DENITRIFICATION ACROSS LANDSCAPES AND WATERSCAPES: A SYNTHESIS

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Abstract. Denitrification is a critical process regulating the removal of bioavailable nitrogen (N) from natural and human-altered systems. While it has been extensively studied in terrestrial, freshwater, and marine systems, there has been limited communication among denitrification scientists working in these individual systems. Here, we compare rates of denitrification and controlling factors across a range of ecosystem types. We suggest that terrestrial, freshwater, and marine systems in which denitrification occurs can be organized along a continuum ranging from (1) those in which nitrification and denitrification are tightly coupled in space and time to (2) those in which nitrate production and denitrification are relatively decoupled.

In aquatic ecosystems, N inputs influence denitrification rates whereas hydrology and geomorphology influence the proportion of N inputs that are denitrified. Relationships between denitrification and water residence time and N load are remarkably similar across lakes, river reaches, estuaries, and continental shelves.

Spatially distributed global models of denitrification suggest that continental shelf sediments account for the largest portion (44%) of total global denitrification, followed by terrestrial soils (22%) and oceanic oxygen minimum zones (OMZs; 14%). Freshwater systems (groundwater, lakes, rivers) account for about 20% and estuaries 1% of total global denitrification. Denitrification of land-based N sources is distributed somewhat differently. Within watersheds, the amount of land-based N denitrified is generally highest in terrestrial soils, with progressively smaller amounts denitrified in groundwater, rivers, lakes and reservoirs, and estuaries. A number of regional exceptions to this general trend of decreasing denitrification in a downstream direction exist, including significant denitrification in continental shelves of N from terrestrial sources. Though terrestrial soils and groundwater are responsible for much denitrification at the watershed scale, per-area denitrification rates in soils and groundwater (kg N·km⁻²·yr⁻¹) are, on average, approximately one-tenth the per-area rates of denitrification in lakes, rivers, estuaries, continental shelves, or OMZs. A number of potential approaches to increase denitrification on the landscape, and thus decrease N export to sensitive coastal systems exist. However, these have not generally been widely tested for their effectiveness at scales required to significantly reduce N export at the whole watershed scale.

Key words: continental shelf; denitrification; estuaries; lakes; nitrogen; oxygen minimum zones; rivers; sediments; soils.

INTRODUCTION

It has long been recognized that denitrification (the microbial production of N₂ from fixed N) affects ecosystems and biogeochemical cycles at local, regional, and global scales (e.g., Codispoti and Richards 1976, Nixon et al. 1976, Seitzinger 1988, Revsbech and Sorenson 1990). At local and regional scales, denitrification removes fixed N that would otherwise be available for primary production or microbial assimilation. In low-N systems, denitrification contributes to N limitation by further decreasing N concentrations and by reducing the N:P ratio of recycled nutrients. In systems highly enriched with N from anthropogenic sources, removal of fixed N by denitrification reduces...
the export of N, and thus reduces eutrophication of downstream ecosystems. Denitrification can help to remove nitrite that can accumulate temporarily to toxic levels, such as in agricultural systems. Denitrification can control organic C sequestration by decoupling the N and C cycles in highly N-limited systems (Falkowski 1997). At the global scale, denitrification may control the amount of fixed N in the world oceans which in turn regulates primary production and hence the dissolved CO₂ in the oceans and atmosphere (Altabet et al. 2002). These linkages to the C cycle both on land and in aquatic systems illustrate the key role that N plays in the productivity of the biosphere and in feedbacks to global climate. As a source of the important greenhouse gas nitrous oxide (N₂O), denitrification affects global climate directly. Also at the global scale, denitrification completes the N cycle initiated by N₂ fixation by returning N to its elemental form, N₂.

The scale of the human perturbation of the natural N cycle is impressive and alarming. Preindustrial inputs of newly fixed N to terrestrial systems were approximately 125 Tg N/yr, of which most was from biological N₂ fixation, with a low percentage from lightning (Galloway et al. 2004). As of the early 1990s, humans had increased fixed N inputs to terrestrial systems by ~17 Tg N/yr. These anthropogenic sources consist mainly of fertilizer production from N₂ via the Haber-Bosch process, increased biological N₂ fixation associated with leguminous crops, and combustion of fossil fuels resulting in increased NOₓ in atmospheric deposition (100, 32, and 25 Tg N/yr, respectively; Galloway et al. 2004). At the same time, natural biological N₂ fixation was decreased by perhaps 10% (from 120 to 107 Tg N/yr) due to a loss in the surface area of natural ecosystems. As a result, land-based N sources of newly fixed N₂ as of the early 1990s were about 270 Tg N/yr, of which most was from biological N₂ fixation occurring in the marine environment. This massive scale of the human perturbation of the natural N cycle poses a series of scientific and management challenges. One prominent question is how rates of denitrification will respond to human intervention in the N cycle.

Both newly fixed N and recycled N (e.g., manure) are processed by terrestrial ecosystems. A substantial portion of this recycled N is subsequently transferred to groundwater, wetlands, lakes, rivers, estuaries, continental shelves, and oceanic waters, a process which has been described as the N cascade (Galloway et al. 2003). At each step along this terrestrial-to-aquatic continuum, there is the potential for denitrification to return a portion of land-based N sources to N₂ (Fig. 1). The oceans receive land-based N inputs (through river discharge and direct precipitation to the water surface), as well as N from marine biological N₂ fixation occurring primarily in the subtropical gyres (Fig. 1). In a hypothetical steady-state world, all the land-based and marine-fixed N sources are eventually denitrified within the terrestrial to marine continuum, and returned to elemental N₂. In the real world prior to major human perturbation, the stocks of fixed N varied over time as climate cycles and other controls affected the relative rates of global N₂ fixation and denitrification. Currently, human acceleration of N₂ fixation raises the urgent question of whether denitrification will keep pace with the extra N₂ fixation.

There have been many studies of denitrification in terrestrial, freshwater, and marine systems. Yet there has been limited communication among denitrification scientists working across the range of terrestrial to aquatic ecosystems. A number of reviews and syntheses have dealt with one ecosystem type such as soils (Stevens and Laughlin 1998, Barton et al. 1999), streams (Mulholland et al. 2004, Bernot and Dodds 2005), temperate riparian wetlands (Martin et al. 1999), freshwater wetlands and riparian forests (Groffman 1994, Mitsch et al. 2001), or continental shelves (Laursen and Seitzinger 2001). Denitrification rates and controls across various terrestrial systems, coastal and/or freshwater systems, or marine systems have also been the focus of analyses (e.g., Seitzinger 1988, Cornwell et al. 1999, Herbert 1999, Codispoti et al. 2001, Saunders and Kalff 2001). However, much remains to be learned about denitrification from comparisons of denitrification rates and controlling factors across the entire range of natural ecosystems. Through comparisons across terrestrial and aquatic systems, we also discover where natural and anthropogenic N is removed along the upland to ocean continuum. This knowledge is needed if...
we hope to understand and manage the N cycle and thus control its positive and negative impacts on both natural and managed systems.

This paper documents similarities and differences in denitrification across terrestrial, freshwater, and marine ecosystems. Within ecosystems, we discuss the range of temporal and spatial relationships between nitrification and denitrification and how these relationships determine where and when denitrification occurs. At the whole ecosystem scale we develop relationships between annual denitrification rates, hydrology, and N loading. In each section, we attempt to find commonalities among systems. At the global scale we present spatially explicit estimates of denitrification in terrestrial, freshwater and marine systems and discuss where and how much N is denitrified along the terrestrial-freshwater-marine aquatic continuum. Finally, we briefly discuss the potential for management of denitrification on the landscape. We have attempted to highlight what we believe are some interesting and useful comparisons that may inspire future syntheses.

Companion review papers in this volume address other topics on denitrification across terrestrial and aquatic systems. These include a review of methods to quantify denitrification (Groffman et al. 2006) and of models of denitrification at various scales (Boyer et al. 2006).

Denitrification, as classically defined, is the microbial oxidation of organic matter in which nitrate or nitrite is the terminal electron acceptor. It is a heterotrophic process of anaerobic respiration conducted facultatively by bacteria that can also respire aerobically, and the end product is N₂. Bacteria capable of denitrification are ubiquitous, and thus denitrification occurs widely throughout terrestrial, freshwater, and marine systems where the combined conditions of nitrate or nitrite availability, low oxygen concentrations, and sufficient organic matter occur. Denitrification generally occurs at O₂ concentrations <~0.2 mg O₂/L; completely anoxic conditions are not required. We use the term suboxic to indicate environments with <0.2 mg O₂/L. Hereafter, nitrite (NO₂⁻) plus nitrate (NO₃⁻) are referred to as nitrate.

In addition to respiratory denitrification, alternative microbial pathways of N₂ production have been identified, including anammox (production of N₂ from the anaerobic oxidation of ammonium with nitrite; e.g., Kuyper et al. 2005) and aerobic denitrification (Robertson et al. 1995). Additional pathways of N₂ production, for example using reduced Fe, sulfides, or Mn as electron donors and acid-catalyzed destruction of NO₃⁻ (chemo-denitrification) can also occur (e.g., Kölle et al. 1985, Postma et al. 1991, Luther et al. 1997, Hulth et al. 1999). In addition to N₂, nitrous oxide (N₂O) and other N gases (NO) can be produced during microbial denitrification. N₂O is an important greenhouse gas, and NO contributes to the formation of harmful tropospheric ozone. In this manuscript, we address total denitrification (including N₂, N₂O, and NO) but do not generally distinguish between the specific gaseous forms. Emissions of N₂O and NO are discussed in detail elsewhere (e.g., Bouwman et al. 1995, 2002, Mosier et al. 1998, Seitzinger et al. 2000). There is still much to be learned about the magnitude of the various biological and chemical pathways of N₂ production in the environment and the microbes and conditions responsible for them (e.g., Zehr and Ward 2002, Megonigal et al. 2004). The data summarized in this paper generally refer to total N₂ production, which we refer to as denitrification; we do not differentiate with respect to the specific pathways involved.

The oxic/anoxic interface as a site for denitrification

Denitrification occurs when three conditions are satisfied: nitrate is available, oxygen concentrations are reduced, and electron donors are available. A major limitation on these factors co-occurring is that the production of nitrate requires oxygen (O₂) while denitrification requires suboxic conditions (<0.2 mg O₂/L). As such, denitrification occurs at oxic/suboxic interfaces, with the interface being a separation in either space or time (or both). The wide range of environments in which denitrification occurs reflects the variety of physical conditions that brings aerobically produced nitrate in contact with denitrifiers in suboxic environments. Denitrification occurs in microsites within well-drained soils in forests, grasslands, and agricultural lands; partially to fully water-saturated soils; groundwater aquifers; surface, hyporheic, and riparian sediments in rivers; intertidal and subtidal sediments in estuaries; continental shelf sediments; permanently and seasonally varying suboxic bottom waters of lakes, estuaries, continental shelves, and enclosed seas; throughout the water column in suboxic river reaches; and in oxygen minimum zones at intermediate water depths in the oceans.

We suggest that the wide range of systems in which denitrification occurs, regardless of whether in a terrestrial, freshwater or marine environment, can be organized along a continuum ranging from (1) those in which the scale of interaction between oxic and suboxic environments is small in space (centimeters or less) and time (<1 d) and therefore nitrification and denitrification are (on average) tightly coupled in space and time to (2) those in which oxic and suboxic conditions are separated substantially in space (tens of meters to kilometers) and/or time (weeks to years) and therefore the production of nitrate is distal in time and/or space from denitrification (Fig. 2a). Furthermore, along this continuum, systems appear to group with respect to the mode of nitrate delivery to the site of denitrification: those in which diffusion dominates transfer of nitrate across a strong, stable gradient in oxygen into the denitrification zone (Group A); those in which advection dominates the transfer of nitrate-containing aerobic water into a region of suboxic water (Group B); and
FIG. 2. (a) Classification of systems according to the magnitude of temporal and spatial separation between nitrification and denitrification. Diffusion-dominated systems are indicated in gray, advection-dominated systems are indicated with heavy outlines, and systems with periodic anoxia are indicated by dashed lines. (b) Schematic groupings of systems according to mechanism of nitrate delivery to denitrification zone. Vertical profiles of oxygen concentrations are indicated.
those in which suboxic conditions occur periodically or episodically, leading to the denitrification of local nitrate produced under oxic conditions (Group C; Fig. 2b). In general, nitrification and denitrification in Group A systems are tightly coupled in space and time. In Group C systems, nitrification and denitrification are often quite separate in space and time, and Group B systems fall somewhere between Groups A and C (Fig. 2a).

Diffusion-dominated systems.—These systems (Group A) have strong, persistent gradients in oxygen, and nitrification and denitrification occur in separate, relatively thin layers near the oxic/suboxic interface (Fig. 2b). The close juxtaposition of nitrification and denitrification result in a tight coupling in space and time of these processes (Fig. 2a). The sharp oxic/suboxic transition is maintained by limited mixing or advection, and therefore diffusion is the primary mechanism by which nitrate is supplied to the denitrification zone. Such seemingly diverse systems as permanently water-saturated soils and sediments with oxic overlying water, microsites within well drained soils, and water bodies that are permanently stratified and have anoxic bottom water are included in Group A.

1. Microsites within soils.—The micro-scale (mm to cm scale) features of well-drained soils such as earthworm castings, particles of decomposing organic matter, and soil aggregates are important for tight coupling of nitrification and denitrification. This is because microsites can support strong gradients in oxygen as organic matter rapidly decomposes. The outside of organic C-rich particles and aggregates is oxic and can support high rates of nitrification while denitrification occurs in the suboxic interior (Svensson et al. 1986, Parkin 1987, Parkin and Berry 1999). Nitrification and denitrification are closely coupled in time because of the small scale spatial separation of nitrification and denitrification (Fig. 2a). These microsites explain why denitrification can occur even in well-drained soils. It also helps to explain why denitrification, as measured in soils, is often quite variable at relatively small spatial scales.

2. Aquatic sediments with oxic overlying water.—Benthic sediments in essentially all aquatic systems with oxic overlying water have strong O₂ gradients near the sediment–water interface (Fig. 2b). Surface sediments in these systems, including lakes, rivers, wetlands, estuaries, and continental shelves, are generally aerobic only in a thin zone of millimeters to a few centimeters thick. In deep-sea sediments, the aerobic zone extends to considerably deeper in the sediments (>25 cm; Bender et al. 1977). Nitrate produced in the aerobic zone (or nitrate from the overlying water) diffuses into the suboxic zone where denitrification occurs (Nielsen et al. 1990, Mengis et al. 1997, Rysgaard et al. 1998). The depth of the aerobic zone in aquatic sediments is controlled by the balance between the rate of O₂ diffusion into the sediments (plus O₂ production if benthic microalgal production contributed [An and Joye 2001]) and O₂ consumption associated with organic matter decomposition and nitrification. The aerial extent of this oxic/suboxic interface can be considerably extended vertically by biological activity such as macrofaunal burrows and macrophyte roots, which may therefore increase the amount of denitrification per unit of horizontal area (Caffrey and Kemp 1990, Nielsen et al. 1990, Pelegri et al. 1994). As with soil microsites, the small scale spatial separation of nitrification and denitrification leads to a tight temporal linkage of these processes (Fig. 2a).

3. Permanently stratified, enclosed, aquatic systems.—Permanently stratified (or rarely mixed) aquatic systems, in enclosed basins, with oxic surface water and anoxic bottom water also demonstrate relatively tight coupling between nitrification and denitrification (Fig. 2b). Permanent stratification occurs in some lakes (e.g., Lake Victoria), semi-enclosed seas (e.g., Black Sea, Baltic Sea, Caspian Sea) and fjords. As with aquatic sediments, nitrate produced in the aerobic layer near the oxic/anoxic transition diffuses into the suboxic zone where denitrification occurs (Codispoti et al. 1991, Brettar and Rheinheimer 1992). In these systems, organic matter fueling denitrification is provided from overlying water. The vertical extent of the denitrification zone is at the tens of centimeters to meters scale, somewhat larger than the centimeter or less scale in aquatic sediments and soil microsites (Fig. 2a).

Advection-dominated systems.—These systems (Group B) have relatively stable low-oxygen regimes with nitrate-rich water advected continuously through them (Fig. 2b). The nitrate is often produced kilometers to thousands of kilometers away from the site of denitrification and separated in time from denitrification by days to years. These systems, therefore, contrast markedly from Group A systems, in that nitrification and denitrification are separated by large spatial and temporal scales (Fig. 2a). Group B systems include OMZs in the oceans, groundwater aquifers, low-oxygen river reaches, and hyporheic sediments. Denitrification occurs continuously in these systems.

1. OMZs.—OMZs in the ocean are characterized by regions of suboxic water (O₂ < ~0.2 mg/L) predominantly found at intermediate water depths in tropical latitudes, underneath regions of high productivity associated with strong upwelling. The three major known OMZs are in the Eastern Tropical North and South Pacific (ETNP, ETSP) and the Arabian Sea. Other smaller regions of suboxic water occur in the oceans, for example off southwest Africa and the Oregon Coast, but estimates of denitrification in these regions are generally lacking (Codispoti et al. 2001, Grantham et al. 2004). Denitrification in OMZs extends over hundreds of meters vertically and over thousands of kilometers horizontally (Codispoti and Richards 1976, Bange et al. 2000, Codispoti et al. 2001, Deutsch et al. 2001). Nitrate for denitrification is primarily supplied by horizontal advection of relatively high nitrate (20–30 μmol/L) water from outside the region
local contributions from nitrate-based fertilizers and source of nitrate is nitrification in overlying soils, with time and space of nitrification and denitrification (Fig. 2a).

2. Groundwater.—In groundwater, the principal source of nitrate is nitrification in overlying soils, with local contributions from nitrate-based fertilizers and NO$_3^-$ deposition. After crossing the water table and leaving contact with oxygenated soil air, ground water nitrate is subject to varying degrees of denitrification depending on the geochemical conditions in the aquifer through which the ground water moves (Hiscock et al. 1991, Korom 1992). Geologic history (e.g., stratigraphy, deformation, mineralogy, and weathering) controls the distribution of flow paths and the mean residence time in the subsurface, as well as the distribution of electron donors for denitrification.

Denitrification in groundwater may be related in part to dissolved organic carbon (DOC) that is carried into the saturated zone with nitrate, but in most aquifers with high nitrate fluxes, the bulk of the denitrification is coupled directly or indirectly with oxidation of solid phases (e.g., organic C, reduced Fe and S minerals, and possibly Mn phases) in the aquifer. Regions of active denitrification in aquifers are typically bounded by upgradient regions of oxygen reduction and downgradient regions of manganese, iron, and sulfate reduction (Frind et al. 1990, Appelo and Postma 1996), but some of these redox zones may be compressed into narrow boundaries that divide the aquifer into separate domains containing relatively oxidized (undenitrified) water or relatively reduced (completely denitrified) water (Postma et al. 1991). Redox domains may be stratified vertically beneath recharge areas where reactive electron donors are distributed in the aquifer. Stratified domains may extend beneath riparian zones to discharge areas or they may be inverted, depending on riparian-zone geomorphology and subsurface lithology. The travel time of nitrate moving from its source in the unsaturated zone to the region of denitrification in groundwater commonly ranges from years to decades or more, and the distances commonly range from meters to kilometers; thus the production of nitrate is separated by large spatial and temporal scales from denitrification (Fig. 2a).

Groundwater nitrate can also be denitrified in riparian wetland sediments as the water moves into floodplains, stream channels (Clement et al. 2003, Kellogg et al. 2005), or estuaries (Tobias et al. 2001). The effectiveness of riparian zones in removing a significant proportion of total groundwater N load depends to a large degree on the proportion of the groundwater that comes in contact with these zones (Böhlke and Denver 1995). Tidal riparian wetlands can also denitrify groundwater-derived nitrate during each flood tide (Howes et al. 1996), as can riparian wetlands downstream of the groundwater discharge site that receive stream water, even if the initial discharge did not directly contact these zones of high denitrification.

3. Suboxic river reaches and hyporheic sediments.—As water enters and moves through fluvial systems, denitrification in stream corridors is typically supported by nitrate that was produced outside of the stream environment, particularly in watersheds with large anthropogenic N inputs. Overland flow and groundwater flow are major pathways for the transfer of water and nitrate from land areas to surface waters. More than half of the total annual discharge of water and nitrate in many streams and rivers passes through groundwater discharge systems before entering surface waters (Rutledge and Mesko 1996, Bachman et al. 1998, Winter et al. 1998, Lindsey et al. 2003). After entering river systems, nitrate from land sources can be denitrified within the surface-water column when it is suboxic, as it can become with high organic matter inputs from anthropogenic sources (Billen 1990, Chestérikoff et al. 1992, Harrison et al. 2005). This situation is somewhat analogous to OMZs, but occurs on smaller temporal and spatial scales, in that nitrate is produced upstream within the watershed and advected into a suboxic river reach. Similarly, nitrate carried by streams from upgradient sources can be advected into hyporheic flow zones where denitrification may occur (Triska et al. 1993, Duff et al. 1998). Hyporheic zones include regions beneath the stream channel and regions adjacent to the channel where stream water is exchanging with interstitial waters at rates and scales larger than those limited by diffusion (Fig. 2a).

Periodic suboxic conditions.—The third group of systems (C) are those that become suboxic periodically or episodically, creating ephemeral conditions that favor denitrification (Fig. 2b). Nitrate in these systems can be produced at the same location that denitrification occurs, but during an aerobic period. Thus, nitrification can be colocated with denitrification, but separated in time. Group C systems range from well-drained terrestrial soils to aquatic systems with seasonally varying anoxic bottom waters such as some seasonally stratified lakes, estuaries, shelf waters, and borderland basins. Many floodplains and wetlands experience temporal variation in water levels that produce periodically suboxic sediments.

1. Well-drained soils.—Well-drained terrestrial soils are largely oxic (except for microsites as discussed previously) and nitrate is generally the major form of dissolved inorganic N. Nitrification is often separated by relatively long time scales (days to weeks) from denitrification in soils, but the location of nitrate production is the same as that of denitrification (Fig. 2a). Nitrate is produced when and where the soils are aerobic, and its accumulation can be ameliorated by plant demand. The supply of oxygen under varying soil
moisture is mediated by properties such as soil texture, porosity, structure, organic matter, and drainage characteristics. The oxygen status and thus denitrification rates in soils can change rapidly depending upon soil moisture and the consequent rate of oxygen diffusion through soils (Tiedje 1988). An example of the rapid changes in denitrification with changing oxygen status is the pulse of soil denitrification often seen after episodic rainfall or irrigation events (Rolston et al. 1982, Ryden, 1983, Sextone et al. 1985, Lowrance 1992, Van Kessel et al. 1996). If anoxic conditions persist, nitrate may become limiting to soil denitrifiers, due to depletion by denitrification.

2. Seasonally stratified aquatic systems.—A number of lakes, estuaries, coastal borderland basins, and shelf regions develop suboxic bottom water following seasonal stratification (Fig. 2b). Nitrate, from in situ production and from external inputs, is distributed throughout the water column during periods of vertical mixing and is available for denitrification when the water stratifies and the bottom layer becomes suboxic (Fig. 2a). Therefore, nitrate production can be collocated with denitrification, or be produced meters (vertically) or tens to hundreds of kilometers (horizontally) away, then mixed or advected into the system before the onset of suboxic conditions. A combination of strong vertical stratification and sufficient organic matter inputs to the bottom water is required to deplete oxygen concentrations. Some of these transiently hypoxic systems have naturally occurring seasonal suboxic bottom water (e.g., Chesapeake Bay, Gulf of Mexico), however, the volume and duration of suboxic waters has increased in many of these as well as in numerous other lakes, estuaries, and shelf waters as a result of increased anthropogenic nutrient loading that supports increased organic matter production (Eadie et al. 1994, Bratton et al. 2003). Denitrification can occur in these suboxic waters or their associated bottom sediments. The extent to which denitrification occurs in the water or sediments in these systems is largely controlled by organic carbon availability in the water (Brettar and Rheinheimer 1992). For example, in the Santa Barbara borderland basin, bottom water organic carbon concentrations are low, and as such, over 75% of the total denitrification occurs in the sediments (Sigman et al. 2003). Comparative studies of the magnitude and controlling factors for denitrification across freshwater and marine systems with periodic suboxic waters are needed. Denitrification in these aquatic systems with periodic suboxic bottom water is similar to terrestrial soils in that nitrification and denitrification are separated temporally by days to months (or longer for some aquatic systems), however they differ from soils in that nitrate in these aquatic systems can originate from proximal or distal sources.

Sediments as a hybrid system.—Though it is useful to think of systems as falling along a gradient with respect to coupling of nitrification and denitrification, in many systems denitrified nitrate is supplied both locally and more distally. Aquatic sediments provide a relatively well-studied example of a system in which both local nitrification (sediment) and distal nitrification (overlying water) can supply nitrate for denitrification. There is considerable variation, however, in the relative importance of local vs. distal sources of nitrate. In some lakes, stream reaches, estuaries, and continental shelf regions, coupled sediment nitrification/denitrification is the major source of nitrate for denitrification (e.g., Jenkins and Kemp 1984, Seitzinger et al. 1984, Lohse et al. 1996, Devol et al. 1997, Nowicki et al. 1997, Rygaard et al. 1998, Laursen and Seitzinger 2001), while in others the water column accounts for 50% or more of the nitrate for denitrification (Devol and Christensen 1993, Nielsen et al. 1995, Cornwell et al. 1999, Herbert 1999, Merrill and Cornwell 2000, Smith et al. 2006).

A compilation of data from a wide range of freshwater and marine systems indicates that the nitrate concentration in the water overlying the sediments can largely explain the wide variability in the proportion of sediment denitrification supported by coupled nitrification/denitrification or nitrate from overlying water (Fig. 3). In systems with bottom water nitrate concentrations less than approximately 10 μmol/L (and with oxygenated bottom water), coupled nitrification/denitrification accounts for 90% or more of the nitrate required to support the denitrification. At nitrate concentrations between

![Figure 3](https://example.com/figure3.png)

**FIG. 3.** Source of nitrate for denitrification in sediments. The percentage of nitrate from overlying water (direct, solid symbols) and from coupled nitrification/denitrification (open symbols) from lake, river, estuary, coastal, and continental shelf sediments is shown. Data sources: Devol and Christensen (1993), Rygaard et al. (1995), Laursen and Seitzinger (2001), and Steingruber et al. (2001).
about 10–30 μmol/L there is considerable variation in the relative proportion of nitrate from bottom water and coupled nitrification/denitrification. At nitrate concentrations of ~60 μmol/L and greater, the bottom water becomes the major source of nitrate, accounting for approximately 80% of the total nitrate required for denitrification. This relationship appears to hold for sediment denitrification across a wide range of lakes, rivers, estuaries, and continental shelf systems. It remains to be shown whether a similar relationship holds for other systems with a relatively sharp transition between oxic and suboxic conditions, such as denitrification at the oxic/suboxic interface of the water column in lakes, estuaries or inland seas that are permanently stratified and have anoxic bottom water or in soil microsites.

Implications of coupled vs. decoupled nitrification-denitrification.—The conceptual organization of systems presented above provides a framework to compare the wide range of systems in which denitrification occurs, regardless of whether it is a terrestrial, freshwater, or marine system (Fig. 2a, b). Whether nitrification and denitrification within a system are tightly coupled, completely decoupled, or somewhere in between affects how we measure and model denitrification (Groffman et al. 2006). Early studies of denitrification often equated denitrification rates in sediments to the rate of disappearance of nitrate from overlying water or the rate of disappearance of nitrate in pore water that originated from the overlying water (e.g., Andersen 1977, Robinson et al. 1979, Christensen et al. 1987). This approach may work in systems where nitrification and denitrification sites are separated, but, as more recent measurements of total denitrification based on N2 fluxes and 15N methods have demonstrated (see Groffman et al. 2006), is likely to underestimate denitrification in systems where nitrification and denitrification are tightly coupled in time. Nitrate disappearance rates also can not be equated to N2 production if there is plant or benthic algal uptake of nitrate (Sundbäck et al. 2004), alternative pathways of microbial N2 production (Kuypers et al. 2005), or dissipatory reduction of nitrate to ammonium (DNRA; An and Gardner 2002).

The degree to which nitrification and denitrification are coupled within a system has implications for the response time of denitrification to changing conditions at the landscape or waterscape scale. For example, there can be lag times of years between changes in N inputs to terrestrial soils (e.g., fertilizer application) and changes in rates of groundwater denitrification (Böhlke 2002, Van Drecht et al. 2003). In terrestrial soils, changes in the frequency of precipitation events may alter the lag time between nitrification and denitrification and affect the total annual denitrification rate.

We are only beginning to understand the diversity of denitrifiers and their distribution in space and time (Wallenstein et al. 2006). Whether systems in which nitrification and denitrification are tightly coupled in space and time have different microbial assemblages than those in which nitrification is distal, or in which denitrification occurs only periodically, remains to be investigated. Similarly, we don’t know whether the coupling between nitrification and denitrification has implications for the predominance of the various pathways of microbial N2 production.

The degree to which nitrification and denitrification are coupled also greatly affects how we model denitrification in natural and agricultural systems (Boyer et al. 2006). One might expect that models of systems with tightly coupled nitrification and denitrification would be strongly influenced by diffusive processes, whereas models of more loosely coupled systems would be influenced primarily by advective (or other ecosystem or climatic) processes (Fig. 2).

Ecosystem-scale controls on denitrification: residence time and N loading

In the previous section, we compared where and when denitrification occurs within systems with an emphasis on the coupling in space and time between nitrate production and denitrification. Here, we address rates of denitrification at whole ecosystem scales, in particular ecosystem-scale controls that may help explain the wide range in denitrification rates across a relatively broad range of systems. Specifically, we address the impact of residence time and N loading, assuming a reactive source of electrons is present. At the ecosystem scale, we suggest that geology and hydrology interact to control the residence time of water and thus the processing time of N within an aquatic system. This, in turn, affects the proportion of N inputs that are denitrified (Fig. 4). At the same time, N loading sets the upper limit on the amount of N available for denitrification.

Water residence time.—In a variety of aquatic systems, water residence time has been recognized as an important factor controlling the proportion of N inputs that are denitrified. For a range of lakes in
Ontario, Canada, Kelly et al. (1987) developed a relationship between the proportion of N inputs that are removed and the geomorphology (bathymetry and depth) and hydrology (water residence time). This relationship was extended in various formulations to a broader range of lakes by Howarth et al. (1996), Saunders and Kalff (2001), Seitzinger (2000), and others.

Rivers are composed of complex networks of reaches ranging from small, shallow, first-order streams to larger, deeper river channels. Geomorphology and hydrology vary throughout a river network as do denitrification rates. Relationships have been developed to explain the variation in the measured proportion of N inputs that are denitrified across a range of stream orders as a function of hydrology and geomorphology (Boyer et al. 2006). For example, in the SPARROW model, the fraction of N removed is described as a first-order rate process whereby N loss varies inversely with stream channel depth (Smith et al. 1997, Alexander et al. 2000). In the Riv-N model, the fraction of N removed per reach varies with the depth/water travel time (Seitzinger et al. 2002b). (The time for water to travel the length of a reach is hereafter referred to as residence time for consistency with other aquatic systems.)

Estuaries can be broadly categorized by their geomorphology and range from shallow (~1 m deep) coastal lagoons to deeper drowned river valley estuaries to fjords. Geomorphology, water discharge from rivers, and tidal flushing affect water residence time in estuaries. The proportion of annual N inputs to estuaries that is denitrified on an annual basis has been described as a function of the water residence time (or water residence time and depth; Nixon et al. 1996). That analysis included nine estuaries that vary in geomorphology and hydrology. Lakes also followed a similar relationship. Other studies in estuaries have also noted the effect of water residence time on the proportion of N inputs that are denitrified (Nielsen et al. 1995, Dettmann 2001).

The studies cited in this section generally describe the relationship between denitrification and water residence time for just one or two system types (except for Saunders and Kalff 2001). When we combine data from lakes, river reaches, estuaries, or continental shelves, we see that water residence time can explain a major portion of the variability in the proportion of N inputs that are denitrified on an annual basis regardless of the system (Fig. 5a). There is a similarly good fit between denitrification and the depth/water residence time across these systems (Fig. 5b). The relationship with water residence time reflects the processing time of N within a system before the remaining N is transported to the next downstream system or offshore (e.g., continental shelf). For example in an estuary, the longer the water residence time, the more times N can be repeatedly cycled through uptake by phytoplankton and deposition of organic matter to sediments and therefore coupled nitrification/denitrification. There are likely numerous exceptions to this relationship. It should be noted that the relationship was developed with data at the annual scale; over short time frames the relationship between residence time and denitrification may not hold (Holmes et al. 2000, Tobias et al. 2003a, b). As data become available it may be fruitful to explore the effect of residence time on denitrification in terrestrial soils.

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In groundwater, the situation is complicated because, in general, the age distribution of groundwater discharging to streams and rivers is poorly known, so the
average time available for denitrification in groundwater is uncertain. Simple aquifer nitrogen models based on exponential age distributions are convenient for some purposes (e.g., Bohlke and Denver 1995, Van Drecht et al. 2003), but they may not represent many real situations (e.g., Cook and Bohlke 2000). Commonly, there are large fractions of very young water (e.g., from quick flow during precipitation and snow-melt events) that are not represented accurately by the exponential age distribution (e.g., Michel 1992), and these young waters may carry large amounts of nitrate through the system without denitrification. Furthermore, although denitrification commonly is modeled with a first-order rate constant, it typically is inhibited by dissolved oxygen, so it may not commence immediately in waters newly entering the system (Vogel et al. 1981, Appelo and Postma 1996, Bohlke et al. 2002). Where oxygen consumption occurs slowly, there may be a large mass of relatively young groundwater that discharges from the aquifer without having been denitrified at all. Finally, because many surficial aquifers have mean travel times (residence times) on the order of decades, and because major changes in N loading have occurred in the last few decades, many aquifers now contain transient records of changing nitrate recharge fluxes (Bohلهke 2002, Lindsey et al. 2003). In these areas, recharge and discharge fluxes may be unbalanced even where sources and sinks are not present in the aquifers. Denitrification rates may be changing in response to these changing inputs (Van Drecht et al. 2003).

N loading.—As N inputs increase, there is more N potentially available for denitrification. A positive relationship between N loading and N retention (largely denitrification) has been found in a range of lakes, rivers, and wetlands (e.g., Fleischer and Stibe 1991, Saunders and Kalf 2001). Across a range of estuaries the rate of denitrification was positively related to N loading (Seitzinger 1988, 2000). When we combine data from all these systems we see that N loading can explain a major proportion of the variability in the total amount of annual denitrification regardless of whether the system is a lake, river reach, estuary, or continental shelf (Fig. 6; linear regression, \( r^2 = 0.77 \)). We also show the regression between N load and N retention for wetlands from Saunders and Kalf (2001) which indicates a somewhat higher denitrification rate per N loading (Fig. 6, dashed line) relative to other aquatic systems. However, the wetland data are not directly comparable to the data from the other aquatic systems shown, because the wetland studies included denitrification as well as plant uptake and other N retention processes.

Agricultural soils with high rates of N input generally exhibit higher denitrification rates than soils not receiving N fertilizer additions (Barton et al. 1999, Hofstra and Bouwman 2005). However, the relationship between N inputs and denitrification rates in agricultural soils is considerably more variable than in aquatic settings (Fig. 6; ellipse). Hofstra and Bouwman (2005) found that N input was an important factor explaining denitrification rates in soils, based on an analysis of 336 soil denitrification measurements. However, denitrification did not show a simple relationship with only N input, because many other factors also were important in explaining the variability in soil denitrification rates, including length of period covered by the measurements, soil type, soil drainage, and crop type, among others.

**GLOBAL-SCALE ESTIMATES OF DENITRIFICATION**

In previous sections of this paper, we addressed denitrification at centimeter-to-ecosystem scales in terrestrial and aquatic systems. In this section, we discuss larger scale spatial patterns of denitrification, at watershed, regional, and global scales. We present spatially distributed global scale estimates of denitrification for the major “system types” including terrestrial soils (agricultural and natural), groundwater, lakes and reservoirs, rivers, estuaries, continental shelves, and OMZs in the oceans. We use a number of approaches
to accomplish this, including using the output from existing global models (e.g., soils and groundwater), applying existing models to global databases (e.g., rivers and continental shelves), and developing new models and applying them to global databases (e.g., lakes). For lakes, continental shelves, and estuaries, these are some of the first spatially explicit global estimates of denitrification. For the others, this is the first time they have been presented spatially and in the context of other systems. Collectively, we use this information to examine global scale patterns in denitrification for each particular system type. We then compare the relative contribution of various system types to total global denitrification. Finally, we address denitrification of land-based N sources and the relative contribution of each system type at global, regional, and watershed scales.

Terrestrial soils

A number of approaches have been used to model denitrification in soils at various scales (see review by Boyer et al. 2006). The spatial distribution of denitrification in terrestrial soils was recently modeled at the global level by Van Drecht et al. (2003). They developed a conceptual model for soils under rain-fed crops that combines the effects of temperature, crop type, soil properties, and hydrological conditions on annual mean nitrate leaching and denitrification rates, relying on simplifications of existing empirical models (e.g., Kolenbrander 1981, Kragt et al. 1990, Simmelsgaard et al. 2000). Van Drecht et al. (2003) assumed that inputs of all reduced N compounds not taken up by plant roots will be nitrified (converted to nitrate) in soils. Hence the quantity of soil nitrate will equal the annual surface N balance surplus. Nitrate is subject to denitrification, and since it is highly mobile in soils, is leached during periods with excess precipitation. This analysis was carried out with a spatial resolution of 0.5 × 0.5 degrees. Since the model assumes no upper limit for denitrification, the surface balance surplus of N is the maximum denitrification rate. We used this model with recent estimates of N inputs for the mid-1990s from Bouwman et al. (2005a) to obtain an estimate of denitrification in surface soils of both natural and agricultural systems.

Globally, denitrification in terrestrial soils calculated with this model accounts for the removal of 124 Tg N/yr (Fig. 7a). This is approximately 46% of the newly fixed terrestrial N (268 Tg N/yr; Galloway et al. 2004) and approximately 33% of the newly fixed plus recycled (e.g., manure) N added to soils annually (379 Tg N/yr; Bouwman et al. 2005b). This is similar to results from mass balance approaches used to estimate denitrification in terrestrial soils at regional scales: 40% for Europe (van Egmond et al. 2002), 30% for Asia (Zheng et al. 2002), and 33% for land areas draining to the North Atlantic (Howarth et al. 1996) as reviewed in Boyer et al. (2006). Furthermore, our estimated global denitrification rate in soils (124 Tg N/yr; or 66 mmol N m⁻² yr⁻¹ based on 135 × 10⁶ km² area of soils) falls well within the range of measured denitrification rates in soils (Fig. 6).

For agricultural systems alone, the new and recycled N inputs for the mid-1990s were 249 Tg N/yr (Bouwman et al. 2005b). Denitrification in agricultural soils was estimated as 66 Tg N/yr (27% of new plus recycled N...
inputs) (Bouwman et al. 2005). This is equivalent to 14 kg·ha$^{-1}$·yr$^{-1}$ (total agricultural area 4900 Mha), which is in line with measurement data for agricultural soils summarized by Hofstra and Bouwman (2005). The global estimate of denitrification for agricultural soils falls toward the high end of the range given by Galloway et al. (2004; 17–68 Tg N/yr) for a nonspatially distributed approach. However, Galloway et al. (2004) did not consider the effect of recycling of animal manure in agricultural systems. A more recent study based on denitrification measurements (Hofstra and Bouwman 2005) estimates the rate in agricultural soils globally as 22–87 Tg N/yr, depending on the technique used to measure denitrification.

We aggregated the spatially distributed estimates of Bouwman et al. (2005b) at the watershed scale to calculate watershed average rates (kg N·km$^{-2}$·yr$^{-1}$; Fig. 8b). We used the STN30 global watershed database to delineate basin boundaries (Vörösmarty et al. 2000a).

Predicted average basin denitrification rates for soils span over four orders of magnitude, ranging from 0.7 kg·km$^{-2}$·yr$^{-1}$ to 19 520 kg·km$^{-2}$·yr$^{-1}$ (0.05 to ~1400 mmol N·m$^{-2}$·yr$^{-1}$). Globally, the distribution of denitrification rates in terrestrial soils reflects mainly N inputs to agricultural systems. High denitrification losses are predicted in countries and regions dominated by intensive agricultural systems such as in India, parts of China, Europe, and North America. In natural systems or non-intensive agricultural systems, denitrification losses reflect rates of biological N$_2$ fixation and atmospheric N deposition.

There is considerable uncertainty in denitrification rates in desert areas. N inputs from biological N$_2$ fixation and atmospheric deposition in deserts are small. However, downward transport of water and nitrate is also very small. The model assumes that there is no net accumulation of N, and thus predicts surplus N is lost via the denitrification pathway. This leads to fairly high

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**FIG. 8.** Model predictions of N loading (kg N·ha$^{-1}$·yr$^{-1}$) and denitrification of land-based N sources in terrestrial and aquatic systems (kg N·km$^{-2}$·yr$^{-1}$). All rates are mapped as watershed area average rates. Note the difference in scale for N loading compared to denitrification.
predicted rates of denitrification in arid regions. Denitrification may be an important loss pathway in deserts (Peterjohn and Schlesinger 1990), which is supported by episodic N\textsubscript{2}O and NO emissions (Bouwman et al. 1993, Davidson and Kingerlee 1997) but other loss routes may not be accounted for, including ammonia volatilization (Bouwman et al. 1997) and accumulation of nitrate in the vadose zone below the root zone (Walvoord et al. 2003).

**Groundwater**

Field studies indicate that the efficiency of denitrification in groundwater ranges from roughly 0% to 100%, that it is spatially heterogeneous, and that it depends locally on aquifer hydrogeology and mineralogy. The denitrification flux depends also on the nitrate recharge flux, which is locally variable and which commonly is not in steady state. Therefore, empirical estimates of groundwater denitrification fluxes (e.g., from pooled field measurements of groundwater denitrification) are not yet possible, and model estimates have large uncertainties. With these caveats, we present two sets of constraints on groundwater denitrification, both of which are based on the spatially explicit global model of Van Drecht et al. (2003), with a spatial resolution of 0.5 × 0.5 degrees, using data presented in Bouwman et al. (2005a, b). First, the total recharge flux of nitrogen was indicated as the upper limit of groundwater denitrification (i.e., if all recharging N were nitrate and denitrification were 100% efficient). The recharge flux of nitrate was calculated as the excess N available for leaching, based on estimates of N loading and soil processes, including soil denitrification, also quite uncertain. Second, the groundwater denitrification flux was estimated by assuming that the groundwater flow system consists of two layers (0–5 m, shallow groundwater) and 5–55 m, deep groundwater) and that denitrification occurs in the shallow layer with a half-life of two years (Van Drecht et al. 2003). The total recharge flux of water into the shallow flow system is assumed to be equivalent to precipitation excess (“total runoff”). The fraction of the total runoff that enters the deep flow system is estimated from characteristics such as soil texture, thickness of aquifers, geology, slope, and other factors (for shallow groundwater this fraction is equal to one; Van Drecht et al. 2003). Water residence times are calculated from the recharge fluxes and pore volumes. The model is based on the assumption that denitrification in groundwater is limited by dissolved organic carbon that is present mainly in the shallow groundwater layer; hence, denitrification rates are assumed to be zero in the deep groundwater layer. Because both groundwater layers may have substantial residence times, the model provides for historical changes in N inputs from animal manure and N fertilizer. Hence, nitrate concentrations in groundwater are related to the year in which the water and nitrate entered the groundwater system. Because nitrate is assumed to have a fixed half-life (2 yr), total denitrification in groundwater with long travel times exceeds that in systems with short travel times. Modeled denitrification rates in a given year in the mid-1990s as presented in this paper depend on the age of the groundwater combined with the fertilizer history and are highest in young groundwater layers with nitrate recently leached from heavily fertilized soils. Denitrification in discharging groundwater in reactive areas such as riparian wetlands is not treated explicitly in the model, but is considered to be included in the overall estimate of “groundwater” denitrification (this is different from denitrification in stream water entering hyporheic zones).

The estimated N flux to shallow groundwater for the mid-1990s is 109 Tg N/yr and modeled denitrification in shallow groundwater is 44 Tg N/yr (Van Drecht et al. 2003, Bouwman et al. 2005a, b; Fig. 7a). The latter is equivalent to the removal of about 16% of all land-based N sources calculated based on newly fixed N (268 Tg N/yr; Fig. 7b), or 12% of newly fixed N plus re-applied N from animal manure (~379 Tg N/yr).

We aggregated results from Van Drecht et al. (2003) and Bouwman et al. (2005a, b) at the watershed scale (resolved at the 0.5° × 0.5° level using STN30; Vörösmarty et al. 2000) to calculate watershed average rates (kg N [km\textsuperscript{2} watershed\textsuperscript{-1} yr\textsuperscript{-1}]) for comparison with denitrification rates in soils at the same spatial scale. Predicted average basin denitrification rates for groundwater range from 0 to 7020 kg N·km\textsuperscript{-2}·yr\textsuperscript{-1} (0–502 mmol N·m\textsuperscript{-2}·yr\textsuperscript{-1}; Fig. 8c). Highest basin-averaged denitrification rates for groundwater are calculated for basins in Europe. In fact, European basins alone account for approximately 30% of the total global denitrification in groundwater. Reasonably high groundwater denitrification rates are also predicted for the southern and central United States as well as parts of East Asia and Japan. There are several causes of the differences in average river-basin denitrification rates in groundwater between Europe and other world regions: (1) the maps in Fig. 8 are aggregations over river basins, resulting in lower average denitrification rates in river basins with a smaller proportion of agriculture than in basins dominated by agriculture such as in many parts of Europe; (2) higher average denitrification rates in Europe are also caused by the high level of surface N inputs in spatially concentrated areas of intensive agriculture; (3) the humid temperate climate in Northern Europe causes higher leaching rates from the root zone to groundwater than in, for example, the United States with lower annual rainfall; and (4) the geohydrological conditions in Europe with large areas of porous material promote longer residence times than in other parts of the world with consolidated rocks.

**Rivers**

N loading to rivers was calculated using the average N loading (kg N [km\textsuperscript{2} watershed\textsuperscript{-1} yr\textsuperscript{-1}]) to surface waters modeled by Van Drecht et al. (2003) based on
data from Bouwman et al. (2005a, b) \((0.5° \times 0.5°)\). The model calculations of N loading included N inputs to surface water from shallow and deep groundwater outflow and from point sources. Groundwater flowing into surface waters or recharging to deep groundwater layers is generally a mixture of water with varying residence times in the groundwater system. The calculation of outflow from shallow and deep groundwater layers therefore accounts for the effects of groundwater residence time, historical fertilizer N inputs and denitrification in groundwater. Residence times are a function of the porosity of the aquifer material, precipitation excess and recharge of the deep groundwater (Van Drecht et al. 2003).

Rivers comprise complex networks of reaches ranging from small, shallow, first-order streams to larger, deeper river channels. As discussed above (Ecosystem-scale controls on denitrification: Water residence time), hydrology and geomorphology are important in determining the proportion of N inputs to a particular reach that are denitrified. Only a small portion (generally \(<20\%\)) of N inputs to a reach are removed in that reach (Fig. 5), however, the remaining N is subject to denitrification during its passage through downstream reaches. For calculating denitrification at the whole river network scale, the cumulative removal of N along the entire flow path in downstream reaches must be accounted for. Models have been used to scale-up sub-reach or reach scale measurements to determine denitrification at the scale of the whole river network and to account for this cumulative N removal (SPARROW model [Smith et al. 1997], Riv-N model [Seitzinger et al. 2002]). Those models have been used throughout various regions of the United States (Alexander et al. 2001, Seitzinger et al. 2002) and in selected regions outside of the United States (Alexander et al. 2002).

While detailed reach-scale information is not currently available for rivers globally, mean whole river water travel time is. Therefore, we used the SPARROW model output at the whole river network scale for 31 watersheds in the eastern United States (Alexander et al. 2001) to develop a relationship between denitrification at the whole river network scale and mean water travel time: percentage of N removed \(= 20.5 \times \ln(\text{mean water travel time}) + 14\), where travel time is in days \((r^2 = 0.72)\). We assumed that this relationship was applicable to rivers globally, while at the same time recognizing the need for information from a wider range of watersheds and geographic regions. We applied this relationship to rivers globally using water travel time in rivers as defined by the STN-30a global river network database (Vörösmarty et al. 2000a, b). TN inputs to each river (basin specific average) were modeled using N input to surface waters from Bouwman et al. (2005a).

The total denitrification in rivers globally based on this spatially distributed approach is 35 Tg N/yr, which accounts for the removal of about 13% of all land-based N sources \((\sim \text{268 Tg N/yr}; \text{Fig. 7a, b})\). This is slightly higher than previous estimates of global N retention in rivers (20–33 Tg N/yr) based on different assumptions and databases (Seitzinger and Kroeze 1998, Green et al. 2004, Bouwman et al. 2005a).

Globally, there is considerable spatial variation in denitrification in rivers, with predicted average basin denitrification rates for river networks ranging from 0 to 2173 kg/(km² watershed)⁻¹ yr⁻¹ (Fig. 8). Highest basin average rates are in central Europe and southern and eastern Asia, wet tropical systems in South America and Africa, and the eastern United States.

**Lakes**

The landscape throughout much of the world is dotted with lakes and reservoirs of varying sizes, ranging from small ponds (<1 km²) to intermediate sized lakes, to great lakes (e.g., Lake Baikal, Lake Victoria, North American Great Lakes). The spatial distribution of denitrification in large lakes and reservoirs was estimated using the relationship between percent denitrification and water residence time from Fig. 5a. N inputs to each lake were calculated in two ways. A high estimate was calculated by multiplying basin-averaged N loading to surface waters (Bouwman et al. 2005a; same as for rivers) by the reported catchment area for each large lake/reservoir (Lehner and Döll 2004). A low estimate was calculated by multiplying basin-averaged N export from river mouths by lake catchment area. We used the global databases of Lehner and Döll (2004) which contain 3067 of the largest lakes (area ≥ 50 km²), 654 largest reservoirs (storage capacity ≥ 0.5 km³) (GLWD-1), plus 250,000 additional permanent open water bodies with a surface area ≥ 0.1 km² (GLWD-2). Lake volume was estimated based on the relationship between surface area and volume for a wide range of lakes based on data presented in Hayes (1957). For large lakes and reservoirs, water residence time was estimated based on the reported water discharge and volume as calculated above. The median residence time of water in GLWD-1 lakes was calculated to be 2.5 yr. For the smaller lakes database (GLWD-2) water surface area was reported, but water discharge was not. Therefore, we estimated denitrification in the group of smaller lakes using the following approach. Large lakes from GLWD-1 were used to develop a relationship between cumulative lake surface area and global lake cumulative denitrification: global denitrification (kg N·km⁻²·yr⁻¹) \(= 0.02 \times (\text{lake surface area in km}^2)^{1.7652}\). We used this relationship along with the global total area of smaller lakes to estimate the additional denitrification in those lakes.

Global lake denitrification was calculated as 31 (19–43) Tg/yr (7–16% of terrestrial N loading). Of this total, we estimate that 11 (6–16) Tg N/yr are denitrified in large lakes and reservoirs and that 20 (14–27) Tg N/yr are denitrified in small lakes. Upper and lower bounds were determined by N inputs. Low estimates were achieved by assuming that lakes only process N after it is
processed in river networks, and the upper estimate assumes that lakes receive N from the landscape before it enters the river system. This is the first global spatially explicit estimate of denitrification in large and small lakes. The magnitude of denitrification in lakes suggested by this analysis indicates the need for further work. Additional development of global databases of hydrological characteristics of lakes and refinement of lake denitrification models are needed.

We mapped the total denitrification in lakes (high-end estimate) at the STN30 basin scale by summing the denitrification in all large (>50 km²) lakes within a basin and then dividing by the total basin area. Small lakes were excluded from spatially explicit analysis because we had insufficient information on small lake location and residence time to place them correctly within basins at the global scale. Mapping lake denitrification at the watershed scale facilitated a comparison of denitrification with terrestrial soils, groundwater, and other watershed scale processes on the global scale. Mapping lake denitrification at the watershed scale permitted a comparison of denitrification with terrestrial soils, groundwater, and other downstream systems. Predicted average basin denitrification rates for large lakes range from 0 to 10 140 kg N-km⁻²-yr⁻¹ (Fig. 8d). Globally, we predict that the highest lake denitrification rates on a watershed basis occur in Eastern Europe (in the Volga and Neva basins) and in North America’s St. Lawrence basin. The high rate of denitrification predicted for these basins is due to the presence of large lakes: the Great Lakes in the case of the St. Lawrence, Lake Ladoga, and Lake Oneh in the case of the Neva, and several large reservoirs in the Volga basin, including the Kuybyshhevskoye and the Volgogradskoye. Though it makes sense that lake denitrification should be high in the St. Lawrence watershed, we have almost certainly overestimated denitrification due to lakes in this basin because our model assumes N application in a watershed is spatially uniform, whereas most of the N loading in the St. Lawrence watershed occurs downstream of the Great Lakes region (Van Drech et al. 2003, Bouwman et al. 2005a). This is probably not the case for the Volga and the Neva basins.

Estuaries

Spatially explicit estimates of denitrification in estuaries were calculated using the relationship between percentage of N removed and water residence time developed using just the estuary data in Fig. 5a ($\gamma = 16.1 \times \text{residence time}^{0.30}$; water residence time is in months, $r^2 = 0.62$). We used TN exported from river systems, calculated as N inputs to surface waters minus river denitrification, as input to our estuarine denitrification model. A number of large rivers discharge directly to continental shelves and thus the N export by those rivers is not subject to estuarine denitrification (Nixon et al. 1996). We therefore subtracted N export by the following large rivers (Amazon, Tocantins, Zaire, Mississippi, Chang Jiang, Huang He, and Columbia; total 11 Tg N/yr; Bouwman et al. 2005a) from the total calculated global river export (46 Tg N/yr) to estimate TN input to global estuaries (35 Tg N/yr). Global estimates of water residence time are not currently available for estuaries. Therefore, we used the median (three months) of water residence time of estuaries from Fig. 5a to calculate denitrification in global estuaries (22%). For a nonspatial estimate of the range of global denitrification in estuaries, we used the range of water residence times for estuaries from Fig. 5a (0.16–7 mo, excluding the Baltic Sea of 240 mo; range of denitrification, 9–29% of TN inputs).

We calculate a global denitrification in estuaries of 8 Tg N/yr, with a range of 3–10 Tg N/yr, based on uncertainty in estuarine water residence times. This is less than several previous nonspatial estimates. Seitzinger and Kroeze (1998) estimated that 50% of the DIN inputs to global estuaries was denitrified, resulting in an estimate that 10 Tg N/yr are denitrified in estuaries. Galloway et al. (2004) assumed that approximately 50% of river export of TN to estuaries (46 Tg N/yr) is denitrified in estuaries, and calculated a global estuarine denitrification rate of 24 Tg N/yr. Neither of those studies considered the amount of N export by rivers that bypasses estuaries and is discharged directly to continental shelves.

We estimate estuarine denitrification as 8 Tg N/yr (Fig. 7a), with lower and upper bounds of 3 Tg N/yr and 10 Tg N/yr, respectively. Thus, estuaries may account for the removal of about 3% (1–4%) of non-recycled land-based N sources (Fig. 7b).

Globally, there is considerable spatial variation in estuarine denitrification. The contribution of estuarine denitrification to the removal of watershed-derived N is predicted to range from 0 to 2095 kg N-(km²-watershed)⁻¹-yr⁻¹ (Fig. 8f). However, the great majority of basins have predicted denitrification rates less than 50 kg (km²-watershed)⁻¹-yr⁻¹. Highest per-watershed area denitrification rates are estimated to occur in the northeastern United States, Europe, and South and Southeast Asia. Relatively high per-watershed area denitrification rates are also predicted throughout Indonesia. (The mapping of total N denitrified in an estuary back to its watershed is unconventional. The source of N to an estuary is, however, from the watershed and thus such an approach permits comparison of the relative amount of N denitrified among the various system types within a watershed.)

Continental shelves

Continental shelves are shallow (average water depth 130 m), gently sloping extensions of the continental crust. Here we use a conventional 200 m depth to define the outer edge of the shelf. The width of continental shelves varies considerably, ranging from tens of meters to a maximum width of about 1300 km. We developed a spatially distributed estimate of denitrification in continental shelf sediments globally using a model previously developed by Seitzinger and Giblin (1996) that has been applied to continental shelves throughout the North Atlantic. That model predicts denitrification rates...
(coupled nitrification/denitrification) in shelf sediments as a function of depth-integrated water column primary production. Data used for the development of that model were from measurements made in shelf sediments in a wide range of world regions. We applied the model globally using SeaWiFS-derived, mean-annual estimates of primary production in shelf waters (J. O’Reilly, personal communication). Primary productivity was estimated for each $9 \times 9$ km grid cell using the VGPM2 model (a slight modification of the VGPM described in Behrenfeld and Falkowski [1997]). Continental shelf area was defined as ocean with a depth between 10 and 200 m using ETOPO 2 (Smith and Sandwell 1997).

The total denitrification in non-polar continental shelves globally based on this spatially distributed approach is 166 Tg N/yr. This does not include estimates for polar shelf regions ($>6^\circ$ N and S), due to a lack of adequate SeaWiFS coverage for primary production in much of the polar region. Denitrification in polar sediments could account for an additional $\sim$44–49 Tg N/yr ($\sim$40–45 Tg N/yr and $\sim$4 Tg N/yr in Arctic and Antarctic shelf sediments, respectively [Devol et al. 1997, Codispoti et al. 2001]). We therefore adjust our global estimate by adding 45 Tg N/yr for polar sediments making our estimate of denitrification in global continental shelves 211 Tg N/yr. We also note that our denitrification model includes only coupled nitrification/denitrification, and not denitrification of nitrate diffusing into the sediments from the overlying water (Seitzinger and Giblin 1996). We roughly estimate that coupled nitrification/denitrification accounts for 80% of total denitrification assuming an average nitrate concentration in continental shelf bottom waters of less than 10 $\mu$mol/L and the relationship between nitrate concentration and denitrification in Fig. 3. Thus we estimate that an additional $\sim$40 Tg N/yr of denitrification supported by nitrate in bottom water occurs in shelf sediments. Our total global estimate of denitrification in continental shelf sediments therefore is 250 Tg N/yr.

The potential importance of denitrification in shelf sediments to the global marine N budget was recognized by Christensen et al. (1987), who estimated global shelf denitrification as 50–75 Tg N/yr by extrapolating denitrification estimates in the Gulf of Maine and northwest U.S. continental shelf based on pore water nitrate profiles to the global shelf area. More recent estimates of denitrification measurements in shelf sediments based on N$_2$ flux measurements from a wider range of locations indicate that denitrification in shelf sediments may be considerably larger (214–300 Tg N/yr; Devol 1991, Devol et al. 1997, Seitzinger and Kroeze 1998, Codispoti et al. 2001, Galloway et al. 2004). Our global estimate of denitrification in shelf sediments (250 Tg N/yr) based on a spatially explicit approach falls well within the range of these recent nonspatial estimates.

The model-calculated spatial pattern of denitrification in shelf sediments reflects not only phytoplankton production rates but also the global distribution of shelf areas (Fig. 9). As such, continental shelves in eastern Asia and Oceania account for 33% of denitrification in shelf sediments estimated by our model globally. Our approach also suggests hot-spots for denitrification in highly productive regions with significant continental
Denitrification in OMZs also exhibits spatial heterogeneity. The three major OMZs are located in the Eastern Tropical North Pacific (ETNP), Eastern Tropical South Pacific (ETSP), and the Arabian Sea. They cover approximately $3 \times 10^6$ km$^2$ (Codispoti and Richards 1976), $1.1 \times 10^6$ km$^2$ (Codispoti and Packard 1980), and $1.2 \times 10^6$ km$^2$ (Brandes et al. 1998), respectively. Globally, denitrification in these regions is estimated to be approximately 81 Tg N/yr, with about 22 Tg N/yr denitrified in the ETNP (Codispoti and Richards 1976, Deutsch et al. 2001); 26 Tg N/yr in the ETSP (Codispoti and Packard 1980, Deutsch et al. 2001) and 33 Tg N/yr in the Arabian Sea (Naqvi et al. 1992, Bange et al. 2000). Average areal-based rates are 7333 kg N·km$^{-2}·$yr$^{-1}$ for the ETNP, 23 636 kg N·km$^{-2}·$yr$^{-1}$ for the ETSP, and 27 500 kg N·km$^{-2}·$yr$^{-1}$ for the Arabian Sea (Fig. 9).

**Comparison of denitrification across terrestrial, freshwater, and marine systems**

In the following section, we integrate the individual analyses described in the previous subsections in an attempt to gain insight into the global distribution of denitrification. First, we consider denitrification of both land-based and marine sources of newly fixed N. Across all terrestrial, freshwater, and marine systems globally, continental shelves are the system where the largest amount of denitrification occurs, followed by terrestrial soils and then OMZs. Approximately 44%, 22%, and 14% of the total denitrification occurs in these three systems, respectively (Fig. 10). Freshwater systems (groundwater, lakes, and rivers) account for most of the remaining denitrification (20%). Estuaries account for only 1% of the global total.

This pattern of global total denitrification is not simply a function of the area of each system. For example, terrestrial soils cover an area approximately five times larger than continental shelves (Fig. 11a), although total global denitrification in terrestrial soils (124 Tg N) is only half that in continental shelves (250 Tg N; Fig. 10). Lakes, rivers, and estuaries combined cover an area that is less than 5% of the area of terrestrial soils, but soils denitrify only twice as much N as these aquatic systems (74 Tg N). The area of continental shelves is five times greater than OMZs, but they denitrify only three times as much N. This is reflected in the differences in the average per-area denitrification rates (kg N·km$^{-2}·$yr$^{-1}$) across these systems. These estimates were obtained by dividing rates shown in Fig. 10 by the areas shown in Fig. 11a. Rates per unit area in soils are approximately 10 times lower than in freshwater or marine aquatic systems (Fig. 11b). Among aquatic systems, there is less than a factor of three difference in global average areal based denitrification rates. (The global area of rivers is very uncertain [van den Berg 1995]; we assumed that 2% of the land area is covered by streams and rivers in the above calculations.) These model estimated rates of average global denitrification fall well within the range of measured rates for each system.

**Denitrification of land-based N sources**

Another perspective is to evaluate the removal of land-based N sources across the landscape for each system type (soils, rivers, lakes, estuaries, and so on). This allows us to estimate where in the land–sea continuum the bulk of terrestrially fixed N is denitrified. Carrying out this analysis in a spatially explicit manner grants insight into spatial patterns of denitrification at regional and global scales.

There is considerable spatial variation in denitrification rates (watershed average) among watersheds for each system type (Fig. 8). In general, the pattern in denitrification reflects that of N inputs to soils from land-based sources, with high denitrification rates predicted for regions with high rates of N input (Fig. 8a). However, the relative importance of different system types as sites for denitrification varies among watersheds and regions.

The amount of N denitrified in a watershed or region is almost always highest in terrestrial soils. Progressively smaller amounts are generally denitrified in groundwater, rivers, lakes and reservoirs, and estuaries (Fig. 8). This pattern is reflected in the global spatially averaged
denitrification rates for each system type mapped back to the watershed area. These rates decrease in a downstream direction from 845 kg N km\(^{-2}\) yr\(^{-1}\) for soils to 359 kg N km\(^{-2}\) yr\(^{-1}\) for groundwater, to 223 kg N km\(^{-2}\) yr\(^{-1}\) for river networks, to 117 kg N km\(^{-2}\) yr\(^{-1}\) for lakes to 45 kg N km\(^{-2}\) yr\(^{-1}\) for estuaries, a decrease of more than an order of magnitude. This trend is evident throughout much of the United States.

However, there are a number of exceptions to this general trend of decreasing denitrification rates in a downstream direction. For example, in Europe, groundwater appears to be the major site of denitrification in watersheds, with lesser amounts in soils and considerably less in rivers and lakes (Fig. 8). In eastern Asia, considerably less N is denitrified in lakes/reservoirs and groundwater than in rivers.

As N cascades down the terrestrial–aquatic continuum, the continued removal of N by denitrification in ecosystems results in less N available for denitrification in each downstream system. This is demonstrated by the relatively small amount of N removed by denitrification in estuaries compared to any of the upstream systems (Fig. 8). In general, this means that denitrification in downstream systems such as estuaries cannot be as important a site for denitrification of land-based N inputs on a global scale as systems with greater N inputs.

This does not mean that denitrification in estuaries is unimportant, however. Within a watershed, estuaries are positioned at the transition between typically P-limited freshwater systems and N-limited marine systems, and they are the focal points where excess N is manifested as eutrophication. Despite the large amount of N removed upstream of estuaries (e.g., in soils, groundwater, lakes, rivers), there is still enough N delivered to the coast to cause a wide range of environmental problems (Rabalais 2002). Therefore, denitrification within an estuary and denitrification in upstream systems contributing N to estuaries can both have critical implications for coastal ecosystems.

Total global denitrification of land-based N sources estimated from our spatially distributed estimates accounts for the removal of approximately 300 Tg N yr\(^{-1}\) (Table 1). Similar amounts of N are denitrified in terrestrial soils (124 Tg N yr\(^{-1}\)) and freshwater systems (rivers + groundwater + lakes + estuaries; 110 Tg N yr\(^{-1}\)). Altogether, we estimate that terrestrial soils and freshwater systems each account for about 35–40% of the total N denitrified from land-based N sources, with marine systems removing another 26% (3% estuaries, 15% in continental shelf sediments and 8% in OMZs; Fig. 7).

In the above calculation, we estimated the contribution of land-based N sources to denitrification in marine
systems as follows. Land-based N inputs to continental shelves (46 Tg N/yr) were from river discharge (11 Tg N/yr), estuarine export (27 Tg N/yr), and atmospheric N deposition (~8 Tg N/yr). We assumed that all land-based inputs to continental shelves are denitrified in shelf sediments since denitrification in shelf sediments (>200 Tg N/yr) greatly exceeds the estimated land-based N inputs to shelves (46 Tg N/yr). Atmospheric N deposition also constitutes a significant land-based source of N to open ocean regions (~25 Tg N/yr; F. Dentener, personal communication). We assumed that all atmospheric N deposition to oceanic regions is eventually transported to OMZs and denitrified. This estimate of atmospheric deposition does not include dissolved organic nitrogen (DON), which could increase N deposition by factor of four (Cornell et al. 1995).

Uncertainties

Considerable uncertainties are associated with all of the above global estimates of denitrification and N inputs; and we have discussed a number of these. Our estimates of total denitrification of land-based N sources across all systems (~300 Tg N/yr) fall within 15% of estimated land-based N inputs to terrestrial systems (Galloway et al. 2004), which is not unreasonable given the uncertainty in the assumptions used to estimate denitrification as well as land-based N sources. The general agreement between total N inputs and total denitrification, however, also reflects the fact that denitrification rates in terrestrial, freshwater, and estuarine systems were calculated as a function of upstream N inputs; therefore, overall estimates of denitrification and N loading in these systems were interrelated. Denitrification downstream of soils (freshwater systems and estuaries) was contingent upon estimates of upstream denitrification. Thus, errors in denitrification estimates can propagate to affect downstream estimates. For example, an overestimation of denitrification in groundwater leads to an underestimation of N inputs to surface water and thus potentially of denitrification in rivers.

The three places in our approach where relatively good global scale data exist are for N inputs to terrestrial systems, N export by rivers to the coast, and denitrification in OMZs. While there is clearly some uncertainty in denitrification rates in OMZs (Codispoti et al. 2001), we believe that at the global scale, denitrification in OMZs, at least by “classical” denitrification pathways, may be one of the better known rates because of their relatively limited geographical location (three major areas worldwide) and because studies of denitrification in these areas over the past 20 or more years converge on similar values. However, based on very recent information on alternative pathways of N₂ production (e.g., anammox) in low oxygen marine waters (Kuypers et al. 2005), this view may change.

N export by rivers to the coasts constrains our estimate of estuarine denitrification. Varying the proportion of N inputs to estuaries that are denitrified within the range of known values does not markedly change the contribution of estuaries to total global denitrification (Table 1) because denitrification can not exceed the N inputs to estuaries. Of course, the spatial distribution of denitrification in global estuaries is considerably more uncertain.

While N inputs to terrestrial systems at regional scales are relatively well known, one of the most uncertain estimates in our global analysis of denitrification is that of denitrification in soils. This uncertainty is due in part to the paucity of measurements of N₂ production under in situ conditions, which reflects the need for better methods for measuring denitrification in terrestrial soils (Hofstra and Bouwman 2005, Groffman et al. 2006). Our estimate of denitrification in groundwater is also quite uncertain at all scales (Table 1). This is due, in part, to the fact that these are relatively few measurements of denitrification in groundwater and to the large spatial heterogeneity of redox conditions in groundwater systems. Measured denitrification rates vary locally by at least eight orders of magnitude, so the selection of a single decay constant representing various reaction zone geometries and rates may not be the best approach for estimating areal fluxes. A more realistic regional or global model for groundwater denitrification will require more detailed (localized) information about subsurface geochemistry and mineralogy (reactivity) controlling the

### Table 1. Denitrification of land-based N sources based on spatially distributed estimates.

<table>
<thead>
<tr>
<th>System</th>
<th>Denitrification (Tg N/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terrestrial</td>
<td></td>
</tr>
<tr>
<td>Soils</td>
<td>124 (65–175)†</td>
</tr>
<tr>
<td>Freshwater</td>
<td></td>
</tr>
<tr>
<td>Groundwater</td>
<td>44 (&gt;0–138)‡</td>
</tr>
<tr>
<td>Lakes and reservoirs</td>
<td>31 (19–43)</td>
</tr>
<tr>
<td>Rivers</td>
<td>35 (20–35)</td>
</tr>
<tr>
<td>Subtotal</td>
<td>110 (39–216)</td>
</tr>
<tr>
<td>Marine</td>
<td></td>
</tr>
<tr>
<td>Estuaries</td>
<td>8 (3–10)</td>
</tr>
<tr>
<td>Continental shelves</td>
<td>46 (&gt;0–70)§</td>
</tr>
<tr>
<td>Oxygen minimum zones</td>
<td>25 (&gt;0–30)¶</td>
</tr>
<tr>
<td>Subtotal</td>
<td>79 (3–145)</td>
</tr>
</tbody>
</table>

Notes: Ranges (the range of uncertainty based on previous estimates and this study) are given in parentheses. The notation “>0” refers to cases in which it is evident from field studies that denitrification takes place in the system, but where data are so sparse that we are unable to make substantive estimates of minimum denitrification.

† Minimum is estimate of N loading to surface waters by Bouwman et al. (2005b); maximum is estimate by Galloway et al. (2004).

‡ Maximum is total new N inputs (268 Tg N/yr) minus minimum soil denitrification minus N loading to surface waters as calculated in Bouwman et al. (2005b).

§ Maximum assumes denitrification in continental shelf sediments cannot exceed N inputs to continental shelves.

¶ Maximum assumes denitrification in marine oxygen minimum zones (OMZs) cannot exceed land-based N inputs to OMZs.
distribution of denitrification, as well as improved understanding of groundwater travel time distributions in different settings.

Our estimate of denitrification in rivers globally is based on a relationship developed from a calibrated model for 30 rivers in the Eastern United States. The appropriateness of this relationship for other geographic regions is not known. In addition, our estimate of denitrification in rivers and lakes and dammed reservoirs could be improved by additional denitrification measurements across the range of stream orders in rivers to improve the models, modeling denitrification within the river network, integrating lakes within the river network, and improving global databases of the hydrological characteristics of river networks, lakes, and reservoirs.

Wetlands are likely to be an important site for denitrification because they provide suboxic, carbon rich environments favorable for denitrification of nitrate inputs, and they often have a high degree of water contact with sediments and biofilms where denitrification takes place. While we have not explicitly modeled wetland denitrification, the contribution of wetlands to denitrification in rivers, soils and estuaries is often included in the approaches used to measure or model denitrification. For example, whole ecosystem denitrification estimates in estuaries or river reaches are often based on mass balance N calculations and therefore would include N removed in associated wetlands. The model we used to estimate denitrification in upland soils included considerations of water saturation and therefore captures some components of wetland denitrification, while a separate approach for wetland rice systems was used (Bouwman et al. 2005).

We have not estimated denitrification in continental slope or deep-sea sediments, although some work suggests that a significant amount of N is denitrified in slope sediments (Middleburg et al. 1996). Neither have we addressed denitrification in wastewater treatment facilities.

Potential for Management of Denitrification on the Landscape

Our increasing knowledge of denitrification presents opportunities for managing ecosystem properties to control where, when and how much N is denitrified. Denitrification can be either bad or good, depending on the particular uses and properties of an ecosystem. In agricultural systems, the loss of nitrate by denitrification in the rooting zone of soils has negative economic consequences for crop production. Alternatively, in freshwater and marine aquatic systems, denitrification can have positive effects by reducing eutrophication associated with excess N inputs from anthropogenic activities on land. In addition to management techniques that affect denitrification directly, there are watershed and landscape management techniques that will affect denitrification indirectly.

A number of reviews and syntheses have addressed the potential for managing N on the landscape (Follet al. 1991, Burt et al. 1993, Martin et al. 1999, Mitsch et al. 2001, Austin et al. 2003, Moldan et al. 2003). Here we highlight a few potential approaches.

One of the systems where nitrogen transformations can be managed most effectively is the agricultural field. This type of nitrogen management has the potential to impact rates and timing of denitrification in these systems. Though many agricultural practices are aimed at minimizing denitrification on fields so that applied N will be available for use by crops, a different suite of techniques can be applied to maximize denitrification along flow-paths from agricultural fields to surface and groundwater systems. One approach is to minimize tile and surface-flow drainage of N-rich waters. Agricultural land in many parts of the world has been drained with either ditches or subsurface tubes to provide better conditions for crop growth, equipment use, or other aspects of crop production. In many areas, drainage has been installed to convert either permanent or seasonal wetlands to cropland (Zucker and Brown 1998, Billen and Garnier 1999, Goolsby et al. 2001, Dinnes et al. 2002). During periods of high precipitation, nitrate that has accumulated in the soil is flushed into streams via tile drainage and surface runoff (Goolsby et al. 2001). Although breakdowns by transport pathway are not generally available, in lands with tile drainage the majority of nitrate leaves via this pathway, thus largely avoiding groundwater denitrification. One potential way to reduce N inputs to surface waters, therefore, is to reduce tile drainage (Billen and Garnier 1999). Although some modifications can be made to lessen drainage intensity (e.g., wider spacing of tubes and ditches), in many regions drainage removal is not feasible because of its negative impact on crop yield.

Alternatively, structures at the ends of drainage lines or ditches can increase the residence time of water leaving drained fields and reduce the nitrate concentration (Gilliam et al. 1979). By holding water in the soil profile longer, controlled drainage can lead to higher denitrification rates under some conditions (Dinnes et al. 2002). The effectiveness of controlled drainage depends on a number of factors including seasonality and climate (Evans et al. 1995, Kliewer and Gilliam 1995, Jacinthe et al. 1999, Dinnes et al. 2002).

Many aspects of fertilizer management may influence denitrification in fertilized soils. For a given amount of N fertilizer applied, management practices that increase the amount of nitrate N may increase denitrification, especially in warm and humid climates. Nitrogen use efficiency can increase as a result of better management and techniques, such as integrated plant nutrition systems, and use of efficient fertilizers, matching application rates with plant demand, precision management, sophisticated schemes for timing and mode of fertilizer application, and crop residue and animal
manure management, as discussed elsewhere (Roy et al. 2002, Bruinsma 2003).

Practices that supply or keep N fertilizer in other forms, primarily NH₄⁺-N will decrease the available nitrate and decrease denitrification. In some cases, applying fertilizer in liquid form may increase denitrification compared to the same fertilizer formulation in a dry form (Paramasivam et al. 1998, Thornton et al. 1998, Marshall et al. 1999). Nitrification inhibitors for N fertilizers are applied to limit the activity and population of Nitrosomonas bacteria that oxidize NH₄⁺ to NO₂⁻ (Dinnes et al. 2002). By eliminating the oxidation of NH₄⁺, nitrification inhibitors will also decrease denitrification, further conserving the inorganic N for plant uptake.

Apart from management and crop yields, the N recovery in agricultural systems depends on many other factors, such as climate and soil conditions and the mix of crops. The potential efficiency, therefore, is not the same for all countries. Field studies by Balasubramanian et al. (2004) indicate that major increases in N use efficiency are possible with existing knowledge on management strategies. Although it is not well documented, the entire suite of management practices designed to increase N use efficiencies should lead to decreases in soil denitrification and leaching (and thus to decreases in denitrification in groundwater, lakes, rivers and estuaries).

Bioreactors have recently been studied as a way to reduce nitrate transport (Dinnes et al. 2002). Bioreactors can range from large barrels to “denitrification walls” such as trenches filled with coarse sawdust (Blowes et al. 1994, Robertson and Cherry 1995, Schipper and Vojvodic-Vukovic 1998). Although a number of bioreactor studies have reported nitrate removal rates for nitrate contaminated drinking water, few have dealt with agricultural drainage water and most of those have not distinguished denitrification from other nitrate removal processes (Blowes et al. 1994, Robertson et al. 1995).

While we have listed a number of possible approaches to increase denitrification on the landscape, it must be noted that none of these have been widely tested or evaluated for their effectiveness at the scales that would be required to significantly reduce N export by rivers to sensitive coastal systems. Another important factor to consider is where in the watershed it is most cost effective to reduce N inputs to rivers. This depends in part on the configuration of land-use within the river network, and the effectiveness of denitrification in various stream orders within the river network.

Due to their potential to act as hotspots for denitrification, both wetlands and riparian buffer strips have been suggested as systems to reduce N entering rivers. Mitsch et al. (2001) estimated that wetlands in the Mississippi River basin would remove about 15 000 kg N·km⁻²·yr⁻¹ and that riparian buffers (bottomland hardwoods) would remove about 4000 kg N·km⁻²·yr⁻¹. N removal in that analysis included denitrification as well as plant uptake and immobilization/burial in sediments. Creating and restoring wetland and riparian buffers was estimated to have the potential to reduce the nitrate load (600–1600 Gg/yr) at a rate comparable to that which could be achieved by changing farm practices (900–1400 Gg/yr [Mitsch et al. 2001]). In addition, diversion of the river flows to floodplains and coastal wetlands in the Mississippi River delta could account for 50–100 Gg/yr of nitrate removal. It must be noted that such studies have primarily been on individual wetlands under highly managed conditions; scaling up such approaches and demonstration that they can effectively reduce N in rivers at the whole watershed scale has not yet occurred. The effectiveness of created or restored wetlands and riparian buffer strips to denitrify significant amounts of N is highly dependent upon the degree to which these systems are maintained for such purposes. In addition, the effectiveness of riparian buffers in general will depend greatly on near-stream hydrogeomorphic characteristics of the fluvial system, subsurface geology (both physical and chemical), and the distribution of flow paths for nitrate-bearing groundwater in the discharge areas.

Treatment of nitrate-contaminated groundwater to enhance denitrification has been proposed (Smith and Duff 1988) and has been tried in a number of pilot projects (Smith et al. 2001, Mailloux et al. 2002). Microcosms constructed from coarse sandy material obtained from the Claiborne aquifer (south central Georgia, USA) had enhanced denitrification rates and nitrate disappearance when nitrate laden water was infused with glucose (Obenhuber and Lowrance 1991). Mailloux et al. (2002) found that either ethanol or acetate could be an efficient source of C to stimulate denitrification. They used a simulation model to estimate that at a site in northern Quebec, Canada, remediation treatment using a C source would lead to nitrate levels below the 10 mg NO₃-N/L threshold four to six years earlier than no remediation. In a different approach, using formate as a hydrogen source, Smith et al. (2001) found that hydrogen-oxidizing denitrifiers were effective at reducing nitrate but less effective at reducing nitrite, leading to a buildup of nitrite in the aquifer.

Given the large size of estuaries and the dominance of tidal exchange in such systems, human modification of estuarine geomorphology or hydrology to significantly increase the proportion of N inputs that is denitrified is probably not realistic at this point in time.

In sum, small-scale studies have suggested potentially effective management approaches for a number of individual systems. However, studies that test strategies for whole watershed-scale management of denitrification are lacking. Such studies must take into consideration where within the watershed denitrification occurs and where it is possible (or desirable) to enhance denitrification through management.
ACKNOWLEDGMENTS

This work was initiated at the International Nitrogen Initiative’s Denitrification Workshop. We thank the following individuals for their contributions to this paper: Donna Falk for assistance with graphics and manuscript preparation; Jay O’Reilly for primary production estimates for continental shelves from SeaWiFS data; Eric Davidson and participants in the Denitrification Workshop for useful discussions; Scott Nixon for discussions over the years; S. K. Hamilton, P. Groffman, R. B. Alexander, and R. Lee for constructive reviews of the manuscript. This work was supported in part by grants from the U.S. National Science Foundation (EAR0355586, DEB0332227, DEB0444349) and National Aeronautics and Space Administration (NN04GL68G). Work of G. Van Drecht and A. F. Bouwman was carried out in the framework of the project Nr. S/550005 entitled “Integrated Terrestrial Modeling” of the Netherlands Environmental Assessment Agency, National Institute for Public Health and the Environment. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the funding agencies.

LITERATURE CITED


