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ECOSYSTEMS

MINI REVIEW

Does Anthropogenic Nitrogen Enrichment Increase Organic Nitrogen Concentrations in Runoff from Forested and Human-dominated Watersheds?

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ABSTRACT

Although the effects of anthropogenic nitrogen (N) inputs on the dynamics of inorganic N in watersheds have been studied extensively, ''the influence of N enrichment on organic N loss'' is not as well understood. We compiled and synthesized data on surface water N concentrations from 348 forested and human-dominated watersheds with a range of N loads (from less than 100 to 7,100 kg N km^{-2} y^{-1}) to evaluate the effects of N loading via atmospheric deposition, fertilization, and wastewater on dissolved organic N (DON) concentrations. Our results indicate that, on average, DON accounts for half of the total dissolved N (TDN) concentrations from forested watersheds, but it accounts for a smaller fraction of TDN in runoff from urban and agricultural watersheds with higher N loading. A significant but weak correlation (r^2 = 0.06) suggests that N loading has little influence on DON concentrations in forested watersheds. This result contrasts with observations from some plot-scale N fertilization studies and suggests that variability in watershed characteristics and climate among forested watersheds may be a more important control on DON losses than N loading from atmospheric sources. Mean DON concentrations were positively correlated, however, with N load across the entire land-use gradient (r^2 = 0.37, P < 0.01), with the highest concentrations found in agricultural and urban watersheds. We hypothesize that both direct contributions of DON from wastewater and agricultural amendments and indirect transformations of inorganic N to organic N represent important sources of DON to surface waters in human-dominated watersheds. We conclude that DON is an important component of N loss in surface waters draining forested and human-dominated watersheds and suggest several research priorities that may be useful in elucidating the role of N enrichment in watershed DON dynamics.

Key words: dissolved organic nitrogen; nitrogen deposition; agriculture; forest; watersheds; urbanization.

INTRODUCTION

Humans have dramatically altered the global nitrogen (N) cycle by increasing N inputs through

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atmospheric deposition and land-use change (Howarth and others 1996; Vitousek and others 1997). The effect of increased N loading on ecosystem inorganic N dynamics has been studied extensively. These studies suggest that current riverine N exports from some regions are as much as five to 15 times higher than preindustrial exports (Howarth and others 1996). Although DON is the dominant vector of N loss from many undisturbed watersheds (for example, Lewis and others 1999; Lewis 2002; Perakis and Hedin 2002; Vanderbilt and others 2002; Kaushal and Lewis 2003), the influence of increased N loading on organic N loss from watersheds is still not well understood.

The effects of elevated N loading on watershed DON loss likely vary with the type and magnitude of human disturbance, as well as inherent ecosystem characteristics. In forested watersheds, there is conflicting evidence of the effects of N enrichment on DON production in soils. Plot-scale N fertilization studies have reported increased DON concentrations in both the forest floor (McDowell and others 2004) and mineral soils (Pregitzer and others 2004), whereas others have shown no clear increase in DON fluxes or concentrations from forest soil plots with increased N fertilization (Raastad and Mulder 1998; Gundersen and others 1998; Hagedorn and others 2001; Pilkington and others 2005).

In watersheds where DON export in surface waters is large relative to inorganic N export, the ''leak'' of DON to surface waters may be an important mechanism sustaining terrestrial nutrient limitations (Perakis and Hedin 2002). Ecosystem N loss as DON is generally believed to be independent of N availability and not controlled by traditional biotic mechanisms in the same way as inorganic N (Vitousek and others 1998). In reality, DON dynamics are regulated by a complex set of factors and may in fact be responsive to the availability of inorganic N. For example, recent work has shown changes in the chemical composition of organic N in response to increasing availability of dissolved inorganic N (DIN) in terrestrial and aquatic ecosystems (Kaushal and Lewis 2003; McDowell and others 2004), as well as decreased uptake of organic N relative to inorganic N in streams (Kaushal and Lewis, 2005). Results from soil N fertilization studies are ambiguous, however, and the effect of elevated N loads on surface water DON concentration and fluxes remains poorly understood at all scales.

Surface water at the catchment outlet represents an integrated signature of the abiotic and biotic controls on N dynamics at the watershed scale (Aber and others 2003). Some parts of a watershed may be disproportionately important in driving whole-system N fluxes, and competing processes of production, consumption, and retention make the interpretation of DON data a challenge at the watershed level (Kaushal and Lewis, 2005; Neff and others 2000). However, we still do not understand the impact of increased N loading on DON loss from catchments. In addition, recent studies have pointed out the potentially important effects of wastewater and fertilizer on surface water DON concentrations (Christou and others 2005; Pellerin and others 2004; Westerhoff and Mash 2002). In light of evidence for higher amounts of bioavailable DON in runoff from human-dominated catchments (Wiegner and Seitzinger 2004; Seitzinger and others 2002), it is critical that we obtain a better understanding of the ecological significance of DON in disturbed watersheds.

Therefore, we synthesized surface water N data from 348 watersheds with varying degrees of human land-use disturbance and inorganic N loading to (a) quantify the relative and absolute losses of DON from catchments, (b) evaluate the role of inorganic N loading on DON concentrations in surface waters, and (c) determine which types of disturbance have the greatest influence on DON losses at the catchment scale. Because DON was historically not included in many ecosystem N budgets, long-term data sets on surface water DON concentration and flux are not common. Therefore, we compiled the data for a large number of catchments in an attempt to overcome confounding factors and evaluate significant relationships among N loading, land use, and surface water DON concentrations (Aber and others 2003). To our knowledge, this study represents the largest and broadest compilation of catchment-scale DON data yet presented in the literature. A better understanding of N enrichment and DON dynamics is critical for assessing marine and freshwater eutrophication, forest N saturation, the quality of drinking water (Westerhoff and Mash 2002), and long-term changes in N cycling through terrestrial and aquatic ecosystems.

Methods

Data Sources

Based on various sources in the literature and a small number of unpublished studies, data were compiled on surface water mean N concentrations from 348 watersheds (Table 1). Watersheds ranged in size from smaller than 1.0 km^2 to 5.0×10^6 km^2, with a median size of 82 km^2. Data are largely from the United States and Canada, but they also include 24

Table 1. Number and Types of Watersheds, Method of Organic Nitrogen (Dissolved or Total) Determination, and References

No. Watersheds	Type	Method	Organic N Form	Source
3[a]	F	Persulfate	Dissolved	Hedin and others (1995)
4	F	Kjeldahl	Dissolved	Lewis (2002)
41	F	Kjeldahl	Total	Clark and others (2000)
3	F	Kjeldahl	Dissolved	Vanderbilt and others (2002)
21	F, M	NA	Dissolved	Lewis and others (1999)
2	F	Persulfate	Dissolved	Kaushal and Lewis (2005)
1	F	Persulfate	Dissolved	McHale and others (2000)
4	F	Persulfate	Dissolved	Hood and others (2002)
15	F	Thermal	Total	Campbell (1996), Campbell and others (2000)
9	F	Thermal	Dissolved	Goodale and others (2000)
39	F	Persulfate	Total	Lovett and others (2000)
10	F, M, A	Kjeldahl	Total	Jordan and others (1997)
13[b]	F	Kjeldahl	Dissolved	Coats and Goldman (2001)
26	F, A	Ultraviolet	Total	Clair and others (1994)
21	F	Persulfate	Total	Mattsson and others (2003)
1	F	NA	Dissolved	Valiela and others (1997)
8	F, M, A	Persulfate	Total	Vuorenmaa and others (2002)
68	F, M, U, A	Kjeldahl	Total	Heinz Center (2002)
17	M, U	Persulfate	Dissolved	Wollheim and others (2005)
5	M, U	Kjeldahl	Dissolved	Chalmers (2002), USGS (2003)
2	M, U	Thermal	Dissolved	Hopkinson and others (1998)
15	M	Kjeldahl	Dissolved	Boyer and others (2002), USGS (2000)
12	M	Thermal	Dissolved	Daley ML and McDowell WH (unpublished)
1	M	Persulfate	Dissolved	Mortazavi and others (2000)
1	M	Kjeldahl	Total	Asbury and Oaksford (1997)

F, forested; M, mixed; U, urban; A, agricultural; N, Nitrogen.
[a]Compilation of 31 watersheds.
[b]Includes references in Table 6 of Coats and Goldman (2001).

watersheds in South and Central America (Perakis and Hedin 2002; Lewis and others 1999; Hedin and others 1995), as well as 29 watersheds in Europe (Mattsson and others 2003; Vuorenmaa and others 2002). Watersheds in the United States represent nearly all geographical regions, but are weighted toward temperate zones. The catchments included also represent a broad range of climatic and geologic conditions, as well as various stages of natural and anthropogenic ecosystem development.

Land-cover data are taken from the literature and therefore may differ in terms of data collection and land-use classification. Forested watersheds were defined as having more than 90% forest cover and accounted for 206 of the watersheds in our data set. Of these, at least 40 were minimally disturbed (little land-use disturbance and low N deposition) (Lewis and others 1999; Lewis 2002; Vanderbilt and others 2002; Perakis and Hedin 2002). Agricultural watersheds were defined as those with more than 50% of the land area in agriculture and accounted for 15% of the catchments (n = 51). Urban watersheds were those with more than 50% urban land area and accounted for 6% of the catchments in our data set (n = 20). The remaining 71 watersheds were defined as mixed land use (less than 90% forested and less than 50% in agriculture or urbanized). Of these, approximately half were influenced largely by agriculture (less than 10% urban) and half by urbanization (less than 10% agriculture). Where reported, wetlands were typically a minor component (less than 5%) of forested and agricultural watersheds, but accounted for up to 27% of some urban and mixed land-use catchments.

Data on total N deposition were available for 180 watersheds, most of which (n = 132) were forested watersheds. Forested watersheds were only influenced by atmospheric N deposition and had inorganic N wet deposition ranging from less than 100 kg N km^{-2} y^{-1} (minimally disturbed) to approximately 800 kg N km^{-2} y^{-1}. Mixed land-use watersheds had total N loads of 700–5,700 kg N km^{-2} y^{-1} and were influenced by atmospheric N deposition, net food and feed import, wastewater discharge, and fertilizer use. Urban and agricultural watersheds had reported total N loads of 2,900–7,100 kg N km^{-2} y^{-1}. Challenges in developing and interpreting total N loading estimates, particularly in urban and agricultural watersheds, are discussed later.

Surface Water Chemistry

Different sampling regimes and analytical approaches are unavoidable in the compilation of any large data set. Mean annual N concentrations were based on 1–30 years of data (Vanderbilt and others 2002), but most of the data in our study were collected between 1990 and 2002. Sampling frequencies in the studies cited typically ranged from weekly or biweekly to seasonally in spatially extensive studies. Several studies reported data as volume-weighted mean annual concentrations, but those without simultaneous discharge data or modeled discharge reported arithmetic means. Several studies also reported total organic N rather than DON concentrations (Table 1), thus representing an unquantified source of error in our study. However, studies in forested watersheds suggest that DON is typically 60–90% of the total organic N pool in surface waters (Coats and Goldman 2001 and references therein; Hood and others 2002; Lewis 2002; Kaushal and Lewis 2003). All surface water organic N data in our study are therefore referred to as DON. However, particulate organic N may be a significant fraction of N losses from disturbed watersheds, particularly during storm events.

Several studies require additional consideration because data collection was not as straightforward. Lewis (2002) noted a potential source of N contamination via mercuric chloride, which was used to preserve samples collected from 1980 to 1982. We therefore used data for the same sites from Clark and others (2000) but for a later period (avoiding contamination) along with the Lewis estimates of atmospheric N load. Volume-weighted mean DON concentrations were not reported in the literature for the sites studied by Boyer and others (2002) and Chalmers (2002) and were therefore calculated from US Geological Survey data as reported by Pellerin and others (2004). In addition, DON concentrations from Wollheim and others (2005) were estimated by a significant relationship between percentage of wetlands and DON concentrations for the same sites during the previous year. A comparison of DON estimates for 2000–2002 with 1999 data (Pellerin and others 2004) indicated that the differences from the predicted values were typically less than 0.1 mg/L for DON concentrations and less than 10% for the ratio of DON/(TDN) (data not shown).

Concentrations of DON were determined by either Kjeldahl N minus NH_4^+ or TDN (measured via persulfate digestion, catalytic oxidation, or ultraviolet oxidation) minus inorganic N (measured colorimetrically or by ion chromatography). Several studies suggest that no clear differences in DON concentrations are generated by the methods described above (Cornell and others 2003; Westerhoff and Mash 2002), whereas Merriam and others (1996) reported slightly higher TDN concentrations via catalytic oxidation (compared to persufate digestion). Uncertainty is inherent in DON calculations as a result of determination by difference and may be particularly high when DON accounts for a small fraction of TDN. Cornell and others (2003) reported SDs greater than 25% of the DON concentration in samples with low DON:TDN ratios (less than 0.25). Very few studies, however, reported the SD of DON concentrations; we are therefore unable to include analytical uncertainty in our data set. The general tendency is to underestimate DON concentrations due to the incomplete conversion of DON to inorganic N during oxidation or digestion or losses during sampling and storage (Cornell and others 2003).

Statistics

Surface water N data were generally not normally distributed in our data set. Therefore, we evaluated significant differences in N concentrations and DON:TDN between land uses (forested, mixed, urban, agricultural) via the nonparametric Wilcoxon rank sum test. In addition, simple linear regression of total N loads and N concentrations or DON:TDN were performed on untransformed and log-transformed data, with both forms of the data yielding nearly identical results. All statistics were at the 95% confidence interval, and the analysis was performed using S-Plus version 6.1. (Insightful Corporation, Seattle, WA)

Challenges in Data Set Compilation

In addition to differences in sampling methodology and analytical approaches, numerous other factors are important in compiling surface water data sets (Cornell and others 2003; Aber and others 2003; Pellerin and others 2004). A significant challenge in data set compilation is the variability in climate, rainfall, and runoff among sites, as well as year-to-year differences at individual catchments (Aber and others 2003). Although the impact of N enrichment on DON flux is ultimately of interest, water runoff is the dominant driver of dissolved organic matter (DOM) fluxes (Campbell and others 2000; Lewis

2002; Mulholland 2003; Harrison and others, forthcoming); therefore, variability in runoff among sites precludes us from a clear analysis and interpretation of N fluxes from the watersheds includes in our study. Runoff variability also affects N concentrations, but it has significantly less influence on concentrations compared to N fluxes (Lewis 2002) and likely plays a minor role in our broad data set.

Differences in tree species composition, disturbance history, bedrock mineralogy, wetland abundance, and hydrologic flowpaths also influence N concentrations in surface waters (Goodale and others 2000; Lovett and others 2000; Aber and others 2003; Pellerin and others 2004). In addition, processes within the aquatic network alter the quantity and composition of inorganic and organic N (Mulholland and others 2000; Webster and others 2003; Brookshire and others 2005), undermining the assumption that surface water chemistry at the watershed mouth is representative of biogeochemical processes in the terrestrial ecosystem. These differences are not explicitly included in our analysis but may influence the interpretation of our data, especially in forested catchments.

Rates of atmospheric N deposition were taken from the literature or, for some sites without literature data, estimated from nearby National Atmospheric Deposition Program (NADP) station data for the same sampling period. Most studies reported only wet inorganic N deposition; we therefore attempted to include only atmospheric input data so we could compare the watersheds. Although the ratio of wet to dry N deposition varies spatially and temporally, studies suggest that dry N is about equal to wet N deposition (Lovett and Lindberg 1993). In addition, DON typically accounts for 10–40% of atmospheric N deposition in rainwater globally (Seitzinger and Sanders 1999; Campbell and others 2000; Neff and others 2002; Cornell and others 2003; Pilkington and others 2005). However, most studies do not include estimates of atmospheric DON deposition; therefore, excluding it from our data (along with dry deposition) results in a significant underestimate of atmospheric N loads to forested watersheds.

In addition to atmospheric N deposition, N loading via fertilizer use and wastewater is critical in human-dominated watersheds. The assumptions and challenges of estimating N loads in agricultural and urban watersheds have been described elsewhere (Valiela and others 1997; Boyer and others 2002; Groffman and others 2004; Wollheim and others, 2005) and are sources of considerable uncertainty in the reported values used in our study. However, these values are the best estimates for the catchments studied. We therefore anticipate that general trends in the data will be apparent across the gradient of watershed loading.

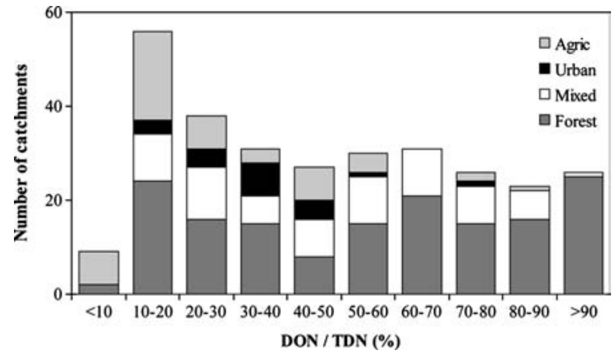

Figure 1. Distribution of catchments of different land uses versus the ratio of dissolved organic nitrogen to total dissolved nitrogen DON:TDN in surface water in our compiled data set (n = 297).

A number of other factors may influence the interpretation of our DON data set and other compiled surface water data sets. However, a complete treatment of all potential caveats for interpretation is beyond the scope of this paper. For example, potential differences due to variability in direct plant uptake of DON (Jones and others 2005) and abiotic transformations of nitrate (NO_3) to DON in soils (Davidson and others 2003) are worthy of further study but difficult to assess in the context of our watershed-scale DON synthesis.

Results

Surface water DON concentrations were greater than DIN concentrations in 46% of the 297 watersheds where both forms of N were reported (Figure 1). Mean DON:TDN ratios were highest in forested watersheds at 0.55 (Table 2) compared to other land uses, with only the Lovett and others (2000) study reporting ratios less than 0.20 in forested watersheds. The ratio of DON to TDN in surface water was lowest in agricultural watersheds at 0.27 as a result of high inorganic N concentrations. Urban and mixed watersheds had DON:TDN ratios intermediate between forested and agricultural watersheds (0.35 and 0.48, respectively). Differences in ratios were statistically significant among all land uses except forested and mixed watersheds (P = 0.07).

Mean surface water DON concentrations ranged from 0.02 to 3.20 mg/L in our data set (mean = 0.34, median = 0.22 mg/L), whereas DIN concentrations ranged from less than 0.01 to 15.0 mg/L (mean = 0.94, median = 0.27 mg/L). On average, forested watersheds had both the lowest concen-

Table 2. Surface Water N Concentrations and DON:TDN for Land Uses

	Land Use	*n*	Mean	Median	SD	25th%	75th%
DON (mg/L)	Forest	201	0.18	0.11	0.17	0.08	0.20
	Mixed	68	0.49[a]	0.35	0.45	0.23	0.59
	Urban	20	0.47[a]	0.41	0.28	0.31	0.48
	Agric	49	0.72	0.60	0.50	0.38	0.88
NO_3(mg/L)	Forest	191	0.14	0.08	0.15	0.02	0.23
	Mixed	64	0.81[a]	0.34	1.11	0.12	0.98
	Urban	17	0.72[a]	0.64	0.33	0.55	0.87
	Agric	49	3.14	2.50	2.92	1.23	3.58
DON:TDN	Forest	160	0.55[a]	0.58	0.29	0.28	0.80
	Mixed	71	0.48[a]	0.49	0.23	0.26	0.66
	Urban	20	0.35	0.36	0.14	0.26	0.41
	Agric	50	0.27	0.19	0.20	0.13	0.40

N, nitrogen; DON, dissolved organic nitrogen; NO_3, nitrate; TDN, total dissolved nitrogen.
[a]No significant difference (P = 0.49, 0.09, and 0.07 for DON, NO_3, and DON:TDN).

trations of NO_3 (dominant form of inorganic N) and DON in surface waters (Table 2). Agricultural watersheds had the highest NO_3 and DON concentrations, with urban and mixed-use watersheds intermediate between forests and agriculture (Table 2). Concentrations of DIN and DON were significantly different for all land uses except mixed and urban watersheds ($P = 0.09$ for DIN and $P = 0.49$ for DON). Concentrations of DON and NO_3 were not significantly correlated with watershed or wetland percentage, whereas DON:TDN was weakly correlated with wetland percentage ($r^2 = 0.07$, $P < 0.01$) but not watershed size (data not shown).

The ratio of DON:TDN was negatively correlated with N loading to forested watersheds (less than 800 kg N km^{-2} y^{-1} as wet atmospheric DIN deposition) and explained 44% of the variability in the data (data not shown). The relationship was heavily influenced by the low DON:TDN data of Lovett and others (2000), which accounted for nearly 20% of the forested watersheds in our data set. The relationship between N loading and DON:TDN is weaker ($r^2 = 0.16$) but statistically significant when those sites are excluded from the forested watershed data set. When watersheds of all land-use types were included, the ratio of DON to TDN in surface waters was weakly correlated with watershed N loads ($r^2 = 0.06$, $P < 0.01$; Figure 2). The relative importance of DON declined when watershed N loading was greater than 2,000 kg N km^{-2} y^{-1}. With the exception of the Lovett data, however, most watersheds with N deposition less than 2,000 kg N km^{-2} y^{-1} had higher concentrations of DOM greater than DIN (Figure 2).

Watershed N loads had a significant positive correlation with both surface water NO_3 and DON

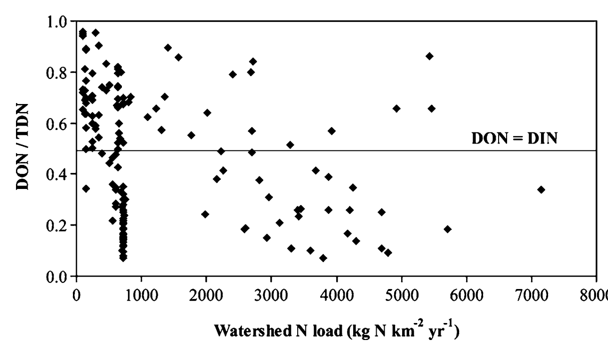

Figure 2. Ratio of DON:TDN versus watershed nitrogen (N) load for 180 watersheds with load data in our study. The DON:TDN ratio of 0.5 (DON = DIN) is indicated by a dashed line. $r^2 = 0.06$, $P < 0.01$. DIN, dissolved inorganic nitrogen.

concentrations in our data set, presumably as a result of the large sample size. In forested watersheds, N loading explained 31% of the variability in surface water NO_3 concentrations, but only 6% of the variability in DON concentrations (data not shown). The variability in NO_3 concentrations explained when all land-use types are included was the same as for forested data alone ($r^2 = 0.31$), but the fraction of the variability in surface water DON concentrations explained by N loading in the larger data set ($r^2 = 0.37$) was greater than for the forested watersheds alone (Figures 3 and 4).

Discussion

Relative Contribution of Dissovled Organic Nitrogen in Surface Waters

On average, DON accounted for approximately half of the surface water TDN concentration in forested

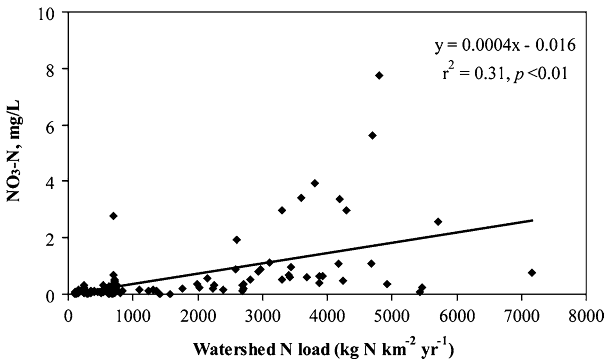

Figure 3. Surface water mean nitrate (NO_3) concentrations versus watershed nitrogen (N) load in our compiled data set (n = 168).

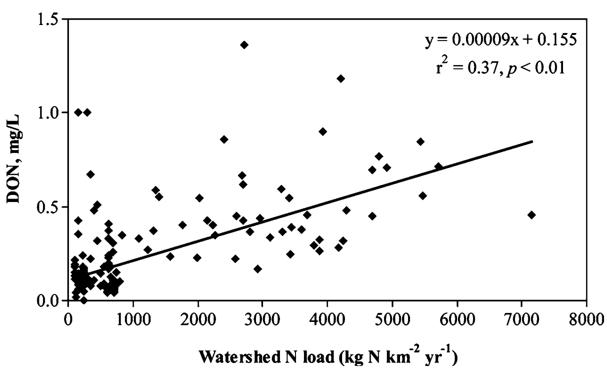

Figure 4. Surface water mean DON concentrations versus watershed N load in our compiled data set (n = 177).

watersheds in our data set (Table 2). Studies comparing DON losses from old-growth forests have reported that DON accounts for 60–95% of TDN losses from minimally disturbed watersheds, but as little as 10–20% of TDN in watersheds impacted by high N deposition (Perakis and Hedin 2002; Van Breeman 2002). Our results contrast with the widely -held view that surface water N is predominantly exported as inorganic N (mainly NO_3) from forested watersheds with elevated N loading. However, our results do supply evidence for declining surface water DON:TDN ratios in forested watersheds as a result of higher N loading, with the large range in DON:TDN (Table 2) likely reflective of differences in loading rates and watershed characteristics, as described previously.

Although the impact of agriculture and urbanization on surface water NO_3 concentrations has been studied for some time, our data show that DON accounts for a relatively high percentage of TDN concentrations in a number of human-dominated watersheds despite elevated N loads (Figure 1). Although higher NO_3 concentrations generally lower the relative importance of DON in disturbed watersheds, our results show that DON concentrations are on average 2.5–4 times higher in surface waters from urban and agricultural waters than in forested watersheds (Table 2). Direct sources of DON runoff such as organic fertilizer and wastewater may be important in disturbed watersheds, but we still lack sufficient information to quantify the relative importance of these DON sources versus DON runoff derived from inorganic N processing in soils and surface waters.

Does Atmospheric Nitrogen Deposition Increase Surface Water Concentrations of Dissovled Organic Nitrogen?

Forested Watersheds. Based on observations from some plot-scale studies (McDowell and others 2004; Pregitzer and others 2004), we hypothesized that surface water DON and NO_3 concentrations in forested watershed runoff increased as a result of atmospheric N loading. Our data set supports a general trend of increasing NO_3 concentrations with higher N loads, explaining 31% of the variability in surface waters draining forested watersheds (data not shown). Similar results have been reported by Aber and others (2003) for a large number of watersheds in the northeastern United States, with 30–38% of the variability in NO_3 explained by N deposition. In contrast to NO_3, our results suggest that N loading explains little variability (r^2 = 0.06, P < 0.01) in surface water DON concentrations in forested watersheds. Therefore, two important questions emerge from our forested watershed synthesis and consideration of plot-scale studies. Does the lack of a strong correlation in our data set indicate that watershed DON dynamics are independent of inorganic N deposition? If so, how can we reconcile evidence from some plot-scale fertilization studies (McDowell and others 2004; Pregitzer and others 2004) showing that inorganic N enrichment increases soil water DON concentrations? The absence of substantial trends in our data set argues against any effect of N loading on DON concentrations in drainage waters from forested watersheds (Aber and others 2003). A complex set of biotic and abiotic factors controlling DON loss, however, could ultimately determine surface water chemistry at the watershed -scale.

Previous studies have suggested limited biotic control on DON concentrations (Campbell and others 2000; Goodale and others 2000; Willett and others 2004), but increased soil water DON in response to N fertilization in some studies suggests at least a partial biotic control (McDowell and others 2004; Pregitzer and others 2004). A decline in microbial demand for N under elevated inorganic N loading is one plausible biotic mechanism that may result in increased soil and surface water DON concentrations. In addition to higher bulk DON concentrations, the decrease in biotic demand for labile DON may also increase the export of higher-quality DON substrates from watersheds. For example, data from forest plots receiving high N fertilization have shown that N enrichment leads to a higher N content in the hydrophilic fraction of DON, suggesting increases in compounds such as amino acids and amino sugars (McDowell and others 2004). Similar processes may also be important in the aquatic network, where increases in the supply of inorganic N correlate with relative decreases in the biological demand for labile DON (Kaushal and Lewis, 2005).

The conversion of inorganic N to organic forms and changes in the Carbon-to-nitrogen (C:N) ratio of soil organic matter (Neff and others 2000; McDowell and others 2004) have also been hypothesized as biotic mechanisms that may lead to increased DON concentrations in soils and surface waters. The rapid biotic uptake of inorganic N and subsequent release in organic form (particulate or dissolved) has been reported in coastal (Bronk and Ward 1999) and freshwater ecosystems (Mulholland and others 2000) and has been suggested as another possible explanation for the two- to threefold increase in forest floor DON concentrations under N fertilization (McDowell and others 2004). Limited data indicate that the microbial assimilation of DIN and release of DON may be rapid and quantitatively significant, with 25–45% of $^{15}N\text{–}NO_3$ added to a sandy forest soil recaptured as DON within 2 days (Seely and Lajtha 1997). In contrast, atmospheric N loading explained little of the variability in forest floor and mineral soil C:N ratios in northeastern US forests (Aber and others 2003), suggesting that changes in bulk C:N are slow and small relative to increased N loads to forested watersheds.

Abiotic controls on DON loss often result in concentrations declining by 50–90% from the surface organic soils to subsurface mineral soils (Neff and Asner 2001). For example, McDowell and others (1998) found no significant increase in mineral soil DON concentrations under experimental N enrichment despite two- to threefold increases in forest floor DON concentrations. Abiotic DON adsorption to mineral soils may be more important than biotic N retention in some soils, particularly those with where iron and aluminum oxyhydroxides are present (Hagedorn and others 2001; Qualls and others 2002; Willett and others 2004). Although we can only speculate, it is plausible that increased DON production or decreased consumption due to N enrichment is not apparent at the watershed -scale as a result of the high retention capacity of mineral soils.

Differences in watershed disturbance history, climate variation, species composition, bedrock mineralogy, and water flowpaths among study sites are important for understanding watershed NO_3 losses (Lovett and others 2000; Aber and others 2003). These factors also likely play a key role in watershed DON dynamics, but they have received considerably less attention than inorganic N. Stream responses in watersheds receiving current levels of atmospheric N deposition may be more strongly influenced by watershed characteristics than those in plot-scale studies, which often receive higher levels of N fertilization (for example McDowell and other 2004). However, the contradictory results emerging from N fertilization studies suggest that controls on DON loss, even at the plot level, are not straightforward (Gundersen and others 1998; Raastad and Mulder 1998; Hagedorn and others 2001; McDowell and others 2004; Pregitzer and others 2004; Pilkington and others 2005).

Urban and Agricultural Watersheds. Surface water draining mixed, agricultural, and urban watersheds typically had higher NO_3 and DON concentrations than forested watersheds in our data set (Figures 3 and 4). Higher NO_3 concentrations in surface waters are likely attributable to increased fertilizer use and wastewater discharge (Howarth and others 1996; Boyer and others 2002), but the reasons for higher DON concentrations are not clear. Battaglin and others (2001) reported higher DON concentrations in agricultural watersheds of the Mississippi River basin and suggested that concentrations have doubled over the last century (Goolsby and Battaglin 2001). In addition, they noted that the relative importance of organic N to total N losses was lowest in agricultural watersheds and had declined from about 0.70 to 0.38 since the turn of the 20th century. Our substitution of spatial data for temporal data suggests a similar result, with DON accounting for 58 and 49% of TDN concentrations on average in forested and mixed watersheds respectively, but only 27% in agricultural watersheds (Table 2). Other studies on the influence of agriculture on DON in surface waters are relatively scarce, particularly at the catchment -scale (Chantigny 2003).

Although N loading explains little of the variability in surface water DON concentrations in forested watersheds, N loads explain 37% of the variability in surface water DON concentrations when all land uses are included (Figure 4). Data from urban and agricultural watersheds are relatively sparse, and watershed N budgets in human-dominated landscapes are subject to significant uncertainty (Boyer and others 2002; Groffman and others 2004; Wollheim and others, forth coming). In addition, uncertainty in DON concentrations is generally higher in urban and agricultural watersheds compared to forests as a result of lower DON:TDN ratios. However, the general patterns in our data set suggest that DON concentrations are influenced by high watershed N loads in human-dominated catchments (Figures 3 and 4).

Abiotic and biotic mechanisms controlling DON dynamics in forested watersheds are presumably important in human-dominated watersheds as well. However, DON concentrations in agricultural watersheds are also influenced by factors such as crop type and land management, which may change over short time scales and alter the amount and composition of soil solutions and organic matter (Christou and other 2005; Chatigny 2003). In addition, the application of inorganic N fertilizer may stimulate plant roots and soil microbes to produce N-enriched organic products over relatively short time- scales (Murphy and others 2000).

The delivery of wastewater and organic fertilizer via surface runoff and point-source discharge represents a potential direct source of DON to streams in agricultural watersheds. This mechanism largely bypasses the biotic and abiotic controls important in terrestrial forest ecosystems and may have contributed to the high DON concentrations found in agricultural watersheds in this study. The relative importance of direct DON inputs versus DON generated via the transformation of inorganic N by plants and microbes is not clear, but this issue has considerable implications for N cycling in downstream ecosystems. Agricultural N fixation by plants such as soybean and alfalfa may also be an important source of organic N, with average fixation rates of 740 kg N km^{-2} y^{-1} for northeastern US watersheds (Boyer and others 2002), but this factor cannot be evaluated with our data set.

Our study also shows that DON concentrations are higher in urban watersheds than in forested watersheds (Table 2). Previous work in urbanizing catchments indicated that surface water DON concentrations were better described by the percentage of wetlands in a watershed than by the percentage of urban land use (Pellerin and others 2004). However, DON concentrations were not correlated with the percentage of wetlands in our larger data set ($r^2 = 0.01$, $P = 0.13$). Few watersheds included in the previous analysis were influenced by direct wastewater inputs to surface waters, with wastewater either exported from the watershed or discharged via septic systems. In watersheds with direct wastewater inputs in that study ($n = 15$), estimates of wastewater loading by Boyer and others (2002) described 74% of the deviation in actual DON concentrations from the wetland-predicted concentrations.

We need to understand the sources of DON in human-dominated watersheds so than we can evaluate anthropogenic impacts on watershed N dynamics and coastal eutrophication. For example, recent studies suggest that there are significant differences in the bioavailability of DON to microbes and bacteria from natural and anthropogenic sources. Although the data are still relatively sparse and lack a standard methodology, urban and agriculturally -derived DON appears to be more labile to aquatic bacteria than forested and wetland-derived DON (Table 3). Wastewater-derived DON may be a significant source of bioavailable N to surface waters in disturbed watersheds (Pehlivanoglu and Sedlak 2004), but this issue has received little attention. Tools for DON analysis, such as DON-^{15}N measurements and chemical characterization, will be useful in answering future questions about the ecological significance of anthropogenically- derived and natural DON in soils and surface water.

Conclusions and Research Priorities

The original hypothesis of our study, based on plot-scale data, was that anthropogenic N enrichment increases DON concentrations in runoff from forested and human-dominated watersheds. Our compiled data set of 348 watersheds shows that DON comprises a large fraction of the TDN in surface waters from most forested watersheds as well as a large number of human-dominated watersheds. However, data from forested watersheds in our study indicate that surface water DON concentrations were not strongly correlated with N loading. Although this finding suggests that N deposition has little impact on DON dynamics, an alternative explanation for the lack of correlation is that abiotic and biotic factors ultimately limit the loss of DON from watersheds. Our results do suggest, however, a stronger relationship between DON concentrations in surface waters and watershed N loading across the entire land-use gradi-

Table 3. Bioavailability of DON from Different Land Uses

Land use	Water Source	DON Bioavailability (%)	Source
F	Boreal stream (baseflow)	19–28	Stepanauskas and others (2000)
F	Mixed hardwood	20	Wiegner and Seitzinger (2001)
F	Coniferous, mixed hardwood	23 ± 19	Seitzinger and others (2002)
F	Minimally -disturbed	15–71	Kaushal and Lewis (2005)
F	Wetland	2–16	Stepanauskas and others (1999)
F	Pristine wetlands	33 ± 25	Wiegner and Seitzinger (2004)
A	Pasture runoff	25	Wiegner and Seitzinger (2001)
A	Agricultural runoff	30 ± 14	Seitzinger and others (2002)
A, U	Polluted wetlands	28 ± 25	Wiegner and Seitzinger (2004)
U	Delaware, Hudson rivers	40–72	Seitzinger and Sanders (1997)
U	Urban, suburban runoff	59 ± 11	Seitzinger and others (2002)
NA	Wastewater	56	Pehlivanoglu and Sedlak (2004)
NA	Rainwater	45–75	Seitzinger and Sanders (1999)

Experimental time course and type of consumer (estuarine or freshwater bacteria or plankton) vary among studies.
DON, dissolved organic nitrogen; F, forested; A, agricultural; U, urban; NA, not available.

ent. Similar biotic and abiotic controls on DON loss may be important in agricultural and urbanizing watersheds. However, we hypothesize that the direct input of wastewater and organic fertilizer runoff may also be an important source of DON that largely bypasses the controls that are active in terrestrial ecosystems.

Although the effect of N loading on surface water NO_3 concentrations has received considerable attention, additional research is clearly warranted on the role played by N enrichment in long-term DON dynamics. Studies have shown that the bioavailability of DON differs depending on its source and composition, with forested watersheds and wetlands typically exporting the least labile DON (Table 3). Therefore, it is critical to also evaluate the changes in the composition and reactivity of DON associated with increased N loading, because small changes in the bulk pool may not be indicative of the altered production and consumption of different DON fractions (Neff and others 2003; Kaushal and Lewis 2003; McDowell and others 2004). It may also be important to determine whether DON is generated internally via the conversion of inorganic N or exported as DON from external sources within disturbed watersheds (for example, wastewater or organic fertilizer runoff) when estimating the total pool of bioavailable N exported to surface waters, but the relative importance of these mechanisms is currently not known.

Riparian and in-stream wetlands are often the main allochthonous DOM source to surface waters and are key features influencing watershed DON dynamics (Pellerin and others 2004). In contrast to forested watersheds, recent studies have reported that DON and inorganic N concentrations in wetland bog waters increase linearly in response to atmospheric N loading (Yesmin and others 1995; Bragazza and Limpens 2004). Wetlands are not subject to the same set of abiotic retention mechanisms as upland soils due to the reductive dissolution of iron and aluminum oxides in anaerobic environments (Hagedorn and others 2001). Therefore, both the biological immobilization of inorganic N and the low retention of DON may result in high DON export even when nutrient inputs are largely in inorganic form (Devito and others 1989; Bischoff and others 2001). The role of DIN uptake and subsequent DON loss from wetlands therefore deserves attention as a potential competing mechanism with denitrification in some wetland environments, particularly in urban watersheds with high NO_3 loads, low available C, and increased aerobic conditions (Groffman and others 2002).

Understanding the differences in DON and DOC cycling may also help to elucidate the role of anthropogenic N loading on DOM quality and its subsequent role in riverine and coastal eutrophication. Several studies have reported an apparent decoupling of DOC and DON in soils and surfaces waters (Hood and others 2002; Kaushal and Lewis 2003; Willett and others 2004; McDowell and others 2004; Wiegner and Seitzinger 2004), but the mechanisms for this decoupling are not yet known (McDowell 2003). Higher rates of microbial assimilation of inorganic N and differences in the main pathways of biotic transformations of DON and DOC (incorporation of DON into the microbial food web and remineralization versus DOC loss to the atmosphere through respiration) may also result in lower DOC:DON ratios in soils and surface water

(Caraco and others 1998; McDowell and others 2004; Wiegner and Seitzinger 2004). Recent work also suggests that differences in predicted DON and DOC exports globally may be due to elevated DON losses from regions with high population densities or intensive agriculture (Harrison and others, 2005). Lower DOC:DON ratios in agricultural and urban watersheds than forested watersheds may reflect anthropogenic N loading, but the importance of biotic N cycling in soils and streams versus direct DON inputs from external sources to surfaces waters is not known.

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