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MODELING DENITRIFICATION IN TERRESTRIAL AND AQUATIC ECOSYSTEMS AT REGIONAL SCALES

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Abstract. Quantifying where, when, and how much denitrification occurs on the basis of measurements alone remains particularly vexing at virtually all spatial scales. As a result, models have become essential tools for integrating current understanding of the processes that control denitrification with measurements of rate-controlling properties so that the permanent losses of N within landscapes can be quantified at watershed and regional scales. In this paper, we describe commonly used approaches for modeling denitrification and N cycling processes in terrestrial and aquatic ecosystems based on selected examples from the literature. We highlight future needs for developing complementary measurements and models of denitrification. Most of the approaches described here do not explicitly simulate microbial dynamics, but make predictions by representing the environmental conditions where denitrification is expected to occur, based on conceptualizations of the N cycle and empirical data from field and laboratory investigations of the dominant process controls. Models of denitrification in terrestrial ecosystems include generally similar rate-controlling variables, but vary in their complexity of the descriptions of natural and human-related properties of the landscape, reflecting a range of scientific and management perspectives. Models of denitrification in aquatic ecosystems range in complexity from highly detailed mechanistic simulations of the N cycle to simpler source–transport models of aggregate N removal processes estimated with empirical functions, though all estimate aquatic N removal using first-order reaction rate or mass-transfer rate expressions. Both the terrestrial and aquatic modeling approaches considered here generally indicate that denitrification is an important and highly substantial component of the N cycle over large spatial scales. However, the uncertainties of model predictions are large. Future progress will be linked to advances in field measurements, spatial databases, and model structures.

Key words: aquatic; denitrification; modeling; nitrogen cycle; regional; terrestrial.

Introduction

Nitrogen inputs to landscapes have been increasing all over the world, stemming from food and energy production activities supporting the growing population (Smil 1997, Vitousek et al. 1997, Galloway et al. 2004). The changing nitrogen cycle and associated abundance of reactive nitrogen (N) in the environment has been linked to many concerns, including the deterioration of air quality related to particulate matter and ground level ozone (Townsend et al. 2003), disruption of forest ecosystem processes (Aber et al. 2003), acidification of lakes and streams (Driscoll et al. 2001), and degradation of coastal waters including high-profile water quality issues such as eutrophication, hypoxia, and harmful algal blooms (National Research Council 2000, Rabalais 2002). The role of denitrification is of utmost importance in this context, as it is the only mechanism by which reactive forms of N in terrestrial and aquatic landscapes are transformed back into dinitrogen (N_2) gas, which is the dominant component of the earth's atmosphere. Understanding factors controlling denitrification and its rates over space and time is crucial for quantifying the effects of human activity on the N cycle,

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and for managing and mitigating the severe environmental consequences associated with N pollution.

Denitrification is a reduction process performed by particular groups of heterotrophic bacteria that are ubiquitous in the environment and that have the ability to use nitrate (NO_3) as an electron acceptor during anaerobic respiration, thereby converting NO_3 in soils and waters to gaseous forms (Firestone and Davidson 1989). At low oxygen (O_2) levels, these microbial communities may use nitrate (NO_3), nitrite (NO_2), or nitrous oxide (N_2O) as alternative electron acceptors to O_2, with molecular N_2 as the final product, given by the following reaction sequence: $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$ (Davidson and Schimel 1995). There remains uncertainty about the conditions favoring the various products of the NO_3 transformation. Understanding these controlling factors is of interest because the intermediate gaseous products are important greenhouse gases whereas the N_2 final product is highly inert and thus has no adverse environmental consequences.

Quantifying where, when, and how much denitrification occurs in ecosystems remains particularly vexing at virtually all spatial scales (Van Breemen et al. 2002, Galloway et al. 2004, Groffman et al. 2006, Seitzinger et al. 2006). It is difficult to detect changes in N_2 in the environment attributed to denitrification amid the very large reservoir of N_2 that makes up the majority (nearly 80%) of earth's atmosphere. At present, there are no scientific methods for making direct measurements of the rates of denitrification at the scale of watersheds or large regions. Even at field scales, there remain large challenges in using direct measurements of denitrification—the measurements are often sparse, sometimes unreliable, and can vary appreciably over short distances. Understanding this variability is complicated by the complex set of environmental variables that control the rates of denitrification and heterogeneity in soils and microbial communities (Firestone and Davidson 1989, Tiedje 1988). Because the dominant controlling factors are highly variable over space and time, they give rise to "hot spots" and "hot moments" of denitrification that are difficult to predict (McClain et al. 2003).

Given these difficulties, terrestrial and aquatic models have become essential tools for integrating current understanding of the processes that control denitrification with broad-scale measurements of the rate-controlling properties so that the losses of N can be quantified within landscapes. Models provide a framework for extrapolating over a wide range of spatial and temporal scales, and over a range of climatic, soil, and land use conditions. Moreover, they are needed to quantify the cumulative effects of the rate-controlling properties on N losses along surface and ground water flow paths; these cumulative losses have important implications for aquatic ecosystems where the effects of N pollution are often observed. Comparisons of model predictions with observational data have been used for verification and to test hypotheses about rate-controlling processes.

In this paper, we give examples of current approaches for modeling denitrification, and identify future needs in measurements and models. Our goal is not to review all of the current models of denitrification in ecosystems. Rather, we chose several mainstream examples to illustrate how denitrification losses of N in terrestrial and aquatic systems are quantified or can be inferred from the various conceptualizations of the N cycle underlying the models. We use the term "loss" to refer to the permanent removal of N from an ecosystem or flow path by denitrification, but may also include, in reference to certain of the models, the effects of long-term N storage in terrestrial or aquatic ecosystems. Note that this definition of "loss" differs from that used in the European literature (e.g., Grimvall and Stalnacke 1996) to refer to N flux in streams or from the terrestrial landscape. We use the term "removal" in this paper to refer to the collection of processes that are responsible for N removal from flow paths, including permanent N losses by denitrification, long-term N storage, and the temporary N removal by heterotrophic or autotrophic processes.

The modeling approaches described herein typically do not explicitly represent or simulate microbial processes and dynamics. Rather, they aim to represent the environmental conditions where microbial denitrification is expected to occur, based on many years of empirical field and laboratory investigations of the dominant controlling processes conducted by ecologists, soil scientists, microbiologists, and agronomists (e.g., Knowles 1981, Tiedje 1988, Groffman and Tiedje 1989*a*, *b*, Mosier et al. 2004). The general conceptual model requires that four conditions are met simultaneously. These include:

1) Nitrogen availability: there must be a source of NO_3 to be transformed to the various gaseous products.

2) A source of energy: organic carbon is what is typically used to fuel this process, but other suitable electron donors may also serve this role.

3) Sub-oxic or anoxic conditions: this typically occurs in waterlogged areas of soil that are therefore low in dissolved oxygen, and in anoxic microsites within otherwise unsaturated (oxic) areas of the soil profile.

4) Availability of denitrifiers: an active population of denitrifiers must be present, usually the facultative anaerobes which are capable of using oxygen or nitrate as an electron acceptor. Denitrifier activity is maximized within an optimal temperature range, and minimized at both low and high temperature extremes.

The combination of these four conditions can arise from different environmental settings, at different times, and to varying degrees in aquatic and terrestrial ecosystems, adding to the challenges of quantifying denitrification.

One key to understanding spatial and temporal rates and patterns of denitrification is the role of soil moisture. In general, denitrification is favored in sub-oxic conditions or in anoxic microenvironments within

larger oxygenated regions. Because NO_3 is preferentially reduced to NH_4 when no oxygen is present, the condition of complete anoxia is not required (or preferred) for denitrification (Firestone and Davidson 1989). Typically, wet areas of the landscape are associated with sub-oxic or anoxic conditions. Thus there is a high potential for denitrification to occur in riparian zones, wetland rice paddies, heavily irrigated lands, and animal manure holding areas (Galloway et al. 2004). While average rates of denitrification in well-drained upland systems are typically fairly low, during precipitation events, anaerobic microsites in the well-oxygenated soils provide potential for significant gaseous N losses over large upland areas (Holmes et al. 1996).

Many of the approaches to model denitrification seek to represent these coupled eco-hydrological controls by describing where and when in the landscape denitrification is likely to occur. Hydrology affects denitrification in several key ways: by transporting and mixing the necessary ingredients such as nitrate, and by changing the oxygen status of the landscape soils and the riparian areas of aquatic ecosystems. Biogeochemical conditions desirable for denitrification are often found at oxic-anoxic interfaces, mediated by hydrology. Oxic conditions are needed for NO_3 production by nitrification, denitrification requires anoxic conditions, and water serves as the transport medium between the oxic and anoxic zones (McClain et al. 2003). For example, in temperate regions, the hydrologically connected soils and land areas that drain to streams expand and contract (both laterally and vertically) during periods of wetting and drying. This causes the expansion of saturated areas in the landscape, especially in riparian zones where flow paths converge (Hornberger et al. 1998). The associated changes in soil redox conditions in these riparian areas often create conditions that are appropriate for denitrification. The hyporheic zone of streambeds is also increasingly thought to be an important hot spot for denitrification. Strong gradients in the oxygen status of streambed sediments occur due to hyporheic exchange; that is, the mixing of the aerated and thus well oxygenated stream water with deeper and anoxic subsurface flows (Bencala 1993). Such redox gradients found in hyporheic regions favor communities of the facultative anaerobes, which can metabolize carbon using either O_2 or NO_3 as an electron acceptor (Duff and Triska 1990, Holmes et al. 1996).

Modeling Denitrification in Terrestrial Ecosystems

We have identified a variety of terrestrial landscape models to illustrate the range of approaches that have been used to quantify the rates of N flux and denitrification in soils and terrestrial ecosystems from field to regional spatial scales. The models include generally similar rate-controlling variables, but vary in their complexity of the descriptions of natural and human-related properties of the landscape. Models that assume unlimited supplies or externally imposed loads of inorganic N can be applied with relatively short periods of record for representation of the rate-controlling variables, while models that represent biogeochemical cycling of N and the associated short- and long-time scales of soil organic matter dynamics require simulations over longer time periods. These differences in model structures reflect a range of scientific and management perspectives, including those of biogeochemists, ecologists, agronomists, agricultural managers, and hydrologists.

A Biogeochemist's Approach: Mass Balance Model

Accounting for inputs, outputs, and changes in storage in landscapes, mass balance budgets have proved useful to explore the magnitude of denitrification occurring over large areas. Howarth et al. (1996) put forth a mass balance budget method to quantify sources of N to large regions and to constrain estimates of N losses in the terrestrial and aquatic ecosystems of these regions. This approach was extended to investigate total N inputs to 16 large watersheds of the northeastern United States from Maine to Virginia (Boyer et al. 2002) and to explore the fate of these N inputs in the soils, vegetation, and ground and surface waters of these watersheds (Van Breemen et al. 2002). The method quantified the mean annual rates of various N inputs (fertilizers, fixation, food and feed, atmospheric deposition), storage (soils and vegetation in agricultural, urban, and forested lands), and outputs (riverine export, ammonia volatilization, and in-stream denitrification), which were estimated using a series of independent modeling approaches (Alexander et al. 2002*b*, Seitzinger et al. 2002, Van Breemen et al. 2002). After accounting for the N sinks, N losses within the soils and ground waters of the terrestrial landscape were calculated as the difference between N inputs and all storage and loss terms; N losses accounted for ~40% of the total N inputs to the northeastern watersheds. Considering the variety of terms included in the mass-balance calculations, Van Breemen et al. (2002) indicated that denitrification was the most likely mechanism for explaining N losses in the terrestrial landscape. Storage in ground waters could account for a portion of the N loss to the extent that the mass balance does not reflect long-term, steady state conditions in the watersheds. The greatest N losses occurred in lands draining agricultural areas, given the greater N inputs available to be denitrified. The denitrification estimates were considered to be highly uncertain because they reflect accumulated errors from the other estimates (Van Breemen et al. 2002). Nonetheless, the results undeniably suggest substantial N losses occurring in terrestrial ecosystems; the process of denitrification must play a substantial role given the mass balance constraints.

Similar mass balance approaches, though based on much coarser resolution datasets, have been used to estimate rates of denitrification at very large regional

scales. The results suggest that huge fractions of N inputs are lost via denitrification in the terrestrial landscape: 40% for Europe (van Egmond et al. 2002), 30% for Asia (Zheng et al. 2002), 33% for land areas draining to the North Atlantic Ocean (Howarth et al. 1996), 37% for land areas draining to the Yellow-Bohai Seas (Bashkin et al. 2002), 40% for the Netherlands (Kroeze et al. 2003), 32% for the United States (Howarth et al. 2002), 16% for China (Xing and Zhu 2002), and 25% for the combined area of continents globally (Galloway et al. 2004).

An Ecologist's Approach: DAYCENT Model

Among the most popular mechanistic models of N cycling in soils used by biogeochemists and ecologists is CENTURY, which simulates the long-term dynamics of N (among other elements) in the landscape (Parton et al. 1994). A related model, DAYCENT, is the version of the model operating on a daily timestep (Parton et al. 1998, Kelly et al. 2000, DelGrosso et al. 2001), which is appropriate for simulation of denitrification in soils given that large losses are associated with changes in soil moisture during short term rain, melt, or irrigation events (Parton et al. 1988). However, because DAYCENT represents the full N cycle and both short- and long-term time scales of soil organic matter dynamics, the representation of soil water content and related parameters (e.g., temperature) needs to be carried out for long time periods. DAYCENT simulates N gas fluxes from soils due to nitrification and denitrification. The model assumes that all NO_x from denitrification will be further reduced to N_2O or N_2 before diffusing from the soil.

The denitrification submodel used in DAYCENT, originally called NGAS, was first presented by Parton et al. 1996. The DAYCENT submodel for N_2O and N_2 flux from denitrification (Parton et al. 1996, 2001, Del Grosso et al. 2000) assumes that N gas flux from denitrification is controlled by soil NO_3^- concentration (e^- acceptor), labile C availability (e^- donor), and O_2 availability (competing e^- acceptor). As soils become more anoxic, a higher proportion of N_2O produced from denitrification is further reduced to N_2 before leaving the soil (Davidson and Schimel 1995). In addition to soil water content, soil parameters related to texture (porosity, field capacity) affect O_2 availability and N gas flux (Groffman 1991). The denitrification model is based on the law of the minimum, i.e., it assumes that denitrification is controlled by the molecular species (NO_3 or labile C) or environmental condition (O_2 availability) that is most limiting. The model first calculates total N gas flux from denitrification, then partitions this between N_2 and N_2O using an N_2:N_2O ratio function. The ratio function assumes that as O_2 availability or the ratio of e^- acceptor to e^- donor decreases, a larger proportion of N_2O from denitrification will be further reduced to N_2 before diffusing from the soil to the atmosphere.

The governing equations were developed using laboratory data from incubations of intact soil cores (Del Grosso et al. 2000). Soil texture, WFPS (water-filled pore space), labile C (dextrose) concentration, and ^{15}N-labeled NO_3 concentration were varied in a full factorial design similar to Weier et al. (1993). N_2O, N_2, and CO_2 fluxes for each core were estimated from measured changes in the gas concentrations in the incubation chamber headspace. Model equations were developed to relate total N gas flux and the N_2:N_2O ratio to the independent variables (WFPS, NO_3 concentration, and CO_2 respiration). Measured CO_2 respiration was used as a surrogate for labile C availability when fitting model equations.

The ability of DAYCENT to simulate N cycling has been tested fairly extensively at field sites and over regional scales (Del Grosso et al. 2001, 2002, 2005). To evaluate the model, isotopically labeled NO_3 was added to the soil, and gaseous N_2 and N_2O fluxes were measured weekly for several years for corn and barley crops in the field. The N_2O emission data from eight cropped sites and NO_3 leaching data from three cropped sites showed reasonable model performance (Del Grosso et al. 2005). However, that is the first time simulated and observed N_2 fluxes have been compared. To simulate N_2 fluxes correctly, the model must also realistically simulate decomposition and N cycling, which rely on proper representation of soil water content and temperature. Reasonable simulation of labile C availability is crucial because most denitrifiers are heterotrophs. Proper simulation of decomposition rates is important because high O_2 demand associated with high decomposition rates can contribute to the anoxic conditions that are necessary for denitrification. Comparisons of observed and simulated N_2 flux rates for the data used in model calibration showed that the denitrification submodel satisfactorily simulated N_2 emissions for the data used for model parameterization. Four independent variables (WFPS, CO_2 emissions, NO_3 concentration, and soil gas diffusivity referenced to field capacity) were able to explain 76% of the variability in N_2 fluxes. This provides evidence that the denitrification submodel is consistent with and can explain most of the variability in the data used for model building. Further, a test of the ability of the overall DAYCENT model to simulate observed N_2 fluxes from an independent data set was tested, using N_2 flux measurements from irrigated corn (*Zea mays* L.) cropping in Colorado (Mosier et al. 1986), showed good model performance. The ability of DAYCENT to simulate N_2 needs to be further tested, but field data describing N_2 fluxes over space and time are extremely limited.

An Agronomist's Approach: DNDC Model

Another mainstream tool for exploring denitrification in terrestrial soils is the denitrification–decomposition (DNDC) model, which was initially developed for quantifying nitrous oxide (N_2O) emissions from agricul-

tural soils in the United States (Li et al. 1992, 1996, 2000). The capability of the model to simulate soil biogeochemistry also allows DNDC to model emissions from other ecosystems through linkages with vegetation models; the model can be applied from field site to regional scales.

The core of DNDC is a soil biogeochemistry model, in which the concept of "biogeochemical field" plays a central role. Biogeochemical field is an assembly of environmental forces or factors that vary in space and time and are controlled by a few primary drivers (e.g., climate, soil properties, vegetation, anthropogenic activity) that result in a series of biochemical or geochemical reactions to determine transport and transformation of the chemical elements in ecosystems (Li 2001). DNDC contains two components to bridge between the primary drivers and the coupled biogeochemical cycles of carbon and nitrogen in terrestrial ecosystems. The first component, consisting of soil climate, plant growth, and decomposition sub-models, predicts the soil environmental factors using the primary drivers as input parameters. The second component consists of nitrification, denitrification, and fermentation sub-models, quantifies production and consumption of N_2O, nitric oxide (NO), dinitrogen (N_2), ammonia, and methane by tracking the kinetics of relevant biochemical or geochemical reactions, driven by the modeled soil environmental factors. The nitrification, denitrification, and fermentation sub-models simulate activities of nitrifiers, denitrifiers, and methanogens by tracking the soil Eh and concentrations of relevant substrates (e.g., dissolved organic C or DOC, ammonium, nitrate, and so forth).

Denitrification is modeled with a series of biologically mediated reductive reactions from nitrate to N_2. The key equations adopted in DNDC for modeling the microbial activities include the Nernst equation and Michaelis-Menten equation. The Nernst equation is a basic thermodynamic formula defining soil Eh based on concentrations of the oxidants and reductants existing in a soil liquid phase (Stumm and Morgan 1981). The Michaelis-Menten equation is a widely applied formula describing the kinetics of microbial growth with dual nutrients (Paul and Clark 1989), which usually include DOC (i.e., energy source) and an electron acceptor (i.e., oxidant) such as nitrate, nitrite, NO or N_2O. The denitrification process will be depressed when either the energy source or the electron acceptor becomes limited. The values of the kinetic coefficients (i.e., Michaelis constant K_m and maximum reaction rate V_{max}) in the Michaelis-Menten equation used in DNDC were adopted from the laboratory incubation experiments done by Leffelaar and Wessel (1998). The Nernst and the Michaelis-Menten equations can be linked because they share a common factor, the oxidant concentration. The Nernst and the Michaelis-Menten equations are linked in DNDC through a simple kinetic scheme called the "anaerobic balloon." By tracking the evolution of soil bulk Eh, DNDC allocates DOC and N oxides into the anaerobic balloon at an hourly time step, defining the effective anaerobic volumetric fraction of a soil. The Eh value for a soil layer is estimated based on the dominant oxidant species with the Nernst equation, determining the size of the anaerobic balloon and the allocation of soil substrates inside and outside of the balloon. Only the substrates allocated within the balloon are involved in the anaerobic reactions (e.g., denitrification, methanogenesis, and so on); substrates allocated outside the balloon are involved in the aerobic reactions (e.g., nitrification, methanotrophy, and so on). The kinetics of transformations from nitrate to nitrite, to NO, to N_2O, and finally to N_2 are then handled by the Michaelis-Menten equation. When the anaerobic balloon grows, more substrates are allocated within the balloon, the rate of the reductive reactions (e.g., denitrification) increases based on the Michaelis-Menten equation, and the probability increases that intermediate product gases (e.g., N_2O, NO, and so on, which take longer to diffuse from the anaerobic to the aerobic fraction) will be further reduced to N_2.

Any change in climate, soil properties and management will simultaneously alter the soil temperature, moisture, pH, Eh, and substrate concentration gradients, which will collectively affect the size of the anaerobic balloon, the substrate availability, and finally the production of NO, N_2O, and N_2. DNDC has been used to model denitrification for both upland and wetland ecosystems. DNDC has been tested against a number of NO and N_2O flux measurements in agricultural and forest ecosystems, and evaluated against datasets of crop yield, C sequestration, and trace gas emissions observed at croplands or grasslands worldwide (Brown et al. 2002, Farahbakhshazad et al. 2002, Zhang et al. 2002, Cai et al. 2003, Xu-Ri et al. 2003, Saggar et al. 2004, Smith et al. 2004, Kesik et al. 2005, Pathak et al. 2005). DNDC currently quantifies N_2 fluxes based on the kinetic parameters observed in the laboratory experiments (Leffelaar and Wessel 1998) as well as the N balance controls. The model has not been adequately validated for N_2 fluxes due to the lack of observations. Increasing direct measurement of N_2 fluxes will provide better opportunities to improve the model performance.

An Agricultural Management Approach: EPIC and Related Models

Various agricultural management models that simulate crop production and related nutrient and C cycling include components that simulate denitrification in soils. One of the more widely used models is EPIC (Williams et al. 1984, Sharpley and Williams 1990)—a dynamic simulation model that describes the influence of agricultural management on crop productivity and erosion. The model has been used in studies of climate change and agriculture (Rosenberg et al. 1992, Mearns et al. 1999) and in evaluations of agricultural policy, water-quality, and field-scale management. EPIC simu-

lates the major N cycling processes in agricultural soils—including mineralization, nitrification, immobilization, ammonia volatilization and denitrification, runoff and surbsurface leaching—at a daily time step based on physical principles and parameter values derived from extensive model testing and specific field validation (Williams 1995).

In EPIC, denitrification is simulated as a function of nitrate availability, C availability, soil temperature, and soil moisture content. If the ratio of soil water content to field capacity in a soil layer is greater than 95% (Williams 1995) or the soil water content is greater than 90% of the saturation value (Marchetti et al. 1997), indicating nearly saturation conditions and likely anoxia, denitrification can occur (Williams 1995). The rate of denitrification (DN, in $kg \cdot ha^{-1} \cdot d^{-1}$) in a soil layer i over time t is determined from the mass of nitrate (NO_3, in $kg \cdot ha^{-1} \cdot d^{-1}$), the organic C content (C_i^{org}, in %) and a soil temperature factor used in other nutrient cycling processes in the model ($\lambda_{T,i}$), such that

$$DN_i = NO_{3i}(1 - \exp[-1.4\lambda_{T,i}C_i^{org}t]) \quad (1)$$

where $\lambda_{T,i} = T/(T + \exp[9.93 - 0.321T])$ for $T =$ the soil temperature. If the soil temperature is less than or equal to zero, no denitrification is assumed to occur.

The field-scale agricultural management model GLEAMS (Leonard et al. 1987, Knisel 1993) was developed from both EPIC and CREAMS and employs a more explicit description of soil water content. In GLEAMS, the concentration of nitrate-N removed via denitrification over a period of time (t) is a function of the factors describing the soil water content (W_f), the soil temperature, and the organic C content, such that

$$DN_i = NO_{3i}(1 - \exp[-W_f\lambda_{T,i}C_i^{org}t]) \quad (2)$$

where $C_i^{org} = 24 \times (0.002C + 0.0042)$ and $W_f = (SW - [FC + 0.1(SAT - FC)])/(SAT - [FC + 0.10(SAT - FC)])$, and where SW is the soil water content, FC is the field capacity, and SAT is the saturation level. Under this formulation, denitrification only occurs if the soil water content is greater than a parameter related to the soil water content at field capacity and saturation. The fraction of soil nitrate-N lost to denitrification increases quickly as soil water content increases beyond the field capacity. As in EPIC, no denitrification occurs if the soil temperature is less than or equal to zero.

The EPIC and GLEAMS method of simulating denitrification neglects denitrification that may occur in anaerobic micro-zones when the soil is not at field capacity or saturation. Therefore, simulation models like EPIC and GLEAMS will tend to estimate a lower frequency of denitrifier activity than observed in the field (Marchetti et al. 1997). Conversely, the models tend to overestimate the magnitude of denitrification when soil water content exceeds the threshold defined for denitrification. For example, Marchetti et al. (1997) found that the simulated denitrification rate in EPIC can rapidly reach the maximum allowable value once soil water content exceeds the assumed 90% of saturation threshold value. The method of representing soil water content is particularly poorly suited to simulating denitrification in well-drained soils where the water content rarely rises to saturation or field capacity.

The popular SWAT (soil water assessment tool) is a physically based mechanistic simulation model that describes processes of water movement, sediment transport, crop growth, and nutrient cycling on land and in water. Input data are required on climate, soil properties, topography, vegetation, and land management practices. SWAT, a modification of the SWRRB model (simulator for water resources in rural basins; Arnold et al. 1990), incorporates features of several United States Department of Agriculture models (i.e., CREAMS, GLEAMS, EPIC) to describe land surface and subsurface processes; it uses components of the QUAL2E model to simulate in-stream and reservoir transport of contaminants. It has been applied at a wide range of watershed scales, including hydrologic units of the United States in the Mississippi River Basin (Brezonik et al. 1999). The N loss from denitrification (mass per area per time) is estimated for individual soil layers as a function of the initial nitrate concentration in the soil water, temperature, and organic C percentage, such as that described in Eq. 1. Denitrification losses increase with increases in temperature and C.

The highly detailed Dutch soil chemistry model ANIMO (Kroes and Roelsma 1998) provides a method for estimating denitrification under both anaerobic and partially anaerobic soil conditions. In ANIMO, denitrification is estimated by either the rate of soil organic matter respiration or the soil nitrate and moisture availability, depending on which is more limiting (Schoumans and Silgram 2003). The aeration status of the soil is determined from the equilibrium between oxygen demand for respiration and nitrification and the oxygen supply, which is based upon soil texture and hydrology. Under fully aerobic soil conditions, nitrification and soil respiration occur at optimal levels and no denitrification occurs. Under fully anaerobic soil conditions, the denitrification rate is estimated via a basic first-order rate equation. In the case of partially anaerobic conditions, soil respiration and nitrification are limited by oxygen availability (in soil and via atmospheric diffusion) and a potential rate of denitrification is estimated from the respiration rate. In these conditions, the final model denitrification rate is assumed to be the lower of the denitrification rates estimated from the respiration and first order rate equation.

Field-scale N models with denitrification components have also been developed that are capable of modeling N dynamics and turnover in agricultural ecosystems and watersheds under various management practices and soil conditions. The DRAINMOD model (Skaggs 1999) and a new N version of the model, DRAINMOD-N II

(Youssef 2003, Youssef et al. 2005), quantify N losses and transport from agricultural lands with shallow water tables where artificial drainage systems (either buried drain tubing or open ditches) are extensively used. Watershed-scale versions of DRAINMOD have been developed and extensively evaluated based on data collected on a 100-km^2 watershed on the North Carolina coastal plain (Skaggs et al. 2004, Fernandez et al. 2005). DRAINMOD is based on water balances in the soil and at the soil surface. It uses functional methods to quantify infiltration, subsurface drainage, surface drainage, evapotranspiration, seepage, freezing, thawing, snowmelt, and seepage. The model predicts the water table depth and soil water contents above the water table, drainage rates and the other hydrologic components on an hourly and daily basis for long periods of hydrologic record. Hydrologic predictions of the model have been tested and found to be reliable for a wide range of soil, crop, and climatological conditions (Skaggs 1999).

DRAINMOD-N II considers both NO_3-N and NH_x-N pools in modeling mineral N and simulates nitrification and denitrification processes. It includes a comprehensive fertilizer submodel that simulates the application of NH_4 and NH_4-forming fertilizers, including urea and anhydrous NH_3, and associated short-term processes such as fertilizer dissolution, urea hydrolysis, temporal change in soil pH, and NH_3 volatilization. It simulates organic C dynamics using a simplified C cycle that includes a description of N mineralization/immobilization processes and the transport of organic N. Denitrification is modeled using Michaelis-Menten kinetics for NO_3-N; the influence of organic C on the process rate is implicitly expressed in the exponential soil depth function. The maximum denitrification rate is site specific and depends on the soil organic matter content and texture and agronomic practices (tillage practices and additional organic C sources). N removal in drainage channels is modeled according to a first order decay process. Modeled daily nitrate loads using DRAINMOD were recently compared with measured loads at the outlet of a 3000-ha forested catchment in eastern North Carolina for the period 1996–2001 (Fernandez et al. 2005). Predicted nitrate loads were relatively unbiased and showed good agreement on average across multiple years with the measured loads during this period, with low prediction errors following calibration.

A Hydrologist's Approach: INCA and RHESSys Models

Two popular mechanistic models are illustrative of approaches that have strong descriptions of catchment hydrology coupled with relatively simple denitrification functions. The INCA (integrated nitrogen in catchments) model is a water and N mass balance simulation model; it estimates the integrated effects of point and diffuse N sources on stream nitrate and ammonium concentrations and loads and also estimates the N loads related to processes in the plant/soil system (Whitehead et al. 1998). It has been most commonly applied to watersheds of 1000–2000 km^2 within the UK, but more recently has been modified for use in smaller European watersheds from 0.005 to 4000 km^2 (Wade et al. 2002). INCA quantifies plant uptake of nitrate and ammonium, nitrification, denitrification, and mineralization and immobilization within each land-use type and subcatchment. The model simulates flow and N transport in 1-km^2 or smaller cells in each of six land-use types. Biogeochemical reactions are limited to the soil zone from which water and N are leached to deeper groundwater. The fraction of stream water flow that is derived from soils and deep groundwater is estimated using a base-flow index method. Long-term changes in soil and ground water storage are modeled using components from the TNT model (Beaujouan et al. 2001); these include estimated terms for water volumes and residence times. Water storage in soils is described by a soil-moisture captured through the use of a "retention" term (which responds slowly and constitutes the majority of soil water storage) and a drainage term (which responds rapidly to water inflows). Estimates of the soil and groundwater contributions to stream flow and the water residence times and storage volumes are generally recognized as having large uncertainties (Wade et al. 2002). Denitrification is modeled according to a first-order function of soil wetness and the nitrate concentration of the soil water; the denitrification rate coefficient is a mass flux expressed as length per time. The denitrification rate and other model coefficients are manually adjusted or statistically estimated, depending on the availability of data and user discretion; INCA models are highly parameterized and unique parameter sets are not always feasible to obtain (e.g., Wade et al. 2002).

The regional hydrological ecosystem simulation system (RHESSys; Band et al. 1991, 2000) is also widely used to explore N dynamics at the watershed scale (Creed et al. 1998, Band et al. 2001). RHESSys simulates the coupled effects of C, N, and hydrological processes using a coupling of biogeochemical dynamics from the BIOME_BGC (Running and Hunt 1993) and the NGAS model used in DAYCENT as described above (Parton et al. 1996). Streamflow generation, including the distribution of surface wetness, saturation areas, and the flowpath partitioning of overland flow, throughflow, and baseflow, is based on the implementation of variable source-area concepts based on topography, quantifying routing of water through the landscape from patch to patch using either a lumped topographic approach adapted from TOPMODEL (Beven and Kirkby 1979) or a distributed approach adapted from the DHSVM model (Wigmosta et al. 1994). For example, one insightful modeling result stems from an application of RHESSys to a forested watershed in Maryland, providing high frequency simulations of denitrification rates over time (Band et al. 2001). During both wet (January)

and dry (August) periods, the downslope, riparian patches typically maintain high soil water suitable for high denitrification. Riparian areas are wetted more frequently than uplands, thus N and organic matter may be accumulating in upland regions during the dry periods. The highest overall denitrification rates were observed in riparian zones in simulations for both January and August. However, significant rates of denitrification were observed in January in upland areas that became transiently saturated during precipitation events, whereas these upland areas have relatively low rates in August when dry conditions prevail. Some of the lowest denitrification rates occur in the well-drained mid-slope areas (Band et al. 2001). The results of this model application highlight the importance of understanding the coupling of hydrologic and biogeochemical processes in identifying denitrification hot spots within the landscape of watersheds. As noted for the INCA model, RHESSys also lacks explicit representation of ground water volumes and residence times, and thus does not quantify N that is denitrified in ground waters.

Similarly, another watershed scale approach uses similar concepts based on variable source area concepts of streamflow generation to quantify denitrification in the landscape, based on new formulations of the model TOPMODEL with coupled C and N components (e.g., Beaujouan et al. 2002, Whelan and Gandolfi 2002). Whelan and Gandolfi (2002) predicted spatial and temporal distributions of denitrification for a 15-year period in a 1-km^2 catchment in southwest England, where denitrification is controlled principally by the soil water regime and available soil C. Stochastic generation of model parameters provided estimates of uncertainties in denitrification. The model developed by Beaujouan et al. (2002), called TNT2 (topography-based N transfer and transformation model), is based on hydrologic and biogeochemical properties of a 5-km^2 catchment in western France. The model combines a fully distributed version of TOPMODEL with the N transformations simulated in an existing agronomic plant-soil model, STICS (Brisson et al. 1998). The results demonstrate the importance of using a relatively simple mode to account for the spatial distribution of biogeochemical processes along flow paths and their effects on denitrification and N flux.

Progress has been made in evaluating various topographic metrics as indicators of the effects of soil properties on soil moisture and denitrifying bacterial populations. The results are generally consistent with those of models based on variable source area concepts. The use of topography as a predictor of denitrification is attractive given the readily available digital elevation model data. Three studies of N_2 and N_20 emissions in northern grasslands of North America (Pennock et al. 1992, Van Kessel et al. 1993, Corré et al. 1996) used digital elevation models (DEMs) to derive slope gradients and curvature and found that the highest predicted emission rates occurred in downslope areas and depressions. This is not unexpected, given that such convergent areas of the landscape are also directly associated with the accumulation of water according to topographic properties (Beven and Kirkby 1979).

Few studies, however, have evaluated the influence of topography on soil microbial activity. In one recent investigation of the effect of topography on the activity of denitrifiers under different humidity conditions at a 1.3-km^2 site in the northern grasslands of Canada, Florinsky et al. (2004) evaluated a rather wide range of topographic and soil properties, including nine topographic attributes, two soil properties, and six properties of soil microbial activity. The resulting regression models indicated that the denitrification rate generally was highest in wetter soils and areas where nutrient supplies to the microbiota were topographically controlled. Topographic properties, especially slope and the relative position of a point on the landscape, influenced the denitrification rate and denitrifier enzyme activity. In dry soils, only the number of denitrifiers was related to topography; various measures of denitrifier activity were generally unrelated to relief and probably reflected soil aeration status. Other recent work clearly demonstrates that nitrification potentials and N cycling in soils are directly related to topographic controls on the distribution of soil moisture (Creed and Band 1998, Laverman et al. 2000, Hefting et al. 2004, Machefert et al. 2004).

Modeling Denitrification in Aquatic Ecosystems

To date, empirical and mechanistic models of the rates of denitrification in aquatic ecosystems have been based on relatively few studies with many of the measurements collected primarily in small lakes and in the headwater and low-order streams of temperate regions (e.g., Howarth et al. 1996, Alexander et al. 2000, 2002*a*, Seitzinger et al. 2002). The estimated rates have large uncertainties related to limitations in the mass balance techniques and the in situ and laboratory measurements of sediment cores; these include the poor accounting of N inputs in some studies and the exclusion of hyporheic flow effects in others (Seitzinger et al. 2002). Little information has been reported on the seasonal variability in denitrification rates (Royer et al. 2004) and the biogeochemical controls on aquatic rates (Seitzinger 1988), including the importance of water-column nitrate concentrations (i.e., saturation kinetics) and properties of the benthic sediment of streams and lakes such as organic C content, grain size, and the density of benthic microbial communities. Moreover, few studies of either heterotrophic or autotrophic processing of N have measured N removal rates along a stream continuum to systematically evaluate the influence of stream dynamics on metabolic processes and especially denitrification rates (Garcia-Ruiz et al. 1998). These limitations have made cross-site comparisons difficult and complicated efforts to generalize denitrification rates over time and space. Only recently have studies of N cycling and loss in streams employed reliable tracer

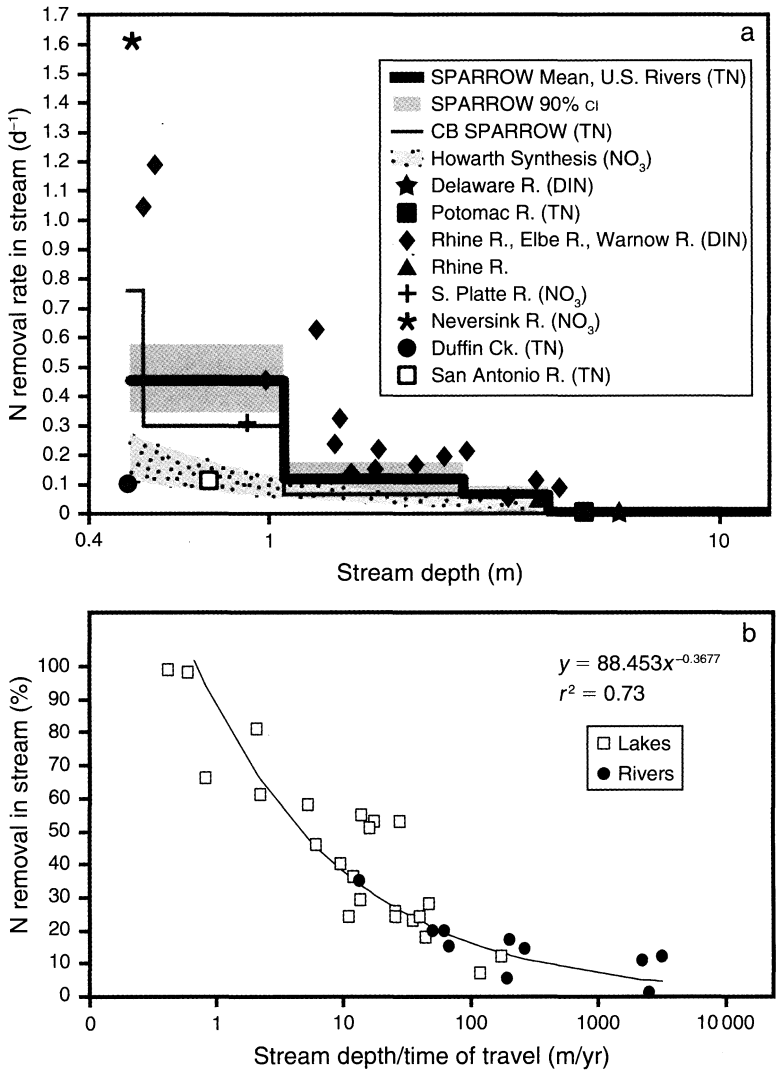

FIG. 1. Estimates of in-stream nitrogen loss with two modeling approaches, showing comparison of modeled and measured rates: (a) SPARROW model (modified from Alexander et al. [2000]); and (b) RivR-N model (modified from Seitzinger et al. [2002]). The literature values plotted in both panels are based on measured denitrification rates in sediment cores or total estimates of N loss from mass balance studies. Both models show a generally consistent relation between in-stream N loss and the hydrologic and physical properties of streams and lakes despite the use of different measures of water hydraulics and stream morphology and different expressions of the N loss rate (i.e., volumetric-based reaction rates in SPARROW vs. fraction of N inputs removed in RivR-N). Note the x-axis log scales.

techniques capable of estimating denitrification and the effects of hyporheic processes on N flux at the reach scale (e.g., Böhlke et al. 2004, Mulholland et al. 2004).

Despite the limitations of many previous studies, recent progress has been made in using the literature data to model N loss rates in relation to hydrologic and physical properties of streams, lakes, and reservoirs (Kelly et al. 1987, Dillon and Molot 1990, Howarth et al. 1996, Alexander et al. 2000, 2004, Seitzinger et al. 2002). Because these properties can be generalized over broad spatial scales (e.g., Leopold and Maddock 1953, Jobson 1996, Alexander et al. 1999, Seitzinger et al. 2002), the empirical models have provided inferences about the importance of hydrologic controls on N loss across a wide range of stream and reservoir sizes. The analyses comparing the available denitrification rates and mass balance estimates from published studies (Howarth et al. 1996, Alexander et al. 2000, 2002*b*, Seitzinger et al. 2002; see Fig. 1) indicate that N loss rates in streams and lakes generally decline with increases in streamflow, water depth, and hydraulic load (computed as the ratio of water discharge to water surface area or as the ratio of depth to water travel time) and decreases in water time of travel (i.e., reciprocal velocity). The results of these analyses show a consistent response of N flux and loss rates to the hydrologic and

physical properties of streams and lakes despite the use of different measures of water hydraulics and stream morphology and different expressions of the N loss rate (i.e., volumetric-based reaction rates, mass-transfer rates, or fraction of N inputs removed).

The empirical relations reported in these studies are consistent with current understanding of the physical and biological mechanisms that explain N loss from the water column (Stream Solute Workshop 1990, Findlay 1995, Harvey and Wagner 2000, Peterson et al. 2001, Thomas et al. 2001)—namely that the hydrological and physical properties of streams and lakes exert a major control on water and N contact with the benthic sediment and exchange in stream hyporheic zones where denitrification and biotic uptake occurs. Greater water-sediment contact and N removal by denitrification and biotic uptake and organic N burial (e.g., expressed as a reaction rate or as a fraction of N inputs) is generally expected in small streams where water volumes are small relative to the benthic surface area. Greater N removal is also expected to occur in poorly flushed lakes and in reservoirs with long water residence times. The conceptual and empirical basis for the importance of small streams and hyporheic zones as metabolically active locations for N processing and removal is found in a growing body of experimental research on autotrophic and heterotrophic processes in streams (e.g., Thomas et al. 2001, Böhlke et al. 2004, Mulholland et al. 2004). The development of nutrient spiraling concepts has provided a mathematical framework (e.g., Newbold et al. 1981, Stream Solute Workshop 1990) for modeling the longitudinal distances in streams over which N is cycled among inorganic and organic forms and permanently removed from waters via denitrification. Notable exceptions have also been reported to these generalizations about the effects of the hydrologic and physical properties of streams on N loss that are related to the effects of floodplains of large rivers. For example, N loss by denitrification in sections of the Mississippi River and southeastern U.S. rivers generally increases with elevated water depth because of the increase in hydrologic connections to microbially active locations on the floodplain (Richardson et al. 2004, Scott et al. 2004).

The models used to quantify denitrification and aggregate N losses in aquatic ecosystems range from highly detailed mechanistic models, which simulate multiple components of the N cycle, to simpler source-transport models that reflect more aggregate N-related processes estimated using empirical functions. Despite these differences, the models are similar in their reliance on two fundamental types of N loss-rate expressions for aquatic ecosystems. Our summary of the principal aquatic modeling approaches is organized accordingly and describes reaction rate and mass flux rate expressions of denitrification and total N loss (i.e., inclusive of organic N storage). We illustrate the use of these approaches for a selected set of reaction and mass-transfer type models that provide a one-dimensional representation of N transport in streams and reservoirs. Other more specialized models are appropriate for use on specific water bodies and provide a more detailed multidimensional representation of aquatic N transport (e.g., Cerco and Cole 1995).

The rate expressions used in the models described below assume first-order kinetics, i.e., the rate of N loss by denitrification from the water column is proportional to the N concentration, such that the concentration declines exponentially according to a specified reaction time (a zero-order process would correspond to a constant rate of N loss per unit of time). In a reaction rate expression, the final N concentration at a downstream location on a stream reach, $C^{\mathrm{N}}_{\mathrm{fin}}$, can be approximated as a function of the initial upstream concentration, $C^{\mathrm{N}}_{\mathrm{init}}$, and the effects of in-stream removal processes acting on the concentration in a water parcel during its transport along the reach, and is expressed according to an exponential function of the reaction rate coefficient, k_c (in units of reciprocal time), and the mean solute time of travel (TR) along the stream reach, such that

$$C^{\mathrm{N}}_{\mathrm{fin}} = C^{\mathrm{N}}_{\mathrm{init}}\exp(-k_c\mathrm{TR}). \tag{3}$$

The reaction rate describes N removal on a volumetric basis and is, therefore, dependent on dimensions of the water volume such as depth (Stream Solute Workshop 1990). Note that, for simplicity, Eq. 3 and subsequent expressions of the in-stream loss functions ignore the incoming supply of N along the stream reach. In many models (e.g., Smith et al. 1997), diffuse nitrogen sources that are introduced at various locations along a stream reach are assumed to travel on average one half the length of the reach, and therefore, are only subjected to one half of the solute time of travel. Also note that in some models as described below the functional form of the relation in Eq. 3 describes first-order reactions related to in-stream load rather than concentration.

Alternatively, N removal has been described as a flux to the benthic sediment, measured according to a mass-transfer coefficient, v, expressed in units of length per time. This depth-independent measure of N removal quantifies the vertical velocity at which N migrates into the sediment. Accordingly, the final N concentration is an exponential function of the mass-transfer coefficient (v) and the reciprocal of the vertical water displacement in the water body expressed as a ratio of the mean water time of travel to the mean depth (d), such that

$$C^{\mathrm{N}}_{\mathrm{fin}} = C^{\mathrm{N}}_{\mathrm{init}}\exp\left(-v\frac{\mathrm{TR}}{d}\right). \tag{4}$$

Different functional forms of this exponential relation have been used in the various models described below. Note that the mass-transfer coefficient is equivalent to the product of the reaction rate coefficient and the mean water depth or may be estimated as the quotient of the measured areal rate of N removal (related to hetero-

trophic or autotrophic processes) and the water-column N concentration (Stream Solute Workshop 1990). Mass-transfer coefficients are frequently used in tracer studies when comparing removal rates among streams of differing size (Stream Solute Workshop 1990, Peterson et al. 2001, Böhlke et al. 2004) and have been used in empirical mass-transport models of denitrification and particulate settling and storage processes in lakes and reservoirs (Kelly et al. 1987, Chapra 1997). The mass-transfer coefficient generally provides a more intrinsic measure of the effects of non-hydrologic properties on N removal (e.g., sediment grain size, organic C, dissolved oxygen, and microbial population densities) than a volumetric-based reaction rate that includes the effect of depth (Stream Solute Workshop 1990). According to first-order assumptions, the mass-transfer coefficient would be expected to remain relatively constant with increases in N concentrations, and thus, the areal rate of N removal (e.g., by denitrification) would rise proportionally with increases in N concentration.

Reaction-Rate Expressions

Applications of the empirical SPARROW water-quality model (spatially referenced regressions on watershed attributes) have used a flow-dependent reaction rate expression to estimate the long-term net N loss in streams (e.g., Smith et al. 1997, Alexander et al. 2000). Alternative mass-flux rate expressions have also been recently developed for the model and are discussed in Schwarz et al. (2006); these give virtually identical estimates of the in-stream N loss as compared with those based on reaction-rate expressions. SPARROW employs a hybrid statistical and process-based approach to estimate N sources and transport in watersheds and surface waters under mean-annual flow conditions. The model structure consists of a detailed stream and reservoir network (e.g., 1:500 000 scale with 1-km^2 grid for the United States [Nolan et al. 2002]; 1:100 000 scale with 30-m grid for New England [Moore et al. 2004]) that supports the quantification of N losses separately for terrestrial and aquatic ecosystems. Model parameters are determined using nonlinear estimation techniques and mass balance constraints on model inputs (sources) and outputs (riverine measurements of nutrient export). The parameter estimation is driven by spatial correlations between measured mean-annual N loads in streams and the geography of N sources (e.g., atmospheric deposition, fertilizers, human and animal wastes) and climatic and hydrogeologic properties of watersheds (e.g., precipitation, topography, vegetation, soils, water routing) that influence N transport. Stream N loads are standardized, in a prior modeling step, to reflect long-term mean conditions by adjusting for intra- and interannual seasonal and flow variability. SPARROW modeling techniques have been shown to appreciably improve the accuracy and interpretability of model parameters and the predictions of N loadings and sources in streams and rivers in comparison to those estimated using conventional regression approaches (e.g., Smith et al. 1997, Alexander et al. 2000, 2002*b*). The models statistically account for 88% to 96% of the spatial variability in stream N loads and the model prediction errors range from 20% to 55% for individual reaches. In modeling in-stream N loss, a depth-dependent reaction rate coefficient is estimated for each stream size class (Fig. 1). Thus, the N mass flux (e.g., kg/yr) at the outlet of a reach i (that results exclusively from the effects of in-stream loss processes acting on the upstream N flux), N_i^S, is estimated in a reaction-rate expression as a function of the upstream N flux entering reach i from reach j (N_j^S), the mean water time of travel (TR_k^S; units of time) in the modeled reach for stream-size class k (defined according to discrete intervals of mean streamflow or depth), and a stream-size dependent reaction-rate coefficient (θ_k^S; units time^{-1}) such that

$$N_i^S = N_j^S \exp(-\theta_k^S TR_k^S). \quad (5)$$

Because SPARROW is based on estimates of the long-term mean-annual flux of total N in rivers, the estimated in-stream loss rates are indicative of permanent or long-term losses of N; this principally includes denitrification, but may also include the long-term storage of particulate and organic N in rivers and floodplains. The in-stream loss rates estimated in the model are generally similar to those estimated from literature denitrification measurements and mass balance studies (Fig. 1). Estimates of the fraction of N input to streams that is removed span a wide range depending on the water time of travel and channel sizes in watersheds, but may range from as little as a few percent in some small eastern watersheds to as much as 90% in relatively arid watersheds of the western Gulf of Mexico region (Alexander et al. 2001). One limitation of this and other models applied at large spatial scales is that the spatial resolution of the stream network and associated maps of landscape properties may not be sufficient to provide a clear separation of the effects on nitrogen loss of in-stream processes from those caused by riparian or terrestrial processes. In addition, SPARROW does not explicitly quantify denitrification in ground water as separate from the processes that affect the long-term storage of nitrogen in soils and ground waters; N storage may reflect the effects of long groundwater residence times that significantly delay the delivery of nitrogen to streams from N sources (e.g., Böhlke and Denver 1995, McIsaac et al. 2001).

In mechanistic source-transport models, the rate of N loss via denitrification in streams is frequently modeled as a first-order reaction process. Mechanistic watershed simulation models, such as HSPF (hydrologic simulation program-Fortran; Bicknell et al. 2001) and INCA (integrated N in catchments; Whitehead et al. 1998, Wade et al. 2002), estimate the N concentration leaving stream reach or cell i ($C_i^{NO_3}$) as a function of the water-column concentration of N entering from the upstream

reach or cell j ($C_i^{NO_3}$), the water temperature (T_i'), and the water time of travel (TR), such that

$$C_i^{NO_3} = C_j^{NO_3} \exp(-\theta^S TR_i^S \theta^{T_i'-20}) \quad (6)$$

where $\theta^{T_i'-20}$ is a simplified temperature-dependent expression of the Arrhenius equation (Chapra 1997) for observed values of temperature (T') in units of centigrade, and $\theta^{T'}$ is the estimated Arrhenius coefficient (values above unity indicate a positive relation between the loss rate and temperature; values below unity indicate a negative relation).

HSPF is the most complex of the available water-quality mechanistic simulation models of watersheds. It originated from the Stanford watershed model and can simulate the hydrologic and water-quality processes on pervious and impervious land surfaces and in streams and well-mixed impoundments (Bicknell et al. 2001). The model operates on a daily time step and includes components that reflect the major N sources in watersheds and the principal N processes in soils, shallow groundwater, and aquatic systems. HSPF is often applied to relatively small catchments; one of the largest applications has been to the whole Chesapeake Bay watershed of 160 000 km^2 (Shenk et al. 1998). INCA also operates on a daily time step and simulates point and diffuse N sources with components that describe soil N transformations and water and N transport in shallow soils and groundwater.

The estimates of denitrification rates in these models may be manually adjusted or statistically derived at the user's discretion, depending on the availability of parameter estimation software and data for calibration or validation; rate coefficients may also vary spatially, depending upon the spatial segmentation of the stream network. The rates of denitrification reported for HSPF model applications to Chesapeake Bay streams range from 0.024 to 0.24 d^{-1} (G. Shenk, *personal communication*), whereas higher rates ranging from 5 to 20 d^{-1} have been reported for large streams in the Ipswich River Basin (Filoso et al. 2004; however, riparian N losses are also included in these estimates). Denitrification rates of less than 0.1 d^{-1} have been reported for certain applications of the INCA model in the River Dee in Scotland (Wade et al. 2001). Less information has been reported on the uncertainties (e.g., standard error of the coefficient estimate) associated with the reported denitrification rates in these models as well as whether the rates change in response to changes in water volume, flow, or depth. Concerns have been previously expressed (Beven 2002, Wade et al. 2002) about the uncertainties in the predictions from detailed mechanistic models related to difficulties in obtaining unique parameter values for large numbers of process rates. Thus, it is unclear from the current literature how accurately mechanistic models separate denitrification from autotrophic and heterotrophic uptake processes (Filoso et al. 2004). In general, the low rates of in-stream denitrification compared to those for biotic uptake processes in many streams (Mulholland et al. 2004) may complicate the ability to statistically resolve differences in these rates in complex mechanistic models, based solely on calibrations to measured N concentrations in streams without the additional use of in-stream measurements of denitrification.

Mass-Flux Rate Expressions

Mass-flux rates have been most commonly used in empirical mass-transport models for lakes and reservoirs to quantify losses from denitrification and organic N burial in the benthic sediments (Kelly et al. 1987, Chapra 1997). In quantifying N loss in reservoirs, a mass-flux expression has been recently used in the SPARROW model (Alexander et al. 2002*a*, 2004, McMahon et al. 2003; mass-flux rate expressions have also been developed for streams in SPARROW, see Schwarz et al. 2006). The N mass flux at the outlet of a reservoir segment i (that results exclusively from the effects of in-stream loss processes acting on the N flux entering from the upstream segment), N_i^R, is estimated as a function of the upstream N flux entering segment i from segment j, N_j^R, and an exponential function of the reciprocal of the areal hydraulic load (q_i^{-1}; units of length time^{-1}) in the reservoir, a mass-transfer coefficient (v^R; units of length time^{-1}), and a water temperature Arrhenius expression, such that

$$N_i^R = N_j^R \frac{1}{1 + (v^R q_i^{-1})} \theta^{T_i'-20}. \quad (7)$$

The areal hydraulic load is computed as the quotient of the outflow discharge to surface area of the impoundment and assumes that the surface area of the impoundment accurately reflects the surface area of the benthic sediments (this expression is equivalent to the ratio of depth to water time of travel, the reciprocal of the term in Eq. 4). In previous SPARROW N models, estimated mass-transfer coefficients have ranged from 3 to 18 m/yr (Alexander et al. 2002*a*, McMahon et al. 2003) and are within the range typical for lakes (Howarth et al. 1996, Alexander et al. 2002*a*). This type of mass flux expression (without temperature) has been widely used to model total phosphorus removal in lakes and reservoirs (Reckhow and Chapra 1982).

Two recent examples, where mass-flux expressions have been applied to streams and rivers, include the quasi-process-based PolFlow model (de Wit 2001) and the THMB (terrestrial hydrology model with biogeochemistry) hydrological model, formerly known as HYDRA (Donner et al. 2002). The former is a source-transport watershed model that has been used to quantify mean-annual total N flux in the watersheds of the Rhine and Elbe Rivers. PolFlow (de Wit 2000) was recently expanded to include water and nutrient routing components similar to those of SPARROW (de Wit 2001). The model accounts for various natural and

anthropogenic N sources, storage and permanent loss of N in soils and shallow and deep groundwater, and N delivery to surface waters. In PolFlow, the N mass flux at the outlet of reach segment i is estimated as a function of the upstream N flux entering reach segment i from segment j and stream and reservoir loss processes, such that

$$N_i^{\mathrm{S}} = N_j^{\mathrm{S}}\left(1 - \frac{1}{1 + \left[a_1^{\mathrm{R}}(S_i + 1)q_i^{b_2^{\mathrm{R}}}\right]}\right) \tag{8}$$

where S_i is the water-level gradient (i.e., channel slope) of the segment (a value of zero is used for reservoirs), q_i is the areal hydraulic load (e.g., ratio of depth to water time of travel) or specific discharge for the stream or reservoir associated with the reach, and a_1^{R} and b_2^{R} are estimated nutrient loss parameters. The estimates of N loss refer to the total form (as in SPARROW), and thus, may include denitrification and sedimentation processes related to storage of organic N in streams, floodplains, and reservoirs. According to the PolFlow model, nitrogen loss in streams would be expected to decrease as the channel slope or specific discharge increases. Because water depth generally increases at a faster rate than the solute time of travel per unit of channel length (i.e., reciprocal velocity) longitudinally in streams (Leopold and Maddock 1952, Stream Solute Workshop 1992), specific discharge would be expected to increase and nitrogen loss decrease in higher-order streams (a relation that is consistent with the water time-of-travel data and the functional relation for in-stream N loss used in SPARROW).

THMB is a mechanistic simulation model of large river systems that has been used recently, in combination with a dynamic terrestrial ecosystem model IBIS (Kucharik et al. 2000), to quantify nitrate flux in the Mississippi River Basin (Donner et al. 2002, 2004*a*, *b*). The coupled models simulate time-varying flow and storage of water and N in rivers, wetlands, and reservoirs at a 5° × 5° spatial scale for an hourly time step, based on major source inputs, subsurface drainage and N leaching, topography, and precipitation and evaporation. Evaluations of the model in the Mississippi basin (Donner and Kucharik 2003) indicated that the model accurately simulated inter-annual variability in the water and N budget from 1960 to 1994, based on historical input datasets. In each river cell, the nitrate mass removed per unit time, $M_i^{\mathrm{NO_3}}$ (kg/s), via denitrification in the benthic sediments in a given reach grid cell i is estimated as

$$M_i^{\mathrm{NO_3}} = C_i^{\mathrm{NO_3}} A_i v^{\mathrm{S}} \delta 10^{0.0293T_i'} \tag{9}$$

where $C_i^{\mathrm{NO_3}}$ is the nitrate concentration (kg/m^3) entering grid cell i, A_i is the river bed area (m^2), and v^{S} is the mass-transfer rate coefficient of 0.04 m/d (based on published literatures rates for stream denitrification from Howarth et al. 1996), and δ is a discharge-related adjustment to the mass-transfer coefficient [min((Q_c/Q), 1.0); for Q, the river discharge, and $Q_c = 120$ m^3/s, the mean discharge for a 2.5 m deep river] that reflects an assumed reduction in sediment contact time with increases in discharge above 120 m^3/s. This discharge adjustment was used to simulate low N loss that is typical in large, deep rivers (Alexander et al. 2000). The loss rate expression, coupled with the time-dependent simulation of water and nitrate flux in each river cell, effectively describes the fraction of water column nitrate that contacts the sediments ($C_t^{\mathrm{NO_3}}$, A_i) and the probability that the NO_3 which contacts the sediments is denitrified ($v^{\mathrm{S}}\delta$, T). The estimates of nitrate loss in streams reflect the general relation with water residence time and seasonal rates indicated in other studies (Donner et al. 2002, 2004*a*, *b*), though the mean nitrate loss rates tend to be lower than those estimated by the empirical models SPARROW (Alexander et al. 2000) and Riv-N (Seitzinger et al. 2002). A recent use of THMB to simulate the effects of annual changes in streamflow on N loss implies that the fraction of in-stream nitrogen removed in large river basins may be much lower during periods of higher rainfall (Donner et al. 2004*b*).

Mass-flux type expressions have also been used in simple empirical models of the literature measurements of N removal rates in streams and lakes (Kelly et al. 1987, Howarth et al. 1996, Seitzinger et al. 2002). A recent version of this model (RivR-N; Seitzinger et al. 2002) was applied to the data from 23 lakes and 10 stream segments, based on measured denitrification rates and mass balance studies. Estimates of the aquatic N loss rates, expressed as a percentage of the N input to the water bodies, were regressed on measures of the areal hydraulic load, computed as the ratio of water depth to water travel time (Fig. 1). This expression of the hydraulic load has the same units as that in Eq. 7 and identical functionality, although it is based on different physical properties. The regression relation accounted for 73% of the variation in the observations of N loss. According to this expression, the N mass flux at the outlet of a reach or reservoir segment i (that results exclusively from the effects of aquatic loss processes acting on the N flux entering from the upstream segment) can be estimated as a function of the upstream N flux entering segment i from segment j, such that

$$N_i^{\mathrm{S}} = N_j^{\mathrm{S}}\left[1 - \left(\frac{1}{100}\left[88.45\left(\frac{d_i}{\mathrm{TR}_i}\right)^{-0.3677}\right]\right)\right] \tag{10}$$

where d_i is the water depth (units of meters) and TR_i is the water time of travel in days. This model provides a generally consistent description of the rate of N loss in both streams and lakes as a function of the hydraulic load. The functional relation of N transport to the hydraulic load is also generally consistent with that of SPARROW and PolFlow given that lower hydraulic loads and higher N loss are generally observed in small

streams in comparison to that for large rivers (see the previous comments on this relation in the discussion of PolFlow). A mass-transfer coefficient is not explicitly estimated in the RivR-N model, but the estimates of N loss reflect a range of values that are implicit in the fitted relation. In general, mass-transfer rates for streams typically range from 20 to 50 m/yr and are higher by a factor of four to ten than those for lakes (5 to 20 m/yr); these higher areal denitrification rates may be explained by the more organic enriched sediments in streams (Howarth et al. 1996). The RivR-N model was applied to 16 northeastern U.S. watersheds with drainage sizes ranging from 400 to 70 000 km^2. The results indicated that from 37% to nearly 80% of the N inputs to streams were removed during transport from headwaters to coastal waters.

Key Uncertainties and Needs in Modeling Aquatic Denitrification

The current methods for using empirically based models to predict denitrification at reach and larger scales in aquatic ecosystems, including approaches for "scaling-up" measurements of denitrification rates, rely primarily on knowledge of the spatial variability in hydrologic or abiotic controlling factors (e.g., streamflow, depth, velocity). These factors are readily generalized over broad spatial scales. Less is currently known about how the non-hydrologic or biotic factors that control the aquatic rates of denitrification vary across different aquatic environments. Improved understanding depends, in part, on the development of more spatially continuous data on the distribution of non-hydrologic controls in streams, although detailed data may be difficult to obtain for some of these factors (e.g., organic C). Improvements may also come from the explicit specification of these properties in mass-transfer rate expressions and the development of experimental investigations that are complementary of these model enhancements.

One area of need is an improved understanding of the linkages between denitrification and the production and cycling of organic N in aquatic ecosystems. Currently, the less complex aquatic models do not provide a separate accounting of the fate of organic and inorganic N forms. For example, INCA and THMB only simulate nitrate transport in streams, whereas SPARROW and PolFlow only describe total N. The models of total N, SPARROW, and PolFlow, are mass balance and reflect long-term, mean-annual conditions. Whereas this provides a complete accounting of the fate of N over long time periods in aquatic ecosystems, the absence of specific N forms in these models limits their ability to identify the specific mechanisms that are responsible for N losses, such as denitrification vs. the storage of organic N in streams, reservoirs, and floodplains. More complex mechanistic models, such as HSPF, describe N cycling processes in detail over daily time periods, but are highly parameterized and have large uncertainties in the estimated rates of denitrification and other N transformations. An improved quantification of these uncertainties will require much more experimental data on aquatic denitrification rates than currently exist and an expanded use of parameter estimation techniques in model calibrations to broaden understanding of the level of complexity that can be accurately represented in mechanistic models of N transformations and cycling. Progress has been made in the measurement of N transformations in streams over relatively short time scales (e.g., Peterson et al. 2001, Hall and Tank 2003, Böhlke et al. 2004, Mulholland et al. 2004), but additional work is needed at seasonal and longer time scales (e.g., Royer et al. 2004) and at reach and larger spatial scales (e.g., especially along stream gradients) to support the use of models to improve understanding of N fate in streams. Advances in understanding the linkages between denitrification and N cycling are also dependent upon the inclusion of labile and refractory C forms in aquatic models. In contrast to the terrestrial models, most aquatic models lack components to describe the dynamic coupling of C and N transformations and provide no mechanisms to account for the accumulation of C in streams. Explicit descriptions of floodplain and riparian processes are also currently lacking in all of the aquatic models reviewed here, although floodplains and riparian areas are recognized as having important metabolically active zones capable of supporting denitrification (e.g., Hill 1996, Richardson et al. 2004, Scott et al. 2004). The exclusion of these processes in aquatic models can be explained, in part, by the poor resolution of mapped information on the physical and biochemical properties of stream riparian areas (e.g., Rosenblatt et al. 2001). However, more experimental observations are needed over space and time in these environments with improved coupling in aquatic models to expand understanding of the separate effects of riparian and in-stream denitrification on downstream N conditions.

Uncertainties also exist in the first-order assumptions that are currently used in virtually all aquatic models to quantify the rates of denitrification. The few studies of the saturation kinetics of denitrification (Garcia-Ruiz et al. 1998) have reported evidence of concentration limitations, but additional research is needed to broaden understanding of these conditions in a range of aquatic ecosystems. Nevertheless, these studies raise questions about how accurately the published denitrification rates apply to streams with especially high nitrate concentrations, such as those found in agricultural watersheds where saturation kinetics may potentially limit denitrification rates. One recent investigation (Royer et al. 2004) of denitrification rates in agricultural catchments with high nitrate concentrations (>400 μM) indicates that the rates of denitrification were one half or even smaller (i.e., mass-transfer rates <10 m/yr) than those that have been measured in streams draining less developed catchments (see also Böhlke et al. 2004).

Additional measurements of denitrification rates in the streams draining highly developed watersheds are especially needed to improve understanding of the saturation kinetics of denitrification. Moreover, there is a need to use existing aquatic and watershed models to empirically evaluate how estimated N loss rates change with N concentrations in streams.

Conclusions

One of the largest uncertainties in knowledge of the N cycle, at all scales, is the amount of reactive N that is converted to N_2 during the denitrification process (Galloway et al. 2004). We illustrate many of the current modeling approaches that are used to shed light on the magnitude of denitrification occurring in terrestrial and aquatic ecosystems. The examples presented here highlight impressive progress by the modeling community in representing couplings among the C, N, and water cycles that control N loss rates. Nonetheless, the models provide only simplified representations of the complex set of processes controlling denitrification, and modeled estimates of the magnitude of N losses via denitrification remain highly uncertain.

It may seem strange to conclude with an observation that future progress in modeling denitrification is very strongly linked to the acquisition of new measurement data and to new experimental work, but that, in our opinion, is the state of the science. Though a sparse number of in-situ field observations and kinetic parameters observed in lab experiments provide some basis for parameterizing N_2 fluxes in models, a major limitation to modeling is a lack of measurements of denitrification at appropriate field scales. Despite the wide range of approaches used to measure and characterize the denitrification process at various scales (Groffman et al. 2006), the modeling community is unanimous in stating that simulated magnitudes of the denitrification trace gas fluxes cannot be adequately calibrated and validated due to the lack of observational data over space and time. There is generally no rigorous way to validate the large-scale terrestrial and aquatic models in terms of their process identification.

To better evaluate model structures and performance, multidisciplinary studies are needed that are comprehensive in terms of measurements over regional spatial scales and long time scales. Detailed field studies are needed where biogeochemical, microbiological, and hydrological measurements are quantified explicitly and are well coordinated. In addition, research is needed that targets an improved understanding of the complex and coupled set of processes controlling denitrification over space and time. Many recent studies have shed new light on mechanisms of N cycling in general, highlighting the importance of aerobic denitrification, alternative denitrification pathways, and other nitrogen loss mechanisms (Robertson et al. 1995, Silver et al. 2001, Thamdrup and Dalsgaard 2002, Davidson et al. 2003). These alternative denitrification and nitrogen loss pathways in the environment may be highly significant at the scale of large regions, and may need to be added to the conceptual paradigms represented in the various modeling schemes. Finally, advancing new methods to enhance the direct measurement of N_2 fluxes at regional scales will provide opportunities to refine estimates of the magnitude of N losses and to improve the capacity of all of the modeling approaches (Groffman et al. 2006).

Further field research and model development is needed to advance scientific understanding of the importance of denitrification along flow paths, and in characterizing the heterogeneity and complexity of subsurface flows. Despite knowledge that N loss in groundwater reservoirs is important in many environmental settings (Puckett 2004), there remain large challenges in characterizing N losses along deep groundwater flowpaths and in aquifers. The highly uncertain quantification of N processes and the residence times of water and N in groundwater in all of the models reviewed here highlight the challenges faced in this area. Models are needed to quantify both the separate and cumulative effects of the rate-controlling properties on N losses at specific locations along both surface and ground water flow paths throughout landscapes. Expanded capabilities for the modeling groundwater N are especially needed because of the importance of subsurface pathways for N transport and denitrification at multiple spatial scales (e.g., Seitzinger et al. 2006).

Advances in quantifying denitrification will also arise from further improvements in the accessibility and availability of synoptic spatial databases providing descriptions of landscape attributes over space and time. Progress in scaling from plot to larger scales has been made by relating N losses to characteristics of the local environmental setting, relating the potential for N removal (that is, N sinks) to characteristics such as the presence of hydric soils for N losses in riparian zones (Gold et al. 2001), topography and soil texture for N loss in large river floodplains (Pinay et al. 2000), and flow regime (as evidenced by stream depth and water travel time) for N losses in streams corridors (Alexander et al. 2000, Seitzinger et al. 2002). Within model structures, new or higher-resolution data sets may prove to be useful toward scaling of denitrification measurements to estimate N losses at regional spatial scales and long temporal scales. These include maps of climate and meteorological variables, soil wetness and moisture, nutrient (organic matter and N) status of soils and streambed sediments, land cover and vegetation, land use history and disturbance, the distribution of topography, geomorphology and flow characteristics of stream reach networks, and flow paths and residence times of water within landscapes.

Recent developments in remote sensing technology will continue to play a significant role in characterizing the landscape and as a tool for modeling. For example, some noteworthy advances in spatial and temporal resolution of information relevant to modeling denitri-

fication at the landscape scale include the distribution of precipitation from the next generation radar (NEXRAD) sensors, the distribution of evaporation, photosynthesis, and primary productivity from moderate resolution imaging spectroradiometer (MODIS) sensors, and the distribution of terrain and geomorphology from light distance and ranging (LIDAR) sensors and airborne laser swath mapping (ALSM). Similarly, the development of other regional scale databases, such as the description of river and reservoir networks provided by the national hydrologic data set (U.S. Geological Survey 1999), provides an important hydrologic framework to assist with the coupling of terrestrial and aquatic modeling approaches. More systematic use of stream networks by the research community (i.e., in reporting experimental observations) could benefit syntheses of the data across multiple sites and support the use of experimental data to calibrate and verify regional-scale N models.

Further development and testing of model structures is also needed. As evidenced by the approaches described here, significant progress has been made in coupling various conceptualizations of the coupled relationships between N, C, and water cycles. However, there remain huge opportunities for better integration and formal coupling of terrestrial and aquatic conceptualizations in integrated and synthetic modeling frameworks, and developing model structures to make use of new information such as the synoptic databases described above. There is increasing interest in the use of spatially distributed models that include mass balance constraints and statistically estimated parameters, which provide an opportunity for the research community to formally test hypotheses about the large-scale importance of various hydrologic and biogeochemical controls on transport and fate of N, and testing of the level of process complexity that is required to explain variations in N export in space and time. Analyses of errors and uncertainties in model predictions, especially comparisons with controlling variables (e.g., Alexander et al. 2002*b*), may also help to identify ways to improve the model specifications. Although there is not detailed information on the spatial distributions of all controlling variables (i.e., organic C, and so on) that are needed to "scale-up" measurements of denitrification rates, modelers may be able to do selected comparisons of model errors in locations where data are available.

In summary, models will continue to serve as essential tools for integrating the current understanding of processes that control denitrification with broad-scale measurements of the rate-controlling properties so that the losses of N can be quantified at regional scales. Despite the uncertainties and model limitations described in this review, scientific information from modeling investigations will continue to provide a critical window into questions of where, when, and how much denitrification occurs in the landscape. The different modeling approaches described herein, though exhibiting a very large range in complexity, all are in consensus in identifying that denitrification is an important and highly significant component of the N cycle in both terrestrial and aquatic ecosystems at regional scales.

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