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Dominance of organic nitrogen from headwater streams to large rivers across the conterminous United States

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[1] The frequency and magnitude of hypoxic areas in coastal waterbodies are increasing across the globe, partially in response to the increase in nitrogen delivery from the landscape (Diaz, 2001; Rabalais et al., 2002). Although studies of annual total nitrogen and nitrate yields have greatly improved understanding of the contaminant sources that contribute to riverine nitrogen loads (Alexander et al., 2000; Caraco and Cole, 1999), the emphasis of these studies on annual timescales and selected nitrogen forms is not sufficient to understand the factors that control the cycling, transport, and fate of reactive nitrogen. Here we use data from 850 river stations to calculate long-term mean-annual and interannual loads of organic, ammonia, and nitrate-nitrite nitrogen suitable for spatial analysis. We find that organic nitrogen is the dominant nitrogen pool within rivers across most of the United States and is significant even in basins with high anthropogenic sources of nitrogen. Downstream organic nitrogen patterns illustrate that organic nitrogen is an abundant fraction of the nitrogen loads in all regions. Although the longitudinal patterns are not consistent across regions, these patterns are suggestive of cycling between ON and NO_3^- on seasonal timescales influenced by land use, stream morphology, and riparian connectivity with active floodplains. Future regional studies need to incorporate multinitrogen species at intraannual timescales, as well as stream characteristics beyond channel depth, to elucidate the roles of nitrogen sources and in-stream transformations on the fate and reactivity of riverine nitrogen transported to coastal seas.

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1. Introduction

[2] Over the last century anthropogenic activities have more than doubled reactive nitrogen inputs in the environment, primarily through increased fertilizer application and the combustion of fossil fuels [*Galloway et al.*, 2004; *Vitousek et al.*, 1997]. A large portion of this nitrogen pool is returned to the atmosphere through denitrification on the landscape; however, nitrate (NO_3^-) is relatively mobile, and a considerable fraction is transported to the freshwater environment. For example, mean nitrogen concentrations in the Mississippi River basin doubled in the last 100 years, primarily owing to increases in NO_3^- (NO_3^- represented less than 55% of the annual riverine load in 1973 to over 75% in 1999) [*Goolsby and Battaglin*, 2001]. The higher nitrogen loads within the Mississippi are caused not only by the doubling of nitrogen inputs, but also anthropogenic changes to the landscape (e.g., tile-drained agricultural fields; levees along main-stem rivers; increased surface runoff into lotic systems within suburban and urban areas), which alter delivery from the land to the stream network [*Turner and Rabalais*, 2003]. Elevated nitrogen loads lead to areas of hypoxia in coastal waters across the globe, including large areas in the Gulf of Mexico, the Chesapeake Bay, and the Black Sea [*Diaz*, 2001; *Hagy et al.*, 2004; *Rabalais et al.*, 2002]. The other reactive forms of nitrogen found in rivers include ammonia (NH_4^+) and organic nitrogen (ON), which are also biologically reactive. Therefore it is the total nitrogen flux that needs to be considered when addressing coastal eutrophication [*Howarth et al.*, 1996, 2002].

[3] The major nitrogen species within the stream network (ON, NH_4^+, NO_3^-) are not transported conservatively downstream, but rather they undergo transformations between inorganic and organic forms as part of biological synthesis and growth (e.g., nitrogen is a required component of both proteins and nucleic acids) or microbial mediated redox transformations resulting in energy release. Nitrogen is primarily delivered to streams through both overland flow during storm events, shallow groundwater flow paths, and point-sources (e.g., WWTP's). The inorganic N delivered to streams will largely be dissolved, where as a portion of the organic N delivered to the stream will be in particulate form (e.g., organic soil, particulate organic matter). The organic carbon molecules containing nitrogen are available for

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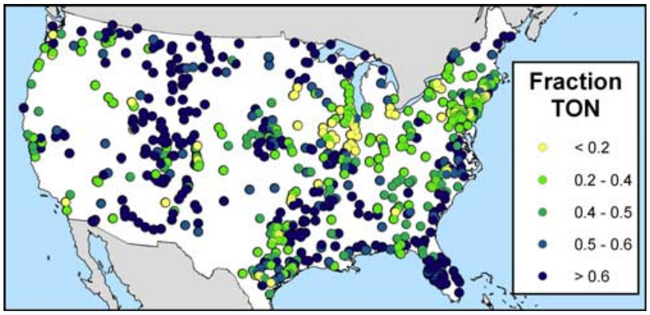

Figure 1. USGS load stations distributed across the United States, depicted with a color coding representing fraction TON for each station calculated for long-term mean annual total organic nitrogen loads.

heterotrophic processes (mineralization), releasing energy and producing NH_4^+. In turn, NH_4^+ is transformed by an energy yielding reaction in the presence of O_2 to produce NO_3^- (nitrification). Both of the dominant inorganic forms of nitrogen (NH_4^+ and NO_3^-) can be cycled back into organic forms through assimilation and subsequently stored for variable periods of time before N is rereleased via decomposition and mineralization. Direct nitrogen fixation of N_2 gas into the biotic pool is also possible via nitrogen-fixing organisms (e.g., cyanobacteria) in some streams [*Grimm and Petrone*, 1997]. One of the most important transformations in high-nitrogen systems is the energy yielding transformation of NO_3^- to NO_2^- (which is usually an intermediate species low in concentration) and then to nitrogen gas (denitrification). Denitrification occurs in stream subenvironments (such as the stream bed) where O_2 is low or absent. Of all the transformations of nitrogen in aquatic systems, denitrification is the only one that results in large amounts of N removal from the aquatic environment. However, because of the close coupling of various nitrogen and carbon reactions in streams, the rate of denitrification in streams is influenced by transport and transformation rates of all of the dominant species of nitrogen in stream environments.

[4] In this study, we examined seasonal and annual nitrogen loads across the conterminous United States in 850 rivers, ranging from less than 1 $m^3\ s^{-1}$ to over 18,000 $m^3\ s^{-1}$ annual mean discharge (Q_m). Nitrogen load estimates for organic nitrogen, NH_4^+, and NO_x were all made in a systematic fashion employing long-term nutrient and discharge data sets, resulting in mean annual load estimates appropriate for spatial analysis. The estimated mean annual nitrogen loads for total organic nitrogen, NH_4^+, and NO_x reveal spatial, temporal, and longitudinal patterns across the United States. These patterns are responsible for altering nitrogen availability and reactivity to downstream ecosystems, including estuaries and coastal ecosystems. In the last decade, nitrogen budget approaches and regional-scale nitrogen models (e.g., SPARROW) identified large nitrogen fluxes from the landscape and high in-stream removal rates as a function of stream size [*Alexander et al.*, 2000; *Boyer et al.*, 2002; *Seitzinger et al.*, 2002a]. These studies identified the need to examine N export on interannual timescales and to explore the interactions between the dominant nitrogen species. Other studies have examined nitrogen export from impacted (northeastern U.S.) and nonimpacted regions in North and South America, highlighting the export of organic nitrogen from these regions [*Lewis*, 2002; *Lewis et al.*, 1999; *Pellerin et al.*, 2004]. These studies have all drawn attention to the increase in N-export to coastal waterbodies, spurring numerous detailed investigations of denitrification within smaller first- through third-order streams [*Bohlke et al.*, 2004; *Mulholland et al.*, 2004]. Most detailed studies have examined denitrification during base-flow conditions, with little emphasis on high-flow conditions. Also, the primary focus has usually been on the fate of NO_3^-, not on transformations involving the other dominant form of nitrogen in lotic systems—organic nitrogen [*Goodale et al.*, 2000; *Perakis and Hedin*, 2002].

2. Methods

[5] Nitrogen concentrations (1975–2004) and discharge records (1970–2004) were acquired for 1300 USGS stream-gaging stations (http://waterdata.usgs.gov/nwis) across the United States (Figure 1). The watershed areas for the stations in this study ranged from less than 5 km^2 to 2.9×10^6 km^2 (mean annual discharge ranged from less than 1 to 1.9×10^4 $m^3\ s^{-1}$). For each record, trend-adjusted annual and quarterly (A = annual; 1 = Jan.–Mar.; 2 = Apr.–June; 3 = July– Sept.; 4 = Oct.–Dec.) nitrogen load and discharge estimates were calculated using an automated estimation routine (FLUXMASTER [*Schwarz et al.*, 2006]) for the period October 1978 through September 2004. The load model on which load estimates are based relates the logarithm of nutrient concentration to the logarithm of daily streamflow, and includes sine and cosine functions of time to account for seasonal patterns. Loads for unfiltered ammonia (NH_4^+), unfiltered ammonia + organic nitrogen (NH_4^+ + TON), and filtered nitrate + nitrite (NO_x) were calculated independently using the water-quality data for each station, and TON was then calculated by difference. A subset of 854 stations was then selected from the entire set that included only stations with (1) estimates of all three loads, and (2) standard deviation divided by the annual load estimate equaling less then 1. The resulting average annual and seasonal loads, discharge, concentrations, and fractions of the dominant nitrogen species were then examined spatially across the United States using the load estimates from the remaining 854 stations that met the above criteria.

[6] A regression analysis was performed to examine nitrogen yields in 131 of 854 watersheds that ranged between 1,000 and 14,000 km^2 (Table 1). The watersheds were dispersed across the country, and the explanatory variables included in each of the initial models were specific runoff (mm yr^{-1}), mean soil organic carbon (Mg C ha^{-1}), total nitrogen fertilizer and atmospheric deposition (kg N $km^{-2}\ yr^{-1}$), and mean weighted riparian land use in woody wetland vegetation. Watershed attributes were calculated using watershed boundaries from the U.S.G.S. enhanced river reach network (RF1)[*Nolan et al.*, 2002]. This digital stream network was initially derived from the E.P.A. at a scale of 1:250,000. The enhanced version, which includes a fully connected stream network with mean velocity and

Table 1. Log-Linear Model Predicting NO_x, TON, and NH_4^+ Yields Using 131 Watersheds Distributed Across the United States Ranging in Watershed Size From 1000–14,000 km^2[a]

Yield, $kg\ km^{-2}\ yr^{-1}$	Log (Specific Runoff),[b] $mm\ yr^{-1}$	Log (N Fertilizer + Deposition),[c] $kg\ km^{-2}\ yr^{-1}$	Log (Soil Organic Carbon),[d] $gC\ m^{-2}\ yr^{-1}/100$	Log (Riverine Wetlands)[e]	Intercept	Adj. R^2
log(TON)	0.35 (0.05)	0.44 (0.05)	0.84 (0.26)	-	−1.1 (0.85)[f]	0.62
log(NO_x)	0.60 (0.1)	0.99 (0.09)	1.1 (0.4)	−0.04 (0.02)	−5.1 (1.5)	0.66
log(NH_4^+)	0.58 (0.06)	0.54 (0.06)	0.85 (0.28)	−0.04 (0.01)	−4.8 (0.9)	0.70

[a]Standard errous are given in parentheses. All *p*-values were less than 0.05 unless otherwise indicated.
[b]Specific runoff calculated from mean annual discharge at each U.S.G.S. stream-gaging station.
[c]Nitrogen fertilizer application was estimated from county sales in 1992, and nitrogen deposition was estimated from total average deposition between 1994 and 2003 from the National Atmospheric Deposition Network (NADP 2006).
[d]Soil organic carbon was estimated from the VEMAP data set [*Kittel et al.*, 2004].
[e]Riverine wetlands within each watershed was estimated for the RF1 stream network by applying the values of woody wetland distribution within 1 km buffer of the RF1 stream network [*Nolan et al.*, 2002].
[f]With *p*-values greater than 0.1.

discharge for each reach and watershed boundaries derived from a 1-km DEM, is used for spatial analysis and water-quality modeling (e.g., SPARROW [*Smith et al.*, 1997]). Although a new digital network at the scale of 1: 100,000 is now available (National Hydrography Dataset, http://nhd.usgs. gov/), the RF1 is appropriate for watershed delineation. For each model, all variables were log-transformed and a stepwise log-linear regression was performed (equation (1)).

$$\log Y_x = \sum_{n=1,z} \log X_n + b. \tag{1}$$

Only variables with a $p \leq 0.05$ were kept in the final regression equation. Specific runoff (mm yr^{-1}), estimated as the mean annual discharge at the outlet divided by watershed area, is representative of the average amount of water delivered to the stream channels throughout the entire watershed. Soil organic carbon was included because areas with high soil organic carbon will also have higher organic nitrogen contents, which may be a source of nitrogen from the landscape through soil erosion/porewater flushing. Terrestrial nitrogen sources (kg km^{-2} yr^{-1}) included within the model were nitrogen fertilizer application rates and atmospheric deposition. Finally, the riverine wetland percentage was included because watersheds with higher percentage of riverine wetlands in their riparian area will have higher floodplain-river connectivity, and these areas can act as a source and a sink for nitrogen.

[7] A second regression model was developed to describe spatial variations in ON and to identify key explanatory factors within each region. The annual fractions of organic nitrogen at each stream-gaging stations calculated from the water quality and stream discharge observations were mapped to illustrate the regional groupings (Figure 1), and then stations were grouped by ecoregion level III [*Omernik*, 1987]. Ecoregions with $\geq$9 water quality stations with a mean-annual load estimate were included in a regression analysis in which ON fraction is expressed as a function of various climate and other watershed properties, including average climatic conditions, soil properties, land use, and nitrogen input data (for full list and source information, see auxiliary Table S1[1]). A stepwise regression approach was then performed to identify parameters that explain the spatial patterns of ON fraction across ecoregions, and only variables with $p \leq 0.1$ were included in the final model. The resulting regression model was then applied across the conterminous U.S. using a grid cell size of 10,000 km^2. The significant explanatory variables in the regression include transmissivity, population density, nitrogen inputs, mean annual precipitation, and woody wetlands land use (Table 2). A subgrouping of four regional data sets (Northeast, Southeast, Midwest, Intermountain West) was analyzed (excluding stations in high population densities, Pop > 1000 people mi^{-2}) to examine differences between systems that are organic rich/organic poor. The corn-belt sites were also further limited to include only sites with high N inputs ($N_{fertilizer}$ > 5000 kg km^{-2} yr^{-1}). Each region was grouped into four stream classes based on mean annual discharge ($1 = 0.28 < Q < 2.8$; $2 = 2.8 < Q < 14$; $3 = 14 < Q < 57$; $4 = 57 < Q < 250$ m^3 s^{-1}). The median depth was calculated for all RF1 streams within each region using the relationship derived by *Alexander et al.* [2000] based on discharge ($D = 0.2612\ Q^{0.3956}$, where D is depth (m) and Q is streamflow discharge (m^3 s^{-1})). Stream width was then estimated using Q_{mean} and V_{mean} from the RF1 stream network and the estimated depth [*Nolan et al.*, 2002].

3. Results and Discussion

[8] Our data illustrate the varying percentages of NO_x and TON in riverine nitrogen loads in the major U.S. river basins. Results from 29 large rivers within the United States highlight the large range in long-term annual total nitrogen yields: from less than 30 kg km^{-2} yr^{-1} at the station on the Colorado River at Lee's Ferry to over 2200 kg km^{-2} yr^{-1} at stations within the Iowa River basin (Table 3). The yield estimates from all 854 stations were derived from the available long-term discharge and water quality records at each site using the FLUXMASTER routine, which provides unbiased detrended results and an associated standard error for each station. This systematic approach to estimating loads is more appropriate for spatial analysis than using shorter-term records or water quality observations from multiple sources that result in unknown errors between stations that are not attributable to any effect other than sampling/calculation errors. Note that the predicted long-

[1]Auxiliary materials are available at ftp://ftp.agu.org/apend/gb/2006gb002730.

Table 2. Linear Regression Model Result for the Estimation of the Fraction of TON in the Average Riverine Load[a]

	Parameter Estimate	Pr > F
Total transmissivity	1.0×10^{-3}	<.0001
Population density	-6.0×10^{-5}	0.0027
Nitrogen fertilizer +nitrogen deposition	-2.4×10^{-3}	0.0176
Mean annual precipitation	-1.5×10^{-4}	0.0199
Land use - woody wetlands	1.7×10^{-3}	<.0001

[a]Linear regression model: dependent variable; TON fraction, $\sum(ax)$; a, parameter value; x, variable.

term mean yields are for the period of observations, 1970–2004. Future uses of these estimates need to consider the relevant period over which these estimates were derived.

[9] The variability in total nitrogen yields observed across all river basins is correlated to differences in the NO_x yields (TN versus NO_x yields, R^2 = 0.89), primarily due to anthropogenic inputs of N (e.g., agricultural fertilizer applications) [*Caraco and Cole*, 1999]. NH_4^+ yields were generally less than 5% of the total nitrogen yield, but organic nitrogen ranged from less than 20% to over 80% of the total annual nitrogen yield (TON yields ranged from less than 15 to over 400 kg km^{-2} yr^{-1}) in these larger river basins. The organic nitrogen pool is composed of a heterogeneous mixture of organic nitrogen compounds, and warrants further investigation given its importance in nitrogen and carbon cycling in riverine systems.

[10] The regression analysis exploring nitrogen yields across the landscape illustrates the importance of water and sources on the material fluxes through riverine networks. For each of the three dominant nitrogen components (TON, NO_x and NH_4^+), mean annual runoff had positive parameter values, which is consistent with runoff as a driver to transport and deliver nutrients to the stream channel. Fertilizer application and atmospheric deposition also had positive parameter values, consistent with the concept that areas with high terrestrial nitrogen loading result in higher nitrogen export from the watershed. Soil organic carbon was also significant for all N yields. Regions that are rich in soil organic carbon will also have high soil organic nitrogen, which depending on the environmental conditions may favor microbial mineralization and subsequent nitrification. The resulting nitrogen in the porewater may then be a source of nutrient delivery to the channels through erosion and flushing of shallow soils during storm events and/or snow melt. Lastly, percentages of riverine wetlands within the riparian zones of the watershed's stream network were significant for NH_4^+ and NO_x yields. Riparian areas high in woody wetlands suggest greater connectivity with the floodplain and river, and these areas have high biogeochemical transformation rates, including mineralization, nitrification and denitrification. While the percentage of riverine wetlands was not significant for TON in this analysis, the negative parameter values for NH_4^+ and NO_x suggest that watersheds with higher flood frequencies result in higher NH_4^+ and NO_x retention. Future spatially based coupled N-models through the stream network need to be developed to capture the interchange between the dominant species

Table 3. Long-Term Mean Annual Discharge and Nitrogen Yields for Selected Major Rivers in the Conterminous United States, Including the Standard Deviation of Each Yield Estimate

			Yield-Mean (Std. Err.), kg km^{-2} yr^{-1}		
River	USGS ID	Q-Mean (Std. Err.), m^3 s^{-1}	NH_4^+	TON	NO_3^-
Mississippi (MS)	07289000	19234 (9938)	11.2 (3.2)	165.4 (14)	348.1 (32.4)
Ohio (KY)	03277200	3040 (2719)	63.4 (11.1)	365.4 (33)	579.7 (24.3)
Missouri (MO)	06934500	2644 (1830)	4.2 (0.8)	74.5 (4)	130.2 (28.1)
Arkansas (AR)	07263450	1370 (1448)	7.4 (0.7)	86.6 (11.9)	53.2 (12.2)
Susquehanna (MD)	01578310	1090 (1243)	48 (5)	193.5 (7.2)	674.2 (12)
Willamette (OR)	14211720	940 (936)	51.3 (7)	329 (19.2)	682 (91)
White (AR)	07077000	859 (557)	19.5 (2.5)	150.6 (16.1)	101.9 (15.2)
Illinois (IL)	05586100	703 (563)	64.2 (8.5)	352 (14.1)	1586.9 (70.7)
Apalachicola (FL)	02359170	697 (502)	10.9 (8.1)	112.2 (11.4)	193.7 (35.9)
Pend Oreille (WA)	12395500	674 (460)	4.1 (0.9)	55.1 (7.3)	6.8 (3)
Connecticut (CT)	01184000	499 (475)	80.4 (7.7)	168.7 (11.3)	225.5 (8.9)
Colorado (AZ)	09380000	423 (208)	0.8 (0.1)	11.3 (0.6)	15.3 (0.5)
Kootenai (ID)	12318500	433 (220)	10.9 (3.7)	184.1 (22)	30.1 (7.9)
Clearwater (ID)	13342500	409 (360)	11.6 (3.5)	101.9 (18.9)	68.1 (32)
Penobscot (ME)	01036390	276 (359)	23.1 (3.7)	169 (21.6)	39.5 (8.3)
Hudson (NY)	01358000	400 (374)	67 (10.9)	255.5 (37.4)	322.3 (29.2)
Monongahela (PA)	03085000	362 (371)	55.4 (4.7)	211.2 (15.6)	511.2 (49.8)
Red (AR)	07341500	359 (375)	6.4 (3.1)	62.8 (9.9)	34.7 (29.4)
Delaware (NJ)	01463500	325 (322)	35.1 (3.7)	276 (17.2)	470.6 (26.8)
Yellowstone (MT)	06329500	314 (275)	3.7 (1.7)	39 (2.9)	15.6 (3.9)
Snake (ID)	13154500	294 (138)	4.7 (1.4)	40.6 (2.2)	127.7 (5.7)
Chattahoochee (AL)	02343801	296 (296)	38.1 (24.7)	141.7 (38.1)	168.2 (36.9)
Iowa (IA)	05465500	282 (301)	42.2 (31.8)	412.1 (40.9)	1829.3 (390.5)
Pee Dee (SC)	02131000	275 (242)	34.1 (12.4)	167.9 (21.9)	140.3 (25.4)
Sacramento (CA)	11370500	280 (232)	6 (2.8)	56.1 (11.2)	58.3 (13.5)
Suwannee (FL)	02323500	258 (182)	9.8 (1.3)	147.8 (25.5)	157.3 (10.1)
Trinity (TX)	08066500	269 (357)	7.8 (2.1)	118.7 (8.9)	127.6 (28.2)
Flathead (MT)	12363000	263 (216)	15.4 (4.9)	116.8 (20)	51.3 (17.5)
Wisconsin (WI)	05407000	258 (164)	23.6 (5.5)	236.2 (14.9)	193.1 (30.3)

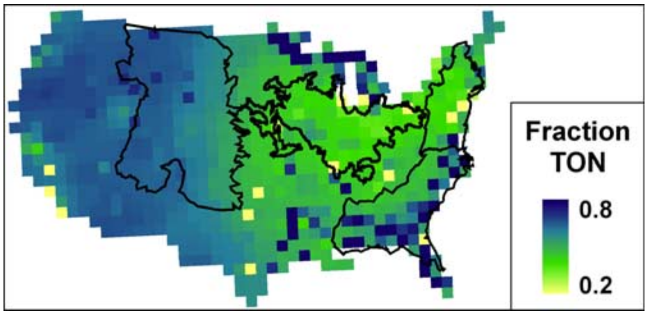

Figure 2. Spatial depiction of the long-term mean annual fraction of the riverine load consisting of TON using the regression model and average properties for the model parameters. The four regions (Midwest, Intermountain West, Northeast, and Southeast) used to examine downstream patterns are outlined in black.

through the river network, including areas of higher hydrologic retention (e.g., riverine wetlands).

[11] Spatially across the conterminous United States, organic nitrogen is the dominant nitrogen fraction within riverine nitrogen loads (Figure 2). Regional nitrogen patterns from 850 USGS stream-gaging stations highlight the spatial variability in the TON fraction within riverine loads, which is a function of nitrogen sources, physical delivery (e.g., hydrologic processes), and in-stream biogeochemical processes. The simple statistical model developed to examine annual TON fractions across the conterminous United States resulted in four major predictive variables: population density, nitrogen fertilizer application and deposition, mean annual precipitation, and woody wetlands (a land-use variable indicative of active floodplain areas) (Table 2 and Figure 2). In areas with higher population density, fertilizer application and nitrogen deposition (Northeast and Midwest regions), TON comprised a low percentage of the total riverine nitrogen. The floodplain metric appears to be the variable that helps relate speciation to a combination of factors, including high natural organic nitrogen sources from the uplands, low organic matter sorption rates, and high rates of biogeochemical processes in overbank floodwaters that have a greater contact area with sediment surfaces in the southeast United States. West of the Mississippi River, organic nitrogen is the dominant fraction because anthropogenic inorganic nitrogen sources are minimal. These patterns illustrate the importance of organic nitrogen within a large portion of the conterminous United States, and point out the need to examine the fate and transport of riverine organic nitrogen. A few studies have shown that the bioavailability of organic nitrogen (utilization via uptake and mineralization) can range from less than 10% in forested catchments to over 80% in urban stormwater [*Kaushal and Lewis*, 2005; *Seitzinger et al.*, 2002b; *Stepanauskas et al.*, 2000, 1999; *Wiegner and Seitzinger*, 2004], demonstrating the importance of organic nitrogen in riverine ecosystems. These patterns illustrate the importance of organic nitrogen within a large portion of the conterminous United States, and point out the need to examine the fate and transport of riverine organic nitrogen at a national scale.

[12] Regional differences in ON concentrations in the nation's rivers are controlled by a combination of factors including: (1) lateral inputs with spatially varying loads into the stream network, (2) in-stream production, and (3) in-stream removal. Rates of in-stream production and respiration vary over the year as nitrogen sources, incoming solar radiation, and temperature fluctuate. Temporal variations in ON and NO_3^- within the river network appear to vary accordingly, showing that ON is highest during the summer months (July–September and NO_3^- lowest during the same period (Figure 3). This is illustrated in both the Intermountain West and the Midwest, where NO_3^- and TON have an inverse seasonal pattern. The summer period has the lowest streamflow (auxiliary Table S1), and in general has the highest primary productivity (from epiphytes, phytoplankton, and macrophytes). Exceptions occur within small, forested headwater streams [*Mulholland*, 2004], where primary NO_3^- uptake is highest during the spring before leaf out. We hypothesize that the general patterns of ON and NO_3^- in summer are controlled by low streamflow and reduced velocity, which results in greater solute contact with streambeds and higher mineralization, as well as high nitrate uptake by the biota within the stream sediments during the summer (which results in net organic nitrogen production). This freshly produced organic matter may in turn be used to drive respiration, including denitrification, when organic carbon is limiting. Furthermore, higher water temperatures within the summer period are expected to also increase denitrification, contributing to the observed patterns [*Holmes et al.*, 1996]. Although the total nitrogen loads are lowest during the summer, nitrogen speciation and

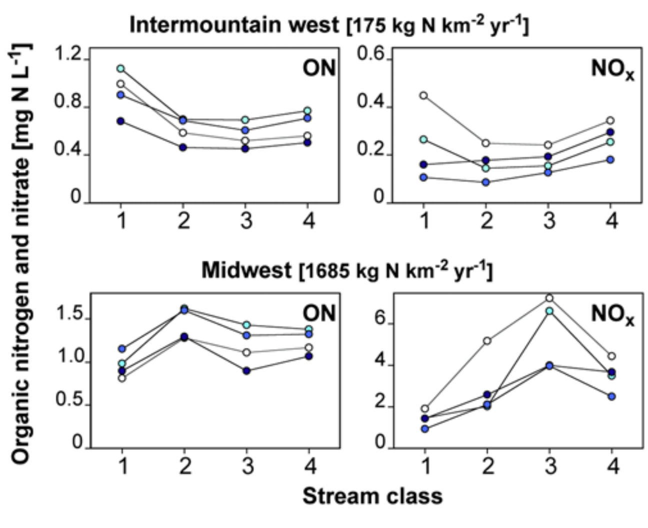

Figure 3. (left) Total organic nitrogen (ON) and (right) nitrate long-term median concentrations grouped by stream class (stream class 1 = 10 < Q < 100; 2 = 100 < Q < 500; 3 = 500 < Q < 2000; 4 = 2000 < Q < 8000) throughout the year (January–March, light blue circle; April–June, medium blue circle; July–September, dark blue circle; October–December, open circle). The long-term mean N-yield is also indicated in brackets.

Table 4. Average TON Fraction in Long-Term Mean Annual Riverine Loads in Stations Within 50 km of a Coastline

Coastline	Average Fraction TON in Stations < 50 km From Coastline
NE Atlantic coast	0.33
SE Atlantic coast	0.83
Gulf of Mexico	0.64
Great Lakes	0.37
Pacific coastline	0.41

reactivity is still important for water-quality concerns (e.g., eutrophication) through the river network.

[13] Organic nitrogen concentrations remain elevated during high-flow periods (rainfall/snowmelt) within the Intermountain West (IMW), Midwest (MW), and Northeast (NE) regions (Figure 3 highlights the IMW and MW regions, although the NE region has a similar pattern). These observations are consistent with detailed observations in streams dominated by snowmelt, where dissolved organic nitrogen increases in concentration during the snowmelt period [*Coats and Goldman*, 2001; *Kaushal and Lewis*, 2003]. The rise in DON during snowmelt is hypothesized to be the result of heterotrophic processing under the snowpack during the winter, and the subsequent flushing during snowmelt of a bioavailable organic nitrogen compartment under the snowpack and another compartment of less labile and more humic-like organic nitrogen from shallow flow paths [*Kaushal and Lewis*, 2003]. Although the humic-like organic nitrogen is less labile, downstream transport and exposure to sunlight will alter the bioavailability of this pool of organic nitrogen through in-stream processing and photochemical oxidation, resulting in organic matter that is available to drive in-stream respiration and potentially result in O_2 depletion.

[14] Downstream longitudinal patterns of organic nitrogen highlight the abundance of this nitrogen pool from headwater streams to larger rivers across all four regions. Although shifts in the abundance of organic nitrogen vary across regions through the stream network, its presence throughout the stream network suggests that this ubiquitous pool of nitrogen may be an important component of ecosystem functioning and trophic dynamics. Although the most labile pool of organic nitrogen may be consumed quickly within smaller headwater streams [*Brookshire et al.*, 2005], organic matter photolysis throughout the stream network will continually produce smaller, labile organic nitrogen compounds, providing both a nitrogen and carbon source for the bottom of the aquatic food chain. Furthermore, the abundance of organic nitrogen in larger rivers across all regions that discharge into N-limited estuaries/waterbodies further underscores the need to consider organic nitrogen fate and transport. This is highlighted by the percentage of TON in the total nitrogen loads in Southeastern rivers in close proximity to coastal waters, where the % TON in total nitrogen load is over 80% (Table 4).

[15] Although temporal patterns of N are relatively consistent across the four regions, downstream longitudinal patterns through the stream network are variable (Figure 4). However, controlling factors behind the ON patterns can be put forward and discussed to stimulate research directions. Firstly, the stream channels within the IMW region appear to be significantly different in channel morphology in comparison to the other 3 regions, as measured by the width to depth ratio (W:D) for each stream class. In the IMW, for any given stream class (categorized by discharge as in Figure 2), the W:D ratios are higher than in the Southeast (SE), MW, and NE regions suggesting that the channels in the IMW are on average wider and/or more shallow. Solutes transported within the IMW streams therefore will have the potential for mineralization due to higher rates of contact with the stream bottom. The sharp decline in ON from the 1st to the 2nd stream class in the IMW region is consistent with the higher W:D ratios in the IMW, resulting in greater solute contact and residence time in areas of the stream with high microbial processing rates (e.g., benthic zone, hyporheic zone). Further downstream, ON concentrations do no show any appreciable change suggesting that ON removal and production rates are in balance with each other although the composition of the ON pool may be changing. Although it appears that a large portion of the delivered terrestrial organic nitrogen from soil flushing is rapidly consumed within smaller channels, the fate of the remaining terrestrial organic nitrogen within the river network is still largely unknown.

[16] Secondly, the contrast between longitudinal patterns in the MW and NE regions is consistent with one of the River Continuum Concept (RCC) [*Vannote et al.*, 1980] tenants, the importance of shading on the balance between in-stream production and respiration. In the RCC, it is theorized that predictable patterns of net ecosystem metabolism and primary production exist from headwater streams to larger rivers, where the switch between a net heterotrophic stream to an autotrophic stream is largely controlled by the amount of incoming solar radiation to the channel and the water clarity. Subsequent studies have shown the importance of both light and inorganic nitrogen availability on primary production [*Mosisch et al.*, 2001]. Changes in primary production (PP) and respiration (R) will alter nitrogen concentrations; a P/R < 1 will decrease organic

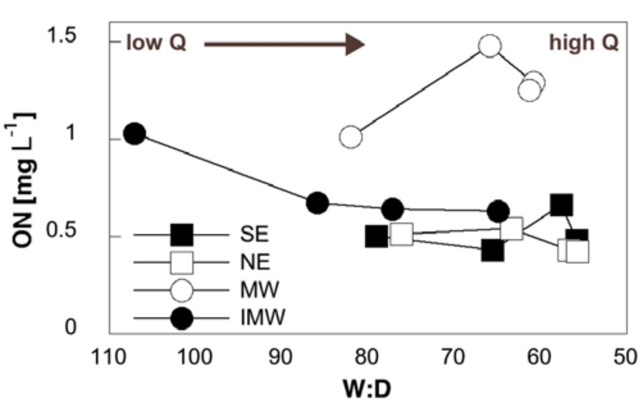

Figure 4. Long-term median annual organic nitrogen concentration for each of the four highlighted regions plotted against the width to depth ratio for the four stream classes.

nitrogen, in contrast to a P/R > 1, which will increase organic nitrogen. In the MW region, which has the highest ON concentrations, the riparian zones are often devoid of larger trees and hydrologic processes are highly altered (e.g., tile drainage) resulting in high inorganic nitrogen loading to streams. Although the NE region also has elevated inorganic nitrogen levels, the riparian zone is generally less altered and contains more trees that provide shading to the water column. We are therefore suggesting that one of the factors contributing to the significant difference in ON patterns is the influence of light on primary productivity, as evidenced by streams in the MW that are not limited by light, which results in high primary productivity. This pattern is consistent with the RCC and the importance of shading on in-stream processes, whether the shading (or lack of) is natural or anthropogenic. However, another important remaining uncertainty is the contribution of ON from the landscape to the stream network, which in addition to any in-stream processes will alter downstream patterns.

[17] Lastly, the SE longitudinal pattern in ON in the SE region suggests the importance of riparian wetlands on downstream nitrogen speciation. The increase in ON within the 3rd stream class (which has an ON > 0.5 mg N L^{-1}) in the SE region is seen in the annual patterns (Figure 4). These riparian wetlands are seasonally inundated and connected with the main stem river, and in turn may be a local source of organic nitrogen but a sink for inorganic nitrogen. The spatial regression model (Figure 2) and the models for NH_4^+ and NO_x yields also suggest the importance of riparian wetlands on nitrogen speciation and transformation. These results are also consistent with the examination of organic nitrogen in the NE region, where the percentage of wetlands was a significant predictor of organic nitrogen concentrations [*Pellerin et al.*, 2004]. These findings point out the need for incorporating and understanding riparian connections within river networks, especially within areas of high connectivity between a river and a floodplain.

4. Conclusion

[18] In conclusion, our results illustrate the importance of considering the annual and seasonal delivery of inorganic and organic N to downstream waterbodies. Seasonal and longitudinal patterns suggest the importance of in-stream processes, and regional patterns draw attention to the importance of organic nitrogen in N-enriched areas and in the Southeast region. A greater emphasis should be placed on the consideration of organic nitrogen, the role of the various types of nitrogen sources delivered to the stream network, and the in-stream biogeochemical processes that alter the distribution between TON, NH_4^+, and NO_x. Storage of N due to spiraling between ON and inorganic nitrogen also has implications for basin-scale nitrogen budgets. The contribution of ON from the landscape versus in-stream generation through river systems remains a large uncertainty. Further exploration is necessary to elucidate and quantify the driving factors altering nitrogen speciation through the stream network, which in turn is critical to understanding the effects of nitrogen loading to downstream ecosystems.

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References

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

Bohlke, J. K., J. W. Harvey, and M. A. Voytek (2004), Reach-scale isotope tracer experiment to quantify denitrification and related processes in a nitrate-rich stream, midcontinent United States, *Limnol. Oceanogr.*, *49*, 821–838.

Boyer, E. W., C. L. Goodale, N. A. Jaworski, and R. W. Howarth (2002), Anthropogenic nitrogen sources and relationships to riverine nitrogen export in the northeastern U.S.A., *Biogeochemistry*, *57*, 137–169.

Brookshire, E. N., H. M. Valett, S. A. Thomas, and J. R. Webster (2005), Coupled cycling of dissolved organic nitrogen and carbon in a forest stream, *Ecology*, *86*, 2487–2496.

Caraco, N., and J. J. Cole (1999), Human impact on nitrate export: An analysis using major world rivers, *Ambio*, *28*, 167–170.

Coats, R. N., and C. R. Goldman (2001), Patterns of nitrogen transport in streams of the Lake Tahoe basin, California-Nevada, *Water Resour. Res.*, *37*, 405–415.

Diaz, R. J. (2001), Overview of hypoxia around the world, *J. Environ. Qual.*, *30*, 275–281.

Galloway, J. N., et al. (2004), Nitrogen cycles: Past, present, and future, *Biogeochemistry*, *70*, 153–226.

Goodale, C. L., J. D. Aber, and W. H. McDowell (2000), The long-term effects of disturbance on organic and inorganic nitrogen export in the White Mountains, New Hampshire, *Ecosystems*, *3*, 433–450.

Goolsby, D. A., and W. A. Battaglin (2001), Long-term changes in concentrations and flux of nitrogen in the Mississippi River Basin, U.S.A., *Hydrol. Processes*, *15*, 1209–1226.

Grimm, N. B., and K. Petrone (1997), Nitrogen fixation in a desert stream ecosystem, *Biogeochemistry*, *37*, 33–61.

Hagy, J. D., W. R. Boynton, C. W. Keefe, and K. V. Wood (2004), Hypoxia in Chesapeake Bay, 1950–2001: Long-term change in relation to nutrient loading and river flow, *Estuaries*, *27*, 634–658.

Holmes, R. N., J. Jones, S. G. Fisher, and N. B. Grimm (1996), Denitrification in a nitrogen limited stream ecosystem, *Biogeochemistry*, *33*, 125–146.

Howarth, R. W., G. Billen, D. Swaney, A. R. Townsend, N. Jarworski, J. R. Freney, V. Kueyarov, P. Murdoch, and Z. Zhao-Liang (1996), Riverine inputs of nitrogen to the North Atlantic Ocean: Fluxes and human influences, *Biogeochemistry*, *35*, 75–139.

Howarth, R. W., D. Walker, and A. Sharpley (2002), Sources of nitrogen pollution to coastal waters of the United States, *Estuaries*, *25*, 656–676.

Kaushal, S. S., and W. M. Lewis Jr. (2003), Patterns in the chemical fractionation of organic nitrogen in Rocky Mountain streams, *Ecosystems*, *6*, 483–492.

Kaushal, S. S., and W. M. Lewis Jr. (2005), Fate and transport of organic nitrogen in minimally disturbed montane streams of Colorado, U.S.A., *Biogeochemistry*, *74*, 303–321.

Kittel, T. G. F., et al. (2004), The VEMAP Phase 2 bioclimatic database. I: A gridded historical (20th century) climate dataset for modeling ecosystem dynamics across the conterminous United States, *Clim. Res.*, *27*, 151–170.

Lewis, W. M. (2002), Yield of nitrogen from minimally disturbed watersheds of the United States, *Biogeochemistry*, *57*, 375–385.

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

Mosisch, T., S. Bunn, and P. Davies (2001), The relative importance of shading and nutrients on algal production in subtropical streams, *Freshwater Biol.*, *46*, 1269–1278.

Mulholland, P. J. (2004), The importance of in-stream uptake for regulating stream concentrations and outputs of N and P from a forested watershed: Evidence from long-term chemistry records for Walker Branch Watershed, *Biogeochemistry*, *70*, 408–426.

Mulholland, P. J., H. M. Valett, J. R. Webster, S. A. Thomas, L. W. Cooper, S. K. Hamilton, and B. J. Peterson (2004), Stream denitrification and total nitrate uptake rates measured using a field ^{15}N tracer addition approach, *Limnol. Oceanogr.*, *49*, 809–820.

Nolan, J. V., J. W. Brakebill, R. B. Alexander, and G. E. Schwarz (2002), Enhanced River Reach File 2, *Rep. 02-20*, U.S. Geol. Surv., Reston, Va. (Available at http://water.usgs.gov/GIS/metadata/usgswrd/XML/erf1_2.xml)

Omernik, J. M. (1987), Ecoregions of the conterminous United States, *Ann. Assoc. Am. Geogr.*, *77*, 118–125.
Pellerin, B. A., W. M. Wollheim, C. S. Hopkinson, W. H. McDowell, M. R. Williams, C. J. Vorosmarty, and M. L. Daley (2004), Role of wetlands and developed land use on dissolved organic nitrogen concentrations and DON/TDN in northeastern US rivers and streams, *Limnol. Oceanogr.*, *49*, 910–918.
Perakis, S. S., and L. O. Hedin (2002), Nitrogen loss from unpolluted South American forests mainly via dissolved organic compounds, *Nature*, *415*, 416–419.
Rabalais, N. N., R. E. Turner, and W. J. Wiseman (2002), Gulf of Mexico hypoxia, a.k.a. "The Dead Zone", *Annu. Rev. Ecol. Syst.*, *33*, 235–263.
Schwarz, G. E., A. B. Hoos, R. B. Alexander, and R. A. Smith (2006), The SPARROW surface water-quality model—Theory, application, and user documentation [CD-ROM], U.S. Geol. Surv., Reston, Va. (Available at http://pubs.usgs.gov/tm/2006/tm6b3/PDF/tm6b3_titlepages.pdf)
Seitzinger, S. P., C. Kroeze, A. F. Bouwman, N. Caraco, F. Dentener, and R. V. Styles (2002a), Global patterns of dissolved inorganic and particulate nitrogen inputs to coastal systems: Recent conditions and future projections, *Estuaries*, *25*, 640–655.
Seitzinger, S. P., R. W. Sanders, and R. Styles (2002b), Bioavailability of DON from natural and anthropogenic sources to estuarine plankton, *Limnol. Oceanogr.*, *47*, 353–366.
Smith, R. A., G. E. Schwarz, and R. B. Alexander (1997), Regional interpretation of water-quality monitoring data, *Water Resour. Res.*, *33*, 2781–2798.
Stepanauskas, R., L. Leonardson, and L. J. Tranvik (1999), Bioavailability of wetland-derived DON to freshwater and marine bacterioplankton, *Limnol. Oceanogr.*, *44*, 1477–1485.
Stepanauskas, R., H. Laudon, and N. O. G. Jorgensen (2000), High DON bioavailability in boreal streams during a spring flood, *Limnol. Oceanogr.*, *45*, 1298–1307.
Turner, R. E., and N. N. Rabalais (2003), Linking landscape and water quality in the Mississippi River Basin for 200 years, *Bioscience*, *53*, 563–572.
Vannote, R. L., G. W. Minshall, K. W. Cummins, J. R. Sedell, and C. E. Cushing (1980), The river continuum concept, *Can. J. Fish. Aquat. Sci.*, *37*, 130–137.
Vitousek, P. M., J. D. Aber, R. W. Howarth, G. E. Likens, P. A. Matson, D. W. Schindler, W. H. Schlesinger, and D. G. Tilman (1997), Human alteration of the global nitrogen cycle: Sources and consequences, *Bioscience*, *7*, 737–750.
Wiegner, T. N., and S. P. Seitzinger (2004), Seasonal bioavailability of dissolved organic carbon and nitrogen from pristine and polluted freshwater wetlands, *Limnol. Oceanogr.*, *49*, 1703–1712.

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