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Temperature controls a latitudinal gradient in the proportion of watershed nitrogen exported to coastal ecosystems

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Abstract Increased export of biologically available nitrogen (N) to the coastal zone is strongly linked to eutrophication, which is a major problem in coastal marine ecosystems (NRC (2000) Clean Coastal Waters: Understanding and Reducing the Effects of Nutrient Pollution. National Academy Press, Washington, DC; Bricker et al. (1999) National Estuarine Eutrophication Assessment. Effects of nutrient enrichment in the nation's estuaries. NOAA-NOS Special Projects Office, Silver Spring, MD). However, not all of the nitrogen input to a watershed is exported to the coast (Howarth et al. (1996) Biogeochemistry 35:75–139; Jordan and Weller (1996) Bioscience 46:655–664). Global estimates of nitrogen export to coasts have been taken to be 25% of watershed input, based largely on northeastern U.S. observations (Galloway et al. (2004) Biogeochemistry 70:153–226; Boyer et al. (2006) Global Biogeochem Cycle 20:Art. No. GB1S91). We applied the N budgeting methodology developed for the International SCOPE Nitrogen project (Howarth et al. (1996) Biogeochemistry 35:75–139; Boyer et al. (2002) Biogeochemistry 57: 137–169) to 12 watersheds in the southeastern U.S., and compared them with estimates of N export for 16 watersheds in the northeastern U.S. (Boyer et al. (2002) Biogeochemistry 57:137–169). In southeastern watersheds, average N export was only 9% of input, suggesting the need for downward revision of global estimates. The difference between northern and southern watersheds is not a function of the absolute value of N inputs, which spanned a comparable range and were positively related to export in both cases. Rather, the proportion of N exported was significantly related to average watershed temperature (% N export = 58.41 $e^{-0.11 * \text{temperature}}$; $R^2 = 0.76$), with lower proportionate nitrogen export in warmer watersheds. In addition, we identified a threshold in proportionate N export at 38°N latitude that corresponds to a reported breakpoint in the rate of denitrification at 10–12°C. We hypothesize that temperature, by regulating denitrification, results in increased proportionate N export at higher latitudes. Regardless of the mechanism, these observations suggest that temperature increases associated with future climate change may well reduce the amount of nitrogen that reaches estuaries, which will have implications for coastal eutrophication.

Keywords Climate change · Denitrification · Eutrophication · Nitrogen budgets · Proportionate nitrogen export · Temperature · Watersheds

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Introduction

The transfer of nitrogen from one ecosystem to another is an emergent property that is of fundamental importance, as export from one system becomes input to another. Given that upstream sources often dominate inputs to coastal areas, nutrient transfer between watersheds and coastal ecosystems is an issue of particular relevance. Indeed, excess nitrogen input from rivers has been identified as one of the most significant problems facing coastal ecosystems, resulting in eutrophication and adverse environmental effects such as hypoxia and harmful algal blooms (Carpenter et al. 1998; Bricker et al. 1999; NRC 2000). There have been several efforts in recent years to develop relationships between watershed input and export to the coast for different areas of the world (e.g., Howarth et al. 1996; Boyer et al. 2002; Parfitt et al. 2006). However, the mechanisms that control the proportion of N exported remain poorly understood.

As part of the International SCOPE N Project, Boyer et al. (2002) developed a methodology for constructing annualized nitrogen budgets for watersheds that took into account inputs from atmospheric deposition, fertilizer, net food and feed import, and biological N fixation. They compiled budgets for 16 watersheds in the northeastern and mid-Atlantic U.S. (Fig. 1), and compared N input with riverine export to estuaries (measured as total N at the most downstream USGS water quality monitoring station). Although there was a strong linear relationship between input and export ($R^2 = 0.62$), riverine export accounted for only about one quarter of N input (Boyer et al. 2002). The predominant pathway for N loss from the watersheds was identified as denitrification, which accounted for an estimated 48% of N loss, with riverine export accounting for the next-largest loss, and a combination of N storage (soil and plants), export (wood and food), and ammonium volatilization accounting for the remainder (Van Breemen et al. 2002; Seitzinger et al. 2002).

Budgets of this type have been used to develop estimates of N loading to the global ocean. Recent estimates have used an average transport efficiency of 25% (Galloway et al. 2004; Boyer et al. 2006), which represents the average nitrogen export of 33, primarily northern temperate, systems throughout the world (including the 16 northeastern watersheds considered by the SCOPE project and several in Canada and northern Europe). However, the range of proportional export spanned from 10 to 40% (Boyer et al. 2006), suggesting that the 25% value may not apply to all regions.

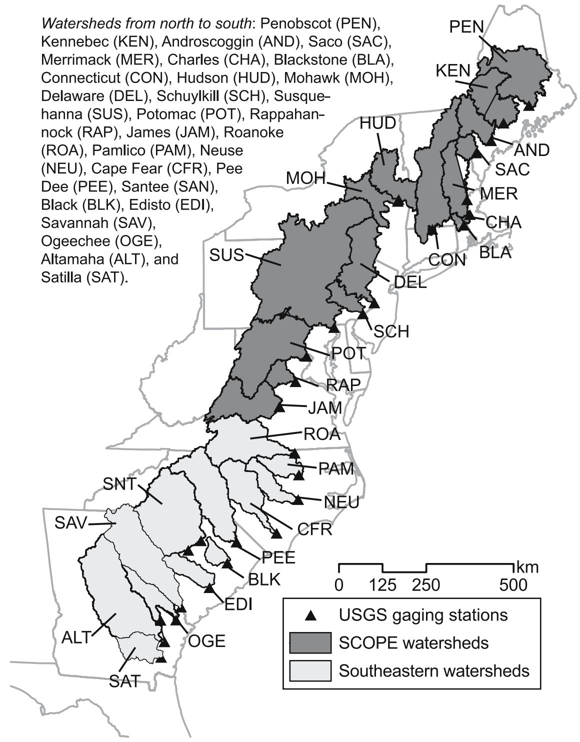

Fig. 1 Eastern U.S. riverine watersheds considered in this study. Watershed areas were delineated to the most downstream USGS water quality gaging stations (represented by triangles) based on data from the National Elevation Dataset (USGS 1999d). For watersheds with two gaging stations, area contributing to either gage was included. Analyses were done using ESRI ArcGis9 software

In this article we apply the SCOPE methodology (Boyer et al. 2002) to 12 watersheds in the southeastern U.S. (Fig. 1) and develop N budgets for the same base year (early 1990s). We use our results, along with those from the SCOPE project, to describe the relationships between input and export of nitrogen to coastal watersheds on the Atlantic coast of the U.S.. We then develop the argument that temperature, by affecting denitrification, exercises a primary control of watershed N export. We expect that this hypothesis will generate further investigations of the biogeochemical controls of N export from watersheds.

Methods

Watershed characteristics

The watersheds considered here were mapped to the most downstream USGS water quality gage based on an overlay of Digital Elevation Models (USGS 1999d) and 8-digit hydrologic unit codes (Steeves and Nebert 1994) performed with ESRI GIS software. The relative proportion of each county located inside each watershed was determined by overlaying the TIGER geographic database (USBoC 2005) on gaged watershed shapefiles, and all county-level data were adjusted according to these proportions. Land cover for the 12 study watersheds was obtained from the 1992 National Land Cover Dataset (USGS 1999a, b, c, 2000), and population density was calculated from 1990 U.S. Census Bureau data (USBoC 1990; Table 1). These are the same datasets used in the SCOPE study (Boyer et al. 2002).

Additional watershed characteristics were obtained for all 28 watersheds (both the SCOPE watersheds and those considered here; Table 2). Climatic information was calculated using gridded DAYMET data (Thornton et al. 1997) and averaged over the years 1988–1993. The average slope of each watershed was calculated from the National Elevation Dataset (USGS 1999d). Dams in each watershed were extracted from a shapefile of major dams of the U.S. (National Atlas 2006).

Nitrogen input

Total N input was calculated by summing external sources of N to a watershed, following the SCOPE methodology (Boyer et al. 2002) and using the same base time period (early 1990s). This period represents typical climatic conditions for the southeast. Sources of N considered were atmospheric deposition, fertilizer, biological N fixation, and net food and feed import.

Net atmospheric deposition

Data from wet (NADP 2005) and dry (USEPA 1995) atmospheric deposition stations in and around the study watersheds, averaged between 1987 and 1996, were interpolated in a GIS to create surfaces. Mean deposition was calculated based on the areal extent of each watershed. The contribution of atmospheric organic N to total N deposition was estimated as 30% of total atmospheric deposition (Neff et al. 2002), which was the estimate used in the SCOPE study. Half of this organic N was assumed to be new input (Boyer et al. 2002).

Fertilizer N input (described below) was used to calculate volatilization losses (Battye et al. 1994) for

Table 1 General characteristics of southeastern U.S. watersheds

Watershed	Abbreviation	Area (km^2)	Persons (km^{-2})	Flow (mm $year^{-1}$)	Forest %	Agric. %	Urban %	Wetl. %	Water %	Other %
Roanoke	ROA	21,984	40	352	69.6	22.2	2.8	1.7	2.5	1.4
Pamlico	PAM	5,748	35	334	58.8	26.5	2.7	10.3	0.6	1.0
Neuse	NEU	7,033	103	341	51.0	29.3	7.6	9.8	1.5	0.7
Cape Fear	CFR	13,599	82	355	62.8	20.8	7.0	6.0	1.5	1.8
Pee Dee	PEE	21,448	62	467	61.2	27.0	5.5	3.8	1.1	1.4
Santee	SNT	32,017	71	433	69.7	18.1	7.0	0.8	2.2	2.1
Black	BLK	3,274	32	286	33.3	43.5	3.0	18.1	0.2	1.9
Edisto	EDI	6,944	39	337	45.0	32.3	1.6	15.2	0.7	5.3
Savannah	SAV	25,488	25	418	65.9	18.0	2.8	4.7	3.6	4.9
Ogeechee	OGE	8,415	29	330	44.9	33.6	0.7	14.2	0.6	5.9
Altamaha	ALT	35,112	51	339	57.9	24.5	3.5	7.3	1.2	5.7
Satilla	SAT	7,348	14	275	45.9	30.4	1.0	14.4	0.6	7.7
Area-weighted average			51.3	379	60.9	23.8	4.2	5.9	1.8	3.4

Population density calculated from U.S. Census bureau data (USBoC 1992), flow from USGS stream flow data (USGS 2005), and land cover from the National Land Cover Database (USGS 1999a, b, c, 2000)

Table 2 Climate and slope characteristics of watersheds of the eastern U.S.

Watershed	Abbreviation	Mean temp. (°C)	Precip. (mm year^{-1})	Mean slope (°)
Penobscot	PEN	4.2	1,145	3.7
Kennebec	KEN	4.3	1,129	5.2
Androscoggin	AND	4.5	1,177	8.0
Saco	SAC	5.8	1,248	8.5
Merrimack	MER	7.4	1,195	6.1
Charles	CHA	9.6	1,241	3.2
Blackstone	BLA	9.1	1,296	4.3
Connecticut	CON	6.2	1,212	7.9
Hudson	HUD	6.2	1,213	8.4
Mohawk	MOH	6.9	1,200	5.7
Delaware	DEL	8.3	1,205	6.9
Schuylkill	SCH	10.6	1,217	5.5
Susquehanna	SUS	8.7	1,091	8.1
Potomac	POT	11.3	1,043	8.9
Rappahannock	RAP	12.7	1,085	6.7
James	JAM	12.2	1,150	10.9
Roanoke	ROA	13.8	1,181	5.9
Pamlico	PAM	15.2	1,155	2.3
Neuse	NEU	15.7	1,200	2.3
Cape Fear	CFR	15.7	1,186	3.2
Pee Dee	PEE	15.4	1,220	4.9
Santee	SNT	15.6	1,276	5.5
Black	BLK	17.4	1,213	0.7
Edisto	EDI	17.9	1,259	1.3
Savannah	SAV	16.5	1,339	4.3
Ogeechee	OGE	18.1	1,260	1.6
Altamaha	ALT	17.8	1,252	2.7
Satilla	SAT	19.3	1,299	0.7

Precipitation and temperature data calculated from DAYMET gridded climate data (Thornton et al. 1997), and slope calculated from USGS elevation data (USGS 1999d) for watersheds of the eastern U.S.

each type of N found in fertilizer (Battaglin and Goolsby 1994). For losses from animal manure, ammonia emission rates (Battye et al. 1994) were multiplied by the total number of animals in the watershed (see below). Following SCOPE (Boyer et al. 2002), we assumed that 25% of both of these emissions were transported long-range as an export from the watershed and subtracted them from total deposition.

Fertilizer input

The 1991 county-by-county fertilizer sales and N content estimates (Battaglin and Goolsby 1994) were weighted by the proportion of agricultural land in each county located inside the watershed. This proportion was calculated from land cover classifications (USGS 1999a, b, c, 2000).

Net food & feed import

Net food and feed import refers to the total amount of N that must be imported into a watershed to sustain resident populations, and is calculated by subtracting total N production (by crops and livestock) from total N consumption (by humans and livestock).

Information on livestock and crops (those comprising 1% or more of harvested cropland in the watershed) grown in each county was obtained from the 1992 Census of Agriculture (USDA-NASS 1992). Crop N contents were calculated using published conversion factors (USDA-NRCS 2005; Lander and Moffitt 1996). N consumption and N excretion by livestock were estimated using published rates (Van Horn 1998); the difference between them was assumed to constitute animal production. Except for hay, forage, and silage crops, 10% of both crop and animal production was subtracted to account for pests, spoilage, and inedible parts (Boyer et al. 2002).

Human population estimates were obtained based on 1990 county data (USBoC 1990). N consumption was estimated using a per-capita annual rate of 5 kg N year^{-1} (Garrow et al. 2000).

Biological N fixation

Crop N fixation was calculated by obtaining 1992 county-wide acreages of hay, pastureland, peanuts, and soybeans (USDA-NASS 1992) and multiplying by published fixation rates (Table 3).

The symbiotically nitrogen-fixing tree species considered by Boyer et al. (2002) are black locust and alder. Black locust was assumed to make up 10% of oak-hickory forest (Boyer et al. 2002) and to have a fixation rate of 5,000 kg km^{-2} year^{-1} (Boring and Swank 1984). Alder was assumed to cover 10% of wetland areas (Boyer et al. 2002) and have a fixation rate of 4,000 kg km^{-2} year^{-1} (Hurd et al. 2001). We obtained the acreage of oak-hickory forest from the USDA Forest Inventory and Analysis (USDA-FS 2005) and derived the wetland areas from land cover estimates (USGS 1999a, b, c, 2000) and applied the same assumptions as Boyer et al. (2002). Non-symbiotic forest N fixation by free-living soil microbes was assumed to be 40 kg km^{-2} year^{-1} (Boyer et al. 2002) and calculated from total forest area (USDA-FS 2005).

An additional N-fixing species found in the southeastern U.S. is kudzu (*Pueraria montana* var. *lobata*), an invasive leguminous vine. Estimates of the area covered by kudzu are preliminary and the N fixation rate of this species is not well characterized, but we estimate that fixation by kudzu could represent as much as an additional 15% of N input to these watersheds (Schaefer 2006). An increase in N fixation would result in a lower N export efficiency for southern watersheds.

Non-food crop export

We assumed that virtually all cotton and tobacco crops are harvested for sale elsewhere and therefore considered them as an export. About 10% of each was assumed to be lost to spoilage or pests. Neither crop is grown frequently in the northeast, so this represents a deviation from the methodology of SCOPE (Boyer et al. 2002). However, this adjustment represented less than 1% of the total N input.

Riverine export

The N export to the coast was estimated from USGS National Water Information System data (USGS 2005). Measurements of total N concentration were obtained for the water quality gage located furthest downstream on each river. In each case, we used all available measurements between the years 1987 and 1996. Whole-water concentrations of TKN (USGS water quality parameter 625) and nitrate + nitrite (parameter 630) were available for almost all cases. In the Canoochee River (a branch of the Ogeechee), nitrate + nitrate was available, as was ammonium (parameter 610), but TKN was not measured so the data do not include DON. The Canoochee only accounts for 18% of the watershed of the Ogeechee so we do not consider this a large source of error. In

Table 3 Biological nitrogen fixation rates used in this study

Crop	kg N km^{-2} year^{-1}	Reference(s)
Hay, alfalfa	22,400	Heichel et al. (1984)
Hay, non-alfalfa	11,700	Lander and Moffitt (1996), cited in Boyer et al. (2002)
Pastureland, all types	1,500	Jordan and Weller (1996)
Peanuts	8,000	Smil (1999)
Soybeans	9,600	Lander and Moffitt (1996), cited in Boyer et al. (2002)

the Santee River, TKN was available but only dissolved nitrate + nitrite (parameter 631) was measured as opposed to total. Differences between total and dissolved nitrate + nitrite were small in the rest of the data (in many cases values reported for dissolved were equivalent or even greater than those for total) so again this is not likely to be a large source of error. N concentrations were multiplied by discharge on the day of observation at the same station to obtain an estimate of load for each constituent. Average loads for each constituent were then summed, to get total N load, and divided by watershed area.

Three of the watersheds posed special difficulties. The water quality station near Eden, GA on the Ogeechee River was unusually far upstream. In order to include as much of the watershed as possible in this study, N export was combined with that from the Canoochee River, whose confluence with the Ogeechee River is below Eden. The same approach was used for the Santee River watershed, where gages on the Congaree and Wateree Rivers were combined. For the Altamaha watershed, water quality data from the Gardi, GA station were combined with flow data from the Doctortown, GA gage located approximately 7 km away.

Results

Southeastern U.S. watersheds are dominated by forest (average = 61% of watershed area), with agriculture as the next most important land use (average = 24%) (Table 1). Total N input ranged from 2,676 to 4,884 kg N km^{-2} $year^{-1}$, with an overall area-weighted average of 3,199 kg N km^{-2} $year^{-1}$. These values are comparable to those observed in the watersheds covered by the SCOPE study (Boyer et al. 2002), which ranged from 835 to 5,717 kg N km^{-2} $year^{-1}$ with an average of 3,088 kg N km^{-2} $year^{-1}$. The relative contributions of the various components of the N budget varied between the two regions: fertilizer was the most important N input in the southeast, averaging 33% of the total, whereas atmospheric deposition was the greatest contributor in the northeast and mid-Atlantic region, averaging 31% (Table 4).

When riverine N export is plotted against N input, the southeastern watersheds fall into a separate group from the more northern systems (Fig. 2). The James and Rappahannock River watersheds, which are the two southernmost systems covered by the SCOPE project, cluster with southern rivers and have been included in this analysis as southeastern watersheds. Both regions show significant increases in N export with increasing N input, but the relationship for the southeastern watersheds has a lower slope than that exhibited by the northern systems. The observed difference in these relationships is not due to methodological differences, as we followed a nearly identical protocol as was used previously. Instead, the different relationships suggest a fundamental difference in the extent of N processing in the two groups of watersheds. This difference is underscored when the proportion of N exported is plotted against latitude (Fig. 3A). On average, 9% of N input to southeastern watersheds was exported, with very little variation (range = 5–12%), as compared to an average of 28% for the more northern systems (range = 19–40%). There was a distinct break between the two sets of observations between about 38 and 39°N latitude.

Our results show a clear difference in proportionate N export between watersheds of the northeastern and southeastern U.S.. We performed an exploratory analysis to examine various factors that could have contributed to this difference. Note that our focus here is on explaining patterns in proportionate N export, which is a property that has received less attention than total export. Some of the factors that have been demonstrated as important predictors of total N export, such as increased population density (i.e. Caraco et al. 2003), would simultaneously increase input as well and so it is unclear how they would affect proportionate export. Factors considered included climate variables (temperature, precipitation); human population density; the amount of wetland/water area; various indicators of the residence time of water (slope, number of dams, area-weighted streamflow); the percent contribution of different N sources; and potential differences in forest N uptake.

Several of these relationships were significant, but only temperature and streamflow could be used to effectively differentiate between northern and southern watersheds (Figs. 3B, 4). In all other cases, although the range of the independent variables was often greater for northern than for southern watersheds, proportionate export from northern

Table 4 N budgets and N export for watersheds of the southeastern U.S.

Watershed	Net atmospheric deposition	Fertilizer	Fixation in forest lands	Fixation in agricultural lands	Net import in food & feed	Non-food crop export	Total watershed input	Riverine export	Percent export (%)
Roanoke (ROA)	758	821	46	697	601	34	2,889	197	7
Pamlico (PAM)	604	1,892	97	848	803	127	4,118	446	11
Neuse (NEU)	560	2,262	89	824	1,178	28	4,884	446	9
Cape Fear (CFR)	516	1,061	81	530	1,458	40	3,604	248	7
Pee Dee (PEE)	428	1,181	62	1,530	888	50	4,039	390	10
Santee (SNT)	661	556	56	496	909	2	2,676	312	12
Black (BLK)	609	2,010	118	839	-210	84	3,282	158	5
Edisto (EDI)	516	1,306	104	551	465	29	2,913	228	8
Savannah (SAV)	481	603	110	521	1,053	5	2,762	272	10
Ogeechee (OGE)	638	1,594	159	730	5	27	3,098	283	9
Altamaha (ALT)	529	1,138	132	572	750	22	3,099	273	9
Satilla (SAT)	468	1,678	111	137	817	8	3,203	365	11
Southeast area-weighted avg.	566	1,057	91	685	827	27	3,199	294	9
SCOPE area-weighted avg.	959	474	167	740	748	–	3,088	718	25

Total N input was obtained by summing all inputs (net atmospheric deposition, fertilizer, N fixation, and net food and feed import) and subtracting non-food crop export. Southeast area-weighted average is the average for the 12 watersheds considered in this study; SCOPE area-weighted average is for 16 watersheds in the mid-Atlantic and northeastern U.S. analyzed previously (Boyer et al. 2002). All numbers are in kg N km^{-2} year^{-1} unless otherwise noted

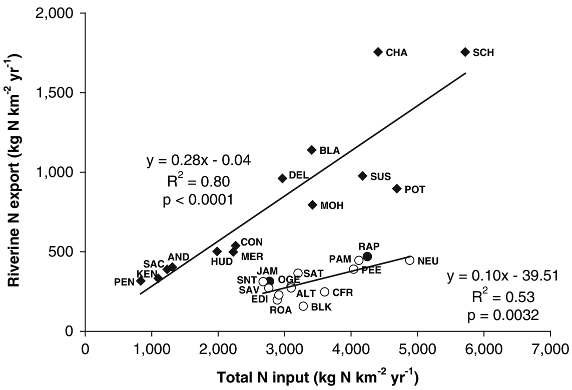

Fig. 2 Riverine N export versus total N input for watersheds of the eastern U.S. (filled symbols, SCOPE watersheds (Boyer et al. 2002); open symbols, this study). Line equations are for northern and mid-Atlantic watersheds (diamonds) and southeastern watersheds (circles). Riverine N export was calculated from observations of total N concentration and flow at the most downstream USGS water quality monitoring gage on each river. N input is the sum of net atmospheric deposition, fertilizer input, net food and feed import, and biological N fixation (see Methods). Watershed abbreviations are listed in Fig. 1. All data have been normalized to watershed area

watersheds was consistently greater than that from southern systems in the portion of the data set where the ranges overlapped. We explore the temperature and area-weighted streamflow relationships in greater detail below, but first we describe the various factors that were eliminated from further consideration.

Population density

Increased N export has been shown to be related to increased human population density (Caraco et al. 2003; Smith et al. 2003). If northern watersheds had higher population densities than more southern systems, it is possible that the attendant increase in N input could potentially result in less watershed processing and hence an increase in proportionate riverine export in northern systems. However, the ranges of population densities in northern and southern watersheds overlapped considerably, and, for a given density, the proportion of N export was always higher in northern systems than in southern ones (Fig. 5B). When all watersheds were considered together, there was a significant relationship between population density and riverine export due only to the influence of the three most densely populated

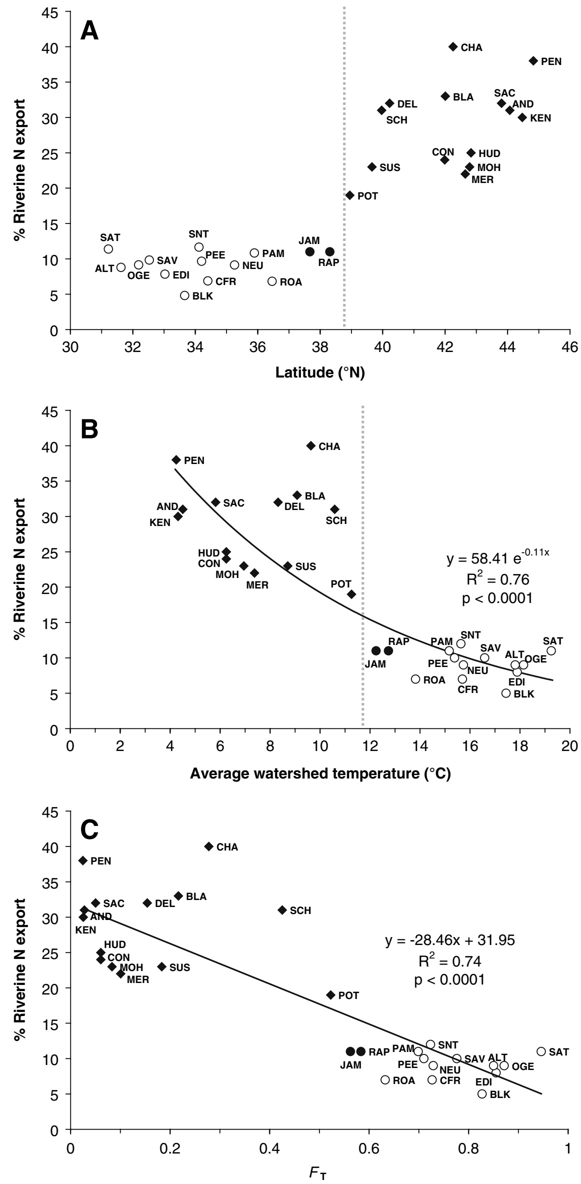

Fig. 3 Riverine N export as a percentage of total input to watersheds of the eastern U.S. versus (**A**) latitude; (**B**) average annual temperature; and (**C**) denitrification temperature factor (F_T). Latitudes are those of USGS water quality stations used to calculate riverine export. Temperature was calculated from DAYMET gridded climate data (Thornton et al. 1997) using ESRI ArcGIS 9.1 software. The dotted lines indicate the breakpoint. F_T, which is normalized to be 1 at 20°C, was calculated (after Hénault and Germon 2000) as: $F_T = \exp\left[\frac{(\text{temperature}-11)\ln(89)-9\ln(2.1)}{10}\right]$ below 11°C and $F_T = \exp\left[\frac{(\text{temperature}-20)\ln(2.1)}{10}\right]$ greater than or equal to 11°C. Symbols and watershed abbreviations as in Fig. 2

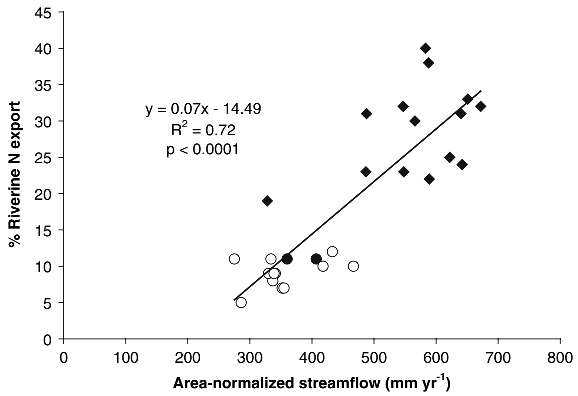

Fig. 4 Riverine N export as a percentage of total input versus annual streamflow. Symbols as in Fig. 2

watersheds (the Charles, Blackstone, and Schuylkill). We conclude that population density cannot explain the difference in N export between northern and southern watersheds, but it is a factor to consider for explaining high N export in some watersheds.

Wetland/water area

Denitrification occurs in aquatic environments, so one might expect a greater proportion of N removal in systems with a greater proportion of wetlands or open water. There were differences in the relative amounts of both of these land cover types across the study (the southern region had several watersheds with a higher percentage of wetland area and the northern region had several with a higher percentage of open water). Where their ranges overlapped, however, the northern systems exhibited proportionately more export, so neither wetland nor open water area could be used to separate the two groups. When taken as a whole, the relationship between percent wetland area and proportionate N export was not significant (Fig. 5C). Although the percentage of a watershed consisting of open water was significantly related to proportionate export, the relationship was positive, implying that watersheds with more lakes and reservoirs process less nitrogen (Fig. 5D). This is counter to what would be expected if water area were the primary control of N processing.

Residence time

Residence time has been shown to be an important factor in regulating denitrification in aquatic environments (Seitzinger et al. 2006), so increases in residence time in a watershed could potentially lead to increases in N immobilization and loss, and hence decreased N export. We therefore evaluated several different indicators of residence time: the proportion of the watershed behind dams (more dams and reservoirs leading to increased processing time); watershed slope (increased slope leading to decreased residence time); and precipitation and streamflow (increased runoff leading to decreased residence time).

The density of dams in the northeastern U.S. is approximately twice that in the southeastern U.S.. This suggests increased processing time in northern areas, which is the opposite of what would be expected if this factor were useful in explaining the differences in N export. However, the relationship between dam density and proportionate export was not significant (Fig. 5E). Although the northeastern group of watersheds had a higher average slope than the southeastern group (7 and 4 degrees, respectively), this factor again was not significantly related to export (Fig. 5F). Note that the northeastern watersheds show a decrease in export with increasing slope, which is again counterintuitive.

Howarth et al. (2006) suggested that precipitation may affect nitrogen export, with higher precipitation leading to greater export due to a shorter flushing time through the watershed. Although this relationship holds true for northeastern watersheds, the relationship with precipitation is not significant when the southeastern group of watersheds is included in the analysis (Fig. 5A).

Proportional N input

Differences in the relative proportions of various N inputs could potentially result in differences in N processing. Neither the percentage of net food and feed import nor that of biological N fixation was significantly related to % N export. The % fertilizer use showed a negative relationship with export (Fig. 5H), and the % input from the atmosphere was positively related to the percentage export (Fig. 5G). However, in both cases the northern systems exhibited proportionately more export in parts of the data set where the independent variables overlapped.

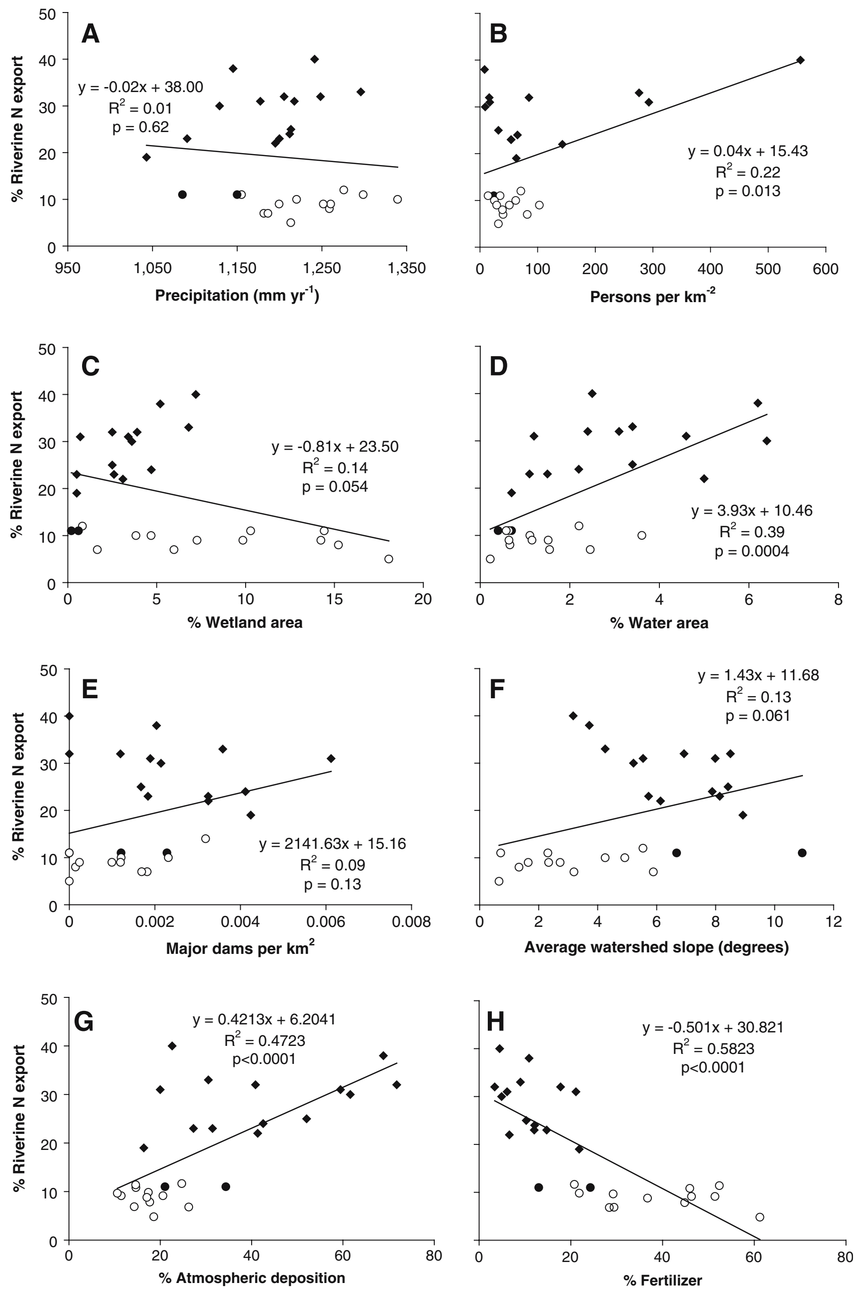

Fig. 5 Riverine N export as a percentage of total input to watersheds of the eastern U.S. versus (**A**) precipitation; (**B**) population density; (**C**) % wetland area; (**D**) % water area; (**E**) density of dams; (**F**) average watershed slope; (**G**) % atmospheric deposition; and (**H**) % fertilizer. Regression equations are for all data combined (both northeastern and southeastern watersheds). Symbols as in Fig. 2

Forest N uptake

It is also possible that differences in forestry practices could account for the latitudinal differences observed in N export. N sinks due to net N uptake by forests (which includes logging residue, harvest export, and net change in biomass) were calculated by Goodale et al. (2002) for watersheds considered in the SCOPE project. This included both the James and Rappahannock, which are grouped here with the southern watersheds. Although the two most northern systems (the Penobscot and Kennebec) had the lowest net N uptake, the highest rates were in the mid-Atlantic (between the Hudson and the Schuylkill). Moreover, differences in net uptake between the James and Rappahannock and other watersheds were generally than less than 400 kg N km^{-2} year^{-1} (Goodale et al. 2002), which is far less than the observed difference in export (southeastern watersheds have inputs of approximately 1,500–3,000 kg N km^{-2} $year^{-1}$ greater than northeastern watersheds with comparable riverine N export).

Temperature and streamflow

Temperature was significantly related to percent export (Fig. 3B). An exponential function of temperature explained 76% of the variance in percent export among watersheds (% export = 58. 41 $e^{-0.11 * \text{temperature}}$; R^2 = 0.76). These data can also be described as having a breakpoint, at an average annual watershed temperature between 11 and 12°C (Fig. 3B), below which proportionate export varies very little and above which it begins increasing.

Area-weighted streamflow was also significantly related to percent N export (R^2 = 0.72; Fig. 4). Howarth et al. (2006) evaluated both discharge and temperature as explanatory variables for fractional N export from the SCOPE northeastern watersheds, and found a better relationship with discharge (R^2 = 0.48) than with temperature (R^2 = 0.17). When the SCOPE data were combined with those presented here, however, temperature was slightly better than streamflow in explaining percent N export for the east coast as a whole. It was not useful to combine these parameters, as neither area-weighted streamflow nor temperature was significantly related to the residuals of the relationships presented in Figs. 3B and 4, respectively.

Flow is strongly correlated with temperature along the east coast of the U.S. ($R = -0.88$), so it is difficult to determine which parameter is driving the observed patterns in % N export. There is a suggestion in Fig. 4 that, for the same streamflow, % export from the northeastern systems might be greater than that from the southeastern ones, which would indicate that differences between the two areas remain regardless of streamflow, but there is not enough overlap in the data to evaluate this possibility. When we performed a multiple regression analysis that considered each of the factors, the best fit was obtained by combining temperature, watershed area, and population (R^2 = 0.85). Although these other predictors may be useful, as might streamflow, we conclude that temperature is the best single predictor for explaining the differences in proportional N export between northern and southern systems.

Our results bear comparison with the findings of Dumont et al. (2005), who developed a global model to estimate DIN export to coastal waters. They considered streamflow (but not temperature), and showed a gradient in proportionate N loading along the east coast of the U.S. but not in other areas of the world (their Fig. 5). It may be that DIN is not representative of total N export, or that factors such as biome type or whether a system is N-limited can obscure temperature-driven patterns in N-processing, particularly at global scales. However, our results suggest that temperature should be incorporated into future models of this type.

Discussion

Denitrification as a potential mechanism

Denitrification is often considered the primary pathway of N loss from watersheds (Seitzinger et al. 2002): denitrification in rivers can range up to 75% of input (Seitzinger 1990), and losses in the terrestrial portions of the landscape can be more than triple those in aquatic areas (Van Breemen et al. 2002). We focused specifically on the relationship between temperature and denitrification to determine whether it could explain the latitudinal disparity in N removal.

The temperature response of denitrification can be described as a piecewise exponential function (Stanford et al. 1975; Hénault and Germon 2000), which reflects the fact that the rate falls abruptly at lower temperatures. The temperature response is often modeled as a continuous Arrhenius function (Van Drecht et al. 2003), but this is less accurate because the fit tends to be poor and observations at low temperatures generally fall below the line (e.g., Westerman and Ahring 1987; Ambus 1993; Holtan-Hartwig et al. 2002). The exact temperature of the breakpoint varies among studies, as there are likely differences in denitrifier communities, but in temperate environments it is usually between 10 and 12°C (Focht and Verstraete 1977). In soil samples from Alberta, Canada, Malhi et al. (1990) found a 3.9-fold decrease in the denitrification rate between 10 and 4°C, as compared to only a 3.5-fold change between 10 and 40°C. More recently, Addy et al. (2005) reported significantly higher denitrification rates in marsh sediment above 12°C than at cooler temperatures.

The accordance between the breakpoint in denitrification activity and the shift in proportionate N export at 10–12°C (Fig. 3B) suggests that the temperature response of denitrification is a potential mechanism for the observed differences in N processing in watersheds. We explored this further by applying a dimensionless factor used in N modeling that scales denitrification to temperature and takes the breakpoint into account (Hénault and Germon 2000; Stanford et al. 1975). When the denitrification temperature factor is calculated based on average annual temperature in each watershed, the resulting relationship with percent export accounts for 74% of the variation among watersheds (Fig. 3C).

Numerous other factors such as soil moisture, crop type and substrate concentration also affect denitrification rates (Focht and Verstraete 1977; Pfennig and McMahon 1997) and likely explain some of the variability in these observations. For example, it is possible that very high N input can overwhelm the ability of denitrifiers to process the material. The three watersheds with the highest population density (the Charles, Schuylkill, and Blackstone) also showed low proportionate removal rates. When these three systems are excluded from the analysis, the relationships in Fig. 3B and C improve (R^2 = 0.84, $P < 0.0001$ and $R^2 = 0.85$, $P < 0.0001$, respectively). Since N export is related to population density (Caraco et al. 2003), the improvement in the model likely reflects the fact that the capacity of the watershed to process N can be exceeded by high total loads.

Implications for coastal N loading

The results reported in this study (an average of 9% N export in the southeastern U.S.) are far below previous global estimates of 25% export (Galloway et al. 2004; Boyer et al. 2002). Although it may be that different mechanisms become important at a global scale, it is likely that some of the scatter observed in other studies (individual watersheds vary from 10 to 40%; Boyer et al. 2006) is due to temperature-driven differences such as those described here. In a modeling exercise that used water residence time and temperature to predict nutrient delivery, Green et al. (2004) derived a global average transport efficiency of 18%. Although they concluded that the empirically determined value of 25% used elsewhere was reasonable, our data strongly suggest that the overall average estimate should be shifted downward.

The results presented here also imply a connection between climate change and eutrophication. With a doubling of atmospheric CO_2, global average temperature is expected to increase anywhere between 1.5 and 4.5°C (Houghton et al. 2001) and by up to 5°C in winter in the northern section of the U.S. (Moore et al. 1997). The relationships presented here predict increased N processing efficiency in warmer watersheds and a northward shift of the breakpoint, resulting in a lower proportionate N export to the coastal zone in the northern and mid-Atlantic states. It must be noted that concurrent increases in N inputs, which are also predicted (Howarth et al. 2002; Bouwman et al. 2005), would act to counterbalance these trends. Nevertheless, the observations presented here suggest that increased temperature would enhance nitrogen removal, thereby decreasing the proportion of N exported to estuaries and potentially reducing eutrophication rates.

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