2008

Chapter 8. The Importance and Role of Watersheds in the Transport of Nitrogen

T. J. Sauer
USDA-ARS

R. B. Alexander
US Geological Survey

J. V. Brahana
University of Arkansas, Fayetteville

R. A. Smith
US Geological Survey

Published in *Nitrogen in the Environment: Sources, Problems, and Management, Second edition,* ed. J. L. Hatfield & R. F. Follett (Amsterdam, Boston, *et al.*: Academic Press/Elsevier, 2008).

Nitrogen in the Environment: Sources, Problems, and Management
J.L. Hatfield and R.F. Follett (Eds)

Chapter 8. The Importance and Role of Watersheds in the Transport of Nitrogen

T.J. Sauer[a], R.B. Alexander[b], J.V. Brahana[c] and R.A. Smith[b]

[a]USDA-ARS, National Soil Tilth Laboratory, Ames, IA, USA

[b]US Geological Survey, Reston, VA, USA

[c]Department of Geosciences, University of Arkansas, Fayetteville, AR, USA

A recent report to Congress concerning water quality in the United States indicated that 35%, 45%, and 44% of the assessed rivers and streams, lakes, and estuaries, respectively, were impaired by one or more pollutants (US Environmental Protection Agency, 1999). Nutrients, primarily nitrogen (N) and phosphorus (P), contributed to the impairment of 30% or 135,000 km of the nation's impaired rivers and streams, 44% of the impaired lakes, and 23% of the impaired estuaries. Excessive nutrient loads are implicated in the eutrophication of lakes and reservoirs in the United States and coastal ecosystems where N is most limiting to primary productivity (Vitousek et al., 1997; Carpenter et al., 1998). Efforts are currently underway to establish Total Maximum Daily Load (TMDL) values for pollutants, including nutrients, of impaired water bodies as described under Section 303(d) of the Clean Water Act of 1972.

The movement of N in the terrestrial environment is intimately related to the movement of water. Water in the form of precipitation, flowing across the soil surface as runoff, and percolating through soil layers to ground water can all be significant carriers of organic and inorganic N constituents. The relative importance of these transport mechanisms is a complex function of N sources and transformations, hydrologic processes, climate patterns, and land use. While some elements of the N cycle can be studied in the laboratory under controlled experimental conditions, many can be studied in a meaningful way only in the natural and culturally affected environments of watersheds. By considering N transport over a range of spatial and temporal scales, it is possible to improve our understanding of the factors affecting the fate of N in watersheds, including the effects of land use and N sources (point, nonpoint, agricultural, urban, organic, and inorganic), N transformations (mineralization, nitrification, denitrification, and immobilization), and transport mechanisms (runoff, percolation to ground water, and ground water transport). Knowledge of the variability in N transport in relation to these factors is critical to developing and implementing effective strategies for mitigating unacceptably high N inputs to receiving waters.

The strengths of watershed-scale evaluations include easily definable hydrologic boundaries, identification of N sources with respect to water flow patterns, and a convenient, integral measure of water-quality response at a single point (the basin outlet). The objective of this chapter is to synthesize current understanding of the major processes and controls affecting N transport in watersheds. The scope is limited to technical issues of flow and chemistry of fixed (i.e., biologically reactive) organic and inorganic N forms in watersheds. We begin with a background discussion of watershed hydrology (Section 1) and the effects of N on ecosystems and human health (Section 2). We then describe the major sources of reactive N to watersheds (Section 3), and summarize the principal terrestrial and aquatic processes affecting N transport (Section 4). Section 5 illustrates the effects of various natural and cultural properties of watersheds on the yield of N in surface waters (N yield is defined as the N mass observed at the outlet of a watershed expressed per unit of drainage area). We conclude with a discussion of the results of empirical modeling methods that have been used to separate the effects of N supply and loss processes and estimate the fate of N sources in watersheds.

1. WATERSHED HYDROLOGY

A watershed (catchment or drainage basin) is an area of land where all of the precipitation that falls, less the water lost to evaporation and deep aquifer recharge, eventually flows to a single outlet. A watershed encompasses both surface and subsurface components of water drainage that contribute to stream discharge. On a global perspective, watersheds vary dramatically in physical features including area, shape, drainage pattern, aspect, orientation, and elevation (Schumm, 1977; Black, 1996). Geomorphic features of watersheds reflect the geologic formations and soils present and the erosive forces that have reshaped these materials. In regions with low relief and homogenous surficial materials such as areas of the Midwestern US, watersheds are often pear-shaped with a dendritic drainage pattern, as there is little difference in resistance to erosion to influence the headward cutting of stream channels (Black, 1996). Other, less random drainage patterns are the direct result of the varying erodibility of soil and rock. Structural differences in underlying formations can create well-defined, regular patterns as the channels develop following the path of least resistance to erosion. Slope aspect and watershed orientation (general direction of main stream channel) become important at higher altitudes and latitudes and especially with regard to snow hydrology. In the Northern Hemisphere, snowmelt will occur later on slopes with a north aspect in steep, east–west oriented watersheds as compared to slopes with a south aspect. Streamflow during snowmelt in watersheds that have a northern orientation may also be impeded by unmelted ice downstream.

Several numerical parameters have been used to describe the physical characteristics of watersheds. These include stream order, drainage density, and area and shape relations (Schumm, 1977; Linsley et al., 1982; Moseley and McKerchar, 1993). A classification of stream order was first proposed by Horton (1945) to describe the amount of branching within a basin. A first-order stream is small with no tributaries, a second-order stream has only first-order tributaries, and a third-order stream has tributaries of first- and second-order, etc. The order of a watershed is determined by the order of its principal stream. Drainage density refers to the total length of streams divided by the drainage area. A highly dissected basin will have a high drainage density and stream discharge that responds more quickly to precipitation events than less-dissected basins. A low drainage density may indicate erosion-resistant or highly permeable soils and low relief. Several area and shape relationships have been developed to create scales with which to compare watershed shapes with each other and with known shapes such as a circle or ellipse. Generally, ratios of basin parameters such as channel length, basin area, perimeter, and relief are calculated to provide indices, which are often dimensionless numbers, to allow relative comparison between watersheds. The numerical parameters used to describe the physical features of watersheds are in turn correlated with storm runoff, as measured by stormflow hydrographs. Functional relationships have been developed between runoff characteristics (e.g., time to initiation of runoff, time to peak flow, discharge at peak flow, total runoff volume, and time to recession) and storm characteristics and physical watershed features (Moseley and McKerchar, 1993).

Streamflow or discharge is a composite of surface (overland flow) and subsurface (baseflow) contributions. On the surface, flow follows the topography, from high elevations to lower elevations along interconnected pathways that provide the steepest gradient down. In the subsurface, discharge to the surface may be concentrated at permeability contrasts such as soil and rock interfaces and through preferential flow paths such as macropores, worm and root channels, bedding planes, fractures, and caves. In the subsurface as on the surface, ground water flow is driven by hydraulic gradients and the favored pathways are those that provide the least resistance to flow. Along all pathways, chemical interaction may occur between the water and solid, liquid, and gas components present in the water. The nature and extent of such interactions depend on the specific biogeochemical environment and residence time. Hydrologic and geochemical processes are rarely uniform over the area of a watershed. This is evidenced by numerous investigations of such features as variable source areas of runoff (Anderson and Burt, 1978; Bernier, 1985), riparian-zone processes (Hill, 1996; Cirmo and McDonnell, 1997; Devito et al., 2000), and karst hydrogeology (LeGrand and Stringfield, 1973; White, 1988). Riparian and karst settings are also notable in that they include frequent and significant interaction between surface and subsurface water, often with important implications for N transport.

2. NITROGEN IMPACTS ON WATER QUALITY

Three well-documented water-quality concerns are related to loadings of N to surface and ground waters. The presence of high levels of nitrate (NO_3) in drinking water has been linked to two different human-health concerns. The risk of methemoglobinemia in infants due to ingestion of high NO_3 drinking water is well understood and recognized. An increased incidence of stomach cancer and nonHodgkin's lymphoma due to NO_3 intake is less certain (US Environmental Protection Agency, 1976; Heathwaite et al., 1993). Nonetheless, a drinking water standard of 10 mg/L for NO_3-N, as established by the US Environmental Protection Agency, is now widely accepted.

A second area of concern is the toxic effect of ammonia (NH_3) on freshwater aquatic life (US Environmental Protection Agency, 1976). It has been known since the early 1900s that NH_3 is toxic to fish and that this effect varies with water pH and temperature. A concentration of 0.02 mg/L as un-ionized NH_3 is the current standard for NH_3 in freshwater for the United States.

The third and perhaps most significant water-quality concern with respect to N is the overenrichment or eutrophication of surface waters. Eutrophication and its attendant problems of algal blooms, subsequent low dissolved-oxygen concentrations, and fish kills have been described in an extensive body of literature. Overabundance of P is the most common cause of eutrophication in freshwaters, although exceptions are known (Hecky and Kilham, 1988; Correll, 1998). In coastal marine waters, either N or P and possibly other nutrients, such as silicon, may be limiting, whereas in the open ocean, N is generally considered the key nutrient controlling primary production (Correll, 1998; Burkart and James, 1999; Council for Agricultural Science and Technology, 1999). Overenrichment of N has been implicated in the development of anoxic and hypoxic zones in shallow coastal waters in Europe, North America, and Asia. Excessive phytoplankton production in these areas leads to oxygen depletion when the organic residues decompose, often with devastating effects on local fisheries.

3. NITROGEN SOURCES TO WATERSHEDS

The inputs of biologically available forms of N to terrestrial and aquatic freshwater ecosystems have increased globally by more than a factor of two over the past two centuries as cultural activities that fix N have rapidly expanded. Nitrogen fixation refers to the conversion of dinitrogen gas (N_2) to NH_3 either naturally via N-fixing plants (legumes), or through cultural processes such as the manufacture of N fertilizer and combustion of fossil fuels. Fertilizer application, cultivation of leguminous crops, and fossil fuel combustion represent 57%, 29%, and 14% of the culturally derived N, respectively (Galloway et al., 1995; Vitousek et al., 1997). Cultural inputs are unevenly distributed around the world, with the highest concentrations in areas of intensive agriculture and industrial processing (Matthews, 1994). The largest increases have occurred in the latter half of the 20th century as the industrial production of N for use as fertilizer increased many fold. More than 50% of all the industrially fixed N applied as fertilizer through 1990 was used during the decade of 1980–1990 (Vitousek et al., 1997). In the United States, fertilizer use has increased by a factor of about 12 since the 1950s, with much of the increase occurring prior to 1980 (Goolsby et al., 1999). Natural sources of N, principally biological fixation by noncultivated leguminous plants and lightning fixation, represent 64–93% (90–140 Tg N) of the total culturally fixed N at the global scale (Galloway et al., 1995; Vitousek et al., 1997), but vary geographically with vegetation and land use. Natural sources of N are typically small (<10%) in relation to cultural sources in many developed regions of the world, such as in the United States (Jordan and Weller, 1996).

The agricultural food chain is the principal pathway for culturally derived N to enter the terrestrial and aquatic ecosystems of developed watersheds. More than 90% of the culturally derived N in the United States enters croplands and pastures through fertilizer application, crop fixation, and atmospheric deposition on agricultural lands (Jordan and Weller, 1996). Nearly 50% of the N applied in fertilizer is recycled in food and feed products (Keeney, 1982; Howarth et al., 1996) that are consumed by livestock and humans. Livestock consume the vast majority of the N in harvested crops and forages, most of which is excreted in feces and urine; 10–40% of the N in animal manures is volatilized (Terman, 1979), and much of that subsequently enters nearby watersheds in NH_3 deposition from the atmosphere (Howarth et al., 1996). Manure that is applied to cultivated or pasture lands enters watersheds in organic-N, NO_3-N, or NH_3-N, (Haynes and Williams, 1993; Jordan and Weller, 1996; Kellogg et al., 2000). Less than 15% of the N consumed by livestock is subsequently ingested by humans in meat, eggs, and milk (Jordan and Weller, 1996). Much of the N in human wastes is recycled into the hydrosphere through on-site septic systems or is discharged to streams and rivers in the effluent of wastewater treatment plants.

In addition to animal manures and human wastes, which largely involve the terrestrial recycling of culturally derived N, mineralized organic N (i.e., N that is biologically converted from organic to inorganic forms) in soil is potentially an important recycled N source to watersheds and aquatic ecosystems (Burkart and James, 1999; Goolsby et al., 1999). Organic N deposits in soils reflect the recent and long-term accumulation of N from fertilizers and biologically fixed N, immobilized by soil microbes and plant residues. Although N mineralization occurs naturally, cultivation may initially expose the soil to much higher rates of mineralization that are equivalent to or even greater than annual N fertilizer application rates (Burkart and James, 1999). On lands that have been cultivated over extended periods, the mineralization of N in soil organic matter may approach equilibrium with agricultural inputs (Paul et al., 1997).

Despite the extensive terrestrial cycling of N in soils, vegetation, livestock, and humans, estimates of N transfers and the net releases of N to watersheds by major cultural activities have been the focus of intensive research and are now known for many areas of the United States (Howarth et al., 1996; Jordan and Weller, 1996; Burkart and James, 1999; Goolsby et al., 1999; US Environmental Protection Agency, 1999; Kellogg et al., 2000). Estimates of N transfers often require assuming average values for N concentrations in organic materials and rate constants for N transformations, the use of state or county level census data, and extrapolation from field-scale measurements. Recent estimates of cultural inputs of fixed N to major regional watersheds of the United States (Jordan and Weller, 1996; Figure 1)

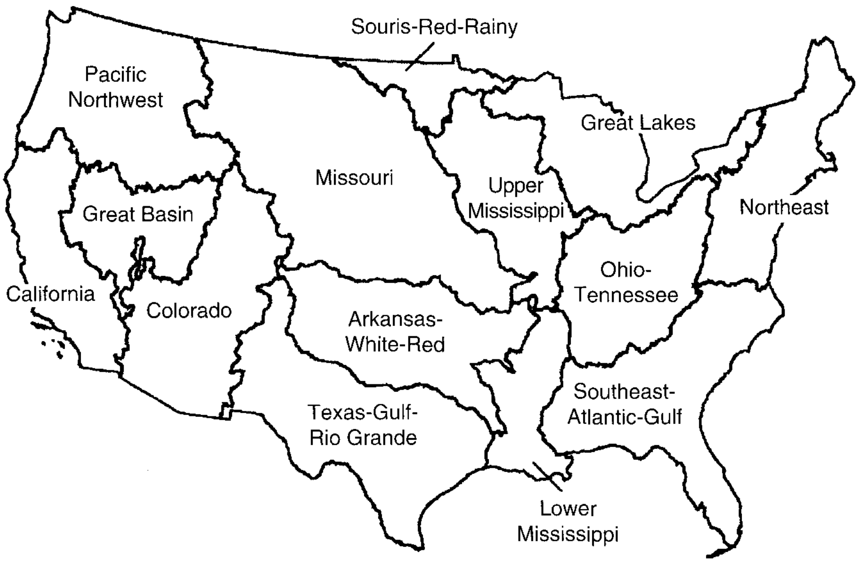

Figure 1. Water-resources regions of the conterminous United States. (Modified from Seaber et al. (1987))

are presented in Table 1. Table 1 separately reports "newly" fixed N inputs, reflecting *in situ* fixation by crops and the initial terrestrial application of N (fertilizer and NO_3 deposition in precipitation), and the releases of previously fixed (terrestrially recycled) N in livestock manure and human wastes. Also reported are estimates of net food and feed transfers by region, which are included in the releases of recycled N in livestock manure and human wastes. Fertilizer typically contributes about 50% of the "newly" fixed N inputs in the watersheds (sum of fertilizer, crop fixation, and deposition) with the highest contributions in the highly agricultural California region and lowest in the highly populated northeast region. Crop fixation accounts for a third or more of the total inputs of newly fixed N, with some of the highest contributions occurring in the Northeast, Upper Mississippi, and Missouri regions.

Atmospheric deposition of NO_3 is much lower than agricultural inputs, typically contributing from 10% to about 20% of the total inputs in most regions. The highest atmospheric contributions (32%) are found in the Northeast region, where deposition rates are high and fertilizer inputs are among the lowest. The inclusion of additional oxidized N compounds (NO_y, including wet and dry deposition) could be expected to increase the estimates of deposition inputs in Table 1 by as much as a factor of 2 (Howarth et al., 1996). Approximately 20% of the total inputs of culturally derived N are transported in agricultural products nationwide in food and feed imports (Table 1). In most regions, exports of N in agricultural products

Table 1.
Cultural inputs of newly fixed and recycled N and net imports of food and feed N in major water-resource regions of the conterminous United States.

		Nitrogen (kg/ha/year)								
								Recycled N releases to land and water		
		Newly fixed N						Point sources		
Region	Total area (10^6 ha)	Fixation by agr. biota	Fertilizer	Nitrate deposition	Total fixed N	Food/feed imports	Total net inputs	Industry	Municipality	Live-stock manure
Northeast	42	8.3	6.0	6.8	21	10	31	1.3	7.7	12.0
Southeast Atlantic-Gulf	68	5.8	13	5.0	24	5.2	29	0.2	1.2	7.4
Great Lakes	30	15	18	6.8	40	−7.2	33	0.7	3.0	5.7
Ohio-TN	52	15	20	5.8	41	−11	30	1.9	2.3	19.6
Upper Mississippi	48	27	40	5.4	72	−37	35	0.2	1.3	18.0
Lower Mississippi	25	13	19	5.4	37	−13	24	1.1	1.2	3.1
Souris-Red Rainy	15	11	23	1.8	36	−19	17	<0.1	0.2	2.6
Missouri	130	12	13	2.8	28	−10	18	<0.1	0.3	8.6
Ark-Red	64	7.4	12	2.8	22	−0.7	21	0.1	0.3	10.6
Texas-Gulf-Rio Grande	80	3.3	7.4	2.8	14	1.1	15	0.3	1.3	9.3
Colorado	65	1.6	1.6	1.4	4.6	0.5	5.1	<0.1	0.2	2.8
Great Basin	36	2.4	0.9	0.9	4.2	0.5	4.7	<0.1	0.1	1.3
Pacific NW	70	3.8	6.4	1.4	12	−1.6	10	0.1	0.4	3.1
California	41	3.4	12	1.4	17	3.5	21	0.2	2.2	6.0

Modified from Jordan and Weller (1996). Municipal and industrial inputs of N from Gianessi and Peskin, (1984); livestock manure N from Puckett et al. (1998).

nearly balance the imports of N in these products. The major exceptions include the Northeast, where imports represent nearly 50% of the newly fixed N inputs, and the Upper Mississippi region, where 51% of the newly fixed N inputs are transported to other regions of the country. The large imports of food and feed in the Northeast can account for the unusually large N releases in livestock manures and municipal/industrial wastes in this region. Nitrogen inputs from municipal and industrial wastes are also relatively high in the Great Lakes, Ohio-Tennessee, and California regions. The Ohio-Tennessee, Arkansas-Red-White, Texas, and Colorado regions show the largest releases of N in livestock manures in comparison to the newly fixed N input to these regions.

4. NITROGEN CYCLING AND LOSSES IN TERRESTRIAL AND AQUATIC ECOSYSTEMS

Biologically available forms of N are highly mobile in the environment, and are subject to extensive biogeochemical cycling in terrestrial and aquatic ecosystems (Vitousek et al., 1997). Nitrogen cycling in terrestrial and aquatic ecosystems involves an intricate array of biogeochemical processes that can vary spatially and temporally in the environment in both rate and direction. Individual processes and the entire N cycle for selected systems have been the subject of numerous studies, many of which have been summarized in comprehensive review articles and monographs including Keeney (1973, 1983), Stevenson (1982, 1994), Floate (1987), Russelle (1992), Powlson (1993), and Vitousek et al. (1997). Discussion here will be limited to a brief description of principal N transformations affecting N transport from watersheds.

Immobilization is the assimilation of inorganic N by plants and microorganisms to form organic N compounds whereas mineralization is the decomposition of organic N to ammonium (NH_4). Nitrification is the microbial oxidation of NH_4 to nitrite (NO_2) and NO_3 whereas, conversely, denitrification is the reduction of NO_3 to NO_2, nitrous oxide (N_2O), and dinitrogen gas (N_2). Nitrification is important from an N transport perspective in that it involves the transformation of a relatively immobile species (NH_4) to a highly mobile one (NO_3). Lastly, N fixation is the conversion of N_2 to NH_3, either naturally via N-fixing plants (legumes), or through cultural processes via the manufacture of N fertilizer.

Nitrogen cycling dynamics and pathways differ within and between terrestrial, freshwater, and marine ecosystems. Nonetheless, some similarities persist and often dominate N dynamics in the environment. Since most agriculturally productive soil environments have extended periods of aerobic conditions, mineralization of organic N to form NH_4 is generally followed by nitrification. Thus, in many terrestrial settings with significant N present, N as NO_3 is commonly found at relatively high concentrations even though it is also the form of N preferred for uptake by many plants. Since NO_3 is also highly mobile in the hydrosphere, it is often the dominant form of N in freshwater systems. Denitrification of NO_3 occurs under anaerobic conditions such as are found in flooded soils, riparian areas, and in the sediment of streams, lakes, and reservoirs. From a watershed perspective, the dominant processes of the N cycle vary not only by location, but also seasonally at the same location.

Nitrogen from natural and cultural sources is removed from runoff and subsurface flows in the terrestrial and aquatic ecosystems of watersheds by many biogeochemical processes. Denitrification permanently removes N from watersheds by converting N to less reactive gaseous forms (NO, N_2O, or N_2) that escape to the atmosphere. Other means of N removal in watersheds, including the uptake of N by vegetation, burial of organic matter on the landscape, and storage of N on floodplains and in reservoirs and ground water, represent temporary storage sites for N over time scales ranging from fractions of a day to decades. Over long periods, these storage sites are likely to gradually release un-denitrified N to streams and rivers. Variability in the reported quantities of N removed in watersheds may in part reflect variations in the temporal and spatial scales over which these loss processes operate in both terrestrial and aquatic ecosystems (Seitzinger, 1988; Correll et al., 1992; Hill, 1996; Harvey and Wagner, 2000). However, most multi-year studies report the loss of large fractions of the N inputs to watersheds for a range of spatial scales, based on comparisons of inputs with the N yields from watersheds in streams and rivers (Galloway et al., 1995; Puckett, 1995; Howarth et al., 1996; Jordan and Weller, 1996; Vitousek et al., 1997; Goolsby et al., 1999). In large North American and European watersheds (basin sizes from 340,000 to 3.2 million km^2), comparisons of total inputs of N with stream yield indicate that 65–90% of the inputs (mean = 75%) are removed by terrestrial and aquatic processes (Howarth et al., 1996). Similar losses of N have also been observed in small watersheds of mixed land use (Jaworski et al., 1992; Jaworski et al., 1997) and in small, forested and agricultural catchments (Howarth et al., 1996). Because forest ecosystems are N limited, forested watersheds are capable of storing considerable quantities of N in biomass and soils. However, large variations have been observed in the percentage of loss, ranging from a few percent to more than 100 percent of N inputs (Johnson, 1992). This wide range may be explained by variations in the biological demand for N, which can fluctuate in response to such factors as N depositional history, forest successional stage, and species composition (Johnson, 1992; Stoddard, 1994; Howarth et al., 1996; Williams et al., 1996) as well as the effects of temperature on nitrification and other N transformations (Murdoch et al., 1998).

Many natural and cultural properties of watersheds may explain spatial and temporal variations in the rates of denitrification, nitrification, mineralization, and N storage and their effects on N transport in streams. These include factors such as land use, climate (precipitation and evaporation), the oxygen and carbon content of soils and stream sediments, and stream morphology (channel density, channel size, and water travel time). Watershed properties that affect the quantity, velocity, and direction of water movement along surface and subsurface flow paths (climate and geology) may have an especially important influence on N transport. Certain flow paths are more likely to remove N from the flow stream than others, such as in stream riparian and hyporheic zones where biochemical conditions may enhance denitrification. The effects of these various watershed characteristics on stream N yield are discussed in the following section.

5. EFFECT OF WATERSHED CHARACTERISTICS ON N TRANSPORT IN STREAMS

The reported N yield from watersheds (in units of kg/km^2/year) throughout the world is highly variable, spanning more than four orders of magnitude (Beaulac and Reckhow, 1982; Meybeck, 1982; Smith et al., 1997; Caraco and Cole, 1999), and may be explained by a variety of watershed characteristics affecting the supply and removal of N in terrestrial and aquatic systems. In this section, we discuss the effects of many of the principal watershed properties on spatial variations in N yield, including stream discharge, climate, geology, soil properties, land surface topography, stream morphology, natural and cultural sources, and land use.

5.1. Stream Discharge

The relation between stream N yield and discharge (the net quantity of water made available to streams via precipitation minus evaporation) illustrates the aggregate effects of surface and subsurface characteristics of watersheds. Streams in watersheds in more humid areas generally transport larger amounts of N and water per unit of drainage area than those in more arid regions. The mean annual yield of N in streams is nearly proportional to the mean annual stream discharge for watersheds around the globe (Caraco and Cole, 1999). For developed watersheds in the United States with a range of cultural N sources (Figure 2), stream discharge and total N yield span nearly four orders of magnitude and display a strong positive relation (R^2 = 0.74) – the exponent on discharge is slightly less than one (0.86). Similar rates of N yield per unit discharge have been observed in developed and undeveloped watersheds of the world (Caraco and Cole, 1999) and for relatively undeveloped watersheds in the United States (R.A. Smith, written communication). The slope of many of the observed relations generally spans a rather narrow range, with exponents from 0.80 to 0.87. Undeveloped tropical watersheds in South America with lower atmospheric N inputs (Lewis et al., 1999) also show similar to somewhat lower exponents for NO_3 (0.80) and total N (0.63). The intercept of the yield-discharge relations differs depending upon the magnitude of cultural inputs of N to the watersheds and units of discharge in the log linear model.

At individual stream locations, N yield also varies considerably in response to storms as well as seasonal and annual fluctuations in precipitation and streamflow. These responses have been extensively documented in the literature (Beaulac and Reckhow, 1982; Mueller et al., 1995; Alexander et al., 1996; Goolsby et al., 1999; US Geological Survey, 1999). Although larger spatial than temporal variability in N yield is generally observed (Beaulac and Reckhow, 1982), temporal changes in

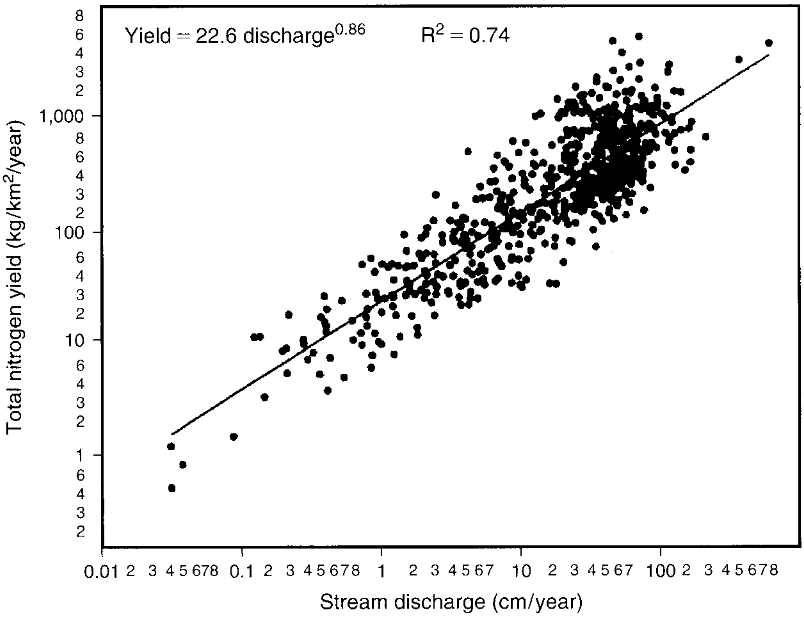

Figure 2. Relation of stream yield of total N to stream discharge for developed watersheds of the United States.

N yield at individual sites have important implications for the management of sources. A recent study isolated the effects of year-to-year variations in streamflow on NO_3 yield at 104 monitoring locations along the East and Gulf coasts of the United States (Alexander et al., 1996). Although the mean annual NO_3 yield at all sites varied by as much as two orders of magnitude in response to year-to-year fluctuations in flow, variations at most sites ranged from 20% to 40% of the mean NO_3 yield. The change in NO_3 yield in response to annual streamflow variations was nearly linear and proportional in most watersheds (i.e., a 1% change in flow corresponded to nearly equivalent percentage change in NO_3 yield), although many streams displayed nonlinear responses. The variance in NO_3 yield at the sites (expressed as a percentage of the mean yield) was negatively correlated with the mean annual streamflow and nonurban land use of the watersheds; the largest variability in yield was observed in watersheds with arid conditions and large diffuse sources of N.

5.2. Climate

Climate explains much of the variability in stream N yield-discharge relations for watersheds. Climate influences the distribution and composition of vegetation and soils, which affect the supply of organic and inorganic N forms to watersheds (Beaulac and Reckhow, 1982; Downing et al., 1999). The productivity of natural and cultivated vegetation tends to be higher in wetter, more temperate climates, and fertilizer-intensive crops are also generally grown in these areas. The rates of water movement over the land surface, through the subsurface, and in stream channels also govern N residence times and loss in watersheds. Water transport may affect the rates of biogeochemical processing of N by controlling the contact and exchange of N-enriched water with sites suitable for denitrification, such as anoxic soils, benthic stream sediments, channel hyporheic and riparian zones, wetlands, and aquifers (Harvey et al., 1996; Hill, 1996). Water travel time, which is strongly correlated with discharge, has been found to be an important predictor of N loss in streams and reservoirs (Kelly et al., 1987; Howarth et al., 1996; Alexander et al., 2000a). Nitrogen losses in streams are also correlated with stream discharge (expressed per unit of drainage area), based on observations in large watersheds in Germany (Behrendt, 1996).

Changes in global climate that may occur in response to recent and anticipated rises in atmospheric levels of CO_2 and other greenhouse gases will potentially affect stream N yield through changes in precipitation and ambient temperatures and their corresponding effects on such factors as stream discharge, biological activity, and land use (Murdoch et al., 2000). Although most general circulation climate models are generally in agreement that temperatures and precipitation will rise over global scales, regional variations are expected to be large (Gleick and Adams, 2000). For example, recent predictions of precipitation through 2030 from two climate models of North America (Gleick and Adams, 2000) indicate large regional differences in the magnitude and even the direction of changes in precipitation, emphasizing the large uncertainty in current predictive models. Nevertheless, the predicted climate-related changes in precipitation or temperature are far reaching and could be expected to have notable effects on nutrient cycling in the terrestrial and aquatic ecosystems of watersheds, the nature of which are discussed in many recent reviews and analyses (Moore et al., 1997; Mulholland et al., 1997; Schindler, 1997; Gleick and Adams, 2000; Murdoch et al., 2000). Stream discharge is one of the major watershed properties likely to be affected by global warming, and is generally more sensitive to changes in precipitation than to temperature-induced changes in evapotranspiration (Wolock and McCabe, 1999). Changes in discharge would affect the quantity and rates of water movement along surface and subsurface flow paths that control the rates of N removal. Both spatial and temporal N yield-discharge relations (e.g., Figure 2; Alexander et al., 1996) suggest that the long-term changes in N yield could be expected to be nearly proportional to the changes in stream discharge, although climate-related changes in land use and the rates of biochemical processing of N may cause more nonlinear, short-term responses in yield. Changes in temperature may also be expected to affect terrestrial and aquatic rates of productivity and N uptake (Mulholland et al., 1997; Murdoch et al., 1998; Murdoch et al., 2000), and could change the density of microbial communities in soils and stream sediments, which govern the rates of nitrification and denitrification (Murdoch et al., 2000).

Moreover, shifts in land use in response to changing precipitation and temperature, such as changes in the location of row-crop agriculture and reservoir construction, are additional factors that could affect N yield from watersheds (Murdoch et al., 2000).

5.3. Physiography and Subsurface Hydrology

Variability in N yield (both explained and unexplained by stream discharge) is related to various physiographic features of watersheds that govern the residence times of water and N, including soil properties, geology, and landscape topography (Beaulac and Reckhow, 1982). Many of these features control streamflow in watersheds according to the concept of variable source areas (Beven and Kirkby, 1979; Wolock, 1993). Such features have been cited as important factors affecting ground- and surface-water interactions and N yield in streams at local and regional spatial scales (Bohlke and Denver, 1995; Winter et al., 1998). Variable-source-area models such as TOPMODEL (Beven and Kirkby, 1979; Wolock, 1993) stress the importance of slope, relief, soil permeability, soil moisture content, and depth to the water table, in defining water infiltration and overland flow. According to these models, overland flow typically occurs where the subsurface movement of water is impeded, such as in low-lying areas and soils of low permeability.

The effects of soil permeability on water and N flow in unsaturated soils have been clearly demonstrated by lysimeter studies in small agricultural watersheds (Howarth et al., 1996). Rates of N leaching in sandy soils have been reported to be 2 or more times than those in loam or clay soils (Sogbedji et al., 2000). In large watersheds with high cultural N inputs, studies have found that permeable soils and rocks result in low NO_3 yield in streams (US Geological Survey, 1999). For example, a relatively low NO_3 yield was observed in the Lost River in Indiana, where the shallow permeable karst bedrock rapidly diverted N into the subsurface (US Geological Survey, 1999). Low N yields in the Prairie and Shell Creeks in Nebraska were explained by a relatively flat terrain and sandy/silty soils that rapidly transport N into the shallow ground water system (US Geological Survey, 1999).

These results are consistent with those from empirical models of stream monitoring data over regional scales (Mueller et al., 1997; Smith et al., 1997). These studies show an inverse relation between mean annual N yields in streams and soil permeability. Tile drainage systems, which have been used extensively on poorly drained croplands in the mid-continent region of the United States (Mueller et al., 1997; Goolsby et al., 1999; Skaggs and van Schilfgaarde, 1999), generally reduce the travel times of N to streams and rivers (Kladivko et al., 1991). Artificial drainage of otherwise poorly drained crop or grazing land by surface channels or subsurface drains can exacerbate N transport from the soil root zone and expedite delivery to surface-water bodies and/or shallow aquifers (Durieux et al., 1995; de Vos et al., 2000). Land drainage networks effectively bypass the natural filtering effects of wetlands and riparian areas and provide direct conduits of surface runoff to streams and lakes. Conversely, any N that is diverted to the subsurface in response to the hydrogeologic properties of watersheds has the potential to be denitrified (Hill, 1996). Subsurface N may also re-appear later in the baseflow of streams. For example, ground waters contribute nearly 50% of the N flux to streams in the Chesapeake Bay watershed; these streams include waters with residence times of 10–20 years (Michel, 1992; Bohlke and Denver, 1995; Focazio et al., 1998). In a study of 27 watersheds in the Chesapeake Bay Watershed, Jordan et al. (1997) found that NO_3 concentration increased with increasing proportion of baseflow to streamflow, suggesting that NO_3 transport was promoted by ground water flow in these areas.

One of the most dynamic responses of watersheds to precipitation and runoff occurs in stream riparian areas and especially in wetlands (Lowrance et al., 1984), where soils rapidly saturate to become the initial sites for overland flow (this is reflected by variable-source-area models of flow generation). The storage and gradual release of water in riparian areas also control baseflow during the recession of peak flows and over more extended periods (Lowrance et al., 1985). Riparian areas have been shown to significantly reduce the quantities of N (more than 80%) transported from upland areas to streams in overland flow and ground waters (Peterjohn and Correll, 1984; Correll et al., 1992; Lowrance, 1992); however, the quantities of N removed are highly variable (Hill, 1996). The age of forests, the types of vegetation and soils, and the geology in riparian areas contribute to this variability. Riparian areas that most effectively remove N have permeable surface soils and shallow impermeable layers that produce shallow subsurface ground water flows with long residence times and extensive contact with roots and soils (Hill, 1996). The removal of N in ground water via denitrification is also controlled by biogeochemical properties of aquifers (e.g., flow paths, organic carbon and oxygen supply, and density of denitrifying bacteria) that are independent of riparian locations, soils, or other land surface characteristics (Postma et al., 1991; Korom, 1992; Bohlke and Denver, 1995; Hill, 1996). Thus, N may be removed in the subsurface by processes that are not readily predicted from land use or other mapped surface features. Moreover, the effect of riparian areas on N transport is uncertain because most studies that report decreases in NO_3 concentration do not report water discharge.

Another type of ground water flow path involves the disrupted drainage patterns characteristic of karst terrain. Karst terrain includes distinctive features such as sinkholes, caves, and springs that develop when soluble rock, often carbonates, occur near the surface. Approximately 15% of the continental United States has karst features, including parts of the Appalachian Mountains, interior lowlands and plateaus in Kentucky, Indiana, and Tennessee, the coastal plain of Florida and Georgia, the Edwards Plateau of Texas, and the Ozark Highlands (Davies and LeGrand, 1972). Karst features allow for rapid conveyance of water from the surface to the aquifer and often within the fractured aquifer itself (LeGrand and Stringfield, 1973; White, 1988). The potentially short water residence time in karst aquifers may limit the opportunity for biogeochemical transformations of N constituents. Owing to the potential for capture of runoff in karst terrain, land-use practices affecting

N distribution and runoff on the soil surface may directly affect N transport to shallow aquifers.

Brahana et al. (1999a) and Sauer et al. (1999a) describe the development of a research watershed (Savoy Experimental Watershed) in karst terrain within the Ozark Highland region of northwestern Arkansas. One subbasin of this watershed has physiographic features (mantled karst, ridge, and valley topography) and land use (hardwood forest and pasture) typical of the Ozark Highlands. Two continuously flowing springs (Copperhead and Langle) discharge on opposing sides of the watershed outlet, which drains directly into the Illinois River. Dye-tracing studies have demonstrated that both springs capture runoff via conduits in limestone beneath porous gravel in the valley floor during storm events and rapidly transmit the intercepted water to the springs and, from there, overland to the Illinois River (Sauer et al., 1998; Brahana et al., 1999b). Figure 3 presents discharge, total Kjeldahl N (TKN) concentration, and NO_3-N concentration for Copperhead Spring during two events over a 20-day interval in 1999. Nitrate was the dominant N species in the spring flow throughout the measurement interval, as concentrations of TKN and NH_3-N (data not shown) were less than 0.1 mg/L. Temporal variations in NO_3-N concentration are typical of runoff events (higher concentrations early with gradual decrease) indicating again that spring flow during storm events is dominated by captured runoff.

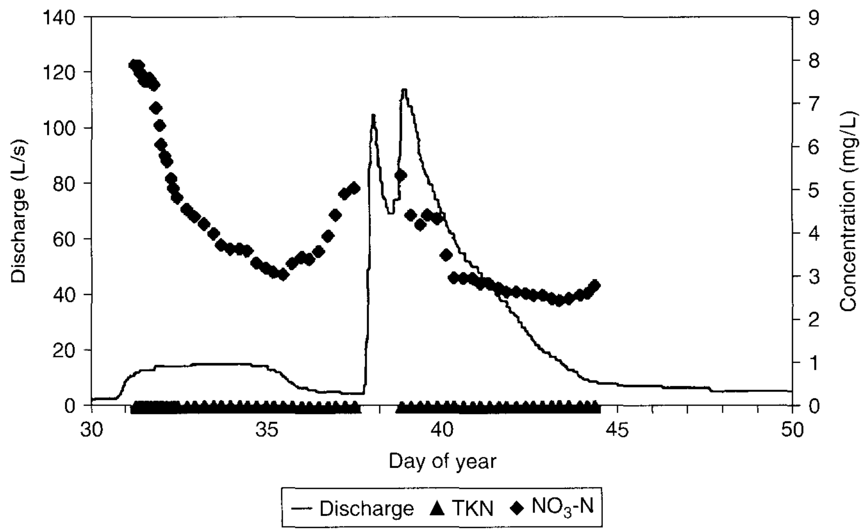

Figure 3. Discharge and TKN and NO_3-N concentrations for Copperhead Spring for a 20-day interval in 1999.

Table 2 lists NO_3-N concentrations in samples taken during base flow conditions for a 2-year period from Copperhead and Langle Springs, a shallow seep discharging in the valley slope above the soil/rock interface, and the Illinois River. Water from the seep represents interflow at the bottom of the root zone, which under nonstorm flow conditions is diluted by ground water already in the shallow karst aquifer. The higher NO_3-N concentrations for Copperhead Spring reflect the more intensely managed grazing lands within its recharge area. Discharge from Langle Spring had lower NO_3-N concentrations than the Illinois River for all sample dates except two whereas, conversely, Copperhead Spring's discharge has higher NO_3-N concentrations for all sample dates except one. These data illustrate the potential interaction between surface and subsurface water in karst settings and the subsequent implications for N transport. Runoff from upland areas flows into the valley but a portion is captured by the springs, mixed with ground water, and discharged from the springs to the Illinois River.

Table 2.
Nitrate-N concentrations in samples taken during base flow conditions over 2 years at four locations in the Savoy Experimental Watershed.

Date	Shallow seep (mg/L)	Copperhead Spring (mg/L)	Langle Spring (mg/L)	Illinois River (mg/L)
02-01-98	2.9	3.4	1.2	2.3
05-22-98	2.0	3.2	0.8	1.1
05-28-98	1.5	0.8	0.4	0.6
06-04-98	4.7	7.6	2.2	2.8
06-11-98	4.7	8.4	2.1	3.0
06-25-98	4.9	9.2	1.2	2.5
09-09-98	6.0	12.4	8.8	3.1
12-08-98	4.8	6.2	2.1	3.3
01-14-99	5.8	6.0	3.3	4.3
04-29-99	2.1	1.6	0.4	1.8
07-27-99	7.0	10.3	3.5	4.1
09-24-99	3.9	7.5	3.2	2.8
Mean	4.2	6.1	2.6	2.7
Maximum	7.0	12.4	8.8	4.3
Minimum	1.5	0.8	0.4	0.6

Water-quality research in karst settings in other locations in the United States has found correlations with land use and has documented interactions between flow dynamics and N losses. Nitrate concentrations measured in several springs of a karst region in West Virginia were found to have a strong linear correlation ($R^2 = 0.96$) with percent agricultural land use in the spring basins (Boyer and Pasquarell, 1995). Kalkhoff (1995) found subbasins of Roberts Creek in northeastern Iowa with karst hydrology generally lost water and had lower NO_3 concentrations in streamflow as compared to those subbasins underlain with till and shale materials. Seepage from the stream to ground water in the karst subbasins of Roberts Creek reduced discharge and flow velocity in the stream thereby causing increased residence time of the water.

5.4. Stream Channels and Reservoirs

The effects of stream channels and their riparian areas on N yield from moderate- to large-sized watersheds (>200 km^2 in size) have been observed in empirical models relating mean annual N yield to point and diffuse sources and various descriptors of stream hydrography (Omernik et al., 1981; Osborne and Wiley, 1988; Smith et al., 1997; Tufford et al., 1998). Several studies (Omernik et al., 1981; Osborne and Wiley, 1988; Tufford et al., 1998) accounted for the effects of channels and riparian areas on N yield by developing measures of the proximity of N sources to stream channels. The researchers reported higher accuracy for models with greater weights assigned to sources in the riparian areas of streams than to sources located outside of these areas.

A study of N transport in rivers of the United States used a mechanistic model structure (Smith et al., 1997) to empirically estimate the attenuation of N sources from upstream watersheds as a function of the physical properties of the watersheds (soils, temperature, and drainage density) and stream channels (water time of travel and channel size). Estimates of in-stream N loss were inversely related to stream channel size and ranged from 0.45 per day of water travel time in small streams to 0.005 per day in large rivers (Figure 4). When stream channel depth was used as an explanatory factor, these estimates were found to generally agree with those

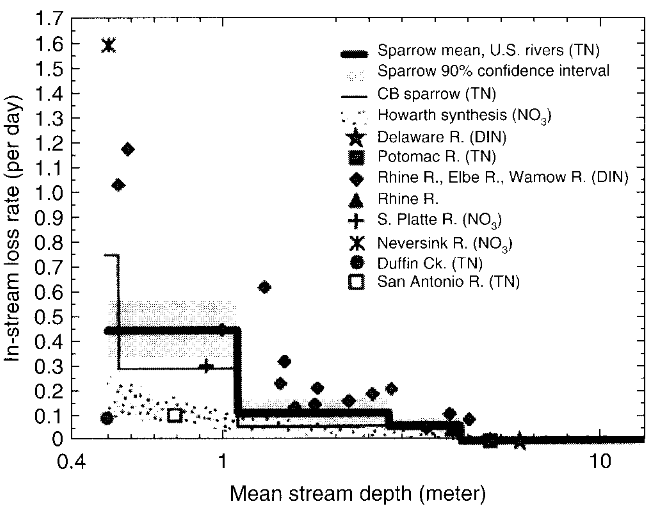

Figure 4. Nitrogen-loss rate in streams (per day of water travel time) in relation to stream channel depth. (From Alexander et al. (2000a).)

from mass balance and experimental studies that are available for selected North American and European streams (Alexander et al., 2000a). The inverse relation between N loss and channel depth may be explained by the effect of channel size (depth and water volume) on particulate N settling times and denitrification (Kelly et al., 1987; Rutherford et al., 1987; Harvey et al., 1996; Howarth et al., 1996; Alexander et al., 2000a). The natural rates of N loss via denitrification and settling are generally expected to be smaller in deeper channels where stream waters have less contact with the benthic sediment. Larger variability is observed in the rates of N loss in shallow streams, which likely indicates variability in the stream conditions responsible for N removal. These conditions include the hyporheic exchange of waters, organic and oxygen content of sediment, density of denitrifying populations, and water column NO_3 concentrations. These results suggest that the proximity of N sources to large streams and rivers, as measured by water travel times in small tributaries, has a major effect on the downstream transport of N. Sources entering large streams and their nearby tributaries may be transported over very long distances in watersheds (Alexander et al., 2000a).

The physical and hydraulic properties of lakes (e.g., water residence time and depth) are also related to the observed rates of N loss in North America and Europe (Kelly et al., 1987; Howarth et al., 1996; Windolf et al., 1996; Seitzinger et al., unpublished data) and in New Zealand (McBride et al., 2000). Rates of N loss varied over a wide range from less than 10% to about 90% in these studies, and declined with increases in measures of the rates of water transport through reservoirs (i.e., the ratio of mean depth to water residence time – water displacement (Kelly et al., 1987; Howarth et al., 1996) and the ratio of reservoir discharge to surface area – areal hydraulic load (McBride et al., 2000)). These lake properties affect the contact and exchange of water with the benthic sediment, which influences the rates of particulate N settling and denitrification (Kelly et al., 1987; Windolf et al., 1996). This implies that the mechanisms for the net removal of N are generally consistent with those in streams (Howarth et al., 1996; Seitzinger et al., unpublished data).

5.5. Cultural Sources and Land use

Human sources of N (fossil fuel combustion, fertilizer, human wastes, and livestock manures) and land use are known to have a major effect on N yield in surface waters (Beaulac and Reckhow, 1982; Peierls et al., 1991; Howarth et al., 1996; Vitousek et al., 1997; Carpenter et al., 1998; Seitzinger and Kroeze, 1998; Caraco and Cole, 1999; McFarland and Hauck, 1999; Arnheimer and Liden, 2000; Castillo et al., 2000). Variability in N yield may be caused by spatial variations in the intensity and timing of N inputs to watersheds as well as differences in land management activities. Nitrogen concentration in streams and rivers of the United States have risen two- to 10-fold since the early part of the 20th century because of increased cultural inputs of N, and similar increases have been noted in European rivers and lakes (Howarth et al., 1996; Vitousek et al., 1997). The N yield of streams in relatively undisturbed watersheds of the North Atlantic region (Howarth et al., 1996) has been recently estimated to range from 0.8 to 2.3 kg/ha/year. A study of background concentrations and yield from 66 relatively undeveloped, forest, grass, and range land watersheds in the conterminous United States (sizes range from 6 to 2,700 km^2) over the period 1976–1997 (Clarke et al., 2000) indicates a range in the yield of total N that is similar to that reported by Howarth et al. (1996) (Table 3). Yield typically ranged from about 0.5 to 2.1 kg/ha/year (based on interquartile range of mean annual yields). Yields larger than 2.1 kg/ha/year and as high as 8.4 kg/ha/year were observed in the eastern United States, where the rates of atmospheric deposition are highest (up to 4 kg/ha/year wet NO_3). The yield of total N, NO_3, and NH_3 all increase with stream discharge (ranging from <1 to about 160 cm/year) and atmospheric deposition.

Comparisons of N yields from relatively undeveloped watersheds with those from developed watersheds in North America reveal significant differences that can be traced to human activities. For example, N yield is frequently reported to be more than a factor of two higher in agricultural and urban watersheds in comparison to less-developed watersheds, including those predominantly in forest and rangeland (Beaulac and Reckhow, 1982; Mueller et al., 1995; US Geological Survey, 1999). Historical data from two US Geological Survey (USGS) water-quality monitoring networks illustrate these effects. These data provide a geographically representative description of N conditions in streams and rivers of the conterminous United States (Smith et al., 1993). The networks include 506 sites in the National Stream Quality Accounting Network (NASQAN) for the period 1975–1992 (Alexander et al., 1998)

Table 3.
Stream yields of N (kg/ha/year) in 66 undeveloped watersheds of the United States. (Nitrate-nitrite and ammonia are dissolved.)

	Percentiles					Percentiles – Fraction of Total N		
Metric	Min.	25th	50th	75th	Max.	25th	50th	75th
TN	<0.01	0.49	0.86	2.07	8.38			
Nitrate-nitrite	<0.01	0.11	0.24	0.52	5.83	0.14	0.27	0.55
Ammonia	<0.01	0.04	0.08	0.12	0.33	0.05	0.08	0.11
Organic	<0.01	0.16	0.33	1.07	5.07	0.32	0.60	0.75
Runoff (cm/year)	0.1	22.0	34.1	58.4	163.1			

Data from Clarke et al. (2000).

and 185 sites in the National Water-Quality Assessment Program (NAWQA) network for the period 1993–1995. The yield of total N was consistently 3–4 times higher in developed watersheds than in undeveloped watersheds (Tables 3 and 4). The median N yield for the developed watersheds (3.3 kg/ha/year) was 3.8 times

Table 4.
Stream yields of N (kg/ha/year) in 691 developed watersheds of the United States. [Nitrate-nitrite and ammonia are dissolved. The stations are located in developed watersheds representing a wide range of land cover types: 191 are predominantly agricultural, 34 are primarily urban, and 455 are classified as containing a mixture of land-cover types. Watersheds in the National Stream Quality Accounting Network range in drainage basin size from about 15 to 2.9 million km^2 with a median size of 11,000 km^2 (interquartile range from 3,100 to 37,000 km^2). Watersheds in the National Water Quality Assessment Program are typically smaller in size, ranging from about 15 to 220,000 km^2 with a median size of 1,300 km^2; interquartile range from 150 to 6,400 km^2].

	Percentiles					Percentiles – fraction of total N		
Metric	Min.	25th	50th	75th	Max.	25th	50th	75th
TN	<0.01	1.05	3.28	7.36	81.08			
Nitrate-nitrite	<0.01	0.22	1.06	3.33	79.02	0.25	0.40	0.60
Ammonia	<0.01	0.05	0.16	0.38	7.84	0.04	0.06	0.08
Organic	<0.01	0.50	1.51	2.88	58.02	0.33	0.52	0.70
Drainage area (km^2)	13	1,585	7,268	28,381	2,953,895			
Runoff (cm/$year^{-1}$)	0.03	6.8	27.7	49.2	598.3			

higher than the median yield for undeveloped watersheds (0.86 kg/ha/year). Some of the highest yields in both developed and undeveloped watersheds occur in the eastern United States, where atmospheric deposition is high. Smaller differences are observed between the stream N conditions in developed and undeveloped watersheds of the western United States than in other regions because of the relatively small inputs of cultural sources of N and more arid conditions in these western regions (Table 1; Clarke et al., 2000).

On the basis of USGS data, the median N yield in predominantly agricultural basins (5.9 kg/ha/year; $n = 191$) and urban watersheds (6.0 kg/ha/year; $n = 34$) was more than twice as large as the median N yield in watersheds of mixed land use (2.7 kg/ha/year; $n = 455$).

Moreover, the median yield from agricultural and urban watersheds was more than six times the median N yield in relatively undeveloped watersheds (0.9 kg/ha/year; Table 3). Figure 5 illustrates the relation between agricultural land area and N yield. An increase in agricultural land area from a few percent to nearly 100 percent corresponded to more than a fivefold increase in stream yields. For watersheds with

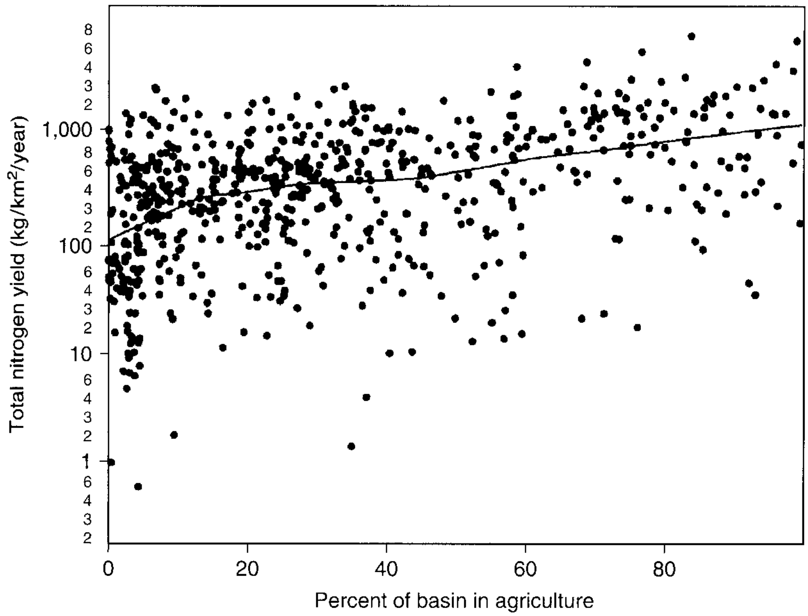

Figure 5. Relation of stream yield of total N to the percentage of basin area in agriculture for developed watersheds of the United States. The fitted line is obtained from a LOWESS smoothing technique (Cleveland, 1979). The LOWESS line displays the central tendency of the data, and provides an approximate description of the univariate relation. A more complex multivariate relation would be required to accurately predict stream N yield as a function of agricultural intensity.

similar percentages of agricultural land, agricultural management practices also can have a major effect on N transport. The addition of fertilizers and organic matter (manure and biosolids) to grassland ecosystems, which are naturally N limited, improves their utility for the grazing of livestock, but contributes to large watershed yields of N. Timmons and Holt (1977) showed that annual stream N yield from ungrazed native little bluestem prairie (*Andropogon scoparius* Michx.) was only 0.8 kg/ha. By contrast, N yield from two grazed rangeland watersheds in Central Oklahoma ranged from 1.7 to 5.2 kg/ha/year (Olness et al., 1980). Higher N yield from grazed watersheds is often due to grazing animal urine, which is known to increase both runoff losses of N and NO_3 leaching (Schepers and Francis, 1982; Stout et al., 1997; Sauer et al., 1999b). Annual N yield of 2–9 kg/ha/year has been observed where fertilizer or manure N additions were made to improve forage production on grazing lands (Kilmer et al., 1974; McLeod and Hegg, 1984; Nelson et al., 1996). Nitrate is typically the dominant form of N transported from grazing lands, often with significant concentrations in both runoff and ground water flow (Sharpley and Syers, 1981; Owens et al., 1983; Cuttle et al., 1992), however, there is a considerable range in N yields because of the effects of other N sources as well as differences in the rates of N processing in watersheds related to many of the factors discussed previously (Beaulac and Reckhow, 1982).

Although N yield from forested watersheds can be low, watersheds disturbed by activities such as logging or development can be a significant source of NO_3 (Hallberg and Keeney, 1993). The high demand for NO_3-N by vegetation can result in a greater proportion of N yield in the organic form. Timmons et al. (1977) measured nutrient transport from an aspen-birch (*Populus tremuloides* Michx., and *Betula papyrifera* Marsh.) forest and found 80% of the total N load in runoff (1.25 of 1.56 kg/ha/year) was organic N. An average of 67% of the N yield in runoff from upland pasture and forest sites in a grazed watershed in the Ozark Highlands was in the organic form (Sauer et al., 2000). Organic N transported to surface-water bodies is subject to further transformations (mineralization, nitrification, and denitrification) in aquatic or benthic environments.

The amount and timing of N loads in streams also have been correlated with row-crop acreage and N management practices. Schilling and Libra (2000) monitored NO_3-N concentrations in 15 Iowa watersheds with row crops covering 24–87% of the watersheds area. Average annual NO_3-N concentrations were directly related ($P < 0.0003$) to row-crop area. Linear regression showed that an estimate of average annual NO_3-N concentration in surface water could be obtained by multiplying a watershed's row-crop percentage by 0.1. Nitrate-N concentrations in streams in 10 states of the upper-midwestern United States were positively correlated with streamflow, upstream areas of corn *(Zea mays* L.), and N fertilizer application rates (Mueller et al., 1997). Others (Becher et al., 2000, David and Gentry, 2000) also have found correlations between N fertilizer use and N yield in agricultural watersheds of the Midwest United States Figure 6 shows seasonal changes in average NO_3-N concentrations in stream water for a 202 km^2 agricultural watershed in central Iowa (T.J. Sauer, unpublished data). Nitrate-N values in Figure 6 are daily means of stream-water samples collected from 13 locations on each date. Ammonia-N concentrations in samples collected on these dates were insignificant (<1 mg/L). All samples except those on days 152, 166, and 194 were collected during baseflow conditions with stream discharge less than 150 L/s. Samples on days 152, 166, and 194 were collected as stream discharge was decreasing following runoff events.

This watershed (Tipton Creek) typifies the intense row-crop management of the upper-Midwest United States, with 84% of the area being in corn or soybean (*Glycine max* Merr.) production. The increase in NO_3-N concentration in streamflow during late spring/early summer in cropped watersheds like Tipton Creek has been attributed to nitrification of N in fertilizers and animal manures (Becher et al., 2000; Castillo et al., 2000). In this instance, fertilizer and/or manure would

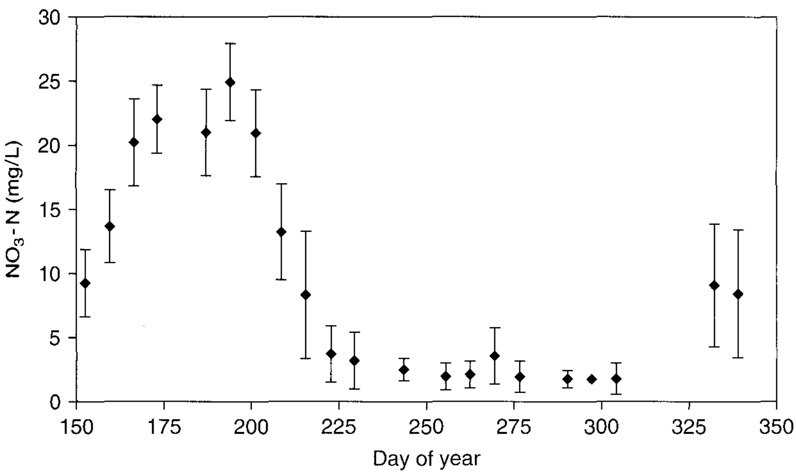

Figure 6. Mean NO_3-N concentration from 13 sampling sites along Tipton Creek in central Iowa during 2000. Error bars represent 1 standard deviation from the mean.

typically be applied to fields sometime between days 100 and 140 to provide nutrients for corn during the growing season. Another process that may contribute to the trends observed in Figure 6 is mineralization of organic N after tillage and as the soil warms in spring.

5.6. Watershed Size

Much of the research on the fate of N in watersheds has focused on small catchments (Sharpley and Syers, 1981; Johnson, 1992; Hill, 1996; Pionke et al., 1996), where the natural and cultural influences on stream N yield are more spatially uniform, and N sources, transformations, and hydrologic flow paths are more readily discerned. Considerable variability has been observed in N yields from these catchments because of the wide range of sampled watershed properties (Beaulac and Reckhow, 1982; Johnson, 1992; Hill, 1996). Relatively little information, however, has emerged about how N yields vary with watershed size. At progressively larger spatial scales, stream yields reflect the effects of an increasingly complex range of N sources and biogeochemical processes. This makes it difficult to quantify how the effect of any individual factor changes with watershed size.

A few studies (Alexander et al., 2000a,b; Seitzinger et al., unpublished data) have used empirical data from a range of watershed sizes to quantify the effects of in-stream N removal processes (denitrification and N storage) on the transport of N through drainage networks. As water is carried downstream, N is continually removed from the water column through contact with the benthic sediment. Although the rate of N removal per unit of water travel time declines significantly with increases in channel size (Alexander et al., 2000a; see Section 6.4), the fraction of N inputs to streams that is removed generally increases with cumulative water travel time in streams, which is positively correlated with drainage basin size (Alexander et al., 2000b). Figure 7 illustrates this concept on the basis of a study of 40 coastal watersheds in the United States in which the SPARROW model was used (Smith et al., 1997; Alexander et al., 2000b). Nitrogen loss, expressed as a percentage of the N delivered to streams, ranged from negligible quantities to 90% or more, and monotonically increased with the mean travel time of water in streams of the watersheds. Travel times can be as much as 24 days in several large, arid watersheds in Texas. Nitrogen losses of less than 10% were estimated for the smaller watersheds with less than about 2–3 days of mean water travel time. More than 50% of the N delivered to streams was removed in watersheds having mean water travel times greater than about 7 days. The estimates of N loss in Figure 7 reflect the cumulative removal of N over the range of stream sizes in these watersheds. Much lower N losses are expected for similar water travel times in large rivers, such as the Mississippi and its major tributaries, for which low first-order N loss rates have been estimated (Alexander et al. 2000a; Figure 4).

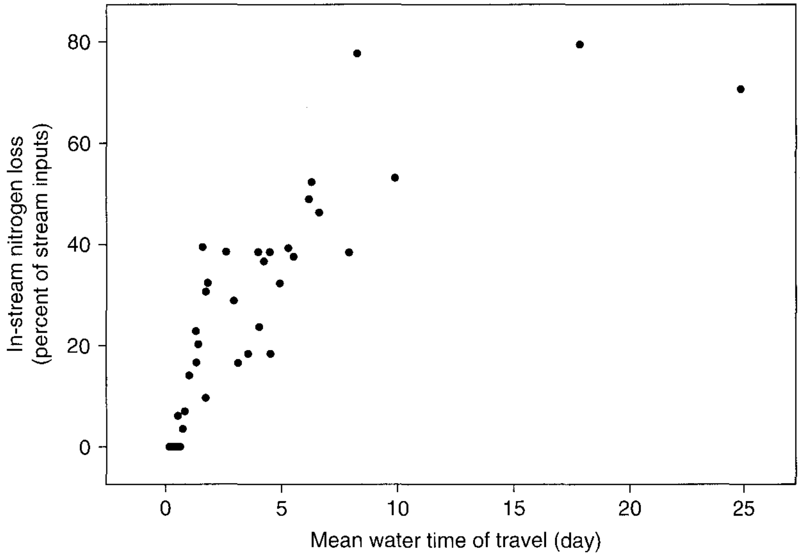

Figure 7. Relation of in-stream total N loss to the water time of travel in coastal watersheds of the United States. (Model predictions from Alexander et al., 2000b.)

Changes in the intensity of land use with watershed size also have discernable effects on stream N yields. Nitrogen yields are typically higher in small, upland watersheds that are intensively managed than in larger, heterogeneous watersheds. In two large US river basins (Figure 8), stream N yields are as much as 2–10 or more times higher in smaller tributary watersheds, many with predominantly agricultural and urban land use, than observed at downstream locations on the mainstem of the two rivers. Two of the mainstem sites located in the upper reaches of the South Platte River show the effects of urban sources. These land-use patterns reinforce the effects of in-stream N removal processes on stream N yields. In some watersheds, increases in the intensity of cultural N sources in lower reaches can cause stream N yield to increase in a downstream direction. For example, Castillo et al. (2000) found that NO_3 concentrations in the River Raisin in Michigan increased from the headwaters to the river mouth and were strongly correlated with the ratio of agricultural to forest land upstream. In such cases, the intensity of land use has a predominant effect on stream N yield, and overcomes the effects of in-stream loss processes.

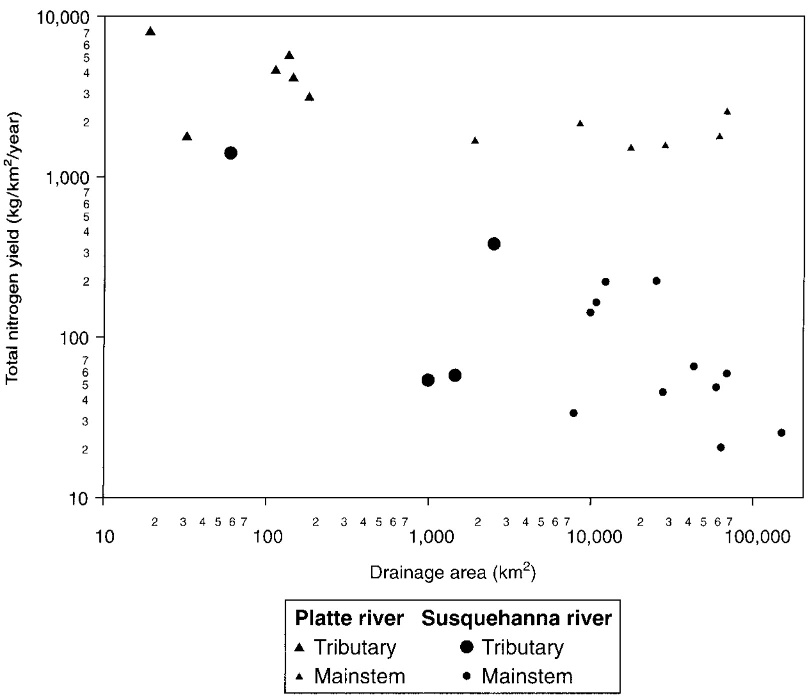

Figure 8. Relation of stream yield of total N to the drainage area for developed watersheds of the United States.

5.7. Nitrogen Forms in Streams

The quantities of stream N in the forms of NO_3, NH_3, and organic N differ with the magnitude of cultural inputs of N and other watershed characteristics. Based on estimates of N yield from relatively undeveloped watersheds in the United States (Clarke et al., 2000; Table 3) organic N typically accounts for more than 60% of the N. Other studies have also noted the predominance of organic N in the streams draining relatively undisturbed forests (Vitousek et al., 1997). However, the organic N content of streams in minimally developed watersheds display considerable spatial variability (Table 3), and large organic fractions are not uncommon in more developed watersheds (Table 4). In undeveloped watersheds, the highest organic N fractions (>70%) were observed in the southeastern and Texas coastal plains and the southern central portion of the United States, whereas the lowest organic-N fractions (<50%) were observed in forested and rangeland watersheds of the Appalachians and arid areas of the northern central portion of the United States (Clarke et al., 2000). Nitrate represents a majority of the remaining N in undeveloped watersheds, typically representing at least a quarter of the total N (Table 3). Ammonia is typically less than 8% of the total.

Larger quantities of NO_3-N are generally transported from developed watersheds (Tables 3 and 4). Nitrate-N represents 40% of all N forms in developed watersheds as compared to 27% in undeveloped basins, based on the median of all stations. In developed watersheds, the organic-N fraction is typically about 50% of all N forms and NH_3 is less than 6%.

The quantities of NO_3-N transported by streams in relatively developed watersheds generally increase with total N yield (Figure 9), providing evidence that large cultural inputs of N are associated with larger fractions of NO_3-N in streams. Greater fractions of NO_3-N in stream N yield are also found in highly agricultural watersheds (median = 60–80% in watersheds with >75% agricultural land use) in comparison to watersheds with little agriculture (median = 30–40% NO_3 in watersheds with <25% agricultural land use). Because NH_3 constitutes a relatively small fraction (median = 6%) of the total N yield, organic forms of N generally decline with increases in the total N yield in streams (Figure 9). The increase in NO_3-N in rivers in response to increases in human activities has been previously observed in coastal rivers in the eastern United States (Jaworski et al., 1997) and in the largest rivers of the world (Peierls et al., 1991; Caraco and Cole, 1999). The availability of NO_3-N can be explained by the inorganic form of many of the cultural sources of N that are supplied to anhydrous ammonia, which are rapidly oxidized to NO_3-N. Large variability is typically observed in N forms across similarly sized watersheds. Large watersheds allow greater mixing of waters from a variety of sources, including less-developed catchments that are more enriched in organic-N. However, in many of the largest US rivers (e.g., Susquehanna, Potomac, Delaware, Ohio, and Mississippi) with high cultural inputs of N, NO_3-N represents significantly more than half of the total N (Goolsby et al., 1999). In the largest rivers of the world (Caraco and Cole, 1999), the proportions of organic N and NO_3-N were found to be roughly equivalent. More complex multivariate relations would be required to accurately predict N forms in streams.

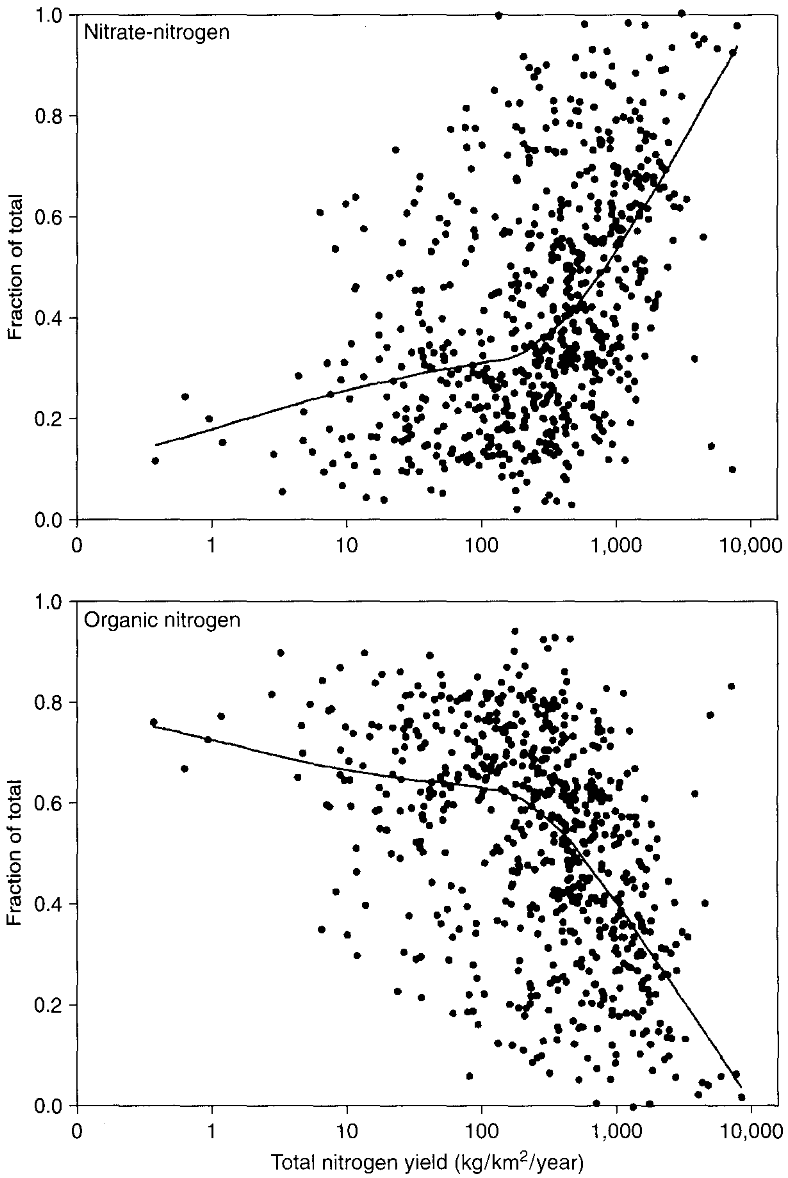

Figure 9. Percentage of NO_3-N and organic N in the stream yield of total N from developed watersheds of the United States as a function of total N yield. The fitted line is obtained from a LOWESS smoothing technique (Cleveland, 1979). The LOWESS line displays the central tendency of the data, and provides an approximate description of the univariate relation.

6. SOURCE CONTRIBUTIONS TO STREAM YIELD

A longstanding problem in quantifying the relative importance of specific natural and cultural sources of N to the stream yield from watersheds has centered on understanding the effects of land use, climate, and the biogeochemical processing of N in terrestrial and aquatic ecosystems over a range of spatial scales. At larger spatial scales, source inputs have commonly been used to characterize source contributions to streams (Jaworski et al., 1992; Puckett, 1995), but these methods do not account for the appreciable differences that exist in the rates of N processing and transport in watersheds as reflected in measurements of stream yield (Beaulac and Reckhow, 1982). A variety of watershed models have been used to resolve the interactions between N supply and loss processes. At large watershed scales, where the applicability and reliability of fine-scale deterministic models is more uncertain (Rastetter et al., 1992), empirical models that are calibrated to stream measurements of N have frequently been used to quantify N sources and losses in watersheds. Examples include spatial regression models of stream N yield on population density (Peierls et al., 1991), net anthropogenic sources (Howarth et al., 1996), atmospheric deposition (Howarth et al., 1996; Jaworski et al., 1997), and models containing a range of explanatory variables describing both N sources and watershed characteristics (Lystrom et al., 1978; Omernik et al., 1981; Osborne and Wiley, 1988; Mueller et al., 1997; Smith et al., 1997; Tufford et al., 1998; Goolsby et al., 1999).

Estimates of the sources of N in streams of the major water-resources regions of the United States (Smith and Alexander, 2000), based on the application of the SPARROW model (Smith et al., 1997; Alexander et al., 2000a,b), are illustrated in Table 5. This model provides separate quantification of a range of major N sources and accounts for the terrestrial and aquatic losses of N as a function of watershed properties. Details of the model structure and calibration to N measurements from 400 stream monitoring sites are given in Smith et al. (1997), and discussions of the model verification are given in Alexander et al. (2000a,b), National Research Council (2000), and Stacy et al. (2000). The major N sources in streams as defined by the model include agricultural diffuse sources (fertilizer and livestock manures), atmospheric deposition, municipal and industrial point sources, and other sources associated with nonagricultural lands. In addition to applied fertilizers, the fertilizer source may also include inputs of fixed N in leguminous crop residues and other mineralized soil N from cultivated lands (Alexander et al., 2000b). Atmospheric sources include wet deposition of inorganic NO_3-N as well as additional N contributions from wet organic and dry inorganic N (Alexander et al., 2000a,b). Nonagricultural runoff includes the remaining sources of N (i.e., not quantified by point sources and other diffuse model terms), delivered to streams in the overland flow and ground water from urban, forested, wetlands, and barren lands. The runoff from forested lands may include N supplied from natural fixation.

The sources of N to stream yield vary greatly among the regions (Table 5), and show a general correspondence to the inputs of newly fixed and recycled N inputs as

Table 5.
Point- and nonpoint-source contributions to total N yield from watersheds in major water-resource regions of the conterminous United States. Total yield is the median stream yield from hydrologic cataloging units in each region. The median and quartile values for the source contributions within each region are expressed as a percentage of the total yield.

Region	Total yield (kg/ha/year)	Percentage of total yield: Point sources		Fertilizer		Animal agriculture		Atmosphere		Nonagricultural runoff	
		Median	Quartiles	Median	Quartiles	Median	Quartiles	Median	Quartiles	Median	Quartiles
Northeast	8.0	4.2	1.5–19	13	6.2–18	10	4.2–19	31	22–40	26	17–36
Southeast Atlantic-Gulf	5.9	2.7	1.1–8.2	26	17–38	14	8.8–21	21	15–28	26	19–34
Great Lakes	8.0	4.3	1.3–12	22	7.8–41	10	4.6–17	25	16–34	17	6.5–40
Ohio-TN	11	2.1	0.7–7.2	26	11–48	15	10–21	25	18–39	16	7.6–25
Upper Miss.	13	0.8	0.5–1.6	55	40–66	21	15–27	13	11–17	3.6	2.1–10
Lower Miss.	7.6	2.3	1.0–11	40	14–64	6.3	3.2–10	22	14–28	18	8.0–28
Red Rainy	3.5	0.3	0.1–0.6	75	57–81	5.2	2.8–9.0	9.3	7.4–14	7.2	3.4–20
Missouri	2.1	<0.1	<0.1–<0.1	30	8.8–51	20	15–25	16	12–20	29	9.5–55
Ark-Red	3.9	0.8	0.2–1.9	29	20–46	23	17–29	18	14–23	20	12–28
Texas-Gulf-Rio Grande	2.1	0.3	<0.1–2.6	20	4–37	15	10–21	16	12–20	37	18–66
Colorado	1.1	0.1	<0.1–0.4	2.0	0.8–8.8	7.7	3.6–12	10	7.7–16	74	64–80
Great Basin	0.9	<0.1	<0.1–<0.1	3.6	0.9–9.2	9.3	5.6–15	6.4	5.4–8.1	78	61–86
Pacific NW	4.2	<0.1	<0.1–<0.1	12	5.5–30	11	7.3–14	13	8.0–16	57	34–69
California	4.8	1.2	0.3–6.7	21	8.9–52	12	7.6–17	8.7	5.5–13	35	16–62
United States	4.7	0.8	0.5–3.4	22	7.5–45	14	8.2–21	16	11–23	28	13–56

Modified from Smith and Alexander (2000).

described in Table 1. Estimates of N loss in watersheds, based on the median stream yield (Table 5) and the total net N input to the regions (Table 1), range from 62% to 89% of the net inputs of N (median = 76%). Agricultural sources (fertilizer and livestock manures) are the largest contributors to stream yield in most of the regions, representing more than 40% in the Ohio-Tennessee, Southeast-Gulf, Upper and Lower Mississippi, Souris-Red-Rainy, Missouri, Arkansas-Red, and Texas regions. Livestock manures contribute large quantities of N in watersheds in the Ohio-Tennessee, Upper Mississippi, Missouri, Arkansas-Red, and Texas regions (Table 5); these contributions are consistent with the estimated large inputs of N in livestock manures in these regions in relation to the total net inputs of N (newly fixed N plus net food/feed imports) as reported in Table 1. Atmospheric N contributes more than a quarter of the stream yield in most of the watersheds in the Northeast region, and is a dominant source in watersheds of the Great Lakes and Ohio-Tennessee region. Nonagricultural diffuse sources contribute a majority of the N to the stream yields in the Colorado, Great Basin, and Pacific Northwest regions, where cultural inputs of N are generally low. Nonagricultural diffuse contributions are also important in the Northeast and Southeast-Gulf, where watersheds generally receive large natural sources of organic N from forest vegetation. Point sources, generally among the smallest contributors in most watersheds, are the highest in the densely populated Northeast, Ohio-Tennessee, and Great Lakes regions; this is generally consistent with estimates of the inputs to watersheds in these regions from municipal and industrial wastewater treatment plants (Table 1). These results are also consistent with other studies of moderate to large watersheds, which find municipal and industrial point sources to be a relatively small source of N to streams (Puckett 1995; Howarth et al., 1996; Goolsby et al., 1999). However, in small, highly urbanized watersheds, municipal and industrial wastewaters frequently account for significantly larger shares of the N in streams (US Geological Survey, 1999; Alexander et al. 2000b).

7. SUMMARY

Stream N yields have been assessed in watersheds through detailed process-oriented studies at the local scale and over larger, regional scales using statistical techniques. These approaches have been applied to natural and culturally affected environments in watersheds to elucidate the hydrologic and biogeochemical factors that affect N transport. The biogeochemical processing of N has been studied over a range of spatial and temporal scales in watersheds to enable the interpretation of data trends and development of conceptual and numerical models of N yield. Surface and subsurface hydrology, climate, physiography, and basin size all affect the partitioning of precipitation between infiltration and runoff and subsequent water flow paths. Natural and cultural sources of N and their subsequent transformations influence the amount and mobility of N constituents in soil, plant materials, and water. Watersheds represent a physical coupling of the hydrologic and source components in a continuous, dynamic system. Management of land resources based on principles derived from watershed-scale studies is a key component of ongoing efforts to improve the efficiency of N use and limit adverse water-quality impacts from excessive N loadings to surface, subsurface, and marine waters.

REFERENCES

Alexander, R.B., R.A. Smith, and G.E. Schwarz. 2000a. Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico. Nature 403: 758–761.

Alexander, R.B., R.A. Smith, G.E. Schwarz, S.D. Preston, J.W. Brakebill, R. Srinivasan, and P.A. Pacheco et al. 2000b. Atmospheric nitrogen flux from the watersheds of major estuaries of the United States: An application of the SPARROW watershed model. *In* R. Valigura et al. (eds) Nitrogen loading in coastal water bodies: An atmospheric perspective, American Geophysical Union Water Monograph 57, Washington, DC.

Alexander, R.B., J.R. Slack, A.S. Ludtke, K.K. Fitzgerald, and T.L. Schertz. 1998. Data from selected US Geological Survey national stream water quality monitoring networks. Water Resour. Res. 34: 2401–2405.

Alexander, R.B., P.S. Murdoch, and R.A. Smith. 1996. Streamflow-induced variations in nitrate flux in tributaries to the Atlantic Coastal zone. Biogeochemistry 33: 149–177.

Anderson, M.G. and T.P. Burt. 1978. Toward more detailed field monitoring of variable source areas. Water Resour. Res. 14: 1123–1131.

Arnheimer, B. and R. Liden. 2000. Nitrogen and phosphorus concentrations from agricultural catchments – influence of spatial and temporal variables. J. Hydrol. 227: 140–159.

Beaulac, M.N. and K.H. Reckhow. 1982. An examination of land use-nutrient export relationships. Water Res. Bull. 18: 1013–1024.

Becher, K.D., D.J. Schnoebelen, and K.K.B. Akers. 2000. Nutrients discharged to the Mississippi River from eastern Iowa watersheds, 1996–1997. J. Am. Water Resour. Assoc. 36: 161–173.

Behrendt, H. 1996. Inventories of point and diffuse sources and estimated nutrient loads—a comparison for different river basins in central Europe. Water Sci. Tech. 33: 99–107.

Bernier, P.Y. 1985. Variable source areas and storm-flow generation: An update of the concept and a simulation effort. J. Hydrol. 79: 195–213.

Beven, K.J. and M.J. Kirkby. 1979. A physically based, variable contributing area model of basin hydrology. Hydro. Sci. Bull. 24: 43–69.

Black, P.E. 1996. Watershed hydrology (2nd edition). Ann Arbor Press, Chelsea, MI.

Bohlke, J.K. and J.M. Denver. 1995. Combined use of ground water dating, chemical, and isotopic analyses to resolve the history and fate of nitrate contamination in two agricultural watersheds, Atlantic coastal plan, Maryland. Water Resour. Res. 31: 2319–2339.

Boyer, D.G. and G.C. Pasquarell. 1995. Nitrate concentrations in karst springs in an extensively grazed area. Water Resour. Bull. 31: 729–736.

Brahana, J.V., P.D. Hays, T.M. Kresse, T.J. Sauer, and G.P. Stanton. 1999a. The Savoy Experimental Watershed – early lessons for hydrogeologic modeling from a well-characterized karst research site. *In* A.N. Palmer et al. (ed.) Karst modeling, Karst Waters Institute Special Publication 5 pp. 247–254.

Brahana, J.V., T.J. Sauer, P.D. Hays, T.M. Kresse, P. Little, and J. Funkhouser. 1999b. Hydrologic monitoring to characterize dominant controls of ground-water flow and transport in an area of confined animal production on a mantled karst terrane, Northwestern,

Arkansas, p. 30. *In* F.D. Wilde et al. (eds) Effects of animal feeding operations on water resources and the environment. US Geological Survey Open-File Report 00-204.
Burkart, M.R. and D.E. James. 1999. Agricultural-nitrogen contributions to hypoxia in the Gulf of Mexico. J. Environ. Qual. 28: 850–859.
Caraco, N.F. and J.J. Cole. 1999. Human impact on nitrate export: An analysis using major world rivers. Ambio 28: 167–170.
Carpenter, S., N.F. Caraco, D.L. Correll, R.W. Howarth, A.N. Sharpley, and V.H. Smith. 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. Issues in Ecology, No. 3. 12pp.
Castillo, M.M., J.D. Allan, and S. Brunzell. 2000. Nutrient concentrations and discharges in a Midwestern agricultural catchment. J. Environ. Qual. 29: 1142–1151.
Cirmo, C.P. and J.J. McDonnell. 1997. Linking the hydrologic and biogeochemical controls of nitrogen transport in near-stream zones of temperate-forested catchments: A review. J. Hydrol. 199: 88–120.
Clarke, G.M., D.K. Mueller, and M.A. Mast. 2000. Nutrient concentrations and yields in undeveloped stream basins of the United States. J. Am. Water Res. Assoc. 36: 849–860.
Cleveland, W.S. 1979. Robust locally weighted regression and smoothing scatterplots. J. Am. Stat. Assoc. 74: 829–836.
Correll, D.L. 1998. The role of phosphorus in the eutrophication of receiving waters: A review. J. Environ. Qual. 27: 261–266.
Correll, D.L., T.E. Jordan, and D.E. Weller. 1992. Nutrient flux in a landscape: Effects of coastal land use and terrestrial community mosaic on nutrient transport to coastal waters. Estuaries 15: 431–442.
Council for Agricultural Science and Technology. 1999. Gulf of Mexico hypoxia: land and sea interactions, Council for Agricultural Science and Technology, Ames, IA.
Cuttle, S.P., M. Hallard, G. Daniel, and R.V. Scurlock. 1992. Nitrate leaching from sheep-grazed grass/clover and fertilized grass pastures. J. Agric. Sci. (Cambridge) 119: 335–343.
David, M.B. and L.E. Gentry. 2000. Anthropogenic inputs of nitrogen and phosphorus and riverine export for Illinois, USA. J. Environ. Qual. 29: 494–508.
Davies, W.E. and H.E. LeGrand. 1972. Karst of the United States, pp. 467–505. *In* M. Herak and V.T. Stringfield (ed.) Karst – Important karst regions of the northern hemisphere, Elsevier, New York.
Devito, K.J., D. Fitzgerald, A.R. Hill, and R. Aravena. 2000. Nitrate dynamics in relation to lithology and hydrologic flow path in a river riparian zone. J. Environ. Qual. 29: 1075–1084.
de Vos, J.A., D. Hesterberg, and P.A.C. Raats. 2000. Nitrate leaching in a tile-drained silt loam. Soil Sci. Soc. Am. J. 64: 517–527.
Downing, J.A., M. McClain, R. Twilley, J.M. Melack, J. Elser, N.N. Rabalais, W.M. Jr. Lewis, R.E. Turner, J. Corredor, D. Soto, A. Yanez-Arancibia, J.A. Kopaska, and R.W. Howarth. 1999. The impact of accelerating land-use change on the N-cycle of tropical aquatic ecosystems: Current conditions and projected changes. Biogeochemistry 46: 109–148.
Durieux, R.P., H.J. Brown, E.J. Stewart, J.Q. Zhao, W.E. Jokela, and F.R. Magdoff. 1995. Implications of nitrogen management strategies for nitrate leaching potential: roles of nitrogen source and fertilizer recommendation system. Agron. J. 87: 884–887.
Floate, M.J.S. 1987. Nitrogen cycling in managed grasslands, pp. 163–172. *In* R.W. Snaydon (ed.) Managed grasslands – Analytical studies, Elsevier, New York.

Focazio, M.J., Plummer, L.N., Bohlke, J.K., Busenberg, E., Backman, L.J. and Powars, D.S. 1998. Preliminary estimates of residence times and apparent ages of ground water in the Chesapeake Bay watershed, and water-quality data from a survey of springs. US Geological Survey Water-Resources Investigations Report 97-4225.

Galloway, J.N., W.H. Schlesinger, H. Levy, A. Michaels, and J.L. Schnoor. 1995. Nitrogen fixation: Anthropogenic enhancement-environmental response. Global Geochem. Cycles 9: 235–252.

Gianessi, L.P. and Peskin, H.M. 1984. An overview of the RFF Environmental Data Inventory: Methods, sources, and preliminary results. Resources for the Future, Washington DC.

Gleick, P.H. and Adams, D.B. 2000. Water: The potential consequences of climate variability and change for water resources of the United States. The report of the water sector assessment team of the national assessment of the potential consequences of climate variability and change. US Global Change Research Program, Pacific Institute for Studies in Development, Environment, and Security, Oakland, CA.

Goolsby, D.A., W.A. Battaglin, G.B. Lawrence, R.S. Artz, B.T. Aulenbach, R.P. Hooper, D.R. Keeney, and G.J. Stensland. 1999. Flux and sources of nutrients in the Mississippi-Atchafalaya River basin. Report of Task Group 3 to the White House Committee on Environment and Natural Resources, Hypoxia Work Group. Federal Register 64: 23834–23835.

Hallberg, G.R. and D.R. Keeney. 1993. Nitrate, pp. 297–322. *In* W.M. Alley (ed.) Regional ground-water quality, Van Nostrand Reinhold, New York.

Harvey, J.W., B.J. Wagner, and K.E. Bencala. 1996. Evaluating the reliability of the stream tracer approach to characterize stream-subsurface water exchange. Water Resour. Res. 32: 2441–2451.

Harvey, J.W. and B.J. Wagner. 2000. Quantifying hydrologic interactions between streams and their subsurface hyporheic zones, pp. 3–44. *In* J.B. Jones and P.J. Mulholland (eds) Streams and ground waters, Academic Press, San Diego, CA.

Haynes, R.J. and P.H. Williams. 1993. Nutrient cycling and soil fertility in the grazed pasture ecosystem. Adv. Agron. 49: 119–199.

Heathwaite, A.L., T.P. Burt, and S.T. Trudgill. 1993. Overview – The nitrate issue, pp. 3–21. *In* A.L. Heathwaite et al. (ed.) Nitrate: Processes, patterns and management, John Wiley and Sons, New York.

Hecky, R.E. and P. Kilham. 1988. Nutrient limitation of phytoplankton in freshwater and marine environments: a review of recent evidence on the effects of enrichment. Limnol. Oceanogr. 33: 796–822.

Hill, A.R. 1996. Nitrate removal in stream riparian zones. J. Environ. Qual. 25: 743–755.

Horton, R.E. 1945. Erosional development of streams. Geol. Soc. Am. Bull. 56: 281–283.

Howarth, R.W., G. Billen, D. Swaney, A. Townsend, N. Jaworski, K. Lajtha, J.A. Downing, R. Elmgren, N. Caraco, T. Jordan, F. Berendse, J. Freney, V. Kudeyarov, P. Murdoch, and Z. Zhu. 1996. Regional nitrogen budgets and riverine N and P fluxes for the drainages to the North Atlantic Ocean: Natural and human influences. Biogeochemistry 35: 75–139.

Jaworski, N.A., P.M. Groffman, A.A. Keller, and J.C. Prager. 1992. A watershed nitrogen and phosphorus balance: the Upper Potomac River basin. Estuaries 15: 83–95.

Jaworski, N.A., R.W. Howarth, and L.J. Hetling. 1997. Atmospheric deposition of nitrogen oxides onto the landscape contributes to coastal eutrophication in the northeast United States. Environ. Sci. Technol. 31: 1995–2004.

Johnson, D.W. 1992. Nitrogen retention in forest soils. J. Environ. Qual. 21: 1–12.

Jordan, T.E. and D.E. Weller. 1996. Human contributions to terrestrial nitrogen flux: Assessing the sources and fates of anthropogenic fixed nitrogen. BioScience 46: 655–664.

Jordan, T.E., D.L. Correll, and D.E. Weller. 1997. Relating nutrient discharges from watersheds to land use and streamflow variability. Water Resour. Res. 33: 2579–2590.

Kalkhoff, S.J. 1995. Relation between stream-water quality and geohydrology during baseflow conditions, Roberts Creek watershed, Clayton County, Iowa. Water Resour. Bull. 31: 593–604.

Keeney, D.R. 1973. The nitrogen cycle in sediment-water systems. J. Environ. Qual. 2: 15–29.

Keeney, D.R. 1982. Nitrogen management for maximum efficiency and minimum pollution, pp. 605–649. *In* F.J. Stevenson (ed.) Nitrogen in agricultural soils, Agronomy Monograph 22, American Society of Agronomy, Madison, WI.

Keeney, D.R. 1983. Transformations and transport of nitrogen, pp. 48–64. *In* F.W. Schaller and G.W. Bailey (eds) Agricultural management and water quality, Iowa State University Press, Ames, IA.

Kellogg, R.L., C.H. Lander, D.C. Moffitt, and N. Gollehon. 2000. Manure nutrients relative to the capacity of cropland and pastureland to assimilate nutrients: Spatial and temporal trends for the United States, USDA-NRCS and ERS, Washington, DC..

Kelly, C.A., J.W.M. Rudd, R.H. Hesslein, D.W. Schindler, P.J. Dillon, C.T. Driscoll, S.A. Gherini, and R.E. Hecky. 1987. Prediction of biological acid neutralization in acidsensitive lakes. Biogeochem. 3: 129–141.

Kilmer, V.J., J.W. Gilliam, J.F. Lutz, R.T. Joyce, and C D. Eklund. 1974. Nutrient losses from fertilized grassed watersheds in Western North Carolina. J. Environ. Qual. 3: 214–219.

Kladivko, E.J., G.E. Van Scoyoc, E.J. Monke, K.M. Oates, and W. Pask. 1991. Pesticide and nutrient movement into subsurface tile drains on a silt loam soil in Indiana. J. Environ. Qual. 20: 264–270.

Korom, S.F. 1992. Natural denitrification in the saturated zone: A review. Water Resour. Res. 28: 1657–1668.

LeGrand, H.E. and V.T. Stringfield. 1973. Karst hydrology – A review. J. Hydrol. 20: 97–120.

Lewis, W.M., J.M. Melack, W.H. McDowell, M. McClain, and J.E. Richey. 1999. Nitrogen yields from undisturbed watersheds in the Americas. Biogeochemistry 46: 149–162.

Linsley Jr., R.K., M.A. Kohler, and J.L.H. Paulhus. 1982. Hydrology for engineers (3rd edition). , McGraw-Hill, New York.

Lowrance, R.R., J. Todd, J. Fail Jr., O. Hendrickson Jr., R. Leonard, and L. Asmussen. 1984. Riparian forests as nutrient filters in agricultural watersheds. BioScience 34: 374–377.

Lowrance, R., R. Leonard, and J. Sheridan. 1985. Managing riparian ecosystems to control nonpoint pollution. J. Soil Water Conserv. 40: 87–97.

Lowrance, R.R. 1992. Groundwater nitrate and denitrification in a coastal riparian forest. J. Environ. Qual. 21: 401–405.

Lystrom, D.J., F.A. Rinella, D.A. Rickert, and L. Zimmermann. 1978. Regional analysis of the effects of land use on stream-water quality, methodology and application in the

Susquehanna River Basin, US Geological Survey Water- Resources Investigations 78-12, Pennsylvania and New York.

Matthews, E. 1994. Nitrogenous fertilizers: Global distribution of consumption and associated emissions of nitrous oxide and ammonia. Global Biogeochem. Cycles 8: 411–439.

McBride, G., R.B. Alexander, S. Elliot, and U. Shankar. 2000. Regional scale modeling of water quality. NIWA, Water and Atmosphere, Auckland, New Zealand.

McFarland, A.M.S. and L.M. Hauck. 1999. Relating agricultural land uses to in-stream stormwater quality. J. Environ. Qual. 28: 836–844.

McLeod, R.V. and R.O. Hegg. 1984. Pasture runoff water quality from application of inorganic and organic nitrogen sources. J. Environ. Qual. 13: 122–126.

Meybeck, M. 1982. Carbon, nitrogen and phosphorus transport by world rivers. Amer. J. Sci. 282: 401–450.

Michel, R.L. 1992. Residence times in rivers basins as determined by analysis of long-term tritium records. J. Hydrol. 130: 367–378.

Moore, M.V., M.L. Pace, J.R. Mather, P.S. Murdoch, R.W. Howarth, C.L. Folt, C.Y. Chen, H.F. Hemond, P.A. Flebbe, and C.T. Driscoll. 1997. Potential effects of climate change on freshwater ecosystems of the New England/Mid-Atlantic Region. Hydro. Processes 11: 925–948.

Moseley, M.P. and A.I. McKerchar. 1993. Streamfiow, pp. 8.1–8.39. *In* D.R. Maidment (ed.) Handbook of hydrology, McGraw-Hill, New York.

Mueller, D.K., P.A. Hamilton, D.R. Helsel, K.J. Hitt, and B.C. Ruddy. 1995. Nutrients in ground water and surface water of the United States – an analysis of data through 1992. US Geological Survey Water-Resources Investigations Report 95-4031.

Mueller, D.K., B.C. Ruddy, and W.A. Battaglin. 1997. Logistic model of nitrate in streams of the upper-midwestern United States. J. Environ. Qual. 26: 1223–1230.

Mulholland, P.J., G.R. Best, C.C. Coutant, G.M. Hornberger, J.L. Meyer, P.J. Robinson, J.R. Stenberg, R.E. Turner, F. Vera-Herrera, and R.G. Wetzel. 1997. Effects of climate change on freshwater ecosystems of the South-eastern United States and the Gulf Coast of Mexico. Hydro. Processes 11: 949–970.

Murdoch, P.S., D.A. Burns, and G.B. Lawrence. 1998. Relation of climate change to the acidification of surface waters by nitrogen deposition. Environ. Sci Technol. 32: 1642–1647.

Murdoch, P.S., J.S. Baron, and T.L. Miller. 2000. Potential effects of climate change on surface water quality in North America. J. Am. Water Resour. Assoc. 36: 347–366.

National Research Council. 2000. Clean coastal waters: understanding and reducing the effects of nutrient pollution. Ocean Studies Board and Water Science and Technology Board, National Academy of Sciences, Washington, DC.

Nelson, P.N., E. Cotsaris, and J.M. Oades. 1996. Nitrogen, phosphorus, and organic carbon in streams draining two grazed catchments. J. Environ. Qual. 25: 1221–1229.

Olness, A., E.D. Rhoades, S.J. Smith, and R.G. Menzel. 1980. Fertilizer nutrient losses from rangeland watersheds in Central Oklahoma. J. Environ. Qual. 9: 81–86.

Omernik, J.M., A.R. Abernathy, and L.M. Male. 1981. Stream nutrient levels and proximity of agricultural and forest land to streams: some relationships. J. Soil Water Conserv. 36: 227–231.

Osborne, L.L. and M.J. Wiley. 1988. Empirical relationships between land use/cover and stream water quality in an agricultural watershed. J. Environ. Manage 26: 9–27.

Owens, L.B., R.W. Van Keuren, and W.M. Edwards. 1983. Nitrogen loss from a high-fertility, rotational pasture program. J. Environ. Qual. 12: 346–350.

Paul, E.A., E.A. Paustian, E.T. Elliott, C.V. Cole, (eds) 1997. Soil organic matter in temperate agroecosystems: Long-term experiments in North America, CRC Press, New York.

Peierls, B.L., N.F. Caraco, M.L. Pace, and J.J. Cole. 1991. Human influence on river nitrogen. Nature 350: 386–387.

Peterjohn, W.T. and D.L. Correll. 1984. Nutrient dynamics in an agricultural watershed: observations on the role of a riparian forest. Ecology 65: 1466–1475.

Pionke, H.B., W.J. Gburek, A.N. Sharpley, and R.R. Schnabel. 1996. Flow and nutrient export patterns for an agricultural hill-land watershed. Water Resour. Res. 32: 1795–1804.

Postma, D., C. Boesen, H. Kristiansen, and F. Larsen. 1991. Nitrate reduction in an unconfined sandy aquifer: water chemistry, reduction processes, and geochemical modeling. Water Resour. Res. 27: 2027–2045.

Powlson, D.S. 1993. Understanding the soil nitrogen cycle. Soil Use Manag. 9: 86–94.

Puckett, L.J., R.B. Alexander, and K.J. Hitt. 1998. County-based estimates of nitrogen and phosphorus content of animal manure in the United States for 1982, 1987, and 1992, version 1.0.0, data available on http://water.usgs.gov/lookup/getspatial7manure

Puckett, L.J. 1995. Identifying the major sources of nutrient water pollution. Envir. Sci Technol. 29: 408–414.

Rastetter, E.B., A.W. King, B.J. Cosby, G.M. Hornberger, R.V. O'Neill, and J.E. Hobbie. 1992. Aggregating fine-scale ecological knowledge to model coarser-scale attributes of ecosystems. Ecol. Appl. 2: 55–70.

Russelle, M.P. 1992. Nitrogen cycling in pasture and range. J. Prod. Agric. 5: 13–22.

Rutherford, J.C., R.B. Williamson, and A.B. Cooper. 1987. Nitrogen, phosphorus, and oxygen dynamics in rivers, pp. 139–165. *In* A.B. Viner (ed.) Inland waters of New Zealand, Science Information Publishing Centre. Department of Scientific and Industrial Research, Wellington, New Zealand.

Sauer, T.J., J.V. Brahana, T.M. Kresse, S.R. Compston, D.K. Winters, J.F. Murdoch, and P.F. Vendrell. 1999a. The Savoy Experimental Watershed: water quality assessment of a basin dedicated to interdisciplinary animal waste management research. *In* Proc. Arkansas Water Resources Center Annual Research Conference. Fayetteville, AR.

Sauer, T.J., T.C. Daniel, P.A. Moore Jr., K.P. Coffey, D.J. Nichols, and C.P. West. 1999b. Poultry litter and grazing animal waste effects on runoff water quality. J. Environ. Qual. 28: 860–865.

Sauer, T.J., T.C. Daniel, D.J. Nichols, C.P. West, P.A. Moore Jr., and G.L. Wheeler. 2000. Runoff water quality from poultry litter-treated pasture and forest sites. J. Environ. Qual. 29: 515–521.

Sauer, T.J., P.A. Moore Jr., K.P. Coffey, and E.M. Rutledge. 1998. Characterizing the surface properties of soils at varying landscape positions in the Ozark Highlands. Soil Sci. 163: 907–915.

Schepers, J.S. and D.D. Francis. 1982. Chemical water quality of runoff from grazing land in Nebraska: I. Influence of grazing livestock. J. Environ. Qual. 3: 351–354.

Schilling, K.E. and R.D. Libra. 2000. The relationship of nitrate concentrations in streams t row crop land use in Iowa. J. Environ. Qual. 29: 1846–1851.

Schindler, D.W. 1997. Widespread effects of climatic warming on freshwater ecosystems in North America. Hydro. Processes 11: 1043–1067.

Schumm, S.A. 1977. Drainage basin morphology, Dowden, Hutchinson and Ross, Stroudsburg, PA.

Seaber, P.R., F.P. Kapinos, and G.L. Knapp. 1987. Hydrologic units maps, US Geological Survey Water Supply Paper 2294.

Seitzinger, S.P. 1988. Denitrification in freshwater and coastal marine ecosystems: ecological and geochemical significance. Limnol. Oceanogr. 33: 702–724.

Seitzinger, S.P. and C. Kroeze. 1998. Global distribution of nitrous oxide production and N inputs in freshwater and coastal marine ecosystems. Global Biogeochem. Cycles 12: 93–113.

Sharpley, A.N. and J.K. Syers. 1981. Amounts and relative significance of runoff types in the transport of nitrogen into a stream draining an agricultural watershed. Water Air Soil Pollut. 15: 299–308.

Skaggs, R.W. and J. van Schilfgaarde, (eds) 1999. Agricultural drainage. Agronomy Monography 38. American Society of Agronomy, Madison, WI.

Smith, R.A. and Alexander, R. B. 2000. Sources of nutrients in the Nation's watersheds. Proc. of the National Resource, Agriculture, and Engineering Service, A conference for nutrient management consultants, extension educators, and producer advisors, March 28–30, 2000. Camp Hill, PA.

Smith, R.A., G.E. Schwarz, and R.B. Alexander. 1997. Regional interpretation of water-quality data. Water Resour. Res. 33: 2781–2798.

Smith, R.A., Alexander, R.B., and Lanfear, K.J. 1993. Stream water quality in the conterminous United States – Status and trends of selected indicators during the 1980s. *In* R. W. Paulson et al. (eds), US Geological Survey Water Supply Paper 2400.

Sogbedji, J.M., H.M. van Es, C.L. Yang, L.D. Geohring, and F.R. Magdoff. 2000. Nitrate leaching and nitrogen budget as affected by maize nitrogen rate and soil type. J. Environ. Qual. 29: 1813–1820.

Stacy, P.E., H.S. Greening, J.N. Kremer, D. Peterson, and D.A. Tomasko. 2000. Contributions of atmospheric nitrogen deposition to US estuaries: summary and conclusions. *In* R. Valigura et al. (eds) Nitrogen loading in coastal water bodies: an atmospheric perspective, American Geophysical Union Water Monograph 57, Washington, DC.

Stevenson, F.J. 1982. Nitrogen in agricultural soils, American Society of Agronomy, Madison, WI.

Stevenson, F.J. 1994. Organic forms of nitrogen. *In* Humus chemistry, John Wiley, New York, pp. 59–95.

Stoddard, J.L. 1994. Environmental chemistry of lakes and reservoirs, pp. 223–284. *In* L.A. Baker (ed.) Advances in chemistry series 237, American Chemical Society, Washington DC.

Stout, W.L., S.A. Fales, L.D. Muller, R.R. Schnabel, W.E. Priddy, and G.F. Elwinger. 1997. Nitrate leaching from cattle urine and feces in Northeast USA. Soil Sci. Soc. Am. J. 61: 1787–1794.

Terman, G.L. 1979. Volatilization losses of nitrogen as ammonia from surface-applied fertlizers, organic amendments, and crop residues. Adv. Agron. 31: 189–223.

Timmons, D.R. and R.F. Holt. 1977. Nutrient losses in surface runoff from a native prairies. J. Environ. Qual. 6: 369–373.

Timmons, D.R., E.S. Verry, R.E. Burwell, and R.F. Holt. 1977. Nutrient transport in surface runoff and interflow from an aspen-birch forest. J. Environ. Qual. 6: 188–192.

Tufford, D.L., H.N. McKellar Jr., and J.R. Hussey Jr., 1998. In-stream nonpoint source nutrient prediction with land-use proximity and seasonality. J. Environ. Qual. 27: 100–111.

US Environmental Protection Agency. 1976. Quality criteria for water, US Government Printing Office, Washington, DC.

US Environmental Protection Agency. 1999. National water quality inventory: 1998 report to congress. EPA 841-R-00-001. Washington, DC.

US Geological Survey. 1999. The quality of our Nation's waters—nutrients and pesticides. USGS Circular 1225.

Vitousek, P.M., J.D. Aber, R.W. Howarth, G.E. Likens, P.A. Matson, D.W. Schindler, W.H. Schlesinger, and D.G. Tilman. 1997. Human alteration of the global nitrogen cycle: sources and consequences. Ecological Applications 7: 737–750.

White, W.B. 1988. Geomorphology and hydrology of karst terrains, Oxford University Press, New York.

Williams, M.W., J.S. Baron, N. Caine, R. Sommerfield, and R. Sanford. 1996. Nitrogen saturation in the Rocky Mountains. Envir. Sci Technol. 30: 640–646.

Windolf, J., E. Jeppesen, J.P. Jensen, and P. Kristensen. 1996. Modelling of seasonal variation in nitrogen retention and in-lake concentration: a four-year mass balance study in 16 shallow Danish lakes. Biogeochemistry 33: 25–44.

Winter, T.C., J.W. Harvey, O.L. Franke, and W.M. Alley. 1998. Ground water and surface water: A single resource, US Geological Survey Circular 1139.

Wolock, D.M. 1993. Simulating the variable-source-area concept of streamflow generation with the watershed model Topmodel. US Geological Survey Water-Resources Investigations Report 93-4124.

Wolock, D.M. and G.J. McCabe. 1999. Estimates of runoff using water-balance and atmospheric general circulation models. J. Amer. Water Assoc. 35: 1341–1350.