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Challenges to incorporating spatially and temporally explicit phenomena (hotspots and hot moments) in denitrification models

Peter M. Groffman · Klaus Butterbach-Bahl · Robinson W. Fulweiler · Arthur J. Gold · Jennifer L. Morse · Emilie K. Stander · Christina Tague · Christina Tonitto · Philippe Vidon

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Abstract Denitrification, the anaerobic reduction of nitrogen oxides to nitrogenous gases, is an extremely challenging process to measure and model. Much of this challenge arises from the fact that small areas (hotspots) and brief periods (hot moments) frequently account for a high percentage of the denitrification activity that occurs in both terrestrial and aquatic ecosystems. In this paper, we describe the prospects for incorporating hotspot and hot moment phenomena into denitrification models in terrestrial soils, the interface between terrestrial and aquatic ecosystems, and in aquatic ecosystems. Our analysis suggests that while our data needs are strongest for hot moments, the greatest modeling challenges are for hotspots. Given the increasing availability of high temporal frequency climate data, models are promising tools for evaluating the importance of hot moments such as freeze-thaw cycles and drying/rewetting events. Spatial hotspots are less tractable due to our inability to get high resolution spatial approximations of denitrification drivers such as carbon substrate. Investigators need to consider the types of hotspots and hot moments that might be occurring at small, medium,

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P. M. Groffman (✉)
Cary Institute of Ecosystem Studies, P.O. Box AB,
Millbrook, NY 12545, USA
e-mail: groffmanp@ecostudies.org

K. Butterbach-Bahl
Institute for Meteorology and Climate Research,
Atmospheric Environmental Research (IMK-IFU),
Forschungszentrum Karlsruhe, Kreuzeckbahnstr. 19,
82467 Garmisch-Partenkirchen, Germany

R. W. Fulweiler
Department of Earth Sciences, Boston University,
675 Commonwealth Ave., Boston, MA 02215, USA

A. J. Gold
Department of Natural Resources Science,
University of Rhode Island, Kingston, RI 02881, USA

J. L. Morse
Department of Biology, Duke University,
Durham, NC 27708, USA

E. K. Stander
Department of Ecology, Evolution, and Natural Resources,
Rutgers University, New Brunswick, NJ 08904, USA

C. Tague
Donald Bren School of Environmental Science and
Management, University of California Santa Barbara,
Santa Barbara, CA 93117, USA

C. Tonitto
Department of Ecology and Evolutionary Biology
and Department of Horticulture, Cornell University,
Ithaca, NY 14850, USA

P. Vidon
Department of Earth Sciences, Indiana University Purdue
University Indianapolis (IUPUI), 723 W. Michigan Street,
Indianapolis, IN 46202-5132, USA

and large spatial scales in the particular ecosystem type they are working in before starting a study or developing a new model. New experimental design and heterogeneity quantification tools can then be applied from the outset and will result in better quantification and more robust and widely applicable denitrification models.

Keywords Denitrification · Nitrogen · Riparian · Sediment · Soil · Stream

Introduction

Denitrification, the anaerobic reduction of the nitrogen oxides nitrate (NO_3^-) and nitrite (NO_2^-) to the nitrogenous gases nitric oxide (NO), nitrous oxide (N_2O) and dinitrogen (N_2), is an extremely challenging process to measure and model (Groffman et al. 2006a). Much of the challenge presented by denitrification arises from the fact that small areas (hotspots) and brief periods (hot moments) often account for a high percentage of denitrification activity (McClain et al. 2003). While we know a lot about the factors that control denitrification activity, i.e., oxygen, nitrate and available carbon (most denitrifiers are heterotrophic), the complex regulation of these factors in the environment creates hotspots and hot moments that are difficult to quantify and model.

The challenges posed by hotspots and hot moments are especially problematic given that denitrification is a process that is carried out by microorganisms but is of interest at a variety of larger scales including crop fields, mixed landscapes consisting of crop fields, forests, wetlands and streams, regional watersheds such as the Chesapeake Bay, Gulf of Mexico and Baltic Sea, and the entire globe. The interest in denitrification at large scales is due to its effects on soil fertility (nitrogen is a key nutrient limiting primary production in many ecosystems), water quality (nitrate is a drinking water pollutant and an agent of eutrophication in marine, especially coastal waters) and air chemistry (nitrous oxide is a greenhouse gas and contributes to the destruction of stratospheric ozone, nitric oxide is a precursor to trophospheric ozone) (Galloway et al. 2003; Kulkarni et al. 2008). Complete denitrification, i.e., reduction all the way to N_2, “closes the N cycle” returning reactive nitrogen to the stable pool in the atmosphere. Unfortunately, it is very difficult to measure the denitrification flux of N_2 given the high atmospheric background of this gas. There are many more measurements of NO and N_2O flux than of N_2 flux, but these do not provide complete information on denitrification (Groffman et al. 2006a).

Recognition of the importance of hotspots and hot moments to denitrification activity emerged in the 1980s along with techniques that allowed for measurement of denitrification in situ, especially in soils. Extremely high spatial and temporal variability in measured rates (Folorunso and Rolston 1984) led to a search for activity centers (hotspots) in the anaerobic centers of soil aggregates (Smith 1980; Sexstone et al. 1985), along growing roots (Woldendorp 1962; Haider et al. 1987), at the aerobic/anaerobic interface of sediments (Reddy and Patrick 1984) and associated with decomposition of labile organic matter (Parkin 1987; Christensen and Tiedje 1990). Parkin (1987) showed that more than 90% of the denitrification activity in a soil core was taking place in less than 1% of the core volume associated with a decomposing leaf (Fig. 1). The close coupling between denitrification and nitrification, an aerobic process that produces the NO_3^- (and also produces NO and N_2O) that is consumed by denitrification, greatly complicates the development of hotspots in both terrestrial and aquatic ecosystems.

The scale of the hotspot concept began to expand with the realization that certain components of landscapes, e.g., riparian zones, or regions, e.g., heavily fertilized watersheds, could be viewed as hotspots of denitrification (McClain et al. 2003). This was a particularly promising development given the need for information on denitrification at large scales and to manage landscapes to achieve water and air quality goals. The motivation for incorporating landscape and regional scale hotspots into existing models is strong, as there are multiple environmental problems driving efforts to depict the convergence of hydrologic, soil and biological factors that create hotspots at these scales (Band et al. 1993).

The hot moment concept is both old and new. There has long been a realization that bursts of activity following drying-rewetting and freezing-thawing events are important to carbon and nitrogen dynamics in soils (Birch 1958; Edwards and Cresser 1992). Recognition of the importance of these events to denitrification came somewhat later, however, (Goodroad

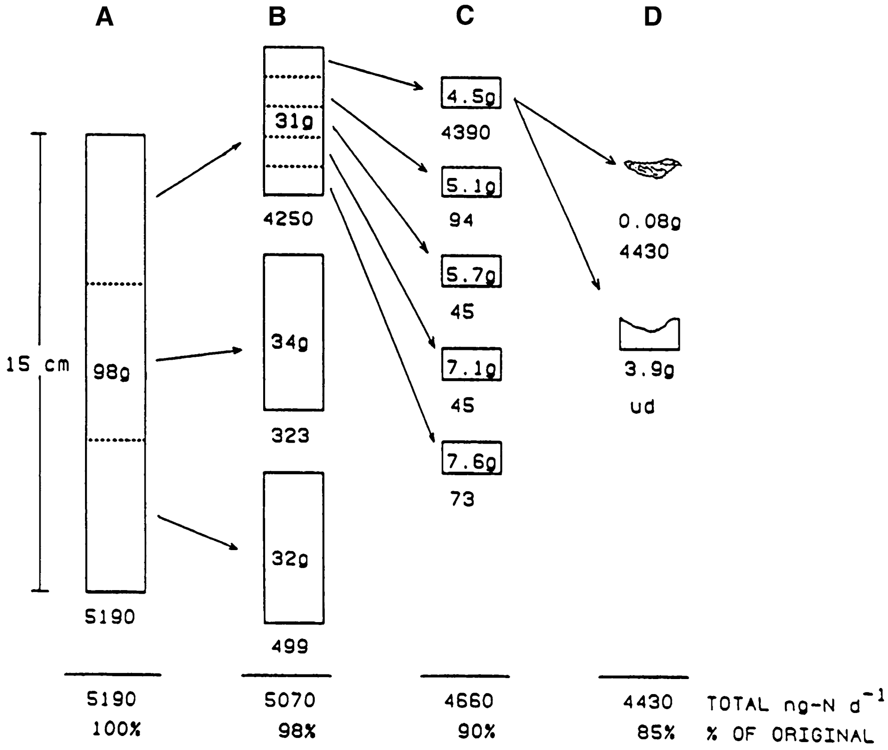


Fig. 1 The distribution of denitrification within a soil core showing the importance of hotspots. Denitrification was first measured on the entire core (*A*). Splitting the core into three segments (*B*) revealed that most of the activity was occurring in the *top segment*, which was then split into five sections (*C*). When this analysis revealed that the vast majority of activity was occurring in the top of the core, this segment was dissected (*D*) to reveal that 85% of total activity in the 5,190 g soil core was taking place in a 0.08 g piece of plant detritus. From Parkin (1987)

and Keeney 1984; Groffman and Tiedje 1988) and was a further impediment to the development of widely applicable denitrification models. As with the concept of hotspots, ideas about hot moments came to be applied at larger scales where particular seasons (e.g., early spring) or hydrologic events (e.g., the confluence of two rivers) came to be viewed as critical to understanding and quantifying denitrification over large areas and time scales (McClain et al. 2003).

While denitrification hotspots and hot moments are widely recognized as important, they are not well incorporated into models of this process in either terrestrial or aquatic ecosystems. Most terrestrial modeling approaches start with temperature and moisture controls on nitrogen process rates, and spatial extrapolations are made using average site parameters for these and other key drivers (Li et al. 1992; Parton et al. 1987; Tague and Band 2004). The interactions among drivers that lead to hotspots and hot moments are either not included or are represented at insufficient resolution in these models. Most terrestrial biogeochemistry models do not incorporate the lateral redistribution of water, nitrogen and carbon within landscapes that cause interfaces between landscape elements to function as denitrification hotspots (Tague and Band 2004). Aquatic denitrification models range from detailed sediment biogeochemical algorithms that highlight individual processes (Di Toro 2001) to larger scale empirically based statistical relationships (e.g., Seitzinger and Giblin 1996; Seitzinger et al. 2002). However, for the most part, these models are not capable of depicting hotspots in unique sediment features (e.g., faunal burrows) or capturing hydrologic interactions within aquatic systems or between aquatic and terrestrial systems (Boyer et al. 2006).

In this paper, we describe the prospects for incorporating hotspot and hot moment phenomena into denitrification models, in multiple ecosystem types, at multiple scales. We start with terrestrial soils and then move downslope to consider the interface between terrestrial and aquatic ecosystems (e.g., riparian zones) and then discuss hotspots in aquatic ecosystems. Our approach follows the analysis of Seitzinger et al. (2006), which showed that the amount of nitrogen denitrified is highest in terrestrial soils, with progressively smaller amounts denitrified in groundwater, rivers, lakes and reservoirs, and estuaries (Fig. 2). This pattern is driven by the large area of terrestrial soils and the importance of fertilizer input as a

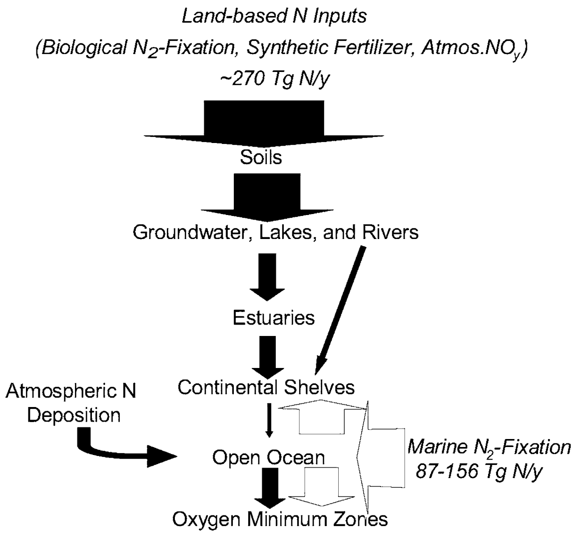


Fig. 2 Denitrification decreases N transfers originating from land-based and marine sources throughout the terrestrial—freshwater–marine continuum. Land-based sources include terrestrial biological N_2 fixation, synthetic N fertilizer, and atmospheric deposition of NO_y; the dominant marine source is biological N_2 fixation occurring in the marine environment. From Seitzinger et al. (2006)

driver of denitrification. The Seitzinger et al. (2006) analysis highlights the importance of hotspots because while it points out that terrestrial soils are responsible for much denitrification at the watershed scale, per-area denitrification rates in soils are quite low compared to rates in downstream aquatic ecosystems, suggesting that much of the terrestrial activity must occur in hotspots and/or at the interface between terrestrial and aquatic systems. Within each section we review the importance of hotspots and hot moments, how they are affected by human activities (e.g., fertilization, land use change) and approaches for incorporating these phenomena into existing denitrification models as well as ideas for new or highly altered models. We end with an applied case study of local land use planning to protect the coastal zone in the northeastern US to highlight the importance of incorporating hotspot and hot moment phenomena into models and environmental management tools.

Hotspots and hot moments in soils

The Seitzinger et al. (2006) analysis clearly showed that a dominant flux in the global nitrogen budget is inputs of reactive nitrogen to land by atmospheric deposition, fertilizer and nitrogen fixation. Further, their analysis showed that most of this nitrogen disappears somewhere in the terrestrial environment (Fig. 2). This result is consistent with numerous mass balance studies that show large "retention" of nitrogen in terrestrial ecosystems—50–80% of reactive nitrogen inputs either stored or lost as gases (Howarth et al. 1996; Boyer et al. 2002; Groffman 2008). Numerous studies to determine just where nitrogen is disappearing in the terrestrial landscape have been hindered by methodological challenges (Groffman et al. 2006a) and by the high spatial (hotspots) and temporal (hot moments) variability of denitrification.

Hotspots in the terrestrial environment develop from the interaction of patches of organic matter with physical factors that control oxygen diffusion and thus anaerobiosis, and the transport and residence time of denitrification reactants. Thus a series of plant and soil factors, e.g., rooting patterns and soil structure at small (0.1–10 m) scales, topography, hydrologic flow paths and geology at larger (>1 km) scales, need to be considered to understand the spatial distribution of hotspots. Hot moments in the terrestrial environment are driven by events that cause a convergence of reactants, e.g., drying-rewetting and freezing-thawing events. Insight into the importance of these events has largely come from studies showing their importance to fluxes of denitrification intermediates (NO, N_2O) that are of environmental concern.

The temporal and spatial phenomena that lead to terrestrial hotspots and hot moments are strongly affected by human alteration of the terrestrial environment for agricultural and urban/suburban land use. In the sections below, we discuss the factors regulating hotspots and hot moments in the terrestrial environment, describe how these are affected by human activities, and list approaches for modifying terrestrial denitrification models to include these phenomena.

Temporal heterogeneity

Insight into the importance of denitrification hot moments has come from studies showing that the annual budgets of nitrogen trace gas (NO and N_2O) fluxes from soils of various ecosystems are often dominated by defined periods (e.g., <5–20 days) with extremely high emissions. As discussed below, in temperate and boreal regions, periods with extremely high N_2O emissions are predominantly at the end of winter, when the soil starts to thaw, whereas in subtropical and tropical regions pulse emissions of N_2O and NO have been observed after wetting of soil following prolonged dry periods. In agricultural ecosystems, pulse emissions of N_2O and NO are also frequently associated with fertilizer additions.

Pulse N_2O emissions during freeze-thaw cycles have received much attention in recent years as they have been shown to be important to, or even dominate overall annual N_2O emission from agricultural and/or forest ecosystems (Christensen and Tiedje 1990; Chen et al. 1995; Kamman et al. 1998; Papen and Butterbach-Bahl 1999; Teepe et al. 2000; Groffman et al. 2006b). Many terrestrial ecosystems, e.g., tundra, boreal forests and steppes, are regularly exposed to long frost periods (Sakai and Larcher 1987). Recurring soil freezing and thawing has great impact on soil physical structure and solute distribution as well as on the activity of plants and microorganisms. During freezing, water and nutrients are redistributed in the soil. Water moves towards the freezing front or point, whereas ions (nutrients) are excluded from the ice grid and accumulate within remaining water films around soil particles (Edwards and Cresser 1992; Stähli and Stadler 1997). The increasing solute concentrations hamper the further freezing of soil water due to freezing point suppression, so that unfrozen water and microhabitats for soil microorganisms can still be found in "frozen" soils down to temperatures of −15 to −20°C (Rivkina et al. 2000; Panikov et al. 2006). Additionally, due to changes in water volume during freezing, soil aggregates are physically disrupted, releasing physically protected organic material (Christensen and Christensen 1991). Freezing also damages soil organisms and plant roots through ice crystal formation and resulting damage to membranes and DNA, or by desiccation. Depending on frost strength, penetration depth and frequency, which are affected by vegetation, litter and snow cover (Edwards and Cresser 1992; Teepe et al. 2000; Groffman et al. 2006b) and adaptation of plants and microbes to frost, a significant amount of plant roots and microbes are killed (DeLuca et al. 1992; Skogland et al. 1988; Tierney et al. 2001; Koponen and Martikainen 2004) providing fresh substrate for mineralization. Upon thawing, the surviving microbes decompose this accumulated easily degradable substrate (Herrmann and Witter 2002) leading to a flush in microbial respiratory CO_2 flux (Christensen and Tiedje 1990; Priemé and Christensen 2001; Mørkved et al. 2006). N_2O production during freeze-thaw cycles has been shown to predominantly originate from denitrification (e.g., >90%, Mørkved et al. 2006) and, thus, the occurrence of N_2O pulses during freeze-thaw largely depends on the nature and extent of anaerobic conditions in the thawing soil. Substantial N_2O emissions during freeze-thaw are only observed if the soil is close to water saturation and/or if microbial respiratory activity is greater than O_2 diffusion into the soil. Depending on environmental conditions, freeze-thaw cycles can re-occur on a daily basis and can create diurnal patterns in N_2O emissions (Fig. 3). However, the magnitude of N_2O emissions declines with repeated cycles due to the progressive utilisation of the accumulated substrate (Skogland et al. 1988; Schimel and Clein 1996; Priemé and Christensen 2001; Kurganova and Tipe 2003; Schimel and Mikan 2005; Ludwig et al. 2006). It is noteworthy that freeze-thaw cycles have not been found to lead to a burst of NO emissions (Gasche and Papen 1999; Koponen et al. 2006), supporting the idea that denitrification is the main source of N_2O during these events.

Freeze-thaw induced N_2O emissions are a major component of annual N_2O emissions from arable (e.g., Christensen and Tiedje 1990; Flessa et al. 1995; Röver et al. 1998), temperate grassland (e.g., Müller et al. 2002), steppe (Holst et al. 2008) and forest ecosystems (e.g., Papen and Butterbach-Bahl 1999; Teepe et al. 2000) with contributions exceeding 50% of the annual budget in some years. However, the frequency of years with N_2O fluxes dominated by freeze-thaw is not well studied. At the Höglwald Forest, Germany, where N_2O emissions have been monitored continuously at sub-daily resolution since 1993 (Butterbach-Bahl et al. 2002), freeze-thaw events dominated (>55%) the annual N_2O budget three out of 12 years (1996, 1997, 2006).

Mechanistic modeling of freeze-thaw induced N_2O emissions requires consideration of (a) the increase in easily degradable substrates following freezing, (b) tight coupling of nitrification and denitrification in the water saturated topsoil, and (c) the breakdown of N_2O reductase activity at low temperature (Holtan-Hartwig et al. 2002). This latter consideration requires detailed stepwise modeling of the denitrification reaction chain, which involves kinetics and differential

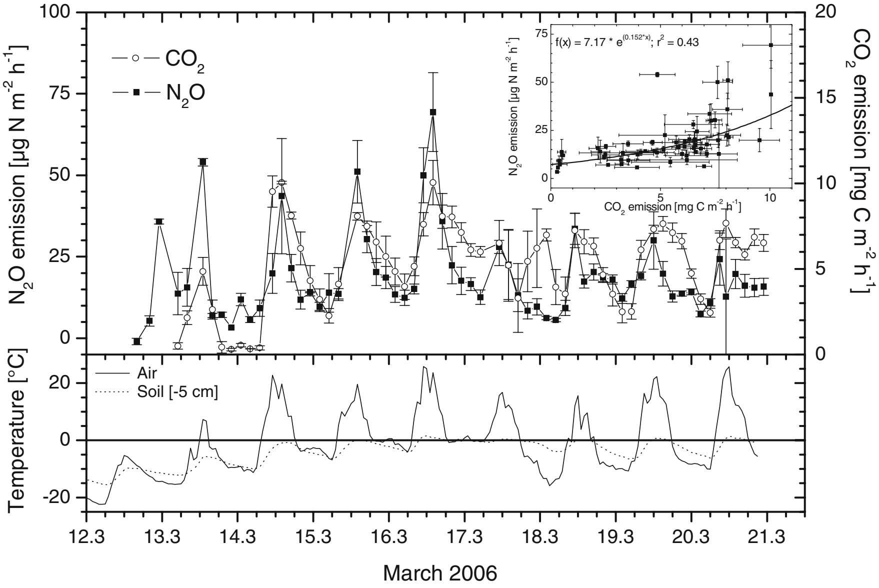


Fig. 3 N$_2$O and CO$_2$ emissions from an ungrazed steppe soil in Inner Mongolia, China, during the period of surface soil thawing in March 2006. Measurements were performed using an automated closed chamber sampling system. The inserted figure shows the close correlation between CO$_2$ and N$_2$O fluxes. Adapted from Holst et al. (2008)

environmental controls of individual denitrification enzymes. Incorporating these factors in the DNDC and COUP models significantly improved simulation of N$_2$O fluxes associated with freeze-thaw events (Butterbach-Bahl et al. 2001; Norman et al. 2008). Further work is addressing uncertainties in the parameterization of the model as well as improving simulation of the physical aspects of freezing, e.g., heat transfer and soil water movement during freeze-thaw events.

Pulse emissions of N$_2$O and NO from soils of natural and semi-natural ecosystems and agricultural soils are frequently observed following re-wetting after periods of prolonged drought (e.g., Slemr and Seiler 1984; Johansson et al. 1988; Davidson et al. 1991, 1993; Garcia-Montiel et al. 2003). Pulses of nitrogen trace gas flux associated with rewetting are particularly frequent in sub-tropical and tropical ecosystems with distinct dry seasons, and seem to be more pronounced for NO than N$_2$O. Similar to freeze-thaw events, easily degradable carbon and nitrogen and/or mineral nitrogen (ammonium, nitrate) are quickly processed via nitrification and denitrification when soil moisture limitations diminish upon rewetting (Davidson et al. 1991; García-Méndez et al. 1991). The magnitude of the NO and N$_2$O emission pulses following re-wetting appear to depend on the length of the preceding drought period and decrease with successive rainfall events (e.g., Johansson et al. 1988; Davidson et al. 1991; Otter et al. 1999; Butterbach-Bahl et al. 2004). During the first re-wetting, NO and N$_2$O emissions have often been observed to increase by several orders of magnitude above fluxes during the preceding dry period (Davidson et al. 1993; Butterbach-Bahl et al. 2004; Van Haren et al. 2005; Werner et al. 2007). However, since pulse emissions following rewetting are mostly brief, lasting in maximum a few days only, they seem to be of minor importance for annual nitrogen trace gas emissions. Davidson et al. (1991) estimated that NO pulses following re-wetting of a seasonally dry tropical forest of Mexico accounted for 10–20% of the estimated annual NO emission of 0.5–1.0 kg N ha^{-1}. In contrast, rainfall driven nitrogen trace gas pulse emissions accounted for only 3.4% (NO) and 1.8% (N$_2$O) of the annual flux for forest and pasture systems in Rondonia, Brazil (Garcia-Montiel et al. 2003). In a modeling study, Yan et al. (2005) estimated that soil moisture change-induced pulse emissions accounted for 4% of global annual NO$_x$ emissions. However, since continuous measurements of nitrogen trace gas fluxes at daily or subdaily resolution are still scarce for tropical and subtropical ecosystems, it is not possible to make conclusive statements on the global importance of pulse emissions to annual fluxes.

Mechanistic modeling of pulse emissions associated with drying and rewetting events requires accurate simulation of moisture changes in different soil layers and complex shifts in utilisation of fast- and slow-cycling soil organic matter pools by microbes that take place during these events (Miller et al. 2005). Moreover, nitrogen trace gas emissions following rewetting are often retarded by several hours to 1–2 days, so daily or sub-daily simulations of both physical and biological processes are required to depict these events (Kiese et al. 2005).

Temporal heterogeneity is accentuated in agricultural relative to non-managed landscapes. Land management causes physical and biogeochemical disturbance of extreme magnitude and in pulsed events. Tillage inverts the soil up to a 25 cm depth, disrupting soil pore structure and aggregation (Aref and Wander 1998; Campbell and Zentner 1993; Mahboubi et al. 1993); soil environmental characteristics important for maintaining access to sufficient moisture and substrate for the bacteria and fungi responsible for soil organic matter (SOM) mineralization and denitrification (Chenu et al. 2001; Chenu and Tessier 1995). Tillage also redistributes SOM in the soil profile and increases its physical degradation, promoting higher mineralization rates (Holland and Coleman 1987; Lundquist et al. 1999; Wander and Traina 1996) and therefore the availability of carbon and nitrogen to microbes. Fertilization adds large amounts of biologically reactive nitrogen to the landscape (Smil 1999; Galloway and Cowling 2002) and is generally applied in 1–3 events. Sub-optimal crop growth following tillage, planting, and fertilization, leads to significant nitrogen loss as nitrogen gas or nitrate leaching, especially following late spring intense precipitation events (Li et al. 2002; McSwiney and Robertson 2005; Wagner-Riddle and Thurtell 1998). Harvest is a further pulse disturbance event, instantaneously removing plant nitrogen demand, leaving a de-vegetated landscape vulnerable to nitrogen loss during fall rains (Dobbie et al. 1999).

The pattern of crop rotation defines the longer temporal-scale heterogeneity of agricultural landscapes. Currently, dominant conventional rotations in temperate North American agroecosystems result in landscapes with 4–8 months of bare fallow annually. While nitrogen loss from these devegetated lands as pulsed nitrate additions to freshwater and estuarine systems has been well documented (David and Gentry 2000; Goolsby and Battaglin 2001; Rabalais et al. 2002), their aggregated contribution to nitrogen gas flux is less well quantified. Carbon availability and aerobic status are particularly important in determining the partitioning between nitrogen leaching and denitrification as well as between denitrification products N_2O and N_2 (Weier et al. 1993). Diversifying the rotations managed on the agricultural landscape, and increasing winter vegetative cover in particular, has the potential to increase SOM (Drinkwater and Snapp 2007; Puget and Drinkwater 2001) and increase nitrogen retention (Tonitto et al. 2006). While promoting increased vegetative cover has clear benefits for reducing eutrophication of aquatic systems, the net effect on terrestrial N_2O release has not been well quantified (Mosier et al. 1998). However, it is logical that a reduction of nitrogen availability for microbial turnover will result in a reduction of N_2O emissions (Mosier et al. 1998).

Spatial heterogeneity

Many studies have investigated how the factors influencing oxygen, nitrate and carbon availability come together to create hotspots in terrestrial environments (McClain et al. 2003). As discussed above, early work focused on characterizing hotspots at the scale of cm in the anaerobic centers of soil aggregates, along growing roots and in patches of labile organic matter. Later work focused on identifying hotspots at the field (e.g., 10–100 m) or landscape (1–10 km) scales (Robertson et al. 1988; Groffman and Tiedje 1989). At the field scale, the distribution of hotspots is affected by the distribution of soil types (Cambardella et al. 1994) and above and belowground plant biomass (Robertson et al. 1997) and by microtopography (Bruland et al. 2006). These factors influence the distribution of water and organic matter through effects on detritus (e.g., litter and dead wood) accumulation (Hafner and Groffman 2005) and soil organic matter. While most studies have focused on organic carbon as the energy source for denitrification, it is important to recognize that a variety of inorganic compounds (e.g., reduced iron, reduced sulfur, methane) can provide energy to support denitrification (Pedersen et al. 1991; Postma et al. 1991, Böhlke et al. 2007). These compounds are particularly important as a source of heterogeneity in subsurface environments. In Europe, coordinated studies of field- and landscape-scale denitrification in floodplain soils have identified soil moisture, temperature, and nitrate availability as important variables for continental-scale denitrification models (Pinay et al. 2007). All of the factors that influence the distribution of hotspots at the field scale are strongly affected by agricultural and urban land use change (discussed immediately below).

At the landscape scale, the focus has been on analysis of variation and interaction among ecosystems or landscape components, i.e., how discrete ecosystem units vary in space, and how flows of denitrification reactants create hot landscape elements (e.g., riparian zones) or hot interfaces between elements. There has been great recent progress in our ability to detect variation among landscape components relevant to denitrification with new remote sensing and modeling techniques, e.g., detection of canopy chemistry using multi-spectral remote sensing and modeling of "wet spots" in the landscape with ecohydrological models (Kulkarni et al. 2008). Analysis of interaction among landscape units to create denitrification hotspots is discussed later in this paper.

Modeling finer scale hotspots within landscape patches, however, remains a key challenge. The nexus of water, labile carbon and nutrients at the scale of cm e.g., along roots, within subsurface soil aggregates or as part of microtopographic variation in accumulated detritus are not explicitly included in terrestrial models of denitrification. Nor is it feasible to directly measure the fine-scale heterogeneity of these variables in multiple landscape patches. Many of the processes discussed as 'hot moments' are also linked to fine-scale 'hot spot' formation. In freeze-thaw cycles, for example, the spatial redistribution and concentration of nutrients plays a key role in creating pulses of N_2O. Given that these fine-scale hotspots may make significant contributions to patch scale fluxes, there is a strong need to develop methods to quantify the factors that account for spatial distributions and co-distributions of environmental conditions and nutrient availability within patches.

Relative to unmanaged ecosystems, agricultural systems appear to be spatially homogeneous landscapes. While the agricultural landscape is in many ways amenable to simplification in modeling studies, temporal and spatial heterogeneity in the soil environment as well as management decisions warrant consideration as important drivers of net landscape-scale denitrification and nitrogen gas flux across agricultural lands. Indeed, agroecosystem management influences all of the soil environmental properties that influence denitrification in ways that create either hot or cold spots for denitrification. Within a field, vegetation cover is dominated by the planted crop. Spatially, plant cover is distributed in rows resulting in a soil environment that alternates between a dense rhizosphere and bulk soil, a distribution in stark contrast to the rhizosphere of wild vegetation (Jackson and Koch 1997). This bimodal distribution, as well as soil compaction by heavy machinery, strongly influences soil biota and activity (Smith and Tiedje 1979; van Elsas and van Overbeek 1996), including N_2O emissions (Flessa et al. 2006). Biota are abundant in the rhizosphere soil due to greater access to organic carbon (Cheng et al. 1996), while the bulk soil is often a C-limited environment (Koch et al. 2001; Rouatt et al. 1960). The biota influence soil structure via macropore development associated with burrowing and root growth (Thorup-Kristensen 2001), as well as aggregate formation (van Elsas and van Overbeek 1996; Angers and Mehuys 1989; Haynes and Beare 1997).

Many agricultural fields are underlain by artificial drainage networks to facilitate removal of water from the root zone. This drainage strongly influences spatial and temporal patterns of soil moisture and denitrification in the landscape. Variation in drainage paths and lack of plant cover, combined with intense spring rains can result in significant ponding in agricultural lands during times of high concentrations of available nitrogen in soil. Model simulations show that these ephemeral events can account for the majority of annual nitrogen gas loss (Tonitto et al. 2007a). These model results are supported by event-based nitrogen gas flux sampling which demonstrates extremely high flux when precipitation follows a fertilization event (Dobbie and Smith 2001; Li et al. 2002; Wagner-Riddle and Thurtell 1998).

At whole-farm, watershed, or landscape scales, crop rotation significantly contributes to the extent of spatial heterogeneity. The dependence of the North American livestock industry on corn- and soybean-derived feed, rather than perennial grasses, results in an agricultural landscape dominated by these commodity crops. These uniform landscapes are especially susceptible to nitrogen loss when erratic climate events coincide with tillage, planting, or fertilization. Additional manifestations of modern livestock production systems are feedlots that are hotspots of reactive nitrogen with their high concentrations of animals and nitrogen-rich wastes.

In urban environments, built or other human altered structures may act as hotspots for denitrification.

These structures include detention basins (which are specifically engineered to capture water, nutrients, and organic matter), drainage ditches and gutters. Denitrification rates in detention basin soils in Phoenix, Arizona, USA were much higher than rates in natural southwestern desert ecosystems (Zhu et al. 2004). Since these detention basins are designed to drain either directly to streams or to groundwater, if denitrification and plant uptake do not remove all nitrate inputs, these structures will still serve as nitrate sources in the urban landscape. Wastewater treatment plants and constructed wetlands are other urban structures that can be specifically engineered to be hotspots of denitrification (Boustany et al. 1997; Baker et al. 2001; Meyer et al. 2005; Faulkner 2005). Urban built structures also include gutters, ditches, and lawns which are not specifically designed to capture water, nutrients, and organic matter but in many cases do this inadvertently (Kaye et al. 2006). The confluence of these three controlling factors on denitrification in many urban built structures suggests that these structures may function as hotspots already, and hold promise for engineered approaches that can promote denitrification while sustaining their hydrologic functions (Kaye et al. 2006; Groffman and Crawford 2003).

Urban ecosystems are often associated with invasions of exotic plant and animal species (Pickett et al. 2001). Several studies have evaluated the effects of invasive plants on denitrification with equivocal results. Windham and Ehrenfeld (2003) found higher rates of denitrification under stands of invasive *Phragmites australis* compared to native *Spartina patens* in a brackish marsh, but Otto et al. (1999) found no differences under invasive *Phragmites* and *Lythrum salicaria* compared to native *Typha angustifolia* in a freshwater marsh. Most studies of biogeochemical impacts of invasives have not looked at denitrification rates (Ehrenfeld 2003), but many have quantified higher rates of litter decomposition (Allison and Vitousek 2004; Ashton et al. 2005; Funk 2005) and nitrogen mineralization and nitrification (Ehrenfeld et al. 2003a; Rice et al. 2004; Hawkes et al. 2005) under invasives. These changes indicate increases in soil nitrogen availability (Rice et al. 2004; Yelenik et al. 2004; Lindsay and French 2005) that could facilitate denitrification hotspots, especially in the case of nitrogen fixers that invade systems with few existing, native N-fixing species (Rice et al. 2004; Yelenik et al. 2004). Even fewer studies have quantified the effects of invasive, exotic animal species on denitrification rates, although some studies have demonstrated that several species, including earthworms in forests (Bohlen et al. 2004), zebra mussels in lakes and rivers (Strayer et al. 1999), and snails in streams (Hall et al. 2003) increase rates of nitrogen cycling processes. Insect species may increase nitrogen availability by converting leaves to frass, e.g., gypsy moths (Lovett et al. 2002), or by increasing concentrations of nitrogen compounds in throughfall, e.g., hemlock stands invaded by hemlock woolly adelgid (Stadler et al. 2005). Few studies have been carried out in urban systems, although Groffman et al. (2006c) did find higher rates of nitrogen cycling and leachate loss in an urban, forested plot which contained more invasive, exotic plant species than less invaded urban plots. More research is necessary to determine whether invaded urban systems are hotspots or cold spots of denitrification at a magnitude that would impact whole watershed nitrogen budgets.

Modeling terrestrial hotspots and hot moments using existing models

Mechanistic terrestrial nitrogen cycle models derive their core mathematical description of flux between nitrogen redox states from biogeochemical process rates observed in controlled experiments conducted using soil cores or field plots (Li et al. 1992; Parton et al. 1987, 1996; Tague and Band 2004). Due to the microbial mediation of the nitrogen cycle, most modeling approaches include temperature and moisture controls on nitrogen process rates (Li et al. 1992, Parton et al. 1987, Tague and Band 2004). The description of the hydrological cycle varies widely across models (Arnold et al. 1994; Gassman et al. 2003; Li et al. 1992; Parton et al. 1987, 1996; Tague and Band 2004; Youssef et al. 2005), and is potentially the greatest source of difference in model outcomes. Central to all terrestrial biogeochemical modeling approaches is the assumption that functional relationships derived from soil core and field plot scale experiments apply at the landscape scale and that dynamic moisture and temperature controls (as determined by site-specific climate and soil texture) sufficiently capture differences between laboratory and field conditions. While it is reasonable to assume biogeochemical processes are the same in the laboratory and the field, in practice, capturing field-scale variation in the soil environment is a daunting task largely ignored in model application. Current widely applied models of the terrestrial nitrogen cycle operate on homogenized landscapes (Arnold et al. 1994; Gassman et al. 2003; Li et al. 1994; Parton et al. 1996) using average site parameters for soil properties and biogeochemical process rates as well as spatially averaged moisture and temperature conditions. These average properties might be used to describe a 100 ha field, or an entire county or watershed. In contrast, field studies have demonstrated that nitrogen flux is highly variable at the field-scale (Clemens et al. 1999; Mathieu et al. 2006). Baker et al. (2007) found map resolution to be a major factor affecting the outcome of nutrient retention models, and argue for the inclusion of high resolution flow path analyses in watershed models. However, sufficient data to adequately parameterize models of high resolution hydrologic flowpaths is rarely, if ever, available (Kirchner 2006).

Model studies of nitrogen dynamics in agricultural systems are generally bounded by known system nitrogen inputs via fertilization and deposition, and nitrogen export in crop yield and nitrate leaching. Though current nitrogen cycle models generally ignore field-scale variation, model outcomes approximate measured patterns of nitrogen export in yield and nitrate leaching (Chung et al. 2001; Du et al. 2005; Li et al. 2006; Tonitto et al. 2007b). However, there are few long-term studies of nitrogen gas flux from agricultural or natural systems and it is rare to find sites with both nitrate leaching and nitrogen gas flux measurements. As a result, model performance is rarely constrained by known nitrogen gas flux or soil nitrogen storage measurements. Model partitioning of nitrogen movement to the atmosphere from soil pools is a significant uncertainty in nitrogen cycle model outcomes. For the cases where we believe our simulations adequately reflect measured values, are we getting the ‘right’ answer because our model accurately captures the distribution of processes, and in particular fine scale hotspots, on the landscape?

Model sensitivity to spatial heterogeneity is relevant when simulating field, farm, or landscape-scale nitrogen dynamics. When simulation model structure does not allow for dynamic representation of spatial variation, multiple simulations can be compared to quantify the importance of spatial diversity. Simulations can be used to consider: 1) environmental property heterogeneity, such as soil texture, porosity, and hydraulic conductivity; 2) diversity of land management, including crop rotation, tillage, and amendment practices; 3) nutrient inputs and exports across the study boundary, such as manure application, crop export, nitrogen volatilization from agricultural lands, patterns of nitrogen deposition from fossil fuel burning, or nitrogen export to waterways. Models of terrestrial carbon and nitrogen cycles are commonly extremely sensitive to soil textural classification (Li et al. 1992; Parton et al. 1987). Soil texture varies within a field, as well as at the landscape scale. Bounding model outcomes across all common soil textures in a landscape, rather than using an average texture, will bound the full range of nitrogen dynamics. Related to soil texture is the consideration of variation in soil porosity and hydraulic conductivity, properties which control water flux and therefore optimal conditions for denitrification.

Questions about “getting the right answer” from spatially lumped models suggest that a clear frontier topic, essential to accounting for hotspot phenomena in models, is the incorporation of spatial heterogeneity into sampling designs and models (Robertson 1987; Lennon 2000). Non-spatial sampling methods and models assume that variability is random, whereas spatial analyses attempt to separate variability due to spatial structure from random variability (Ver Hoef 2002). Wider application of spatial analyses may improve our ability to include hotspots in denitrification models, especially if we can apply new tools available for these types of analyses, such as distributed networks of environmental sensors, high-resolution databases of field- and remote-sensed data, and advances in computation and geostatistics (Burrough 2001; Clark et al. 2001; Legendre et al. 2002). Yet spatially explicit analyses in ecological studies bring additional complexity, parameters, and thus potential sources of errors (Peters and Herrick 2004). Whether and how to incorporate these approaches into experimental designs depends in part on ecosystem characteristics. The magnitude and causes of the spatial heterogeneity strongly influence how variability can be addressed at different spatial scales (Levin 1992; Parkin 1993; Wagner and Fortin 2005).

Interestingly, terrestrial and aquatic ecosystems generally are abstracted and modeled differently, with less emphasis on connectivity and flowpaths between landscape patches due to the more static nature of soils compared to the dynamics of flowing water (McClain et al. 2003). In terrestrial ecosystems, the landscape is generally represented as a mosaic of contiguous polygons or grid cells, with point- or area-referenced data (Perry et al. 2002). Aquatic ecosystems are driven by hydrologic and topographic gradients and dominated by lateral connections and fluxes, such that dynamic, spatially referenced models are more common (Burrough 2001; Boyer et al. 2006). This broad distinction between model representations of land and water helps us address the issue of spatial heterogeneity in denitrification in these environments.

A non-spatial approach may be valid in many cases, including the following: (1) for larger areas, where variability in denitrification can decrease with increasing extent of measurement (Groffman et al. 1987); (2) for apparently homogenous areas without major lateral fluxes or internal environmental gradients (e.g., Van Hoewyk et al. 2000); and (3) when the spatial distribution of predictor variables is too expensive to measure (Peters and Herrick 2004). Many field-scale and ecosystem models adopt the spatially implicit perspective, with empirically or mechanistically derived equations driven by georeferenced input parameters measured on a grid (e.g., Burke et al. 1997). This category also encompasses field studies along gradients, such as toposequences and transect approaches (e.g., Davidson and Swank 1986; Groffman and Tiedje 1989; Pinay et al. 1993; Silver et al. 1994). Distributed applications of one-dimensional models of terrestrial denitrification (reviewed in Boyer et al. 2006) could prove fruitful. Indeed, DRAINMOD-GIS is the result of coupling a watershed-scale model to a geographic information system (GIS) to predict nitrate losses from drained lands (Fernandez et al. 2006). DRAINMOD-N II, which is a related but more complex representation of the nitrogen cycle, could also be adapted to function in a spatially implicit GIS framework (Youssef et al. 2005). DNDC and DAYCENT are examples of other denitrification models that could be applied in a spatially distributed GIS framework, because lateral connections within the grid and neighborhood effects (effects of nearby grid cells on a particular cell) are not represented in these models. The advantage of the spatially implicit application would be that more accurate spatial maps and extrapolations of denitrification over the area of interest might be achieved.

Spatially explicit models include neighbor effects, which are important when there are large fluxes of materials with locally mediated, variable transfer rates (Peters and Herrick 2004). Geostatistical methods and certain hydrologic models fall into the category of spatially explicit models. Hydrologic simulation models such as RHESSys (Band et al. 2001) that route water and materials across the landscape based on digital elevation models and soil characteristics are especially relevant where there are significant topographical and hydraulic gradients in surface and subsurface flow (Poole et al. 2004). Both geostatistical and hydrologic simulation models require intensive sampling and large datasets for parameterization; this has been a major limitation to their wide adoption in ecological research (Peters and Herrick 2004).

To select the appropriate modeling approach, trade-offs between sources of error inherent in spatial and nonspatial models should be considered (Peters and Herrick 2004). Simple models are prone to errors of omission (key parameters are missing), while more complex models with many parameters (and associated uncertainties) tend to yield errors of commission through error propagation (Peters and Herrick 2004). Spatial models (implicit and explicit) may be preferable when the following conditions exist: (1) non-linear processes; (2) threshold responses; (3) positive feedbacks; and (4) neighborhood interactions (Peters and Herrick 2004). When viewed through this framework, modeling denitrification would appear to benefit from spatially dependent modeling because spatial interactions, such as lateral hydrologic fluxes, and non-linear responses to changes in substrate availability commonly influence denitrification rates.

In contrast to the situation with hotspots, fine-temporal scale climate data are increasingly available to support the modeling of hot moments. In general, terrestrial ecosystem models are designed to track the temporal complexity of climate and management cycles. Models can be run at higher temporal resolution to include fine-temporal scale climate data. However, fine-temporal scale management changes farmers make depending on localized weather and field conditions will remain difficult to generalize. As nitrogen models are increasingly applied to understand N dynamics in response to a variable climate, we can use simulations to test the sensitivity of modeled nitrogen flux to: (1) the frequency and magnitude of precipitation and irrigation events, (2) the proximity of precipitation to fertilization and tillage events, (3) the benefits of dividing fertilizer applications across multiple events, (4) the occurrence of extreme climate and (5) variation in crop growth. Rigorous consideration of model sensitivity to these and other episodic events, e.g., freeze/thaw events and dry/rewet cycles will expand our ability to characterize the true distribution of nitrogen pools and fluxes, as well as bound model uncertainty.

The importance of ephemeral conditions to annual nitrogen flux was observed in simulations of corn-soybean rotations of the US Corn Belt. Simulation using the DNDC model showed that the highest nitrogen gas flux events coincided with poor crop growth early in the growing season (Tonitto et al. 2007a). In this agroecosystem, the extent to which there is a mismatch of nitrogen availability and crop uptake drives the actual rate of nitrogen flux. At the landscape-scale, variation in crop growth is spatially patchy and these processes are acting over short time scales (days). Both simulation modeling and event-based field sampling suggest that a significant proportion of the annual nitrogen gas flux can occur over the course of days.

Terrestrial/aquatic boundaries as hotspots

Boundaries between land and water have received lots of attention as landscape-scale hotspots of denitrification. It is convenient to distinguish between "riparian" boundaries where the direction of flow is from the land to the water (Fig. 4) and "hyporheic" boundaries where the direction of flow is from streams into the terrestrial environment. Riparian zones are potential hotspots for denitrification of NO_3^- moving from upland land uses, especially agriculture, while hyporheic zones are potential hotspots for denitrification of NO_3^- moving in streams.

Hyporheic zones can process significant amounts of the water, C and N in a stream (Boulton et al. 1998; Fisher et al. 2005). Many studies have characterized dynamic gradients of dissolved oxygen, NO_3^- and dissolved organic carbon availability along upwelling

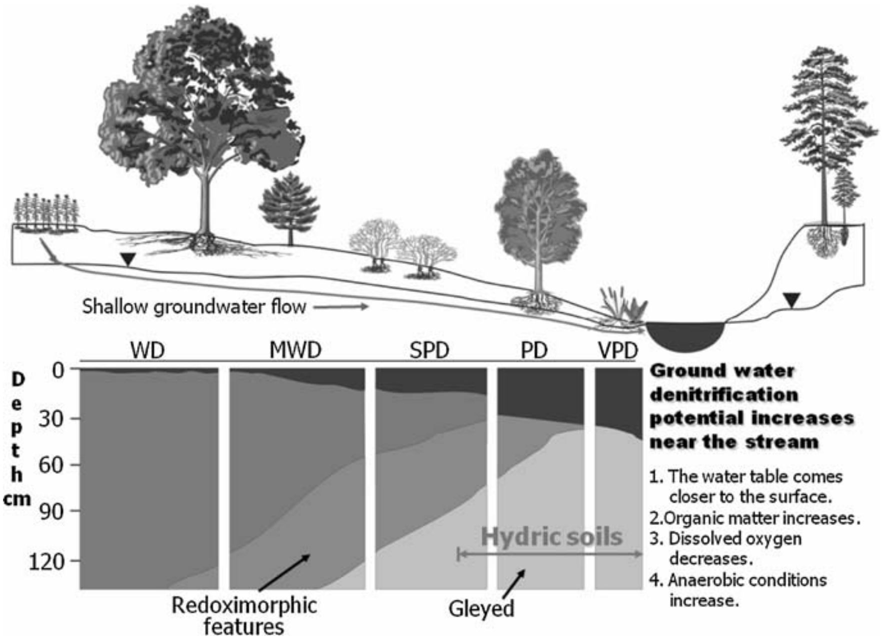


Fig. 4 Cross section of a riparian zone showing how flow paths and soil properties converge to create a denitrification hotspot at the interface between terrestrial and aquatic components of a landscape. Denitrification of nitrate moving in shallow groundwater from the upland agricultural field will be denitrified when it interacts with denitrifiers in poorly (PD) and very poorly drained (VPD) soils. The figure also illustrates that not all riparian zones are likely to function in the same way, i.e., the opposite side of the stream, dominated by well (WD), moderately well (MW) or somewhat poorly (SPD) soils is much less likely to function as a denitrification hotspot. Adapted from Gold et al. (2001)

and downwelling areas in hyporheic zones, suggesting that there are hotspots of denitrification within hyporheic zones, and that not all hyporheic zones will function as hotspots of denitrification within stream ecosystems and landscapes (Jones and Holmes 1996; Hedin et al. 1998; Hill et al. 1998; Sobczak and Findlay 2002; Sobczak et al. 2002). The functional significance of hyporheic zones is ultimately controlled by their hydrologic "connectivity" with the stream channel (Boulton 2007; Kaushal et al. 2008), which varies markedly within and between streams, and is sensitive to environmental changes, e.g., hydrologic regime, land use in the watershed.

Riparian zones can be broadly defined as semi-terrestrial areas regularly influenced by freshwater, and normally extending from the edges of water bodies to the edges of upland communities (Naiman et al. 2005). Because of their potential role as nitrogen sinks, protection of riparian zones is widely recommended as a best management practice by federal and local agencies around the world to mitigate the impact of nitrate pollution from agriculture on stream water quality (Welsch 1991; Hill 1996; Lowrance et al. 1997; Dosskey 2001; Puckett 2004; Naiman et al. 2005). Multiple studies have reported nitrate removal efficiencies >90% in the USA (Maryland, Georgia, North Carolina, Pennsylvania, Rhode Island, Illinois), New Zealand, Switzerland, France, Spain, Denmark and Canada (see reviews in Hill 1996; Vidon and Hill 2006). In many instances, most nitrate removal occurs within 10–20 m from the field-riparian boundary (Haycock and Pinay 1993; Lowrance et al. 1984; Peterjohn and Correll 1984; Böhlke et al. 2002) or abruptly at the interface of highly conductive sediment layers with organic rich deposits (e.g., peat, buried channel sediments) (Devito et al. 2000; Hill et al. 2000). In a comparative study of riparian zones in Canada, France, Denmark, Switzerland, Spain and the United States (Georgia, Maryland, Oregon), Vidon and Hill (2006) report that unless riparian sediments are coarse sand and/or gravel, 90% nitrate removal is often achieved in less than 20 m in most riparian zones. Research also suggests that although riparian zones may only represent a small area of the landscape, they are perhaps one of the most important elements of the hydrological landscape given that they can act both as a conduit and barrier for nutrients between upland communities and stream ecosystems (Burt 2005) and that nitrate concentration in subsurface flow often decreases dramatically in the riparian zone (Peterjohn and Correll 1984; Lowrance 1992; Haycock and Pinay 1993; Jordan et al. 1993; Gilliam 1994; Hill 1996).

Although nitrate removal and denitrification can vary tremendously between sites depending on local conditions (Peterjohn and Correll 1984; Brusch and Nilsson 1993; Jordan et al. 1993; Gilliam 1994; Hill 1996), research suggests that overall, riparian zones are often hotspots for nitrogen removal in the landscape. Nevertheless, the cumulative effect of riparian zones on nitrogen removal at the watershed scale remains poorly understood. The role of a riparian zone as a nitrogen sink in the landscape indeed depends on the amount of nitrogen ($\mathrm{g\ day}{-}^{1}\ \mathrm{m}^{2}$) removed daily compared to other landscape units such as streams, lakes, agricultural and forested soils, and on the temporal and spatial variability of nitrogen removal in riparian zones for an entire watershed. In addition, both the amount of nitrogen transported through the riparian zone and the nitrogen removal efficiency of the riparian zone must be taken into account to estimate the potential impact of a riparian zone on water quality at the landscape scale. For instance, one riparian zone may have a high nitrate removal efficiency but fluxes may be very small or seasonally absent, while another may display a lower efficiency but receive high nitrate loading throughout the year and therefore be a larger nitrate sink at the watershed scale (Table 1, Vidon and Hill 2004). The fate of nitrogen within the riparian zone is also important. While nitrogen converted to gas is removed from the system, nitrogen taken up by plants and microbes is available for recycling and release at a later time. The environmental effects of riparian zones also depend on the ratio of gases produced during denitrification, i.e., N_2O is a potent greenhouse gas. It is therefore crucial to develop strategies to estimate the spatial and temporal variability in nitrogen removal in riparian zones and the cumulative effect of individual riparian zones on water and air quality at the watershed scale.

Recent advances in our understanding of the hydrological and biogeochemical functioning of riparian zones have shown that landscape hydrogeomorphic characteristics can be used as indicators of the potential of riparian zones for nitrogen removal at the landscape scale (Lowrance et al. 1997; Hill 2000; Gold et al. 2001; Rosenblatt et al. 2001; Vidon and Hill 2004). In a recent comparative study, Vidon and

Table 1 Water and nitrate inputs per meter of riparian perimeter and nitrate removal at eight riparian sites in Ontario, Canada

Site name	Water input ($L\ day^{-1}$)	Nitrate input ($g\ N\ day^{-1}$)	Nitrate removal ($g\ N\ day^{-1}$)	Duration of upland/riparian connection (months)
Eramosa	390	4.2	4.1	12
Boyne	320	9.4	8.7	12
Road 10	34	1.5	1.5	12
Speed	52	0.27	0.26	12
Maskinonge	74	1.3	1.29	12
Ganatsekiagon	218	3.4	2.0	7–9
Highway 27	20	0.11	0.11	6–8
Vivian	0.67	<0.001	–	5–7

The duration of the upland-riparian hydrologic connection per year is also indicated for each site. Variation in all parameters shows the spatial and temporal complexity of riparian hotspot behaviour. From Vidon and Hill (2004)

Hill (2006) showed that riparian zones that are large nitrogen sinks at the watershed scale have large amounts of water flowing through them (300–1,200 $L\ day^{-1}\ m^{-1}$ of stream length), sufficient organic matter pools to sustain denitrification, and high nitrate concentration entering the riparian zone under anaerobic conditions. Riparian zones located in outwash valleys where organic matter has accumulated and where a confining layer (low hydraulic conductivity sediment layer, $Ks < 10^{-6}$ cm/s) forces nitrate rich groundwater to interact with organic rich sediment layers (e.g., peat, buried river channel sediments) often fall in this category. Amounts of nitrogen removed daily in these riparian zones are typically between 4 and 10 $g\ N\ day^{-1}\ m^{-1}$ stream length (Vidon and Hill 2004). This rate can be easily converted into $g\ N\ day^{-1}\ m^{2}$ based on riparian zone width, if necessary for model applications.

At the other end of the spectrum are riparian zones that have little to no effect on nitrogen removal at the watershed scale, or that even act as a nitrogen source to the stream (cold spots). Riparian zones in the former category typically have low groundwater fluxes owing to a low hydraulic gradient and/or a low soil hydraulic conductivity (nitrogen removal is then transport limited). For instance, Wigington et al. (2003) report low water (12 $L\ day^{-1}$ meter stream length) and nitrate (0.03 $g\ N\ day^{-1}\ m^{-1}$ stream length) fluxes in a riparian zone on nearly level clay terrain in Oregon. Vidon and Hill (2004) report similar small water and nitrate fluxes in a nearly flat riparian zone in a glacial till landscape in southern Ontario. Riparian zones in this category have little impact on nitrogen removal at the watershed scale owing to the small amount of nitrogen removed daily. Riparian sites which act as N sources include riparian zones where nitrogen rich groundwater bypasses the riparian zone at depth owing to deep riparian sediments with low organic matter content and high hydraulic conductivity. For instance, Puckett et al. (2002) report results for a riparian zone in Minnesota, USA where sand overlies a confining unit 16 m deep and groundwater with considerable nitrate concentration is able to move along flowpaths under the riparian zone to the river with limited nitrate removal. Similarly, on the Delmarva Peninsula in Maryland, USA, nitrate-rich groundwater flowed at depth in a thick sand aquifer beneath a riparian area and discharged upward through the stream bed (Böhlke and Denver 1995).

Some riparian zones may also be sources or sinks of nitrogen in the landscape depending on local conditions at the time of measurement. Riparian zones that typically have close to a 100% nitrate removal efficiency most of the year can have cold moments, i.e., moments when the riparian zone efficiency decreases dramatically, and the riparian zone becomes less of a sink or even a source of nitrogen in the landscape. For instance, Wigington et al. (2005) report that nitrate rich water in overland flow bypasses a riparian zone with clay soil in Oregon, USA during storms. Vidon and Hill (2004) reported that nitrate removal dropped from >90 to 60% as the water table rose and groundwater fluxes increased from 1.8 to 244 $L\ day^{-1}\ m^{-1}$ of stream length in a riparian zone in southern Ontario. In that riparian zone, a gravel layer near the soil surface allowed water to bypass organic rich sediment in the riparian zone during episodic high water table periods. Cirmo and McDonnell (1997) reported that in some forested catchments, seasonal water table drawdown can stimulate mineralization of organic nitrogen in surface soils which results in nitrogen input to the stream.

Hydrogeomorphic characteristics related to geologic setting and hydrologic flowpaths can be helpful in generalizing riparian zone functions. Landscape hydrogeomorphic characteristics can often be mapped (Gold et al. 2001; Rosenblatt et al. 2001) and hotspots for nitrogen removal can therefore potentially be represented in spatially explicit models of nitrogen cycling at the watershed scale (discussed below). The total amount of nitrogen removed by riparian zones in a watershed could also be estimated based on the hydrogeomorphic characteristics of the landscape. By applying hydrogeomorphic mapping to riparian zone modeling we can estimate the relative potential of riparian zones to remove nitrogen at the watershed scale compared to other landscape units such as streams, lakes, forest or agricultural soils. Ultimately, such work could drive model development and help modelers focus efforts on areas of the landscape with the most potential for nitrogen removal. One complication is that land use change can affect hydrology and therefore N cycling processes such that landscape-scale hydrogeomorphic characteristics are no longer accurate predictors of denitrification (Stander and Ehrenfeld 2008).

The interface between terrestrial and aquatic ecosystems is strongly affected by land use change. In urban and suburban watersheds, high storm flows erode streambanks and incise stream channels, thus drawing down water tables in riparian wetlands. Urban wetlands display high rates of net nitrification as a result of lower water tables (Groffman et al. 2002; Ehrenfeld et al. 2003b; Stander and Ehrenfeld 2008). Stander and Ehrenfeld (2008) found lower rates of denitrification in urban wetlands with dry and/or flashy hydrology compared to wetlands with normal hydrology. These results suggest that urban wetlands may function as denitrification "cold spots" in urban landscapes. However, Groffman and Crawford (2003) did find high rates of potential denitrification in urban riparian zones, suggesting that if normal hydrological regimes could be restored to these systems, denitrification would likely occur.

Ecosystems dominated by human settlements are engineered to move water off landscapes quickly before flooding of heavily trafficked areas can occur. Rainfall is channeled from impervious surfaces directly to streams, dramatically altering the flow of water and denitrification reactants across the landscape (Paul and Meyer 2001). Urban wetlands and streams display flashy hydrological patterns (Ehrenfeld 2000; Ehrenfeld et al. 2003b), characterized by low baseflow and low water tables between rain events punctuated by episodic high flow and flood events during even relatively small rainfall events. Thus urban storm events may move water and NO_3^- across the landscape too quickly to allow for denitrification to occur. However, in some areas, especially in the arid Southwest, storm water management is increasingly focused on retaining water within landscapes rather than enhancing drainage to surface waters, as is the focus of storm water management in humid urban systems (Baker et al. 2001; Zhu et al. 2004). Conserved water is often used for irrigation, causing soils in urban parks, detention basins, and residential grassy areas to be wetter than natural desert soils, and therefore have higher capacity for denitrification.

Incorporating interface hotspots into models

The spatial interaction between and within land parcels is a defining landscape characteristic with limited representation in models. Many terrestrial models account for nitrogen export from terrestrial landscapes to freshwater and marine systems but do not incorporate lateral redistribution of water, nitrogen and carbon within the terrestrial landscapes. In these models, the coupling of the pedosphere, lithosphere and hydrosphere only occurs through net nitrogen loss below the rooting zone or through surface runoff. Riparian and hyporheic hotspots typically occur due to lateral redistribution of water and nutrients as the result of topographic convergence of flowpaths within a terrestrial environment. To account for these landscape scale hotspots, within watershed lateral redistribution must be included within models. Spatially distributed hydrologic models account for lateral redistribution, but few of these models incorporate linkages with nitrogen cycling. The RHESSys model (Tague and Band 2004) is one example of a coupled ecosystem-hydrologic model that explicitly considers hydrologic exchange between land parcels.

While ecohydrological models such as RHESSys show promise for characterizing hotspots that arise from lateral redistribution of denitrification reactants in the landscape, accounting for the emergence of hotspots due to flowpath convergence, however, remains challenging (Beven 2001, 2006; Richardson et al. 2007). Many studies have demonstrated that accurate prediction of streamflow by distributed hydrologic models does not necessarily mean that internal hydrologic processes (including spatial distributions of soil moisture, internal connectivity, surface—groundwater interactions) are accurately represented (Grayson and Blosch 2000; Kirchner et al. 2000). A parallel conclusion can be made about the limits of relying on aggregate watershed fluxes such as nitrogen loss to the stream for the validation and parameterization of terrestrial denitrification models since these rely on the distribution of internal watershed conditions. Recent advances within hydrology apply remote sensing of soil moisture (Moran et al. 2004) and isotopic tracers (Vitar et al. 2005), allowing for better constraint of model representation of within-watershed moisture redistribution and flowpaths. Linking advances in spatially distributed hydrologic modeling with nitrogen cycling models should improve estimates of terrestrial denitrification and should improve the ability of these models to account for landscape scale hotspots that occur as a result of lateral moisture fluxes.

Hotspots and hot moments in aquatic ecosystems

Water has been described as the primary driver of “hotspots” in biogeochemical cycles because it can transport important constituents across landscapes and provide ideal conditions for nutrient transformations (McClain et al. 2003). Regardless of the environment, denitrification is influenced mainly by temperature, oxygen concentration, and the supply of organic matter and nitrate. With this in mind, aquatic systems in general could be considered “hotspots” of denitrification activity because they often have high nitrate concentrations, plentiful organic matter, and anoxic conditions in sediments or in micro sites within suspended particulate matter (Galloway et al. 2004).

It is not our purpose here to describe all of the factors affecting denitrification in aquatic systems; that has been done elsewhere (i.e., Seitzinger 1988; Hebert 1999; Seitzinger et al. 2006). But a brief review of major factors may be useful in order to understand what might create hotspots and hot moments. Temperature has been shown to correlate with denitrification rates, especially when nitrate is not limiting (Smith et al. 1985; Hebert 1999). In some cases, nitrate concentrations are dependent on episodic inputs like the spring freshet or storm run off from agricultural land. In these cases denitrification rates do not respond in a simple linear or exponential fashion with temperature (Sorensen et al. 1979). In many systems, a decrease in water column oxygen concentration is concurrent with warming water temperature. At first, one might assume this would increase rates of denitrification. But in systems where denitrification is tightly coupled with nitrification, low oxygen conditions reduce the amount of available nitrate and thus reduce denitrification. For example, Jenkins and Kemp (1984) showed that in the Patuxent River Estuary, the majority of nitrate from nitrification was denitrified in the spring, with denitrification rates experiencing a two order of magnitude decrease during summer. Over the course of a season, then, one area can switch from being a hotspot to being a cold spot of denitrification.

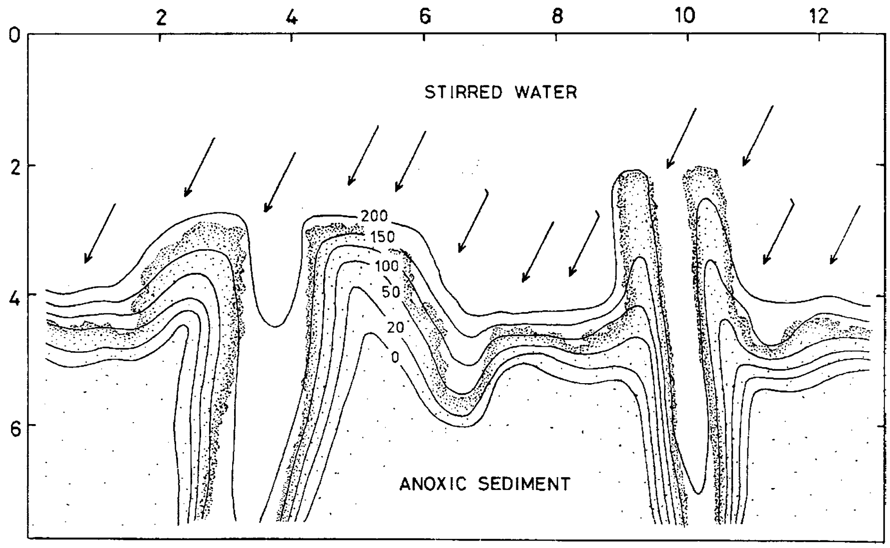
Organic matter is a known regulator of denitrification rates in both freshwater and marine systems (e.g., Tiedje et al. 1982; Caffrey et al. 1993; Seitzinger and Giblin 1996; Cornwell et al. 1999; Fulweiler et al. 2007). Rysgaard et al. (1998) reported that after the break-up of sea-ice in Young Sound, Greenland, benthic metabolism was rapidly stimulated by a significant peak in the sedimentation of organic matter. When sea-ice covered the sound, denitrification was approximately 0.2 mmol m^{-2} day^{-1} but it quickly jumped to 0.6 mmol m^{-2} day^{-1} when the sea ice broke apart. During the period of rapid increase, denitrification was largely supported by nitrate from sediment nitrification (Rysgaard et al. 1998). Episodic inputs of carbon stimulate denitrification in freshwater systems as well. A winter ice-storm struck the Hubbard Brook Experimental Forest in New Hampshire, USA, in January of 1998 causing extensive damage. While nitrate export from the watershed did increase, it is thought that the nitrate export would have been even greater were it not for in-stream processing. Specifically, nitrate removal by denitrification may have been stimulated by the large inputs of organic matter in the form of woody debris into the stream (Bernhardt et al. 2003).

An essential difference between fresh and marine sediments is the dominant mode of organic carbon metabolism (Seitzinger 1988). Anaerobic metabolism is dominated by sulfate reduction in marine sediments and by methanogenesis in freshwater sediments (Capone and Kiene 1988; Schelsinger 1996). The end product of sulfate reduction (sulfide) is a known inhibitor of nitrification. On the other hand, sulfide can be an energy source to support denitrification (Burgin and Hamilton 2007). Therefore, in systems where coupled nitrification-denitrification is dominant, sulfide could play a critical role in regulating denitrification rates. Joye and Hollibaugh (1995) found that sulfide reduced nitrification rates by 50–100% in estuarine sediments.

Macrophytes and benthic algae are also known to influence nitrogen transformation dynamics. Macrophyte root and rhizome systems (i.e., eelgrass) can trap organic matter, thus providing a rich site for denitrification. In addition, dissolved organic carbon exudates from the roots can stimulate denitrification (Christensen and Sorensen 1986). By releasing oxygen, root and rhizome systems can stimulate nitrification and ultimately indirectly stimulate denitrification by increasing substrate availability (Iizumi et al. 1980; Hebert 1999). Benthic micro-algae in sub-tidal and inter-tidal environments can increase surface sediment oxygen concentrations, thus inhibiting denitrification during the day (Jørgensen and Sorensen (1985). Freshwater systems can be affected by similar processes. In algal mats growing in a stream, denitrification was lower in the light than in the dark (Triska and Oremland 1981; Seitzinger 1988). And a similar pattern found in Lake Hampen, Denmark was thought to be due to oxygen produced by benthic microflora (Christensen and Sorensen 1986). One might also expect that in systems which rely on coupled nitrification-denitrification, the increased oxygen could stimulate rates of nitrification during the day, perhaps leading to higher denitrification rates at night.

In both fresh and marine systems burrowing infauna can play an important role in nitrogen transformations (Seitzinger 1988 and references therein). Infauna can increase the rate of exchange of nitrate and oxygen between the sediment and the water column by burrowing into the sediment and by water pumping (Fig. 5). Nixon (1988) reported that compared to freshwater systems, marine sediments maintain larger populations of benthic fauna that increase sediment mixing and lead to a more complete degradation of organic matter in these systems. The increase in oxygen penetration associated with burrowing can stimulate nitrification, while the increase in nitrate stimulates denitrification. In addition, the infauna concentrate organic matter in the sediment by depositing fecal pellets (Hebert 1999). Pelegri and Blackburn (1994) found denitrification was 1.5 times greater in microcosms with the amphipod *Corophium volutator* than in those without. For the Kertinge Nor estuary in Denmark, the overall denitrification rate

Fig. 5 Vertical section through a sediment surface. *Contour lines* indicate sediment oxygen isopleths (O_2, m mol L^{-1}) measured using an oxygen microelectrode. *Angled arrows* indicate direction of O_2 movement. *Numbers* on *x*- and *y*-axes indicate millimeters. Two polychaete worm tubes are evident. Adapted from Jørgensen and Revsbech (1985)



was decreased by the inhibitory effects of benthic microalgae (taking up ammonium and nitrate) and the stimulating effects of bioturbating benthic infauna (Rysgaard et al. 1995). Thus the seasonal distribution of infauna may create hotspots of denitrification activity.

Land use change can greatly alter spatial and temporal patterns of denitrification in aquatic systems. Agricultural, and especially urban, streams often display symptoms of reduced nitrogen retention capacity. While we expect high nitrate concentrations common in agricultural streams to stimulate denitrification (Inwood et al. 2005), agricultural and urban streams which are hotspots with respect to nitrate availability can have low denitrification rates due to low levels of organic matter (Arango et al. 2007). Meyer et al. (2005) found lower nutrient uptake velocity in urban streams close to Atlanta, Georgia, USA and Grimm et al. (2005) found longer nutrient uptake lengths in urban streams in Phoenix. However, Teissier et al. (2002) found higher denitrification rates in incubations of epilithic biofilms sampled downstream of wastewater treatment plant outflows in Toulouse, France compared to biofilms from an upstream reference station. Sediments in headwater streams in urban-dominated subwatersheds in southwestern Michigan, USA had higher rates of potential denitrification than streams in forested watersheds, but urban sediments removed a smaller percentage of the stream nitrate load than sediments from forested streams, suggesting that urban streams are not nitrogen sinks based on sediment denitrification alone (Inwood et al. 2005). Groffman et al. (2005) found high rates of potential denitrification in urban stream sediments associated with organic debris dams, suggesting debris dams as denitrification hot spots. However, debris dams may not remain in place very long, due to high flow volumes and velocities in urban streams during rain events. Along those lines, Hale and Groffman (2006) found that debris dams were most often found in urban streams which did not have incised channels. However, while the overall rates of denitrification may be higher in organic rich sediments, the much greater area of low organic matter pools and riffle sediments might make them important nitrate sinks (Groffman et al. 2005). In such cases, the “cold spots” might turn out to be just as important to overall stream denitrification as the “hotspots”.

Incorporating aquatic hotspots and hot moments into models

A search on the ISI Web of Science for “hotspots and/or hot moments” combined with “aquatic denitrification modeling” comes up empty. It appears that the idea of hotspots and hot moments has yet to be explicitly incorporated into modeling denitrification in aquatic systems. Perhaps this is because, as stated earlier, aquatic systems may be considered “hotspots” of denitrification in general. Aquatic denitrification models range from detailed sediment biogeochemical algorithms that highlight individual processes (Di Toro 2001) to larger scale empirically based statistical relationships (e.g., Seitzinger and Giblin 1996; Seitzinger et al. 2002). Many of the empirical and mechanistic models for rivers and lakes are based on only a few studies with limited seasonal and spatial coverage (Boyer et al. 2006). In addition, the same problems that plague denitrification measurements (i.e., technique limitations, large uncertainties, etc.) are transferred into the models. Nevertheless, as Boyer et al. (2006) point out, recent progress has been made in estimating denitrification based on the physical properties of streams, lakes, and reservoirs (Kelly et al. 1987; Dillon and Mollot 1990; Howarth et al. 1996; Seitzinger et al. 2002). Studies consistently link water residence time with nitrogen cycling—the longer the water has contact with the benthos the more nitrogen is removed through denitrification. In addition, small streams were the water volume is small relative to the benthic area appear to have greater nitrogen removal. Currently, most models do not include bacterial biomass, diversity, structure, or function. A recent study by Iribar et al. (2008) suggest that including the development and community structure of denitrifying bacteria may be a necessary step to understanding and successfully modeling biogeochemical dynamics.

According to Boyer et al. (2006), most aquatic denitrification models rely on two fundamental nitrogen loss rate expressions: reaction-rates and mass flux expressions. Reaction rate expressions usually rely on first order kinetics assuming that the rate of nitrogen loss is proportional to the concentration of N. The water quality model SPARROW (spatially referenced regressions on watershed attributes) uses a flow-dependent reaction rate expression to approximate nitrogen loss in streams (Smith et al. 1997; Boyer et al. 2006). Recent versions of SPARROW have also included mass flux rate expressions. In mass-flux models, the loss of nitrogen is described as a flux to the benthos. These expressions are most often used in empirical mass transport models that quantify denitrification and organic nitrogen burial in sediments of lakes and reservoirs (Boyer et al. 2006, and references therein).

Fennel et al. (this volume) discuss the importance of incorporating diagenetic processes into models of aquatic denitrification. Diagenesis, the sum changes to materials incorporated in sediments from physical, chemical, and biological processes, has important implications for our understanding of sediment denitrification. Diagenetic modeling focuses on understanding individual processes instead of the net result, and is thus probably the best possibility for including the concept of hotspots and hot moments in aquatic denitrification models.

Hotspots, hot moments and environmental decision making: a case study from the northeastern US

Incorporating hotspot and hot moment phenomena into denitrification models is not merely an academic exercise. Translating complex scientific understanding of variation and uncertainty for environmental decision makers is challenging. Yet our analysis above suggests that if we hope to manage nitrogen flows in the landscape to protect nitrogen-sensitive coastal ecosystems, there is a strong need for hotspot and hot moment phenomena to be considered and incorporated into management tools and local decision making.

In the northeastern US, local communities often control a host of decisions that can reduce risks to water quality and aquatic resources. Local issues, such as the location and density of residential developments, the extent and placement of shoreline buffers and the approaches selected for water supply and wastewater and stormwater treatment, warrant thoughtful consideration of watershed features to sustain ecological values. However, local decision making can be confounded by a lack of scientific expertise, a paucity of local data, an aversion to complex regulations, and a fear of lawsuits. Communities in rural areas and at the rural-urban interface typically have few professional staff trained in watershed management and water quality (Arnold 1999). These communities need tools that evaluate the extent and location of nitrogen sinks within their specific watersheds so that they can target best management practices (BMPs; e.g., intensive source controls or stream reach ecosystem restoration) in subwatersheds that lack nitrogen sinks. In subwatersheds with important nitrogen sinks, such tools can provide guidance to protect critical areas.

In addition to site-specific information, local decision makers need information on the effect of incremental decisions on larger scale dynamics. For example, Last (1995) found that rezoning decisions at the local level often occur incrementally, without a sense of the influence of the decision on the “big picture.” GIS and nonpoint source water quality models can help to clarify the water quality risks of land use decisions (Corwin et al. 1998). The challenge is to provide communities with information on their land and water resources that is relevant to the temporal and spatial scales associated with the scale of decision-making (Last 1995), which range from small individually owned parcels to subwatersheds and aquifer recharge areas of >400 ha.

In the past decade, there has been a great increase in the emergence of high resolution geospatial data that is available for public use. At the same time, GIS software has become more user friendly and suited for the type of personal computers that are increasingly used by all segments of society. New GIS systems can examine water quality effects from both small and large land areas. Important landscape features related to denitrification are now available through widely available geospatial databases like the SSURGO (1:15,840) soil geographic database (soil wetness, surficial geology), Land Cover data (1:24,000, Andersen Level III system), wetlands (USFWS NWI, 1:24,000) and digital elevation (1:24,000, USGS Digital Line Graphs). These data or similar GIS products (e.g., National Hydrography Dataset, National Land Cover Database) are readily available for most watersheds along the east coast of the US and are at scales that have proven to be useful for land management and planning at the local level (Fernandez et al. 1993).

Land use planning to protect aquatic hotspots of denitrification, especially streams, is particularly challenging to local decision makers. Small channels and intermittent streams convey nitrogen from sources to downstream locations and may serve as important nitrogen sinks. Baker et al. (2007) have used accumulation grid techniques with digital elevation models to extend stream networks to headwater streams and ephemeral flowages that are not generally depicted on available hydrography databases. Such analyses afford opportunities for the use of high resolution spatial data for management that targets stream reaches likely to function as hotspots for nitrogen removal in the landscape (Fig. 6). Local decision makers can also influence land use practices that indirectly reduce nitrogen processing within stream reach ecosystems. Many land practices reduce water retention times and alter the timing and pathways of water flow. New subdivisions and roads restrict groundwater recharge and stream baseflow and limit the amount of nitrogen that can undergo riparian groundwater denitrification. As discussed above, urbanization creates flashy streams that reduce retention times and deepen stream channels, diminishing the capacity for stream nitrogen processing. Storm water drainage systems—in agricultural or urban/suburban development—alter flow paths within natural swales and ephemeral streams that constitute the expanded stream network during rain events, thereby bypassing potential nitrogen removal.

A particularly promising development at the interface between science and environmental decision making are Environmental Spatial Decision Support Systems (ESDSS). ESDSSs provide quantitative and visual tools to decision makers to assist them in describing, understanding, and forecasting how specific human activities or physical processes change across a landscape and over time (Cova and Church 1997; Davis and Keller 1997; Thumerer et al. 2000; van der Perk et al. 2001). ESDSSs are based on GIS, geographic visualization, exploratory data analysis tools, and spatial statistical analysis and modeling (Armstrong et al. 1992). ESDSSs hold special potential to connect scientists with decision makers because they establish a shared understanding of problems, allow the exploration of alternative solutions in group settings (Carver et al. 1996; Zigurs et al. 1999), and generate solutions and consensus-building (Reitsma et al. 1996; Zigurs et al. 1999). They therefore have great potential to translate our understanding of denitrification hotspots into decision support tools for local communities. These tools might be interactive where trained users will be able to define initial conditions, establish geographic parameters as inputs to the model, generate maps, manipulate maps, connect instantaneously from the maps to data, and repeat selected steps under different scenarios. By instantaneously linking maps to data, decision makers will better visualize and understand data relationships. Spatial statistical analysis and modeling provides tools to quantify spatial and temporal processes, generate "what if" scenarios, and lead to improved management of nitrogen pollution problems in the coastal landscape.

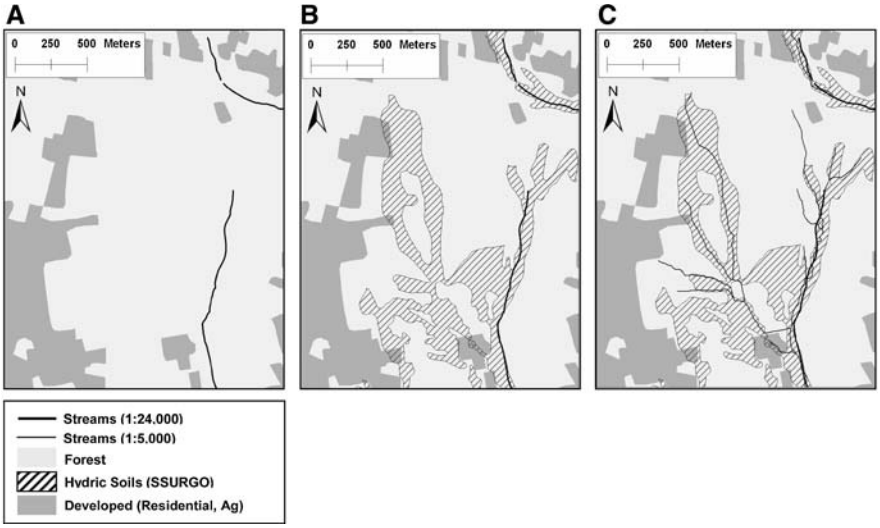


Fig. 6 High resolution environmental data improve our ability to model hotspots in the *landscape*. **a** Shows the presence of a "first order" stream channel as indicated on a USGS 1:24,000 map. **b** Shows the presence of potential riparian hotspot *hydric soils*. **c** Is a high resolution depiction of the actual first order stream network showing functionally important interactions between residential land uses, *hydric soils* and *streams* that dictate hotspot and hot moment phenomena in a changing landscape

Conclusions

One general conclusion is that more field measurements are needed in order to construct better models. As Boyer et al. (2006) state, “the modeling community is unanimous in stating that simulated magnitudes of the denitrification trace gas fluxes cannot be adequately calibrated and validated due to a lack of observational data over space and time (p. 2137).” Our analysis suggests that the need for data is especially critical for hot moments. While we have lots of data illustrating the importance of hotspots, and conceptual and practical approaches for including them in experimental designs, we have made much less progress identifying and quantifying hot moments in both terrestrial and aquatic ecosystems. This is not to say that we are accounting for the importance of hotspots on a routine basis, but rather that we at least have an idea of what to look for, and what we might be missing, at multiple spatial scales.

Somewhat ironically, while we have done a better job measuring hotspots than hot moments, we argue that hot moments are more amenable to model representation given current modeling frameworks and available data. Given the increasing availability of high temporal frequency climate data, models are promising tools for evaluating the importance of hot moments such as freeze-thaw cycles and drying/rewetting events. Spatial hotspots are less tractable due to our inability to get high resolution spatial approximations of denitrification drivers such as carbon substrate (i.e., the single decaying leaf issue).

Denitrification models that include hotspots and hot moments are greatly facilitated by tight coupling between models and data. New GIS-ready versions of biogeochemical models create the ability to incorporate new data coverages on the variables that create hotspots and hot moments, e.g., high resolution soil and stream maps. These models can then readily be translated into ESDSS that allow for consideration of detailed spatial and temporal patterns of denitrification in environmental decision making.

Our analysis suggests that enough information is available to provide a framework for thinking about hotspots and moments before starting a study or developing a new model. Investigators need to consider the types of hotspots and hot moments that might be occurring at small, medium, and large spatial scales in the particular ecosystem type they are working in, and then make some preliminary estimates of the magnitude of denitrification processes or nitrogen gas emissions that result from those hotspots and moments. In a managed system, this analysis should consider the effects of a range of possible management decisions and regimes. If the analysis determines that hotspots and hot moments are important in the system under study, the new experimental design and heterogeneity quantification tools discussed above should be applied from the outset. Such an approach will result in better quantification and more robust and widely applicable denitrification models.

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