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Role of wetlands and developed land use on dissolved organic nitrogen concentrations and DON/TDN in northeastern U.S. rivers and streams

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Abstract

Previous studies have shown that watersheds with significant human development (i.e., urban and agricultural land use) generally have higher concentrations and fluxes of dissolved inorganic nitrogen (DIN) in comparison to less-developed or forested watersheds. However, the impact of watershed development on dissolved organic nitrogen (DON) concentrations in drainage waters has received little attention. We present data from 39 watersheds in Massachusetts (Ipswich River watershed) encompassing a gradient of developed land use (0%–92% urban plus agriculture) and wetland abundance (0%–32%) to assess controls on mean annual DON concentrations and DON/total dissolved nitrogen (TDN) in drainage waters. In addition, we compiled published data from 119 northeastern U.S. watersheds to evaluate broader-scale relationships between DON, developed land use, and wetlands. The percentage of developed land is a poor predictor of DON concentrations in the Ipswich watersheds ($r^2 = 0.09$) and the compiled dataset ($r^2 = 0.27$). In contrast, wetland percentage explains 56% of the variability in DON concentrations in the Ipswich watersheds, and 60% when all literature data are included. Excluding watersheds with direct wastewater inputs to surface waters improves the regional relationship significantly ($r^2 = 0.79$). The DON : TDN ratio is best explained by a multiple regression of wetland percentage and developed land use percentage for both the Ipswich watersheds ($r^2 = 0.73$) and the compiled dataset ($r^2 = 0.50$). Watersheds with abundant wetlands may therefore have high DON concentrations and DON : TDN ratios despite elevated anthropogenic nitrogen inputs associated with human development.

Humans have significantly altered the global nitrogen (N) cycle in the temperate northeastern United States (Howarth et al. 1996; Boyer et al. 2002) via elevated atmospheric N deposition and inputs of anthropogenic N associated with land use change. As a result, current riverine N exports from the region are estimated to be 5–15 times higher than preindustrial exports (Howarth et al. 1996). Previous studies have assessed the potential influence of atmospheric N deposition on the concentration and relative fractions of dissolved inorganic (DIN) and dissolved organic N (DON) in stream export from temperate forested watersheds (Hedin et al. 1995; Campbell et al. 2000; Goodale et al. 2000; Perakis and Hedin 2002). Several studies have also evaluated the impact of urbanization and agriculture on DIN concentrations and fluxes from temperate rivers and streams (Jordan

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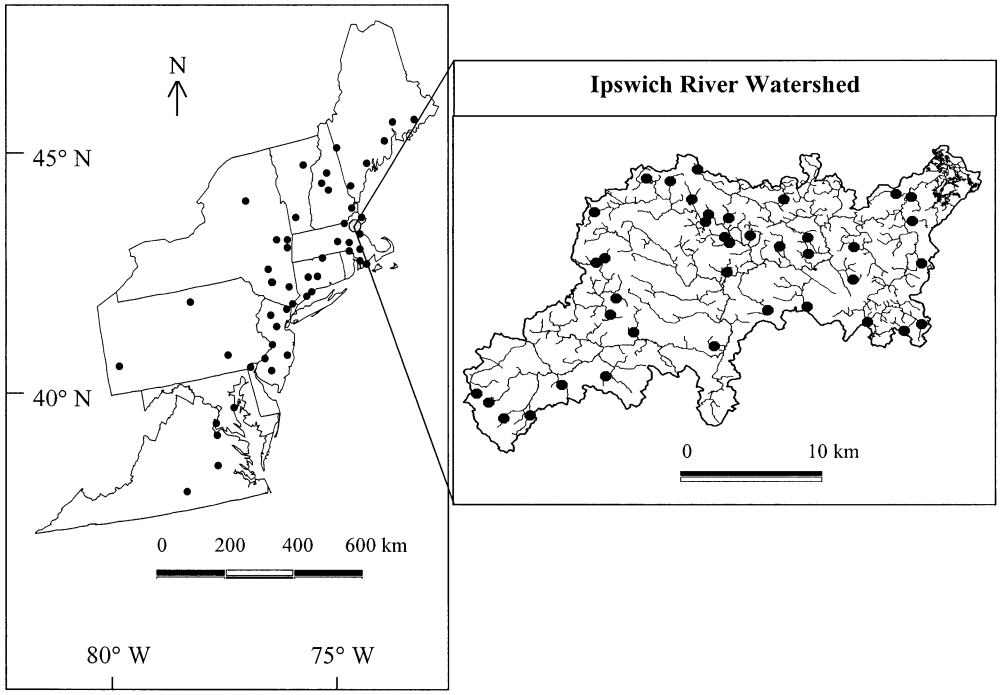

Fig. 1. Location of watersheds sampled within the 404-km^2 Ipswich River watershed and the location of watersheds included in our compiled dataset. Points outside of the Ipswich River watershed may represent more than one sampled catchment.

et al. 1997; Valiela et al. 1997; Herlihy et al. 1998; Boyer et al. 2002). Few studies, however, have evaluated the impact of human development (i.e., urbanization and agricultural development) on DON concentrations and DON : TDN ratios in drainage waters.

Urban and agricultural land use within watersheds has been linked to increased inorganic N concentrations in drainage waters via wastewater, fertilizer use, cultivation of N-fixing crops, and atmospheric deposition (Howarth et al. 1996; Jordan et al. 1997; Herlihy et al. 1998; Boyer et al. 2002). In addition to elevated DIN concentrations, wastewater discharge and runoff from intensive agricultural activity may contain elevated concentrations of DON (Westerhoff and Mash 2002). Seitzinger et al. (2002) have reported that a higher proportion of anthropogenically-derived DON was bioavailable to estuarine bacteria relative to forest-derived DON. Therefore, urban and agricultural activity may not only alter the importance of DON in hydrologic N losses, but they may also have serious implications for our understanding of estuarine and coastal eutrophication.

Our current knowledge of relationships between natural landscape features and DON concentrations in streams and rivers is also critically lacking. Wetlands have been shown to function as sinks for inorganic N through denitrification (Hill, 1996), as well as sites where inorganic N may be converted to organic N (Devito et al., 1989). Although regional studies linking DON to natural landscape features have had limited success (Clair et al., 1994), relationships between stream water dissolved organic carbon (DOC) (Mulholland and Kuenzler 1979; Eckhardt and Moore 1990; Raymond and Hopkinson 2003) and wetland abundance suggest that wetlands may play an important role in hydrologic DON losses from forested and developed watersheds.

Here we present data from forested and developed watersheds in northeastern Massachusetts to assess the importance of DON in hydrologic N losses. The specific goals of this paper are to: (1) determine the concentration and proportion of DON in total N losses from 38 subcatchments and the mouth of the Ipswich River watershed, (2) assess the influence of wetlands and developed land use on DON concentrations and DON as a fraction of total N in drainage waters, and (3) incorporate results from previously published studies in forested and mixed land use watersheds to assess the role of wetlands and human development on DON losses in the northeastern United States.

Methods

Site description—Samples for N analysis were collected from 38 subcatchments and the mouth of the 404-km^2 Ipswich River watershed in northeastern Massachusetts (Fig. 1). The watershed is one of three that drain into the Plum Island Sound estuary, and is part of the Plum Island Ecosystem Long Term Ecological Research (LTER) project. The Ipswich River watershed lies within the coastal lowland section of New England and is characterized by low to moderate relief and relatively poor drainage. Bedrock is mainly igneous and sedimentary rock (Paleozoic and Precambrian), and shallow soils are developed largely on surficial till, gravel, and sand deposits (Baker et al. 1964). Average annual precipitation is 1180 mm yr^{-1} and is uniformly distributed throughout the year. Mean monthly air temperature ranges

from −2°C in winter to 23°C in summer. Atmospheric N deposition (inorganic, wet plus dry) is approximately 700–800 kg N km^{-2} yr^{-1} (Ollinger et al. 1993). Organic N wet deposition is assumed to be a minor component (<5%) of total N deposition in eastern North America (Keene et al. 2002), although some studies in northeastern U.S. watersheds have considered DON to be as high as 15%–30% of N deposition (Boyer et al. 2002). Land use in the Ipswich River watershed (in 1999) is 37% forest, 35% urban, 7% agricultural, and 16% wetlands. Wetland area and land use were delineated from 1:5,000 orthophotography and 1:25,000 aerial photography (MassGIS) and were analyzed using geographic information system software. Urban land use in our study included land classified as residential, commercial, industrial, and transportation.

Subwatersheds sampled as part of this study are all headwater catchments (0.5–4.2 km^2) ranging from 0% to 92% developed (urban plus agriculture). Residential land use is the dominant form of development, with agriculture (mainly as pasture) totaling <10% of the land area in most watersheds. Wastewater from developed areas is released to septic systems or to municipal sewer systems that discharge directly to the Atlantic Ocean. Wetlands account for 0%–32% of the watershed area in the subcatchments (MassGIS) and are typically located along stream channels and in scattered small, upland depressions.

Sampling frequency—River water samples for N analysis were collected monthly at the mouth of the Ipswich River (42°39′35″ N, 70°53′39″ W) from 1998–2002, with higher frequency sampling (≈biweekly) from February 1999 to September 2000. In the 38 subwatersheds, samples were collected on four to five sampling dates from February 1999 to September 2000 and were distributed throughout the sampling period (February, April, September, and November). The number of samples collected from each site is a limitation in our dataset, but one that is often required when using spatially extensive sampling to discern broad scale patterns (Hedin et al. 1995; Lovett et al. 2000; Perakis and Hedin 2002). However, intensive sampling at the mouth of the Ipswich River was used to determine whether averaging N concentrations from the reduced sampling frequency provided a reasonable estimate of volume-weighted mean (VWM) DIN and DON concentrations. VWM concentrations were calculated as

$$\mathrm{VWM} = \left(\sum C_i Q_i\right) / \sum Q_i$$

where C_i is the measured nutrient concentration at time i, Q_i is the discharge volume for the period with the sample collection date as the midpoint, and $\Sigma\ Q_i$ is the sum of the annual discharge.

For the Ipswich River, arithmetic mean concentrations of DON collected on the five sampling dates and VWM concentrations based on approximately biweekly samples differed by 5% in 1999–2000 (477 vs. 452 μg L^{-1}). Similarly, DIN concentrations differed by only 8% (202 vs. 188 μg L^{-1}). This suggests that reduced sampling was adequate to characterize mean annual DON and DIN concentrations in our subwatersheds. Discharge was not measured from subwatersheds during the sampling period and differences in land cover preclude estimating discharge based on discharge from the mouth of the Ipswich River (U.S. Geological Survey gauging station 02102000). Fluxes are therefore not calculated for the subwatersheds in this study.

Sample collection and analysis—Samples from the mouth of the Ipswich River were collected in 1-liter polyethylene bottles or 10-liter polyethylene carboys, and filtered within 12 h of collection through precombusted Whatman 24-mm GF/F glass-fiber filters (pore size = 0.7 μm). Samples were stored on ice until transported to the laboratory and frozen in acid-washed polyethylene bottles until analysis. Similar methods were used for subwatershed sampling except that all samples were filtered into acid-washed polyethylene vials in the field.

NO_3^- and NO_2^- were measured using the cadmium reduction method on a Lachat QuikChem 8000 flow injection analyzer. NH_4^+ was measured colorimetrically by the indophenol method. Total dissolved N (TDN) was determined via persulfate oxidation with subsequent measurement of NO_3^- following the methods of Valderrama (1981). DON is quantified as TDN minus DIN (NH_4^+ + NO_3^- + NO_2^-). Analytical precision for NH_4^+ and NO_3^- is ±5% and instrument detection limits are typically <1.5 μg L^{-1} (C. Hopkinson pers. comm.). The reported percent N recovery following persulfate digestion generally ranges from 90% to 110% (Merriam et al. 1996; Bronk et al. 2000; Sharp et al. 2002; Westerhoff and Mash 2002).

Statistical analysis—Watersheds in this study were grouped by the fraction of developed land use (0%–20%, 21%–40%, 41%–60%, and >60%) to describe DON and DIN in each category. Because data were generally not normally distributed, significant differences in mean N concentrations and DON percentages were determined via the nonparametric Wilcoxon signed rank test at an alpha level of 0.05. In addition, N concentrations and DON percentage were regressed on developed land use or wetland fractions (or both) to evaluate relationships in our data. All statistics were performed using JMP software (version 4.04; SAS Institute, Inc.).

Results

Land use influence—Estimated VWM annual DON concentrations from the Ipswich River and 38 subcatchments ranged from 170 to 825 μg L^{-1} and did not differ statistically among land use categories (Fig. 2). DON concentrations for individual watersheds had a weak but significant negative correlation with the percentage of developed land use (r^2 = 0.09, p = 0.04; Table 1). In contrast to DON, watershed DIN concentrations varied by two orders of magnitude (16–1,314 μg L^{-1}) and were correlated with the percent of development (r^2 = 0.51, p < 0.01). Higher DIN concentrations in developed watersheds were largely due to NO_3^-, which accounted for half of the DIN in the least-developed category, and increased to 90% of DIN in the most-developed land use category (data not shown). The high standard deviation in the 21–40% developed category (Fig. 2) is due to

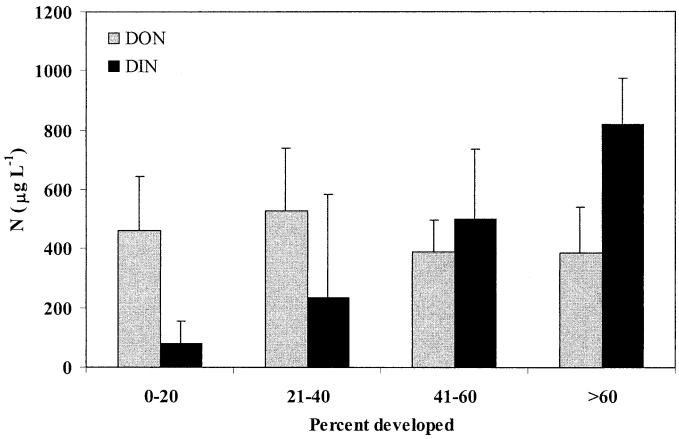

Fig. 2. Mean concentrations and standard deviations of DON and DIN in stream water and river water at the Ipswich River watershed sampling locations. Watersheds are grouped by the percentage of developed land use.

one outlier with consistently high DIN concentrations (mean = 1,233 μg L^{-1}, range for other 11 sites in this category = 13–239 μg L^{-1}). The DON percentage (as a fraction of TDN) ranged from 17% to 97% in individual watersheds and decreased as developed land use increased ($r^2 = 0.63$, $p < 0.01$). DON was the dominant form of N in watersheds with little to moderate development, accounting for 87% (±7%) and 73 (±24%) of TDN in the two categories with <40% developed land (Fig. 2). DON was a smaller fraction of TDN in more developed categories, accounting for 46% (±18%) and 32 (±10%) of TDN.

Wetland influence—Watersheds in this study had a range of wetland percentages (0%–32%), allowing for an assessment of the wetland influence on concentrations of DON and DIN and the DON percentage. Mean annual DON concentrations were significantly correlated with wetland percentage in Ipswich River subwatersheds ($r^2 = 0.56$, $p < 0.01$; Fig. 3, Table 1). DIN concentrations had a weak but significant negative correlation with wetland percentage ($r^2 = 0.27$, $p < 0.01$). Wetland percentage has a significant positive correlation ($r^2 = 0.42$, $p < 0.01$) with DON as a fraction of TDN in stream water. Multiple regression analyses, including both wetland percentage and the percentage of developed land, improved the r^2 for DON as a fraction of TDN ($r^2 = 0.73$), but did little to improve relationships with DON and DIN concentrations. Including agriculture as a separate land use rather than including it in ''developed'' did not substantially improve our results (data not shown).

Discussion

DON dynamics in the Ipswich River watershed—In this study, DON accounted for more than half of the hydrologic TDN losses from 54% of the watersheds sampled and more than one-third of TDN losses from 77% of the watersheds. Therefore, our data clearly indicate that DON can be a significant and often dominant fraction of TDN losses from watersheds influenced by moderately high atmospheric deposition and human development (Fig. 2). However, both land use and wetlands are critical landscape features for understanding the role of DON in hydrologic N losses.

Effect of land use on DON—Individual watershed (Valiela et al. 1997; Williams et al. unpubl.) and regional studies (Howarth et al. 1996; Boyer et al. 2002) in the northeastern U.S. have shown wastewater and fertilizer inputs to be important sources of inorganic N to surface waters. In addition, elevated surface water DON concentrations have been linked to wastewater treatment discharge and intensive agricultural activity in the United States (Westerhoff and Mash 2002). Our results, however, indicate that DON concentrations in streams are not strongly influenced by urban and agricultural land use in the Ipswich River watershed despite significant anthropogenic N inputs (Fig. 2, Table 1). In the Ipswich River watershed, wastewater is either discharged via septic systems or exported out of the catchment. In addition, fertilizer is mainly applied to urban lawns, which may leach a significant fraction of deposited N to subsoils (Valiela et al. 1997). Mineral forest soils are a major sink for DON (Ait-

Table 1. Adjusted r^2 values and p values (*in italics*) for DON, DIN, and DON/TDN as a function of percent wetlands and percent developed land use (simple regressions) and a multiple regression including both variables. Compiled regional data include Ipswich River watershed data. Regional sites without wastewater lack direct agricultural and human wastewater inputs.

				Compiled data			
	Variable	Ipswich only (n = 39)		W/out wastewater (n = 139†)		All sites (n = 156‡)	
DON (μg L^{-1}) vs.	wetlands	0.56	*	0.79	*	0.60	*
	developed	0.09	*(0.04)*	0.26	*	0.27	*
	wetlands, developed	0.55	*	0.80	*	0.65	*
DIN (μg L^{-1}) vs.	wetlands	0.27	*	−0.01	*(0.69)*	0.01	*(0.20)*
	developed	0.51	*	0.38	*	0.35	*
	wetlands, developed	0.55	*	0.53	*	0.45	*
DON/TDN vs.	wetlands	0.42	*	0.39	*	0.38	*
	developed	0.63	*	0.01	*(0.11)*	0.02	*(0.04)*
	wetlands, developed	0.73	*	0.50	*	0.50	*

† Wetland n = 112 (114 for DON).
‡ Wetland n = 139 (141 for DON).
* $p < 0.01$.

Table 2. Number of watersheds, watershed type, method of DON determination, and references for all data compiled for the northeastern U.S. Watershed types: For = entirely forested, Dev = developed (range in %). DON is calculated as TDN (measured by thermal oxidation or persulfate digestion) minus DIN of Kjeldahl N minus NH_4^+.

Number of watersheds	Watershed types	DON method	Source
10	For	Thermal oxidation	Goodale et al. (2000)
1	For	Persulfate digestion	McHale et al. (2000)
1	For	NA	Valiela et al. (1997)
15	For	Thermal oxidation	Campbell et al. (2000), Campbell (1996)
39	For	Persulfate digestion	Lovett et al. (2000)
5	For, Dev (<20%)	Kjeldahl nitrogen	Clark et al. (2000)
15	Dev (2–30%)	Kjeldahl nitrogen	Boyer et al. (2002), USGS (2000)
12	Dev (3–30%)	Thermal oxidation	Daley and McDowell (unpubl.)
2	Dev (38–53%)	Thermal oxidation	Hopkinson et al. (1998)
14	Dev (45–99%)	Kjeldahl nitrogen	Heinz Center (2002)
5	Dev (14–70%)	Kjeldahl nitrogen	USGS (2003), Chalmers (2002)

kenhead-Peterson et al. 2003) and we therefore hypothesize that significant abiotic soil retention of human-loaded DON is occurring in our watersheds. Long-term N-fertilization studies at the Harvard Forest in Massachusetts have shown, however, that DON concentrations in the forest floor (McDowell et al. 1998) and mineral soil solutions (Currie et al. 1996) increased as a result of experimentally elevated inorganic N deposition. The conversion of NO_3^- to DON in soils and the subsequent leaching of DON is possible in developed watersheds with high anthropogenic N inputs, but is not indicated by our data.

Although the percentage of developed land use is a poor predictor of DON concentrations in streams at our sites, it does explain a significant percentage of the variability in stream water DIN concentrations (r^2 = 0.51; Table 2) and therefore influences the ratio of DON : TDN. Mean DON concentrations across all land use categories varied by only 27%, whereas DIN concentrations increased by more than an order of magnitude with increasing development (Fig. 2). As a result, DON accounted for 32–87% of TDN, on average, with the highest values in the least-developed land use categories.

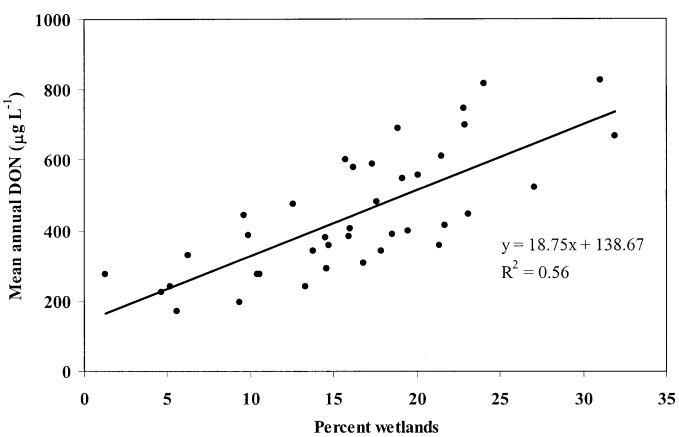

Fig. 3. Percent wetlands versus mean stream water DON concentrations (μg L^{-1}) from watersheds draining into the Ipswich River.

Effect of wetlands on DON—Wetlands are important sources of dissolved organic matter to streams and rivers, particularly when they fringe stream channels or discharge directly into streams (Mulholland and Kuenzler 1979; Eckhardt and Moore 1990; Fiebig et al. 1990; Fölster 2000; Raymond and Hopkinson 2003). Shallow flow paths from wetlands to streams bypass most mineral soils, which are known to retain DON as well as DOC (Aitkenhead-Petersen et al. 2003). In addition, the refractory nature of wetland-derived DON and DOC (Stepanauskas et al. 1999) likely limits its biological utilization en route to and in the stream channel. Several studies have related stream water DOC concentrations to the fractional area of wetlands in multiple watersheds (Mulholland and Kuenzler 1979; Ekhardt and Moore 1990). However, previous attempts to link hydrologic DON losses to landscape characteristics have been less successful. For example, Clair et al. (1994) found that basin slope and precipitation, both of which are factors in wetland development, explained only 30% of the variability in DON fluxes from Canadian watersheds.

Our results show that the percentage of wetlands within the Ipswich River watershed and subcatchments explains 56% of the variability in DON concentrations (Fig. 3). Wetland percentage also had a significant negative relationship with DIN concentrations in our study watersheds (r^2 = 0.27, Table 2). Although weak, this relationship suggests that wetlands at our study sites may be transforming inorganic N via denitrification (Hill 1996) or the conversion of inorganic N into organic forms (Devito et al. 1989). However, the relationship between DIN and wetlands might also be an artifact of a weak but significant (r^2 = 0.20) negative relationship between developed land use percentage and wetland percentage in our watersheds. The DON : TDN ratio increased as wetland percentage increased, although the relationship was not as strong (r^2 = 0.42) as that using developed land use as a predictor of DON percentage (r^2 = 0.63). However, combining both land covers in a multiple regression explains 73% of the variability of mean annual DON percentage for the Ipswich catchments.

Based on our data, the mean percentage contribution of DON to TDN losses from watersheds with up to 40% urban

and agricultural land (78% ± 20%; $n = 19$) was comparable to that reported by Perakis and Hedin (2002) for unpolluted, temperate old-growth forests in South America (mean = 80% DON). DON was only a small fraction of total N export from five eastern U.S. old-growth watersheds studied by the same authors, suggesting that chronic atmospheric N inputs may have caused a shift over time from organic to inorganic N (largely as NO_3^-) as the dominant N species in drainage waters. Our results suggest that watersheds receiving elevated N inputs due to urbanization and agriculture in addition to nearly 10 times higher atmospheric N deposition relative to the unpolluted South American watersheds (Hedin et al. 1995) may still overwhelmingly export N in the form of DON if wetlands occupy a significant fraction of the watershed.

Regional patterns of DON and DIN losses—In order to assess the role of land use and wetlands on hydrologic DON losses regionally, we compiled a dataset of 119 watersheds in the northeastern U.S. from various sources in the literature (Fig. 1, Table 2). Watersheds ranged in size from <1 to 70,000 km^2 and included 69 forested watersheds and 50 watersheds with developed land use (defined as urban plus agricultural). Mean annual precipitation ranges from 900 to 1,250 mm yr^{-1}, and mean annual temperatures range from approximately 13°C in the south to 4°C in the north (Boyer et al. 2002). The gradient of atmospheric N deposition (inorganic, wet plus dry) generally decreases from about 1,200 kg N km^{-2} yr^{-1} in southwestern Pennsylvania to 500 kg N km^{-2} yr^{-1} in northern Maine (Ollinger et al. 1993). Sites were characterized by 0–99% development and 0–12% wetlands. Land use and wetland cover data were taken from the published literature or obtained via personal communication (J. Campbell, C. Goodale, M. McHale) and may differ slightly in terms of data collection and land use classification.

Methodological issues—Different sampling methodologies are inherent in compiled datasets and need to be addressed before comparisons are made. Sampling frequencies ranged from weekly or biweekly (Campbell 1996; Campbell et al. 2000; Clark et al. 2000; McHale et al. 2000) to monthly (Goodale et al. 2000; Daley and McDowell unpubl.) or seasonally in spatially extensive studies (Lovett et al. 2000). DON concentrations for the SCOPE study sites (Boyer et al. 2002) and the New England Coastal Basins (NECB) study sites (Chalmers 2002) were not available in the literature and were therefore calculated from U.S. Geological Survey data at the stations reported in the literature. Volume-weighted mean DON and DIN concentrations were calculated for 1988–1992 at sites described by Boyer et al. (2002) and 1998–2000 for NECB study sites (Chalmers 2002). Sampling frequency varied by sites, but most samples were collected on a monthly basis. Volume-weighted N concentrations were calculated as previously described for the Ipswich River watershed. At all other sites except those in the Catskills (Lovett et al. 2000), discharge was either measured or modeled by the authors and used to calculate mean annual flow-weighted N concentrations. With the exception of two studies (Campbell et al. 2000; McHale et al. 2000), all samples were filtered through 0.45- to 0.7-μm pore-size filters before analysis. Both authors estimated that total organic N equaled DON (based on the lack of turbidity in unfiltered samples), and we therefore refer to total organic N from these studies as DON.

Analytical methods—A consideration for compiling data on DON is the lack of a standard analytical methodology. In our dataset, DON was either determined as the difference between TDN and DIN ($NO_3^- + NH_4^+$) or as the difference between Kjeldahl N (NH_4^+ + organic N) and NH_4^+ (Table 1). Inorganic N was measured colorimetrically or by ion chromatography, whereas TDN was measured by persulfate digestion or high-temperature catalytic oxidation. Method comparisons for TDN analysis indicate that both persulfate digestion and high-temperature oxidation typically produce similar results for freshwater and seawater samples, with N recoveries of 90–110% (Merriam et al. 1996; Bronk et al. 2000; Sharp et al. 2002; Westerhoff and Mash 2002). Cornell et al. (2003) noted that there were no clear differences in rainfall DON concentrations generated by Kjeldahl, ultraviolet, or oxidation methods, suggesting that concerns over different analytic methods may be overestimated.

The major uncertainty in DON concentrations comes from the TDN analysis and typically results in an underestimation of DON concentrations (Cornell et al. 2003). Cornell et al. (2003) found the precision and reproducibility of DON concentrations in rainwater improved as the DON : TDN ratio in samples increased. In samples with DON : TDN greater than 0.25, the percent standard deviation of DON concentrations was less than 25% (Cornell et al. 2003). Approximately 70% of the watersheds in our compiled dataset had DON : TDN ratios >0.25, suggesting that the uncertainty in DON concentrations in our database should not dramatically alter our conclusions.

Effect of land use on regional DON and DIN losses—Our literature dataset of 119 watersheds indicates that DON concentrations were higher on average from developed watersheds than forested watersheds in the northeastern United States (Fig. 4). Most forested watersheds in this study did not have wetlands, which may explain lower DON concentrations (as will be discussed in the following section). Combining the literature data with our Ipswich River watershed data shows that developed land use explains only a small percentage (27%) of the variability in mean DON concentrations in northeastern U.S. rivers and streams. Although there was a general trend of increasing DIN concentrations with development in both the Ipswich River watersheds (Fig. 2) and the literature data (Fig. 4), the percentage of urban plus agricultural land was not a strong predictor of DIN concentrations ($r^2 = 0.35$, $p < 0.01$) or DON/TDN ($r^2 = 0.02$) at the regional scale. A multiple regression with agricultural and urban land use as separate cover types improves these relationships only slightly (data not shown).

There are several possible factors influencing our ability to predict DIN and therefore DON/TDN based on land use in our compiled dataset. These include: (1) data limitations, (2) use of a simple predictive model, (3) land use history, and (4) confounding land cover–land use relationships. Nearly 60% of the watersheds in our literature dataset are

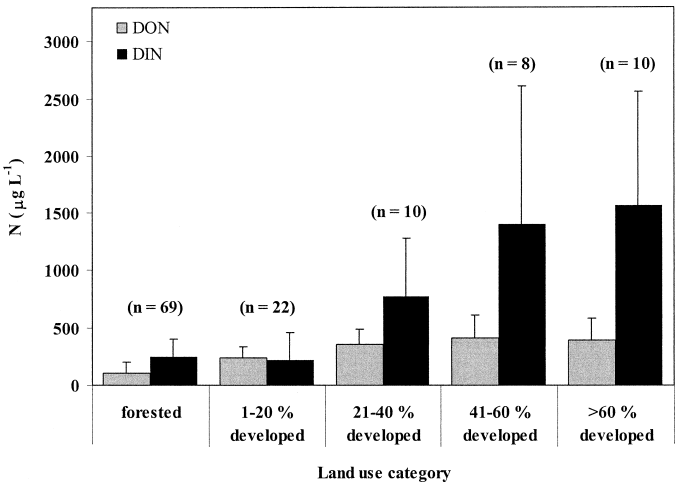

Fig. 4. Mean DON and DIN concentrations from watersheds in the northeastern U.S. based on the percentage of developed land use. Error bars are standard deviations. n = number of watersheds. See Table 1 for data references.

entirely forested. The limited amount of published N data for developed watersheds in the northeastern U.S. likely contributes to the high standard deviation in DIN concentrations in the literature data (Fig. 4). However, this observation also highlights the importance of our Ipswich River watershed data, which includes 39 watersheds influenced by human development.

The use of a single land feature (percentage of developed land) to predict DIN concentrations is another challenge in our analysis. Caraco et al. (2003) found that a simple model based on population density failed to explain NO_3^- export for watersheds less than 100 km^2 in size. In contrast, they found that a simple loading model based on fertilizer, wastewater, and atmospheric inputs was a good predictor of NO_3^- export in watersheds ranging from 0.1 to more than 1,000,000 km^2. For the Ipswich River sites, developed land use percentage is strongly correlated with population density (Wollheim et al. unpubl.). In addition, our compiled dataset incorporates a wide range of watershed sizes and N inputs. Therefore, our simple model based on developed land use percentage may be inadequate at broad spatial scales. Quantifying N loads to watersheds in our compiled dataset may improve our ability to predict DIN concentrations and therefore DON/TDN at the broader scale, but is beyond the scope of this paper.

Data from forested watersheds in our study highlight the potential role of land use history on our ability to predict hydrologic N losses. While DON fluxes from forested watersheds are typically low, DIN fluxes are variable and may account for 0–100% of atmospheric N inputs (Galloway et al. 2003). In our data, the DON : TDN ratio was particularly low in Catskill Mountain watersheds studied by Lovett et al. (2000), many of which show symptoms of N saturation (Aber et al. 1989). Although these sites receive high N deposition and lack wetlands, the authors attribute high stream water NO_3^- concentrations (319 ± 119 μg L^{-1}) from many watersheds to forest species composition and forest history. Other forested watersheds in the northeastern U.S. generally have lower NO_3^- concentrations (104 ± 95 μg L^{-1}) and higher DON : TDN ratios despite differences in forest type, successional status, and atmospheric deposition (Campbell 1996; Campbell et al. 2000; Clark et al. 2000; Goodale 2000; McHale et al. 2000). Therefore, the role of land use history in determining hydrologic DIN losses is unclear, but we assume that our compiled dataset will allow for us to discern general land use trends without directly considering past land use.

Interrelated land cover—Land use relationships may also influence the interpretation of our DIN and DON values. Human development in the northeastern U.S. is concentrated in coastal lowlands, which are also typically characterized by low slopes and abundant wetlands. Although urbanization is historically associated with wetland loss, an analysis of the percentage of wetlands and population in the Gulf of Maine indicates that approximately 80% of the population and 50% of the wetlands are located within 100 km of the coast (data not shown). Wetlands act as both sources of DON and sinks of DIN, and may confound relationships between human development and N concentrations. However, these results indicate that in areas with significant urban development, DON may still be a large fraction of TDN losses due to the influence of wetlands on stream water chemistry.

Effect of wetlands on regional DON losses—Our literature dataset included 95 northeastern U.S. watersheds for which wetland data were available. Watersheds were 0–12% wetlands, with many forested sites (n = 57) lacking wetlands. This limited range in wetland percentage also highlights the value of our Ipswich River data, which has 0–32% wetlands in the subcatchments studied. Despite challenges inherent in compiling datasets, our results indicate that the percentage of wetlands within a watershed explains a significant proportion (r^2 = 0.60, p < 0.01) of the variability in mean annual DON concentrations in drainage waters from forested and developed watersheds in the northeastern U.S. (Fig. 5). The observation that forested watersheds lacking wetlands had low stream water DON concentrations (range = 39–127 μg L^{-1}) is particularly interesting. In a recent review, Aitkenhead-Peterson et al. (2003) reported mean DON concentrations of 1,100–1,560 μg L^{-1} in organic soil solutions from cool deciduous and coniferous forests. The one-to-two order of magnitude reduction in DON concentrations between organic soil solution and stream water supports significant mineral soil adsorption in forested watersheds. In forested watersheds without wetlands, the transport of DON (and DOC) to streams therefore largely depends on shallow hydrologic flow paths through organic-rich soils during hydrologic events (Aitkenhead-Peterson et al. 2003).

Data used for this analysis also included 17 developed watersheds with direct anthropogenic N inputs to the rivers as human and animal wastewater (Boyer et al. 2002; Daley and McDowell unpubl.). We assume that entirely forested watersheds do not have significant wastewater inputs. Developed watersheds without direct wastewater inputs to the rivers either discharge wastewater via septic systems or discharge wastewater outside of the watershed. DON concentrations from the watersheds with direct wastewater inputs

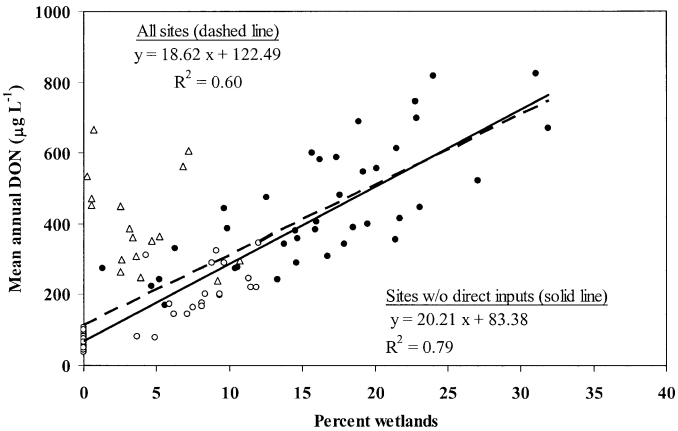

Fig. 5. Percent wetlands versus mean stream water DON concentrations ($\mu g\ L^{-1}$) in the northeastern U.S. Watersheds with direct human and animal wastewater inputs to rivers (Boyer et al. 2002; Daley and McDowell unpubl.) are indicated by open triangles. Black circles represent our Ipswich River watershed data, while open circles are literature data from watersheds without significant direct wastewater inputs (Campbell 1996; Campbell et al. 2000; Goodale et al. 2000; Lovett et al. 2000; McHale et al. 2000; Daley and McDowell unpubl.; Chalmers 2002).

were typically higher than predicted by the wetland–DON relationship (open triangles, Fig. 5), suggesting that wastewater represents a significant input of DON directly to some streams and rivers. The quantity of wastewater N inputs as estimated by Boyer et al. (2002) explained 74% of the difference between wetland-predicted DON concentrations and measured DON concentrations at these sites (data not shown). The relationship between wetland percentages and mean annual DON concentration is strong ($r^2 = 0.79$) when sites with direct wastewater inputs are excluded from our analysis. Adding the fraction of developed land use in a multiple regression explains little additional variability (Table 2), suggesting that wetlands are the primary landscape feature determining riverine and stream water DON concentrations.

Extrapolating the slope of the DON-wetland relationship to a 100% wetland watershed indicates that as a land use, wetlands contribute approximately 25 times more DON than other combined land uses. Seitzinger et al. (2002) reported that a substantially higher percentage of anthropogenically derived DON was bioavailable to estuarine microbes as compared to agricultural- and forest-derived DON. Wetland-derived DON may be even less bioavailable than forest-derived DON, with only 8–15% of the bulk DON from a wetland in Sweden taken up by estuarine bacteria (Stepanauskas et al. 1999). Therefore, additional research on the quantity and bioavailability of anthropogenic and wetland-derived DON is needed to better understand the current and future eutrophication of coastal waters.

References

ABER, J. D., K. J. KNADELHOFFER, P. STEUDLER, AND J. MELILLO. 1989. Nitrogen saturation in northern forest ecosystems. BioScience **39:** 378–386.

AITKENHEAD-PETERSON, J. A., W. H. MCDOWELL, AND J. C. NEFF. 2003. Sources, production, and regulation of allochthonous dissolved organic matter inputs to surface waters, p. 25–70. *In* S. Findlay and R. Sinsabaugh [eds.], Aquatic ecosystems: Interactivity of dissolved organic matter. Academic Press, Amsterdam.

BAKER, J. A., H. G. HEALY, AND O. M. HACKETT. 1964. Geology and ground-water conditions in the Wilmington-Reading Area, Massachusetts. U.S. Geological Survey Water-Supply Paper No. 1964.

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 **57/58:** 137–169.

BRONK, D. A., M. W. LOMAS, P. M. GLIBERT, K. J. SCHUKERT, AND M. P. SANDERSON. 2000. Total dissolved nitrogen analysis: Comparisons between the persulfate, UV and high temperature oxidation methods. Mar. Chem. **69:** 163–178.

CAMPBELL, J. L. 1996. Processes affecting the acid-base status of surface waters in the Lye Brook Wilderness, Vermont. M.S. Thesis, University of New Hampshire.

———, J. W. HORNBECK, W. H. MCDOWELL, D. C. BUSO, J. B. SHANDLEY, AND G. E. LIKENS. 2000. Dissolved organic nitrogen budgets for upland, forested ecosystems in New England. Biogeochemistry **49:** 123–142.

CARACO, N. F., J. J. COLE, G. E. LIKENS, G. M. LOVETT, AND K. C. WEATHERS. 2003. Variation in NO_3 export from flowing waters of vastly different sizes: Does one model fit all? Ecosystems **6:** 344–352.

CHALMERS, A. 2002. Trace elements and organic compounds in streambed sediment and fish tissue of coastal New England streams, 1998–1999 U.S. Geological Survey Water Resources Investigations Report 02-4179.

CLAIR, T. A., T. L. POLLOCK, AND J. M. EHRMAN. 1994. Exports of carbon and nitrogen from river basins in Canada's Atlantic provinces. Global Biogeochem. Cy. **8:** 441–450.

CLARK, G. M., D. K. MUELLER, AND M. A. MAST. 2000. Nutrient concentrations and yields in undeveloped stream basins of the United States. J. Am. Water Resour. As. **34:** 849–860. Data: http://water.usgs.gov/nawqa/nutrients/pubs/awra_v36_no4/.

CORNELL, S. E., T. D. JICKELLS, J. N. CAPE, A. P. ROWLAND, AND R. A. DUCE. 2003. Organic nitrogen deposition on land and coastal environments: A review of methods and data. Atmos. Environ. **37:** 2173–2191.

CURRIE, W. S., J. D. ABER, W. H. MCDOWELL, R. D. BOONE, AND A. H. MAGILL. 1996. Vertical transport of dissolved organic C and N under long-term N amendments in pine and hardwood forests. Biogeochemistry **35:** 471–505.

DEVITO, K. J., P. J. DILLON, AND B. D. LAZERTE. 1989. Phosphorus and nitrogen retention in five Precambrian shield wetlands. Biogeochemistry **8:** 185–204.

ECKHARDT, B. W., AND T. R. MOORE. 1990. Controls on dissolved organic carbon concentrations in streams, Southern Québec. Can. J. Fish. Aquat. Sci. **47:** 1537–1544.

FIEBIG, D. M., M. A. LOCK, AND C. NEAL. 1990. Soil water in the riparian zone as a source of carbon for a headwater stream. J. Hydrol. **116:** 217–237.

FÖLSTER, J. 2000. The near-stream zone is a source of nitrogen in a Swedish forested catchment. J. Environ. Qual. **29:** 883–893.

GALLOWAY, J. N., J. D. ABER, J. W. ERISMAN, S. P. SEITZINGER, R. W. HOWARTH, E. B. COWLING, AND B. J. COSBY. 2003. The nitrogen cascade. BioScience **53:** 341–356.

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.

HEDIN, L. O., J. J. ARMESTO, AND A. H. JOHNSON. 1995. Patterns

of nutrient loss from unpolluted, old-growth temperate forests: Evaluation of biogeochemical theory. Ecology **76:** 493–509.

HEINZ CENTER. 2002. National nutrients summary for the Heinz Center report: The State of the Nation's Ecosystems, 2002. Available at: http://water.usgs.gov/nawqa/nutrients/datasets/nutconc2000/.

HERLIHY, A. T., J. L. STODDARD, AND C. B. JOHNSON. 1998. The relationship between stream chemistry and watershed land cover data in the mid-Atlantic region. US Water Air Soil Pollution **105:** 377–386.

HILL, A. R. 1996. Nitrate removal in stream riparian zones. J. Environ. Qual. **25:** 743–755.

HOPKINSON, C. S., AND OTHERS. 1998. Terrestrial inputs of organic matter to coastal ecosystems: An intercomparison of chemical characteristics and bioavailability. Biogeochemistry **43:** 211–234.

HOWARTH, R. W., AND OTHERS. 1996. Regional nitrogen budgets and riverine N & P fluxes for the drainages to the North Atlantic Ocean: Natural and human influences. Biogeochemistry **35:** 75–139.

JORDAN, T. E., D. L. CORRELL, AND D. E. WELLER. 1997. Nonpoint source discharges of nutrients from Piedmont watersheds of Chesapeake Bay. J. Am. Water Resour. As. **33:** 631–645.

KEENE, W. C., J. A. MONTAG, J. R. MABEN, M. SOUTHWELL, J. LEONARD, T. M. CHURCH, J. L. MOODY, AND J. N. GALLOWAY. 2002. Organic nitrogen in precipitation over eastern North America. Atmos. Environ. **36:** 4529–4540.

LOVETT, G. M., K. C. WEATHERS, AND W. V. SOBCZAK. 2000. Nitrogen saturation and retention in forested watersheds of the Catskill Mountains, New York. Ecol. Appl. **10:** 73–84.

MCDOWELL, W. H., W. S. CURRIE, J. D. ABER, AND Y. YANO. 1998. Effects of chronic nitrogen amendments on production of dissolved organic carbon and nitrogen in forest soils. Water Air Soil Pollution **105:** 175–182.

MCHALE, M. R., M. J. MITCHELL, J. J. MCDONNELL, AND C. P. CIRMO. 2000. Nitrogen solutes in an Adirondack forested watershed: Importance of dissolved organic nitrogen. Biogeochemistry **48:** 165–184.

MERRIAM, J., W. H. MCDOWELL, AND W. S. CURRIE. 1996. A high-temperature catalytic oxidation technique for determining total dissolved nitrogen. Soil Sci. Soc. Am. J. **60:** 1050–1055.

MULHOLLAND, P. J. AND E. J. KUENZLER. 1979. Organic carbon export from upland and forested wetland watersheds. Limnol. Oceanogr. **24:** 960–966.

OLLINGER, S. V., J. D. ABER, G. M. LOVETT, S. E. MILLHAM, R. G. LATHROP, AND J. M. ELLIS. 1993. A spatial model of atmospheric deposition for the northeastern U.S. Ecol. Appl. **3:** 459–472.

PERAKIS, S., AND L. HEDIN. 2002. Nitrogen loss from unpolluted South American forests mainly via dissolved organic compounds. Nature **415:** 416–419.

RAYMOND, P. A., AND C. S. HOPKINSON. 2003. Ecosystem modulation of dissolved carbon age in a temperate marsh-dominated estuary. Ecosystems **6:** 694–705.

SEITZINGER, S. P., R. W. SANDERS, AND R. STYLES. 2002. Bioavailability of DON from natural and anthropogenic sources to estuarine plankton. Limnol. Oceanogr. **47:** 353–366.

SHARP, J. H., AND OTHERS. 2002. A preliminary methods comparison for measurement of dissolved organic nitrogen in seawater. Mar. Chem. **78:** 171–184.

STEPANAUSKAS, R., L. LEONARDSON, AND L. J. TRANVIK. 1999. Bioavailability of wetland-derived DON to freshwater and marine bacterioplankton. Limnol. Oceanogr. **44:** 1477–1485.

UNITED STATES GEOLOGICAL SURVEY. 2000. National Water Information System Data Retrieval [online]: http://waterdata.usgs.gov/nwis-w/US/. Last accessed: September 23, 2003.

———. 2003. National Water Quality Assessment (NAWQA) Program: New England Coastal Basins (NECB) Study Unit [online]: http://nh.water.usgs.gov/CurrentProjects/nawqa/nawqaweb.htm.

VALDERRAMA, J. C. 1981. The simultaneous analysis of total nitrogen and total phosphorus in natural waters. Mar. Chem. **10:** 109–122.

VALIELA, I., I. G. COLLINS, J. KREMER, K. LAJTHA, M. GEIST, B. SEELY, J. BRAWLEY, AND C. J. SHAM. 1997. Nitrogen loading from coastal watersheds to receiving estuaries: New method and application. Ecol. Appl. **7:** 358–380.

WESTERHOFF, P., AND H. MASH. 2002. Dissolved organic nitrogen in drinking water. J. Water Supply Res. Technol. AQUA **51:** 415–448.

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