller tributaries were sampled during and after a storm (May 31-June 2, 1992), after the application of pesticides and fertilizers. Broad Brook, one of the tributaries studied, was sampled monthly during 1993-94, as a regular NAWQA sampling station.

Water samples collected from the Scantic River subbasins in 1992 had concentrations of dissolved nitrite-plus-nitrate nitrogen and the herbicide metabolite desethyl atrazine that decreased with increasing river stage, indicating that the ground-water-runoff component of streamflow contained larger concentrations of these constituents than the surface-water-runoff component. Concentrations of total ammonia plus organic nitrogen, atrazine, and metolachlor increased with river stage, indicating that storm-water runoff from fertilizer- and pesticide-treated fields was the primary source.

During the monthly sampling in 1993-94, at Broad Brook at Broad Brook, Connecticut, concentrations of dissolved nitrite-plus-nitrate nitrogen and total ammonia plus organic nitrogen fluctuated with changes in river stage and discharge. Concentrations of dissolved nitrite-plus-nitrate nitrogen ranged from 1.3 to 4.9 mg/L (milligrams per liter). The largest concentrations were measured during baseflow periods. The instantaneous load of nitrite-plus-nitrate nitrogen, which ranged from 84 to 827 kg/d (kilograms per day), was largest during the periods of high flow that were sampled. Concentrations of total ammonia plus organic nitrogen ranged from 0.2 to 4.2 mg/L and instantaneous load, which ranged from 8 to 1,654 kg/d, was also largest during the highest flow periods that were sampled.

Analysis of these data shows that large variations in concentrations of nitrogen species can occur even during small storms and that it is important to sample such events at different times of the year and at different storm intensities and durations in order to quantify loads.

In the subbasins studied, the sources of nitrite-plus-nitrate nitrogen include ground-water inflow from beneath treated agricultural fields and storm-water runoff. The primary source of total ammonia plus organic nitrogen is storm-water runoff. Ground-water samples collected as part of the NAWQA program and previous studies support these conclusions and show that nitrite-plus-nitrate-nitrogen concentrations in agricultural parts of the subbasins range from 1.5 to 60 mg/L and that total ammonia plus organic nitrogen was rarely detected.

[1] U.S. Geological Survey, Hartford, CT
[2] U.S. Geological Survey, Marlborough, MA

Nitrogen and Sediment Loadings and Streamflow Variation Due to Thunderstorm Runoff into Lake Tahoe from Incline Creek Basin in Nevada, September 1994

Timothy G. Rowe[1]

The U.S. Geological Survey, in cooperation with the Tahoe Regional Planning Agency, established the Lake Tahoe monitoring network in 1988. The network now has 32 sampling sites and 20 streamflow-gaging stations on 14 tributaries. Data and samples from the network are used for estimating nutrient and sediment loadings from major tributaries to Lake Tahoe. In 1993 and 1994 (water years), the U.S. Geological Survey in cooperation with the University of Nevada, Reno, collected additional samples of summer thunderstorm runoff at the upper Incline Creek sampling and streamflow-gaging location. Nutrient samples were collected to determine dissolved (ionized) ammonia (NH_4), dissolved nitrite plus nitrate (NO_2+NO_3), and total ionized ammonia plus organic nitrogen (NH_4-N). Suspended-sediment samples were collected also, and instantaneous streamflows were calculated from the gaging-station data by using the stage–discharge relation.

Few thunderstorms occurred in Incline Creek Basin during the summers of 1993 and 1994. Then three thunderstorms occurred in late September 1994. Recorded rainfall and instantaneous peak streamflows for each storm were 0.70 in and 2.3 ft^3/s, 1.12 in and 2.7 ft^3/s, and 0.70 in and 2.3 ft^3/s respectively. Although greater than the summer base flows (0.3 to 1.0 ft^3/s), these peak streamflows were less than the instantaneous peak for 1994, 11 ft^3/s, which occurred during spring runoff.

Summer thunderstorms provided the highest loading of dissolved NH_4^+, total NH_4-N, and suspended sediment for the 1994 water year, although peak streamflows were substantially less than spring runoff. Peak loading of dissolved NH_4^+, 0.50 lb/d, occurred during runoff from the first thunderstorm, on the rise of the peak streamflow. This peak loading compares to a range of less than 0.01 to 0.13 lb/d for the rest of the 1994 water year. Peak loading of dissolved NO_2+NO_3 occurred during spring runoff. The peak associated with late-September thunderstorm runoff, 0.38 lb/d, occurred at peak streamflow of the first thunderstorm. It compares to a range of 0.03 to 0.98 lb/d for the rest of the 1994 water year. Peak loading of total NH_4-N, 22.4 lb/d, occurred at peak streamflow during runoff from the second thunderstorm. This peak loading compares to a range of 0.8 to 13.5 lb/d for the rest of the 1994 water year. Peak loading of suspended sediment, 1,740 lb/d, also occurred at peak streamflow during runoff from the second thunderstorm. This peak loading compares to a range of less than 20 to 1,460 lb/d for the rest of the 1994 water year.

[1] U.S. Geological Survey, 333 W. Nye Lane, Carson City, NV 89706

Water Quality of Springs and Their Effects on Nitrogen Loads in the Snake River, South-Central Idaho

Gregory M. Clark[1]

The 150-kilometer middle reach of the Snake River (middle Snake) in south-central Idaho receives significant recharge from springs discharging along the north side of the river. From 1984 to 1994, recharge to the middle Snake from springs averaged 162 m^3/s, or about 55 percent of the mean annual streamflow in the reach. Land-use practices along the Snake River, primarily irrigated agriculture and confined-animal feeding operations, have degraded the water quality of the springs. Water-quality samples collected from nine springs in 1994 contained total nitrogen concentrations ranging from 0.93 to 2.9 mg/L, of which more than 90 percent was dissolved nitrate. Concentrations of ammonia and organic nitrogen in the springs were near or less than analytical detection limits. Springs in the upstream part of the reach had larger concentrations of total nitrogen and nitrate than the downstream springs. The chemical differences among springs are attributable to differences in the spring source water, the direction of ground-water flow, and spatial variations in land- and water-use practices along the river. Historical discharge and water-quality data from three springs indicate that, although discharge from the springs fluctuated slightly from 1984 to 1994, nitrogen concentrations in individual springs did not change significantly.

Because of the magnitude of the recharge, the springs have a large effect on the water quality of the Snake River. In some parts of the middle Snake, the springs degrade the water quality in the river, and in other parts, the springs improve the water quality. From 1984 to 1994, the springs contributed an annual average of 6,750 metric tons of nitrogen as nitrate, 590 metric tons of nitrogen as organic nitrogen, and 53 metric tons of nitrogen as ammonia to the middle Snake. Loads of nitrogenous compounds transported in the Snake River were estimated by regressing concentrations with several predictor variables. The results indicate that total nitrogen loads decreased by 52 percent from about 29,000 metric tons in 1984 to about 14,000 metric tons in 1994. Most of the load decrease in the river is attributable to decreased streamflow resulting from drought conditions in the Snake River Basin from 1987 to 1994. Mean annual streamflow in the middle Snake decreased from 510 m^3/s in 1984 to 230 m^3/s in 1994. As a result, total contributions of recharge and nitrogen from the springs have remained relatively constant, whereas the percentage of the total river streamflow and nitrogen load derived from the springs has increased. From 1984 to 1994, the annual contribution of recharge from the springs to the river increased from 33 to 65 percent and the annual contribution of the total nitrogen load increased from 24 to 45 percent of the total transported from the middle Snake reach. Because the springs provide a large percentage of the nitrate in the Snake River, nitrate loads in the river decreased by only 19 percent from 1984 to 1994. In contrast, loads of total organic nitrogen and dissolved ammonia decreased by 86 and 78 percent, respectively, during this period.

[1] U.S. Geological Survey, 230 Collins Rd., Boise, ID 83702

Appendix

Group 1 Summary Report:
Scope of the Nitrogen Problem in Ground Water

Chairperson: David K. Mueller

Work Group: Eric F. Vowinkel, Michael G. Rupert, Abraham H. Chen, Hilda H. Hatzell, and Gerald L. Feder

The primary area of concern for nitrogen in ground water has been the impact of high nitrate concentrations on human health. The 10 mg/L nitrate standard has been an overriding consideration in analysis of ground-water nitrogen data. However, we should not assume the situation will not change. Several questions should be considered when establishing the objectives of future research. Is the 10 mg/L standard still the most appropriate criterion for determining impairment of ground water? Are there significant impacts from other nitrogen species? Should we be concerned about the contribution to ecosystem health or surface-water eutrophication from nitrate in ground-water baseflow?

Issues Expected to be Important in the Near Future

The general issues of sources of nitrogen in ground water, effects, and remediation will continue to be important in the future, and may be expanded as concerns broaden or change. An emerging issue related to potential sources is nitrogen oxides in emissions from utilities, industries, and automobiles. Because this source is in the atmosphere, there may be a possibility of global contamination of surface water and ground water. An ongoing issue is the impact of nitrogen contamination on drinking water or industrial/agricultural uses. The issues of remediation are how to reduce impacts from human activities and what can we do in areas that are already severely impacted.

Current information about the effect of fertilizer applications on nitrate in ground water is primarily from agricultural areas. An emerging issue is that same effect in urban areas. Several research questions could be addressed. For example, what are the effects of lawn care on nitrogen in shallow ground water? Is increased use of fertilizer by homeowners related to increased nitrate in urban water-table aquifers? Is there any mitigating effect from increased reliance on lawn care professionals? What is the best scale (single aquifer, single urban area, regional) to investigate potential impacts?

Related to these environmental issues are monitoring and data analysis issues. First of all, we must be able to design ground-water sampling networks at various scales and within cost constraints. We need data and methods for efficient detection of trends in nitrogen concentration, especially in moderately contaminated areas, so we can identify impacted areas before they exceed water-quality standards. Correlation of potential contamination with ancillary factors such as land use, soil characteristics, and hydrogeology also could help prioritize areas for alternative management practices or remediation. Modeling the nitrogen potential of ground water might help prioritize vulnerable areas so that monitoring and remediation can be cost effective. Nitrogen-species concentrations might be useful as low-cost indicators of the presence or absence of related contaminants, such as pesticides, which would greatly expand the scope of and interest in analysis of nitrogen data from ground-water samples. Thorough data analysis will require integration of surface-water and ground-water modelling, including both chemistry and contaminant transport. Presently, ground-water and surface-water contaminant transport modeling are separate disciplines. Merging the disciplines will require new or expanded models.

Along these lines, continued research is needed on ground water-surface water interactions. Related questions are:

1. Are ground-water nitrate plumes near streams transient or stable?
2. If nitrate reductions occur near the stream boundary, are they caused by denitrification or by dilution from stream leakage?
3. What data or ancillary information should be routinely collected to quantify these effects?
4. At what spatial scale do these processes occur? For example, is denitrification of nitrate in ground water common in the southeastern United States, or does it vary so much from one watershed to the next that regional generalizations cannot be made?

Information and Expertise Needed to Address These Issues

In addition to primary data from ground-water sampling (nitrogen-species concentrations, depth to water, and depth of the screened interval) certain ancillary data are necessary. These include other chemical measurements on the samples and information about the well location. Some chemical information, such as concentrations of dissolved oxygen, silica, and dissolved organic carbon, can be obtained from standard measurements and analyses. Analyses that can provide age dating of the sample are not as common, but possibly should be required for all samples. The age of the sampled ground water is equally important as the depth of the sample, which is determined from the water level and the screen depth. When the age of the ground water is known, water quality can be tied to the history of land use in an area (e.g., increasing fertilizer application rates with time). Ancillary information about the well site includes depth to water, land use, soil properties, and estimates of nitrogen loading. Fertilizer and manure inputs can be obtained on a county basis, but more local information might be necessary. Export of nitrogen in harvested crops is more difficult to determine, but of equal importance. Other loading information relates to atmospheric interactions, such as deposition, nitrogen fixation, and nitrogen-gas flux to the atmosphere.

More information about denitrification along ground-water flow paths also is necessary. Obtaining this information will require research efforts. One question that could be addressed is the significance of denitrification in deeper ground water or for regional ground-water systems. Current information only applies to shallow systems or local effects. Additionally, how variable are nitrogen transformation processes from one stream to the next, or at different locations along the same stream? In one stream, nitrification in the hyporheic zone can be a nitrogen source, whereas in another stream with a smaller zone of hydrologic exchange, denitrification can provide an important nitrogen sink.

Producing the necessary ancillary data will require expertise in the development of new chemical methods for analyses such as identifying denitrification, nitrification, dilution effects, determining atmospheric contributions of N to hydrologic systems, age-dating techniques, and fingerprinting sources of N in ground water. Maintaining data interpretation expertise will be important, particularly in statistical methods of trend analysis. Expertise also will be needed in the GIS area of integrating geographic data and geostatistics into interpretation of ground-water data. In order to accomplish any of this, expertise is needed in project planning and network design at various scales (local, regional, and national), particularly for trend monitoring.

Potential Roles for the U.S. Geological Survey

Several traditional roles of the USGS could provide a lead in addressing the issues related to nitrogen in ground water. These roles include research, development of methods for chemical analyses, and interpretation of large (regional or national) data sets. The primary research and development roles involve studies of nitrogen cycling processes and methods to quantify these processes. Intermediate-scale investigations might be developed to determine the importance of processes within individual ground-water basins.

Data interpretation roles could include:

1. Identification of national or regional trends and differences related to land use or other factors, and

2. Process-related assessments of regional hydrogeologic and land-use factors leading to nitrate contamination of ground water. It also might be possible to scale up transect data to investigate or define regional processes of nitrogen contamination and movement.

One role in which the USGS might establish a lead is development of methods to quantify the effects of N contamination. Such methods could then be used in remedial investigations by the USGS, other agencies, or contractors.

The USGS performs other roles that support the primary needs of research, development, and data interpretation. These secondary roles include sampling and network design and dissemination of information.

Suggested Low-Cost Products

A fact sheet could be published to summarize the major points discussed at the nitrogen workshop. For ground water, these are:

1. Consistently higher ground-water nitrate concentrations are found in agricultural areas, but elevated levels can also be found in residential areas.

2. Nitrate is more concentrated in the upper levels of many aquifers.

3. The hydrogeological factors leading to preferential movement of nitrate to ground water include sandy soils, high DO, and low DOC.

4. Some factors associated with or leading to nitrification or denitrification have been identified, but more research is necessary on these important parts of the nitrogen cycle.

Also, examples of nitrate in ground water from national, regional, and local studies could be summarized.

Another low-cost product would be a procedure for sharing literature, including annotated bibliographies and synthesis reports. This could be done using a news group or a home page on the World Wide Web. A home page could also include:

1. Latest news from USGS studies and ongoing research on nitrogen cycling.
2. Listing of published reports.
3. Listing of available expertise.

A product that would require slightly more effort, but still be low cost, would be creation of a nitrogen (or nutrient) data base. The questions would be what would this data base include and who would administer it.

The simplest product might be providing suggestions to Districts for nitrogen-related studies and advice on District coop proposals or existing projects.

Potential New Program Areas for the U.S. Geological Survey

Remediation of nitrogen contamination in ground water is not new, but it is something the USGS has traditionally left to other agencies and contractors. However, certain aspects of remediation could fit into the traditional mission of the USGS. We could develop concepts and methods of remedial treatment and provide evaluation of remedial results through monitoring, research studies, and data interpretation. We could then provide education on these methods to others who are implementing large-scale remediation efforts.

Group 2 Summary Report: Scope of the Nitrogen Problem in Surface Water

Chairperson: Patrick J. Phillips

Work Group: Elaine C. Todd Trench, Larry J. Puckett, Patricia L. Lietman, Charles J. Patton, and Gregory C. Johnson

Information on the transport, form, and fate of nitrogen in surface water is critical to both human use of surface-water resources and the health of aquatic ecosystems. After reviewing and discussing the papers presented in the workshop, the surface-water group identified four major issues for nitrogen cycling monitoring and research in the U.S. Geological Survey:

1. Synthesis of findings from different scales and environments
2. Analytical techniques and quality assurance data
3. Biologic measures and stream chemistry
4. Long-term water-quality monitoring and trend analysis

The first part of this group's report gives a detailed analysis of these issues, and also identifies the major expertise that the USGS has in these areas. The last few paragraphs of this report identify possible solutions that would address these issues.

Synthesis of Findings from Different Scales and Environments

Synthesizing results across spatial scales and different environmental settings emerged as a major issue in the workshop. For example, it is not clear how to relate data from small plots up the spatial scale to midsize watersheds, large watersheds, lakes and reservoirs, and finally to estuaries. The linkages between these different scales have rarely been developed, and although there is sentiment to do such work, there are few programs that address this question. NAWQA's National Synthesis component does recognize the importance of this issue, although intermediate scale comparisons have not been emphasized.

Fluxes from rivers to estuaries is another important scale issue. Much estuary monitoring includes extensive monitoring in the estuary, but little monitoring in large tributaries. It seems logical that the USGS could work better with estuary researchers to address the importance of riverine nitrogen inputs to estuaries. For example, NASQAN II is designed to address nutrient issues on large rivers and provide information on the flux of nutrients from the continent; this is likely an area where the Water Resources division can coordinate efforts with the Coastal Marine Branch of the Geologic Division.

Finally, many agencies and individuals are interested in using USGS data for monitoring the affects of Best Management Practices (BMPs) on water quality. In some cases, agencies may assume that USGS studies can address such questions, even though our studies were not designed to answer such questions. Our monitoring programs should do a better job of identifying monitoring objectives so that we minimize misuse of our data.

Analytical Techniques and Quality Assurance Data

Quality assurance and the development of new analytical techniques are two important issues that the U.S. Geological Survey must address so that our data are useful for monitoring nitrogen cycling.

The usefulness of our nitrogen data would be improved if there were better communication between the lab and district projects with regards to using quality assurance (QA) data. There is much QA data collected that could help projects evaluate their results, yet this data has no repository or curator. Furthermore, the comparability of USGS results with results of other labs is another important analytical issue. Improving the comparability of USGS results with those generated from other State and Federal agencies would help improve the transferability of results. Blind blank data could also be better used in order to determine confidence intervals for data.

The trade-off between implementing new analytical techniques versus maintaining current techniques is another key analytical issue, and is one that continues to be a topic for the ITFM lab committee. Some recent examples include studies on the comparability of different treatment procedures for nutrients. Changing analytical techniques can have a substantial affect on the ability to detect trends. The balance between using new or improved methods versus maintaining the continuity of our databases must be determined. If new methods are developed, priorities must be set for which methods are implemented, and how quickly they are implemented. One possibility is that the field scientist can decide what constituent to measure, but the lab should decide how to measure a constituent at a given concentration range. Further, when new methods are implemented, the lab should release guidance on the potential effects the change in method will have on the comparability of the existing and new data. We further recommend that both methods be maintained at the National Water Quality Lab for a specified period of time for those cases where significant data changes occur due to the implementation of new methods.

Biologic Measures and Stream Chemistry

Eutrophication, because of its resulting growth in biological indicators to noxious levels, has been a driving force in the clean-up of the Nation's waters since the early 1970s. Improved understanding of the nitrogen cycle will require better understanding of the link between biologic characteristics and water chemistry. Unfortunately, because so few biologists were present at the meeting, this topic did not receive adequate attention. Because the USGS has recently added a number of biologists, there may be greater opportunities to improve our understanding of the link between nitrogen cycling and biologic systems within the next few years.

Identification of key biologic measures that can help understand the link between chemistry and biology should be made a priority. Many studies are beginning to assess the importance of biology in nitrogen species transformations, but there needs to be better understanding of the roles of macrophytes and algae in nitrogen species transformation. Simple cost-effective biological, physical and biochemical measurements need to be identified and added to monitoring programs. Some simple chemical measurements, including dissolved organic carbon, chlorophyll-A, and silica, can also help in understanding the role of biologic systems in nitrogen cycling.

Opportunities for development of programs linking nitrogen cycling and biology have dramatically increased with the increased numbers of biologists in District operations, the potential addition of the National Biological Service, and better coordination with National Research Program experts in the field. Two future issues that may present opportunities for interaction between hydrologists and biologists include the effect of zebra mussels on nitrogen and the transport and fate of nitrogen in estuaries. Because so few biologist attended the workshop, potential collaboration between hydrologists and biologists that work in water quality issues is not clear.

Long-Term Water-Quality Monitoring and Trend Analysis

Long-term monitoring of water quality is an important issue in the U.S. Geological Survey because of our mission to characterize our nation's water resources. In some parts of the country, the only long-term water quality monitoring programs have been the NASQAN and Benchmark programs. However, these programs have been severely cut-back, and it is not clear that the NAWQA projects will replace these data. The U. S. Geological Survey need to reassess all of its long-term data collection activities to insure that these data will continue to be generated. The worth of such data has recently been shown by the use of U.S. Geological Survey data for providing the long-term data for estimation of historical nutrient inputs to the Gulf of Mexico.

General Long-Term Monitoring Issues

The U.S. Geological Survey needs a program wide emphasis on long-term monitoring. However, there is no widely accepted criteria for requirements for productive long-term monitoring, nor is there guidance for the effect of censored data and lab changes on long-term trends. In many cases, trend information needs to be considered in light of other data, including hydrologic information. In addition, many locations have inadequate data for trend analysis, and planning horizons for managers rarely account for long-term trend monitoring. Hence, when questions are asked about long-term trends, data are often inadequate to answer those questions. In the case of NAWQA projects, there is concern that decisions on determining long-term trend sites should include input from the scientists from study units and National Synthesis.

Trend Analysis of Existing Data

The USGS should try to evaluate existing data for long-term trends, with appropriate qualifications in terms of changes in analytical methods. Detected trends may be caused by changes in environmental factors, changes in methods, or some combination of both. Multiple lines of evidence, including biological data, can be used to evaluate the environmental significance of detected trends. Trends detected in existing data can provide guidance in determining constituents that merit continued long-term monitoring.

Planning Appropriate Data Collection for Future Trend Analysis

Long-term monitoring for biologic measures in conjunction with nutrient monitoring is sorely needed. Biologic measures that reflect nitrogen cycling need to be identified and these measures need to be made at long-term monitoring sites. Such measures could include monitoring of population shifts in algae or invertebrate populations in waters. Data collected from long-term networks need to be periodically interpreted so that monitoring can be improved.

Understanding of long-term trends can often be hampered by the lack of data for other constituents. For example, low-intensity sampling for NAWQA may not include dissolved organic carbon or major ions (including silica). If monitoring for long-term trends includes monitoring for just nitrogen, and no additional monitoring of other constituents that are crucial to understanding the causes of changes in nutrient trends, these data will likely not be sufficient to explain observed trends. In Connecticut, for example, analysis of nitrogen trends was aided greatly by analysis of flow trends. Long-term monitoring of light penetration, chlorophyll A, silica, and dissolved organic carbon can be crucial to understanding nitrogen trends.

Communicating the Importance of Long-Term Data

The U. S. Geological Survey must do a better job of demonstrating to the public (including state and local officials) the importance of long-term data for determining trends. A fact sheet could be written to illustrate how long-term monitoring has shown the positive effects of the Clean Water Act. Such a publication could emphasize the need for chemical, biologic, and discharge data to address long-term nitrogen trends. Such a publication could emphasize the need for chemical, biologic, and discharge data to address long-term nitrogen trends. We should emphasize that environmental indicators are analogous to economic indicators, and that such indicators can act as an early warning system that may indicate initial declines in water quality, before degradation becomes severe.

Panel Suggestions

After considering existing programs and approaches, the surface-water working group identified a number of proposals, and grouped them according to their cost. These proposals follow:

Low Cost

1. Compile a list of specialists working on Nitrogen questions.
2. Create a Nitrogen or Nutrient special interest group in WRD.
3. Write a fact sheet detailing long-term nitrogen trends (and why they are important).

Moderate Cost

1. Create teams working on regional synthesis investigating nitrogen cycling at different scales.
2. Organize a workshop on the link between biology and nutrient cycling, or a workshop on linkage between nitrogen and other chemical systems and biology.
3. Develop and implement new methods for measuring organic nitrogen and dissolved organic carbon.
4. Insure funding for long-term NAWQA stations to collect dissolved organic carbon, silica, and chlorophyll A at low-intensity sites.

High Cost

1. Develope an initiative on linking biology to water quality, using both WRD and NBS personnel.
2. Develop a thrust proposal to investigate major sources of nitrogen and other nutrients to estuaries and the potential affect on biologic systems.
3. Identify, develop, and implement biologic methods to assess status and trends in nitrogen and other nutrients in U.S.G.S. data collection networks.

Groups 3 and 4 Summary Report: Atmospheric Deposition and Nitrogen Cycling in Soils and Uses of Isotopes for Determining Sources

Chairpersons: Douglas A. Burns and Carol Kendall

Work Group: Donald H. Campbell, Charles A. Cravotta, Patricia Ging, Carol J. Lind, Gregory B. Lawrence, Peter S. Murdoch, Steve Silva, and Donald Wilkison

This report reflects the views of both watershed and isotope geochemists. The professional interests and experiences of the group extended beyond just forested watersheds, so this report will reflect those broader concerns as well as issues related to forested watersheds.

Introduction

The magnitude of the problems associated with human-induced leaching of nitrogen into surface and ground waters are just beginning to be realized. The issue of excessive nitrogen in waters is likely to receive more attention in coming years, and the U.S. Geological Survey is uniquely poised to provide quantitative information on the magnitude of the problem. The problems associated with elevated loads of nitrogen vary with the ecosystem of concern. In agricultural ecosystems, 10 mg/L as NO_3-N is often used as a frame of reference because this is the EPA recommended maximum concentration for potable water. Ecosystems vary in sensitivity, and concentrations of NO_3-N as low as 1 mg/L or less are of concern in forested ecosystems, because such levels may reflect that atmospheric deposition is exceeding the biological demand for nitrogen. Any process or activity that increases nitrogen loads in surface waters is of concern because of the potential to affect saline estuaries where nitrogen has been related to eutrophication.

Scientific Issues of Importance

Our group identified a number of scientific issues related to nitrogen in aquatic environments that have not been adequately addressed. We will present these in list form:

1. Dissolved (and particulate) organic nitrogen has not been measured frequently enough, and our knowledge of how rapidly organic nitrogen is transformed to inorganic forms and vice versa, in aquatic environments is inadequate at present.
2. Our knowledge of the interactions of nitrogen (particularly NO_3^-) with reactive surfaces in natural environments is inadequate. Laboratory studies indicate that NO_3^- does not adsorb readily to positively charged surfaces, yet there is evidence to suggest that significant amounts of NO_3^- are abiotically adsorbed in soils.
3. There is a need for accurate nitrogen budgets in a variety of small and large ecosystems.
4. The double isotope technique for analyzing NO_3^- shows tremendous potential, and may provide insights into nitrogen cycling processes.

Expertise that the USGS Currently Lacks in Nitrogen Cycling Studies

1. We do not currently have enough microbial ecologists or microbiologists to adequately understand nitrogen dynamics at many of the sites we are studying. Institutional biases against hiring microbial ecologists should be changed as they have been for aquatic biologists.
2. We do not have a soils analysis lab. Currently, investigators must contract with a Department of Agriculture Lab somewhere to get soil analyses done. At such labs, we usually have very little control or input for quality assurance and quality control. If the demand is sufficient, we should consider an agency-wide contract with a soils lab to provide quality analyses.

Strategies for Gaining the Expertise We Are Lacking in Nitrogen Cycling

1. Under tight manpower restrictions, we should look more closely at cooperating with scientists at other Federal agencies. Often, there are Federal scientists with necessary expertise who may be able to work at some of our study sites at no charge to us. We should pursue this more aggressively as an agency by developing strategies based on the success of other USGS scientists who have developed cooperative relationships with other Federal scientists.
2. We must continue to emphasize to the powers that be that we need a stronger student coop program. As long as students count against our FTE ceiling, this program will be inadequate to serve our needs. There are many examples of how we have used this program in the past to get the expertise we needed on a project.
3. We need to be less selfish with our cooperators and suggest university scientists where appropriate to carry out portions of a study that we do not have the expertise to undertake. Too often we are competing with university scientists for funds. We could both benefit by working more cooperatively.

Major Scientific Issues Raised in Panel Discussions

Do we have an adequate balance between monitoring and assessment process studies in the USGS?

1. We need more cooperation between districts and NRP.
2. We need to share our money and expertise with entities outside our "own" groups rather than try to hold onto all of it for our own projects (especially when we don't have all the needed expertise inside our own group). This is hard to do because of budget and hiring problems. By pooling expertise with outside scientists, you can also enhance chances for obtaining support from outside sources.
3. We must have continuity -- cannot keep chopping out parts of programs to pay for others.
4. We must get beyond needing to find an "issue" for monitoring and convince folks that continuous monitoring is needed for answering problems that we don't even know about yet.
5. We cannot do without either monitoring or research. Some research stems form databases produced through long-term monitoring.
6. We should put forward monitoring concerns within WRD.

7. We need better coordination of site selection; when possible, use existing sites for new programs.
8. USGS should focus on hydrologic/geochemical aspects of N cycling for remediation studies; we have lots of expertise in this area.

Does the USGS have critical gaps in knowledge, experience, or expertise to conduct state-of-the-art nitrogen cycling research?

1. We especially need biologists, microbiologists, soil scientists, oceanographers. The NBS biologists will soon be joining the USGS, but they are mostly macro-biologists instead of microbiologists.
2. A big survey to determine where is/is not N the limiting nutrient in fresh surface waters would be very useful.

What are the next steps for watershed nitrogen studies?

1. We need to identify, separate, and understand influences of various processes, particularly biological.
2. We need to have a scale-up plan for our watershed research; we need to work at scales ranging from small to big, but most of our research is in small pristine watersheds. Where is our research most applicable?

   Probably agricultural pollutant and urban runoff studies. We should be making more linkages with EPA and USDA for such studies.
3. We need long-term monitoring to separate small scale perturbations from long-term changes.
4. We need to determine the sources of atmospheric NO_3 and NH_4. Perhaps O^{18} of nitrate will prove to be useful for this. Kendall wants to collect snow samples from a network of sites (including NAWQA sites) as a preliminary assessment of the potential usefulness of this tool.
5. We need more information about geology and lithology (reactivity) of local flow systems for regionalization of N cycling information.
6. We need to define a new thrust area: N cycling processes. Use the merit program approach. This could incorporate many of the elements that our agency has defined as important, namely: District-NRP collaboration, inter-disciplinary research, relevancy to local issues, lots of bang for the bucks since money is matched by district.

Can plants be used as isotopic integrators of water/nutrient sources? Especially algae?

1. There has been lots of work on using O^{18} and H_2 of plant water in the arid southwest as a tool for determining what waters (soil verses ground water) plants are using.
2. N^{15} of algae may be a good indicator of N source if source is consumed quantitatively. Preliminary work with a University of Colorado student shows that algae from streams with sewage input are isotopically heavier than algae in pristine streams. This is consistent with the presumed N^{15} values of the N sources.
3. Using C^{13} is more complicated because of photosynthetic fractionations.

4. For organisms higher up the food chain, "you are what you eat plus 1 to 4 permil" applies (if source is consumed quantitatively); hence, diet can often be related to total composition. Perhaps analyzing organisms that use particulates would be less complicated (less fractionation because particulates are less labile).
5. Compound specific stable isotope mass spectrometry may allow much better determination of specific sources of organic compounds, including information about land-use.

Do isotope fractionations pose problems for interpretation?

1. Yes. Sometimes the fractionations are so large and variable that nothing quantitative can be determined. Other times, the fractionations are minimal and may even provide useful process information. Isotopes cannot be applied mindlessly.
2. In studies of sources of N in small watersheds or in surface runoff, these are probably less critical than in large ground water systems because of the shorter residence times and generally oxic conditions.
3. Urea applied to agricultural fields can be volatilized, causing appreciable fractionation in many instances. Studies thus far indicate that most snow ammonium is not nitrified very quickly, so does not appear to be an important source of NO_3 to the system very quickly.
4. Use of N^{15} is complicated by the fact that each recycling step can cause a little enrichment. One advantage of the use of O^{18} for tracing sources of NO_3^- is that the O^{18} signature of NO_3^- is reset with each cycling step.
5. We may be able to use O^{18} and N^{15} together as a tracer of extent of denitrification, and to determine the original source value. Also can measure N_2/Ar ratios, and measure the N^{15} of residual NO_3^- and dissolved N_2.
6. Pool effect: when there is a large pool of nitrate, isotope fractionations may have little effect. In contrast, little pools can be drastically affected. However, if pools are so small that all the substrate is used up, then there is no fractionation because kinetic fractionations usually change with reaction speed.
7. Use of N^{15} labeled materials eliminates most of the fractionation problem. Thus far, labeled studies have been limited in the USGS because of the cost of the analyses. Recent methods developed in a MO MSEA-Isotope Tracers Project collaboration have reduced the costs for such analyses. The new elemental analyzer/mass spectrometer system purchased in Menlo Park further reduces costs.

Low/moderate/high cost options to promote cooperative studies in the agency

Low- or no-cost options

1. Set up interest groups; possible topics: nitrogen (nutrient?) cycling, isotopes, watersheds, etc. Have the leader download interesting stuff from continuums and the NET to the interest group distribution list.
2. A newsletter similar to those that have arisen in other areas of interest within WRD.

3. Technology transfer: Assign to the regional water quality specialists the responsibility for providing technology transfer between NRP and District scientists on the topic of N cycling (and other topics!). These folks should attempt to keep people aware of what is going on and who is doing what. The research advisers could be more helpful, too, in providing "match-ups" of people and programs. They receive a tremendous amount of information that is rarely ever distributed to possibly interested folks. For example, handouts distributed at research meetings are almost never circulated within the NRP.
4. Try to arrange a special session at AGU or GSA on N cycling every year or two.
5. Initiate a discussion of what sorts of research and monitoring topics are ideal for an agency with a broad geographic distribution of offices, like the USGS. This is our natural turf and we should be taking advantage of this. Perhaps we could look for OFA funding for "good" ideas.
6. Try to free up more operating money for productive NRP scientists. Currently scientists that are busy bringing in outside money are subsidizing large numbers of folks who are unable or unwilling to shift gears to bring in outside money. And large projects are being penalized to provide "some" money for all. One way to free up some money is to re-assign less productive or poorly focused NRP scientists to other projects where OFA funding would otherwise be used to hire similar expertise.
7. Have workshops like this one periodically, but broaden to the wider topic of nutrient cycling.

Moderate-cost options

1. Reinstate the Merit Program, strongly advising that District folks seek NRP collaboration. Provide some token amount of money to the collaborating NRP project (maybe $5K).
2. Provide "sabbatical" money for District scientists to have opportunity to synthesize data sets of national interest. As an agency, we do lots of gathering of data but not enough evaluation.
3. EPA is currently downsizing; are there areas where we could now become the lead Federal agency?
4. Provide a few weeks of funding for the occasional District scientist to come work in an NRP lab; this would greatly facilitate District and NRP collaboration.
5. Provide funding for occasional post-doc to bring in new expertise in hot-issue areas (e.g., compound-specific stable isotope geochemistry).
6. Provide some equipment money for isotope laboratories. Most isotopers in the NRP are actively collaborating with District scientists; hence, any equipment purchased for the isotope labs will be widely used. However, in the last 5 years, almost no NRP or NWQL money has been supplied to any of the isotope labs for capital improvements related to nutrient-cycling research. During this same period, other Federal agencies (and universities) have purchased significant quantities of new equipment, resulting in a situation where USGS scientists no longer have access to state-of-the-art equipment.

Major-cost options

1. Recent work by USGS researchers (Plummer, Busenberg, Böhlke, etc.) has shown that age-dating young ground waters can provide critical information about the timing of recharge of pol-

lutants, the time required for natural remediation, and the processes responsible for NO_3^- removal. This information then can lead to changes in best-management practices. These and other workers have shown that CFCs can provide useful age data, but that helium isotopes (and helium/tritium) are a superior (although more expensive) age-dating tool because they are not affected by biological reactions and can be applied in polluted environments where CFCs cannot be used.

The USGS currently has recently found a contract lab for such analyses. In the future, it may be more practical to set up an in-house research/production lab for noble gas isotopes. Both Divisions could share such a facility.

2. Use our national distribution of personnel to initiate new regional studies that cannot be undertaken by OFA or universities. For example, monitoring of atmospheric gases of interest to greenhouse research (N_2O, CO_2, CH_4). Or sampling of %C and C^{13} of soils in temperate forests. Or O^{18} and N^{15} of atmospherically derived NO_3^-.

3. Join with University scientists to purchase an tandem accelerator (AMS) for measuring cosmogenic isotopes.

Groups 5 and 6 Summary Report: Nitrogen Transformations in Ground Water and Nitrogen Transport and Fate in Riparian Areas

Chairperson: Richard L. Smith

Work Group: Stephen P. Garabedian, Brigid Rea Kumler, J.K. Böhlke, Lan H. Tornes, Larry J. Puckett, and John R. Mullaney

The Ground Water/Riparian Zone discussion panel identified 5 key issues facing the Nation and the USGS regarding nitrogen contamination. These are topics that the USGS should be addressing during the next 5-10 years to understand the impact of nitrogen loading on subsurface systems, and ultimately, the contribution to the eutrophication of surface water systems, to which ground water is eventually discharged. While this is not necessarily a comprehensive list, these issues were considered to be among the most important, though not necessarily in the order listed.

Regional Aquifer Susceptibility

Where is nitrate in ground water a major problem, where might it become a problem in the future, and where is it a non-issue and likely to remain so? How does nitrate contamination in the East compare to the West, or the North versus the South? And what are the factors that control any differences that might be evident? How many of these differences are due to land use practices, how many are due to the physical environment, e.g. the hydrology and the subsurface formation, and how many are due to biological differences?

A key to all of these questions is the issue of scale. This workshop demonstrated that there are small-scale studies in progress that focus on nitrogen cycling in various hydrologic systems. Each study is addressing, to varying degrees, some or all of these questions. But what is the transferability of these studies to the regional scale? How useful will the results of these studies be to managers at different sites? As a group and as an Agency, we must be able to put our results into a broad perspective. Larger-scale assessment studies, such as NAWQA, are also in progress, but it can be very difficult to determine factors controlling nitrogen susceptibility with such studies.

The conclusion is that unified, comprehensive compilations of the small-scale studies are in order. These should be done in an integrative fashion and in conjunction with the large-scale assessment studies. This workshop on nitrogen cycling is one step in that direction. However, much more is needed. These compilations should be in a variety of formats and geared towards a variety of end-users, including scientists, managers, regulators and the lay public. In addition, application of existing technology could prove to be particularly appropriate. Nitrogen susceptibility maps could be prepared that incorporate existing information on land use, soil type, lithochemistry/geochemistry of bed rock material, subsurface formation, including grain size distribution, regional hydrology, and climatic conditions. These maps could serve as the foundation for the transfer of information from our study sites to the regional scale, would serve as a useful tool for the management of the Nation's water resources, and would represent a cost-effective product that could include all of the Divisions of USGS.

Nitrogen in the Hydrosphere--Linkage Between Ground Water and Surface Water

Nitrogen transport in ground water and subsequent discharge to surface waters can potentially play a major role in the eutrophication of surface water ecosystems. The extent to which this happens, the role of riparian zones in nitrogen removal, and the transformation of nitrogen by hyporheic zone processes are topics that need a great deal more research. These types of studies must be interdisciplinary in nature, in part because hydrology plays a pivotal role in the path of travel and the geochemical conditions encountered by the nitrogen.

At present, there is a general lack of recognition by regulators and the public at large about the connectedness between ground water and surface water, which is pertinent not only to nitrogen, but all other forms of water contamination. This an area in which the USGS could play a leadership role both in research and in heightening awareness of the continuity of the hydrologic cycle vis a vis ground water surface water interactions. The presence of nitrate in ground water is not just a drinking water issue.

Remediation

Considerable amounts of money are currently being spent in the U.S. on remediating contaminated water, both for pre- and post-discharge of the water to the environment. Nitrogen is often involved in some aspect of the remediation. In some cases it is one of the constituents that is targeted for removal. For instance, constructed wetlands are designed to remove not only carbon, but nitrogen and phosphorus as well. Additional treatment systems to remove nitrogen that are installed between a septic system and its drain field are currently being marketed and have been proposed as mandatory for some water districts. In other cases, nitrogen is added as the remediation agent. The degradation of toluene or other aromatic solvents present in ground water or soils has been proposed and attempted by adding nitrate to stimulate denitrification. However, remediation is commonly instigated with little prior testing as to the efficacy of the process that has been selected or its overall effect upon water quality and with little or no monitoring of the overall effect of the remediation process once the remediation has commenced. Surprisingly little is known even about the effect of the most common remediation practice, household septic systems. There is a great need for objective, integrated, interdisciplinary studies on the utility of the various types of remediation approaches. These studies should be holistic and include hydrology, water chemistry, sediment geochemistry, biology, etc., i.e. all of the discipline specialties of the Water Resources Division. The USGS should take a leadership role in assessing water remediation practices.

Microbial Processes

Microbial processes are crucial factors that control the speciation, and therefore the transport, of nitrogen in the entire hydrosphere. Uptake and release of nitrogen by plants and other higher organisms are also significant in watersheds and riparian zones. There was a clear recognition by the workshop attendees of the role of biological processes in their nitrogen studies. But there was also a perception that WRD has a paucity of process-oriented specialists, and that there is a general lack of information regarding the function of these processes in rivers, streams, reservoirs, and water-saturated systems. Most of our knowledge about biological processes, such as nitrification, denitrification, or nitrogen uptake by plants, come from agricultural research in soils, which are relatively organic-rich. Yet, soils are much different environments than ground water, rivers, or streams. Consequently, the biological processes will function much differently. Characterizing and understanding ground water, rivers, and streams is the purview of WRD. This purview should include the necessary (i.e. more) expertise needed to support our studies on the fate and transport of nitrogen in water. Much more research is needed to develop techniques to assay and characterize the processes and the (micro)organisms that mediate the processes.

There is a direct consequence of the shortage of process-oriented expertise. Often, it appears that the processes affecting nitrogen cycling are considered only after a project is well underway, or even completed. This can mean that the additional data needed to infer what processes might be operating at a study site were not collected, thus leaving certain aspects of the study as incomplete or inconclusive. Education and training are needed to help overcome this problem. If there is sufficient interest, specific process-oriented training courses could be developed. Or, these could be in the form of hands-on training in individual research labs to learn how to measure or assess the processes of interest. Another alternative would be to establish a specific fund, for which individuals could apply (say based upon a proposal or justification) to travel to the appropriate research center (or field site) for a short (1-2 week) hands-on, one on one, training session with a process-oriented scientist. These instructional tools would also be appropriate not just for biological processes, but for acquiring other types of expertise, such as experience with analytical techniques or with using stable isotopes.

Nitrate Concentrations in Ground Water

There is a general perception that nitrate concentrations in ground water are increasing nationwide. While this is probably the case, a great deal remains unknown regarding this issue. How do these trends vary historically as agricultural practices and urban development have changed? What well location and frequency of sampling are sufficient to document these trends? How much of the perception is simply due to an increased awareness of the issue?

Over the "short term", these are questions being addressed at NAWQA study sites. However, the technology now exists for reconstructing these trends over much longer terms by age-dating ground water along known aquifer flow paths. This information, coupled with isotopic data, nitrogen speciation, and key geochemical and hydrological data offer an important new approach for reconstructing these trends and for predicting the ultimate fate of nitrogen in ground water. This approach has proven effective in the few studies in which it has been attempted. It needs to be expanded and developed further and incorporated into more studies. In addition, a direct comparison with the trends in the NAWQA studies is clearly warranted and could prove insightful. The technology needed for this long term trend analysis is currently present within WRD. The investment needed to incorporate it into other studies would be modest.

Finally, the panel briefly discussed organizational interactions regarding nitrogen in water. This workshop on Nitrogen Cycling was a very good first step in coalescing what up until then, had been only individual efforts. We realized that WRD has a great deal of interest and active studies regarding nitrogen in the environment and that collectively we can have a much greater impact upon the scientific community and the public at large, and do a better job in our own individual studies. We strongly urge that a forum be found to continue this interaction. Ideas proposed to do so included adding a session at the Toxics Meetings on nitrogen (and publicizing that this was being done), additional workshops which could dovetail nitrogen with other topics, such as carbon, repeat sessions of this workshop, and training classes or mini-classes with nitrogen as the central focus. The inertia has been overcome, and we thank WRD management and the workshop organizers for doing so; let's keep the momentum going.

Group 7 Summary Report:
Nitrogen-Cycling Processes at the Sediment-Water Interface

Chairperson: Frank J. Triska

Work Group: Edward Callender, James E. Cloern, John H. Duff, Kevin F. Dennehy, Karla S. Pfenning, Robert L. Runkel, and P.F. Wang.

The sediment interface work group addressed three questions posed under the original objectives of the workshop:

1. What is the extent of nitrogen cycling research within USGS?
2. Are there any critical gaps in our expertise?
3. What high, medium and low cost options are required or available to enhance nitrogen cycling research within USGS.

Prior to addressing the above questions we established the central theme that:

> *Nitrogen is a reactive and critical element in the biosphere which has important, social, political and ecological implications.*

Management Issues/Extent and Distribution of N-Cycling Expertise

Nitrogen's reactivity, critical need in biosynthesis, and extensive application to the biosphere has resulted in at least three important management issues related to nitrogen cycling. The USGS is equipped to address all three at some level of expertise.

Issue 1: Nitrate Contamination in Ground Water and Surface Water

Current and increasing nitrate contamination of ground water and surface water raises numerous questions of national significance. For example: At what rate is nitrate increasing in ground water and surface waters of the United States? Are any regions approaching or exceeding drinking water standards? Within large watersheds are certain locations, stream orders, or riparian land uses likely to be impacted more than others? What is the role of reservoirs in transporting and cycling of nitrogen along a river corridor? These questions are best addressed using long-term data sets, collected consistently, and analyzed using standard analytical protocols in the context of national or regional monitoring and assessment programs. Both historically and currently the USGS is well situated and equipped to address such issues. Much of the required expertise is centered on the operational and NAWQA programs.

Issue 2: Eutrophication

By eutrophication we mean the general biological response to enhanced nitrogen input. Eutrophication has both management and basic ecological implications. At the heart of the biological response is the identification of nutrient cycling processes, both biological and physical-chemical, and the determination of their rates. Important biological nitrogen cycling processes include assimilation (primary production) nitrification, denitrification, ammonification and fixation. Physical-chemical processes include sorption and sedimentation. Addressing biological response requires a process-oriented approach. Process-oriented activities are often centered in the NRP, although outstanding process-oriented scientists can also be found in district and NAWQA Programs. In essence, the process approach is not uniformly distributed throughout USGS programs.

Issue 3: Gas Flux (N_2, N_2O)

This issue concerns the production of biologically generated gases especially N_2O which can damage the atmosphere. Flux of nitrogenous gases has not been a common component of monitoring programs at USGS. This is partly because measurement of gases is a different specialty than aquatic chemistry and because other gases such as CFC's CH_4 and CO_2 are generally considered more destructive to the atmosphere either by virtue of their activity or high level of production. Estimates of nitrogenous gas flux has been neglected and should be expanded to more locations, especially where nitrate contamination is an issue. Gas flux is ecologically important both as a sink for nitrate in transport, and for its potential damage to the atmosphere. Most activity in this area has been concentrated in NAWQA and NRP.

In addressing issues related to nitrogen cycling, the USGS, particularly WRD, has important assets critical to developing a regional or even national perspective. These include: (1) a national network of monitoring stations with long-term data sets and (2) a strong cadre of hydrologic expertise. With these assets WRD is uniquely positioned to provide a hydrologic, solute-transport perspective to nitrogen cycling research.

Conceptual Framework/Identifying Gaps

The sediment interface work group felt that development of a simple, consistent, conceptual framework was a critical prerequisite for developing a watershed perspective in nitrogen cycling, identifying gaps, synthesizing extant data and proposing future programs. The work group felt-that such a framework should cross spatial and temporal scales, and serve as guide wherein each researcher could rapidly chart his spatial position, identify his research contribution and determine gaps in N-cycling data from his site. A sample model, quickly developed by the group is shown in Figure 1.

Our goal was to develop an ecosystem-watershed approach, emphasizing linkage between the terrestrial and aquatic environment, upstream to downstream reaches, and freshwater to maine systems. Within this spatial continuum we wanted to link hydrologic transport, retention (biologic and geomorphic), and biogeochemical transformation. The continuum begins in upland (N-application to crops), and riparian areas. Hydrologic sources include subsurface transport of nitrogen via ground water to the channel. Retention features include plant uptake into biomass, transformation (e.g. nitrification, denitrification, and atmospheric flux (N_2, N_2O). Transport from upland to low order streams includes both dissolved nitrogen in ground water (DIN, DON) and particulate nitrogen (litterfall, blow-in etc.).

As stream order increases particulate sources become less significant. Within the channel, transport includes concentration of various nitrogen species both particulate and dissolved. Retention includes nitrogen incorporation into biomass (e.g. periphyton, macrophytes) physical retention by geomorphic features, such as pools and beaver dams in low order streams, and dams and associated reservoirs in higher order streams which are sites of nitrogen storage via sedimentation. Atmospheric flux includes N_2 and N_2O as products of denitrification during transport through the river continuum. Transformations include the above, atmospheric losses, assimilation to biomass, and also shifts in DIN (NO_3, NH_4) and DON concentration. As stream order increases algal communities shift from lotic to lentic forms and the dominant N-cycling process might shift in response. The total river continuum extends from headwater to estuary including coastal marine environments.

The purpose of this type of conceptualizing is to:

1. Identify positions along the continuum emphasized past work as well as those neglected.
2. Serve as a guide to synthesize data and concepts,
3. Identify gaps in our knowledge, and
4. Ultimately to formulate and test hypotheses. For example: What order reaches along the continuum have typically been used for monitoring, compared to process studies? Are certain orders along a continuum typically higher or lower in dissolved nitrogen than others? What is the molar ratio of nitrate to ammonium, and how does it vary along a river corridor?

Using Figure 1, the work group proposed the hypothesis that nitrification in riparian zones and channels is the dominant nitrogen cycling process in low-order streams(1-3 order), biomass production is dominant in mid-order streams (4-6 order), and denitrification in the dominant N-cycling process in higher (6-7) order rivers (are sites of high atmospheric nitrogen flux). Is our agency positioned to test such hypotheses? In fact is there a complete data site anywhere in the country for a single river network? Future development of a general conceptual framework is an essential prerequisite for planning any new large-scale program in nitrogen cycling. It may also be a valuable organizing tool in data syntheses for existing monitoring and assessment programs.

Recommendations

The sediment-interface work group did not see immediate establishment of new large-scale initiatives or thrust programs due to funding uncertainties. However, we attempted to suggest low-cost options which might provide valuable insights at modest cost.

1. We recommend that, to the extent possible, additional low cost analyses be included in routine nitrogen related monitoring. These analyses include chloride, dissolved oxygen, dissolved organic carbon, dissolved organic nitrogen and silica. These parameters are linked to important consideration of nitrogen cycling within a hydrologic context including water source (chloride), redox requirements for nitrogen transformation (dissolved oxygen), organic nitrogen mineralization (dissolved organic carbon, dissolved organic nitrogen), and algal community structure (silica). Gas flux (N_2O) could be an important component of nitrogen flux especially at sites where nitrate input is high. At such sites gas flux should be measured at least periodically.
2. Linkage between various element cycles should be considered in planning N-cycling studies. For example C/N provides information about the biological quality of organic matter sources, and can identify potential nutrient limitation of N-cycling processes. The ratio N/P can determine the structure of algal communities. For example, in low N/P environments one would expect greater composition of blue-green algae. Dissolved N/Si, ratio should be determined. Large inputs of nitrate to river water can result in effective stripping of silica higher in the river

continuum lowering its availability to estuarine and coastal diatom communities.

3. A small funding "set aside" should be made to support merit-based, small-scale cooperative studies. While the USGS and particularly WRD has extensive expertise in N-cycling, the talent is not evenly distributed throughout operational, research, and NAWQA programs. Small grants to fund travel and supplies would foster cooperation between various agency programs and supply small supplements to address research questions that could not otherwise be examined.
4. A small funding "set aside" should be established to take advantage of research opportunities related to episodic events such as floods.
5. At this time the Survey does not have a strong expertise on remediation. Additional expertise is required to translate scientific data, such as loading rates, pool sizes and process rates into recommendations for environmental improvement; especially in ground water and riparian settings.

Group 8 Summary Report: Role of Special Events

Chairperson: Norman E. Peters

Work Group: Gregory M. Clark, John R. Mullaney, Timothy G. Rowe, and James M. Thomas

The work group addressed the following questions, as requested by the organizers:

1. What are the major scientific issues regarding nitrogen cycling?
2. Which of the issues identified in question 1 will be major national issues?
3. In which of the issues identified in question 1 should have USGS involvement and what role should the USGS play in the issue?
4. For the issues identified in question 1, is USGS infrastructure sufficient? Expertise? Equipment? Methods development? Instrumentation?
5. What no cost/low cost products can be derived from this workshop?
6. Moderate cost products and programs, i.e., add-ons and travel costs?
7. What major new programs should be initiated to address emerging issues per question 1?

Major Scientific Issues, National Issues, and USGS Involvement

Of the issues listed below, the work group prioritized items 2 through 6 in that order as those which are or will become national issues. Item 1 is general and critical to identifying and quantifying nutrient-cycling processes that need to be evaluated regarding specific issues as per 2 through 6. The USGS should be involved in each of these issues, but the level of involvement varies among issues. Other Agency's that also should be involved and in one case should take the lead are listed after the issue.

1. Quantifying transformation and transport of N and P species.

We've identified that agriculture, atmospheric deposition and urban water quality can have a major impact on nitrogen species in water. Assessments are similar among studies, but can we quantify the different pathways?

- Volatilization of N species
- Identify sources in homogeneous areas, possibly using a small watershed approach
- Cycling of nutrients in reservoirs and lakes
- Chronic effects on terrestrial and aquatic systems, e.g., exhaustion of soil cation nutrients due to acidification from fertilizer, compaction and resultant water logging of soils and eutrophication. Chronic effects may result from continually high applications of fertilizer, high levels of atmospheric deposition, and ground water leaching of wastes.
- Episodic effects on terrestrial and aquatic systems, e.g., fish kills, blow downs from

high wind, algal blooms, and acidification. Episodes include forest fires, floods, droughts, spills, hurricanes, other high wind and rain events, volcanic eruptions, and stormwater runoff

2. Use of manure and inorganic fertilizers in agriculture (with USDA taking the lead)
3. Delivery of nutrients to estuarine systems (other Agencies apparent but not identified by the work group)
4. Atmospheric deposition of nutrients (with NOAA and EPA)
5. Health
    - Domestic water supplies and shallow ground water (local water authorities, EPA, and State Regulatory Authorities)
    - Episodes (CDC, State Health Departments, EPA)
    - Atmospheric deposition (USGS Wet Deposition through NTN/NADP, and NOAA and EPA for Dry Deposition)
6. Eutrophication of receiving waters as it effects recreation, fisheries (estuarine), public supply, shipping and navigation, (NOAA, Corp of Engineers, Bureau of Reclamation)

USGS Infrastructure (Needs)

1. New hire(s) having expertise in biological and chemical aspects of agricultural systems
2. Develop low level analysis for organic N
3. Develop methods for field measurements of N_2O monitoring and transport
4. Develop methods for quantifying transformation rates and sources of N such as the use isotopes
5. Develop methods for real time, i.e., in-situ, monitoring of N species

Products and Programs

Low Cost

- Nutrient home page listing USGS experts, publications and project summaries
- Add bibliography of N papers of each workshop participant to workshop open file
- Research-directions congressional report -- joint venture with important Federal and State partners
- Lay-reader four-page color fact sheet on the scope of N cycling research in the USGS

Moderate Cost

- A key factor here and in high cost section is to create an environment of interdisciplinary research on various issues related to nutrient cycling
- Provide travel/incentives or other incentives, such as equipment, to experts (internal –

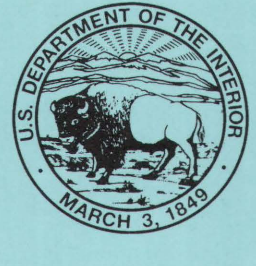
NRP & District researchers, and external – researchers in Universities or other Federal Agencies) to participate in targeted research projects.

- Provide emergency funding for studying impacts of episodes
- Establish Federal merit funds for add-on research
- Establish discretionary program funds to support “hot” topics -- interesting and potentially fruitful areas of research are uncovered in many projects that never are pursued, because they either fall outside the scope of a project or funds are not available for the additional investigation.
- Develop process-orient models within the framework of the Modular Modeling System (MMS) -- this may be a high cost item

High Cost

- Investigate processes of nutrient cycling in agricultural systems including the effects of best management practices and remediation in collaboration with USDA
- Investigate the fate of nitrate in ground water
- Establish a core data collection and monitoring network of watersheds as a core USGS function for long-term investigations of various aspects of N cycling or broader on hydrologic, biogeochemical and ecological aspects of terrestrial and aquatic systems.

*U.S. Government Printing Office: 1996 — 545-579



U.S. DEPARTMENT OF THE INTERIOR

MARCH 3, 1849