

## Groundwater-transported dissolved organic nitrogen exports from coastal watersheds

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### Abstract

We analyzed groundwater-transported nitrogen (N) exports from 41 watershed segments that comprised 10 Cape Cod, Massachusetts watersheds to test the hypotheses that chemical form of N exports is related to land use and to length of flow paths through watersheds. In the absence of human habitation, these glacial outwash–plain watersheds exported largely dissolved organic N (DON) but at relatively low annual rate. Addition of people to watersheds increased rates of both total dissolved N (TDN) and DON export through groundwater. Percent of TDN as DON in groundwater was negatively related to path length of groundwater through aquifers, but %DON was not significantly related to population density on the watersheds. DON was often the dominant form of N exported from the watersheds, even at high population densities. Our results suggest that natural sources are not entirely responsible for organic N exports from watersheds, but, instead, a substantial portion of anthropogenic N introduced to watersheds is exported as DON. This finding is in disagreement with previous results, which suggest that anthropogenic N is exported from watersheds largely as  $\text{NO}_3^-$  and that DON exported from watersheds is from natural sources.

Eutrophication associated with increasing land-derived nitrogen (N) loads is perhaps the greatest agent of change that alters coastal waters (Howarth et al. 2000). Because of this important role, efforts have been made to quantify and model N inputs to watersheds, retention and losses within watersheds, and exports from watersheds to receiving waters. Much has been learned in recent years about N sources and patterns of N cycling at watershed (Valiela et al. 1997), regional (Alexander et al. 2002), and global scales (Galloway 1998). However, the roles of dissolved organic N (DON) and of groundwater remain as two of the largest unknowns in watershed N budgets.

### Role of DON

Little information is available about the chemical form of watershed N exports (here, chemical form refers to the contributions of the major forms of dissolved, fixed N—dissolved organic N, nitrate+nitrite, and ammonium) or about factors, including human impacts, that regulate the chemical form of N transported from mixed-land-use

watersheds. Chemical form of land-derived N loads, and, in particular, the contribution of DON, is an important aspect of the coupling between watersheds and receiving waters because extent and rate of reactivity of the N forms differ. Inorganic N forms,  $\text{NO}_3^-$  and  $\text{NH}_4^+$ , are immediately available to primary producers. DON from terrestrial sources may show substantial biological availability, perhaps 10% to 70%, but mineralization and assimilation occurs relatively slowly over several days (Qualls and Haines 1992; Seitzinger et al. 2002). Because behavior of the N forms differ, quantification and understanding of controls on the chemical form of watershed N exports are important.

The mix of  $\text{NO}_3^-$ , DON, and  $\text{NH}_4^+$  exported from watersheds might depend on the mix of land uses within the watersheds. Forests are generally thought to export primarily DON (Perakis and Hedin 2002), and increased atmospheric deposition of N to forests (Likens and Bormann 1995; Perakis and Hedin 2002) and addition of wastewater and fertilizer associated with human habitation of watersheds (Peierls et al. 1991; Robertson and Cherry 1992) are thought to increase exports of inorganic N. This pattern has led to the conclusion that sources for DON exports from watersheds are natural and that anthropogenic N is exported from watersheds largely as inorganic N (Gildea et al. 1986; Caraco and Cole 1999, 2001).

### Role of ground water

Past studies on watershed N exports have largely focused on transport by streams and rivers. However, recognition that groundwater transports a substantial portion of water, often with elevated N concentrations, from watersheds to receiving waters has increased. Processes that occur within aquifers, including storage, transformations, and transport, are often among the largest unknown terms in watershed N budgets (van Breemen et al. 2002). Groundwater and nutrient discharges directly to the coastal zone, which bypass stream and river transport, are often large (Burnett

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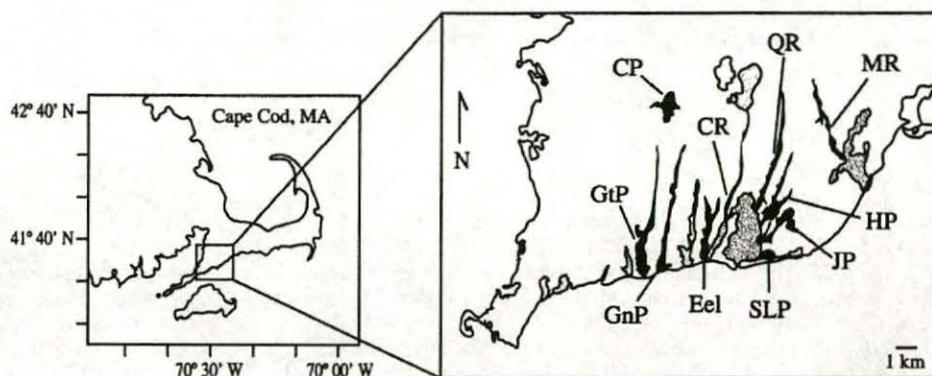


Fig. 1. Map of western Cape Cod shows locations of receiving waters and watersheds included in this study. All receiving waters are estuaries, with the exception of CP, a freshwater pond. Abbreviations: GtP = Great Pond, GnP = Green Pond, Eel = Eel Pond, CP = Coonamessett Pond, CR = Childs River, QR = Quashnet River, SLP = Sage Lot Pond, JP = Jehu Pond, HP = Hamblin Pond, MR = Mashpee River.

et al. 2003). In addition, for the United States as a whole, 30% of streamflow may be supplied by groundwater seepage (WRC 1978). Groundwater seepage is often responsible for a much larger portion of total transport of freshwater (up to 80% or more) and associated nutrients to streams in coastal areas with unconsolidated sandy soils, such as the coastal plain that comprises much of the East Coast of the United States (Modica et al. 1998).

Transformations of N during transport by groundwater through watersheds may influence the chemical form of N before discharge to streams, rivers, or coastal waters. Mineralization, sorption, and complexation of DON (Cronan and Aiken 1985; Pabich et al. 2001) and sorption and nitrification of  $\text{NH}_4^+$  (Wilhelm et al. 1994; DeSimone et al. 1996) during transport of N through vadose zones (the unsaturated sediment layer above the water table) and aquifers may diminish concentrations of DON and  $\text{NH}_4^+$  in groundwater. A generally held conception is that N in aquifers occurs almost exclusively as  $\text{NO}_3^-$ , on the basis of knowledge that ammonification and nitrification occur in unsaturated sediments above aquifers and that  $\text{NO}_3^-$  is mobile enough in soils to be transported to aquifers in quantity (Freeze and Cherry 1979; Bouwman et al. 2005). However, contrary to this conception, we and others have found that DON concentrations in some cases are quite high in groundwater (Kroeger et al. 1999; Valiela et al. 2000; Corbett et al. 2002; Kroeger et al. 2006).

To understand attenuation and transformations of N during transport through watersheds, we must consider sources of N loading to watersheds and processes that occur during groundwater recharge through vadose zones to aquifers and transport through aquifers. The goals of this study were to examine the chemical form of groundwater-transported N exports from watersheds and to identify possible mechanisms that control the contribution of DON to TDN exports. Our approach was to measure concentrations of TDN and DON and proportion of TDN as DON in groundwater samples collected from a set of watersheds on Cape Cod. We then examined

relations between the N concentrations and watershed variables, including population density and length of water-flow paths through the vadose zone and aquifer.

## Materials and methods

**Study design**—We selected nine estuaries and a freshwater pond in western Cape Cod, Massachusetts (Fig. 1), collected multiple groundwater samples along the land margin of each source, and analyzed N concentrations in the samples. We then related variations in N concentration and chemical form to variations in watershed land uses, population densities, vadose-zone path lengths (average vadose-zone thickness in the watershed), and aquifer path length (the average distance water parcels travel through the aquifer). To avoid averaging N concentrations from watershed segments with substantial differences in land use or other attributes, we divided the 10 watersheds into 41 watershed segments (Fig. 2).

**Site description**—The study area is located in western Cape Cod, Massachusetts, and the watersheds comprise much of the Town of Falmouth and portions of Mashpee and Sandwich (Fig. 1). The watersheds are located almost entirely within the Mashpee pitted-plain geologic unit, which is composed of gravelly sand and pebble-to-cobble gravel. Soils are of glacial origin and are mostly sandy loam (Oldale 1992). The sandy soils allow rapid percolation of rainwater into the aquifer, and groundwater discharge accounts for 90% or more of freshwater inputs from watersheds to Cape Cod estuaries (Valiela et al. 2002). The aquifer is composed of unconsolidated quartz and feldspar sand and gravel (Oldale 1992). Typical groundwater velocity is  $146 \text{ m yr}^{-1}$  (LeBlanc et al. 1991). Annual rainfall averages  $1,130 \text{ mm}$  (Lajtha et al. 1995). Atmospheric deposition of TDN, wet plus dry, is  $\sim 1500 \text{ kg N km}^{-2} \text{ yr}^{-1}$  (Valiela et al. 1997). Naturally vegetated areas range from grass and shrublands to pitch pine and mixed-oak forests (Lajtha et al. 1995).

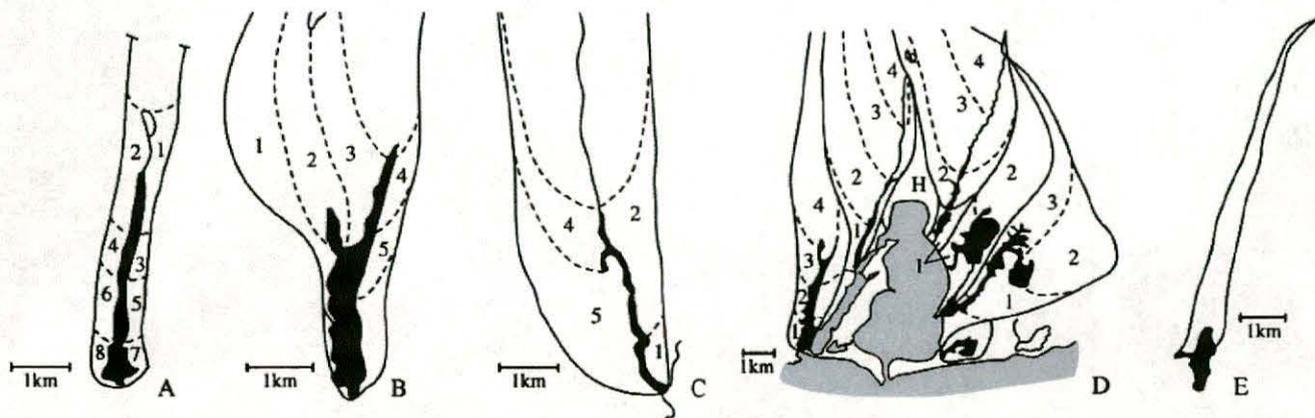


Fig. 2. Watershed delineations for the 10 ponds and estuaries included in this study. Solid lines show outline of whole watersheds and dashed lines separate watershed segments. Black fill indicates receiving water. Numbers that identifying segments correspond to those listed in Tables 1, 2, and 3. (A) Green Pond; (B) Great Pond; (C) Mashpee River; (D) (clockwise from left) Eel Pond, Childs River, head of Waquoit Bay (H), Quashnet River, Hamblin Pond, Jehu Pond, Sage Lot Pond; (E) Coonamessett Pond. Note that scale varies by panel.

#### Groundwater N concentrations and watershed N exports—

To comprehensively define N concentrations in groundwater just before seepage from the watersheds, we collected samples every 30 to 60 m along the shoreline (stream, river, estuary, or pond) of each watershed. The freshwater pond was sampled only along the upgradient shore, to collect groundwater discharging from the aquifer to the pond. Fringing wetlands were considered to be part of the receiving water, and groundwater samples were collected landward of these features. To collect groundwater samples, we inserted a piezometer into the water table at or above the high-tide mark and pumped groundwater into a collection vessel. We rejected groundwater samples with a salinity  $\geq 1$  (an indication that the sample was collected from the zone of mixing between fresh and saline groundwater) and resampled landward from the high-tide mark until we obtained a fresh groundwater sample. Samples were stored on ice until return to the laboratory, where they were filtered through combusted glass-fiber filters (0.7  $\mu\text{m}$  nominal pore size) and frozen or acidified and stored at 4°C until analysis.

We measured  $\text{NH}_4^+$  concentrations colorimetrically by the phenol/hypochlorite method or fluorometrically (Holmes et al. 1999). Nitrate + nitrite (in this paper referred to as nitrate) concentrations were measured colorimetrically after cadmium reduction to  $\text{NO}_2^-$  by use of either a manual method or a Lachat autoanalyzer. To measure TDN concentrations, we used a modification of the persulfate-digestion method (D'Elia et al. 1977) to oxidize all nitrogen forms to nitrate. DON concentrations were calculated as  $\text{TDN} - (\text{NO}_3^- + \text{NH}_4^+)$ .

Nitrogen concentrations in individual groundwater samples, even collected in close proximity to each other, are extremely variable (e.g., Kroeger et al. 1999). Therefore, rather than analyze N concentrations at the level of the individual sample, nitrogen concentrations were analyzed as averages of all samples collected from each watershed or watershed segment, and N exports were calculated as

average concentration multiplied by annual groundwater discharge. Annual groundwater-discharge volume was calculated as annual average atmospheric precipitation corrected for loss caused by evapotranspiration (Valiela et al. 1997). On Cape Cod, average annual rainfall is 1,130 mm (Lajtha et al. 1995), and 55% of precipitation is evapotranspired (Running et al. 1998).

Nitrogen-concentration data used in this study were based on groundwater collections conducted specifically for this study during the years 1998 to 2000 and on previous collections conducted in the early 1990s for the Waquoit Bay Land Margin Ecosystem Research Project (Valiela et al. unpubl. data). Some uncertainty is associated with combining N-concentration data from two different studies. However, the range of measured concentrations (0 to  $10^3 \mu\text{mol L}^{-1}$ ) was very large relative to error associated with the analytical methods (at most a few  $\mu\text{mol L}^{-1}$ ).

**Watershed attributes**—We quantified watershed land uses on the basis of aerial photographs and the Town of Falmouth GIS database of land uses, and on the basis of those land uses, we estimated the contributions of the major N sources (atmospheric deposition, fertilizer applications, and wastewater disposal) to watershed TDN exports by application of the Nitrogen Loading Model (NLM), a watershed land-use-based N loading model (Valiela et al. 1997, 2000). Watershed delineations (Fig. 1) for Waquoit Bay subwatersheds were determined by use of a groundwater-flow model (MODFLOW). For other watersheds, delineations were drawn on the basis of water table-elevation contours from the United States Geological Survey (Savoie 1995) with flow lines perpendicular to the contours. We then overlaid watershed boundaries on aerial photographs or GIS land-use maps (from the Town of Falmouth GIS database) and collated land uses within, including number of residential buildings and coverage by commercial and agricultural land and by wetlands, ponds,

and golf courses. Human-population density was calculated on the basis of the number of residential buildings and average occupancy per building in these watersheds (Valiela et al. 1997).

As a measure of the distance that average groundwater parcels and associated solutes traverse through the aquifer in these watersheds, we calculated the aquifer path length as the watershed area/length of the seepage face along the shoreline of the receiving surface water, multiplied by 0.5. This quantity estimates the areally weighted average distance between all points within the watershed and the seepage face. If we ignore any curvature in groundwater flow paths, the computed quantity provides an estimate of the average distance that water parcels must traverse through the aquifer before discharge. Examination of the degree of curvature in flow paths in Waquoit Bay watersheds, for which particle-tracking analysis has been performed by application of MODFLOW (Valiela et al. 2000), suggests that ignoring curvature in flow paths results in an error in estimated path length of at most a few percent.

The path length, or thickness, of the vadose zone (the unsaturated sediment layer above the water table) was calculated from a database of vadose-zone thickness for Cape Cod generated by D. Walters and colleagues (USGS Marlborough, Massachusetts). The database was developed on the basis of field measurements and by overlaying topographic maps on modeled water table-elevation maps and calculation of the difference between the land surface and the water table. We used GIS software to overlay our watershed delineations on the map of vadose-zone thickness and calculate areally weighted average vadose-zone thickness for each watershed.

*Statistical analyses*—Simple and multiple linear regressions and correlations were calculated by application of StatView statistical software from SAS and according to the texts from Daniel (1987) and Neter et al. (1996). Graphical methods were used to test assumptions for parametric regression of linearity, homoscedasticity, and normality of residuals. We tested for multicollinearity, or strong correlations between independent variables used in multiple correlation and regression analyses, by use of pairwise correlation analyses and on the basis of the variance inflation factor (VIF) (Neter et al. 1996). VIF was calculated as  $VIF_k = 1/(1-R^2_k)$ , where  $R^2_k = R^2$  for the regression of the  $k$ th predictor on the remaining predictors.  $VIF > 4$  suggests that multicollinearity should be further investigated, and  $VIF > 10$  suggests a high degree of multicollinearity. Results of multiple correlation and regression analyses were interpreted on the basis of Daniel (1987). For each combination of independent and dependent variable, we calculated the partial correlation coefficient ( $r$ ) as a measure of the strength of the correlation between the two variables when the effects of other variables were held constant. The significance of each  $r$  was tested by application of a  $t$ -test. The coefficient of partial determination ( $r^2$ ) was calculated as a measure of the proportion of the remaining variability in the dependent variable that can be explained by each independent

variable after all other independent variables have explained as much as they can of the total variability.

## Results

*Watershed attributes*—The primary watershed land covers were residential and natural vegetation (Table 1). Areas of agriculture and ponds and wetlands in this portion of Cape Cod were quite small. Average population density on the watershed segments was 430 people  $\text{km}^{-2}$ , with a range of 0 to 1,440 people  $\text{km}^{-2}$  (Table 1). Population densities on these watersheds are, therefore, representative of many coastal watersheds throughout the world. Ninety percent of global coastal populations occur outside of major urban centers, at population densities that average 500 to 600 people  $\text{km}^{-2}$  (Nicholls and Small 2002), similar to the average 430 people  $\text{km}^{-2}$  in the watersheds studied here. Further, in many cases, such residential areas with low-to-moderate population density may be likely to dispose of wastewater through decentralized, on-site systems, as is the case in our study sites.

The watersheds ranged in surface area from 0.08 to 13.62  $\text{km}^2$ . Average aquifer path length and average vadose-zone thickness in watersheds (Table 2) ranged from 109 to 2,334 m and 1.4 to 18.3 m, respectively. Significant but weak correlations occurred among physical attributes of the watersheds and human-population density. Vadose-zone thickness and aquifer path length increased as watershed area increased, and population density decreased with increased aquifer path length and vadose-zone thickness (Kroeger 2003).

*Nitrogen concentrations in groundwater*—N concentrations in groundwater leaving the watersheds varied widely (Table 3). Average total-dissolved N (TDN) concentrations in groundwater samples collected from each of the 41 watershed segments ranged from 5 to 293  $\mu\text{mol L}^{-1}$  (Table 3), with a relatively uniform distribution of observations (Fig. 3). Average DON concentrations ranged from 5 to 182  $\mu\text{mol L}^{-1}$  (Table 3; Fig. 3). Percent of TDN as DON (%DON) ranged from 10 to 93, but on the whole, N exports were dominated by DON, which comprised a median of 62% of TDN (Table 3; Fig. 4). Associations between land uses in these watersheds and groundwater-nitrate concentrations and natural abundance stable-isotope ratios in nitrate are the subject of a separate article (Cole et al. in 2006) and will not be discussed in here.

*Associations between land uses and nitrogen concentrations*—A full examination of associations between watershed attributes and magnitude and chemical form of N exports (Kroeger 2003) indicated that concentrations of TDN and DON in groundwater leaving the watersheds showed relations only to population density, vadose-zone path length, and aquifer path length. Concentrations of both TDN and DON were positively related to population density (Fig. 5), whereas percent land cover by agriculture and by ponds and wetlands were small and were not related to N concentrations. DON concentrations were also negatively correlated with lengths of flow paths through

Table 1. Percent of watershed cover by four categories of land use and population density on the watersheds.

	Residential	Natural* vegetation	Agriculture	Pond/wetland	People km <sup>-2</sup>
Average	15	81	1	2	430
Standard deviation	8	9	2	3	380
Median	19	77	0	0	280
Range	0-59	41-100	0-9	0-9	0-1,440
Green Pond whole watershed	32	62	2	3	740
1	31	58	3	8	510
2	24	60	9	8	560
3	42	58	0	0	1,060
4	39	61	0	0	990
5	13	87	0	0	270
6	48	52	0	0	1,220
7	17	83	0	0	390
8	59	41	0	0	1,440
Great Pond whole watershed	23	74	0	3	400
1	19	75	0	6	330
2	21	76	0	3	320
3	23	77	0	0	400
4	37	63	0	0	610
5	36	64	0	0	860
Mashpee River whole watershed	12	87	0	0	110
1	9	90	0	1	160
2	9	91	0	0	170
4	14	84	0	1	20
5	13	86	0	0	110
Eel Pond whole watershed	26	73	1	1	450
1	30	70	0	0	740
2 East	40	60	0	0	930
2 West	19	81	0	0	450
3 East	55	45	0	0	1,410
3 West	22	78	0	0	510
4	22	75	2	1	250
Childs River whole watershed	24	75	0	1	260
1 West	38	62	0	0	700
2 West	22	78	0	0	230
3 West	20	77	0	3	220
4 West	27	71	0	2	250
Head of Waquoit Bay (segment)	16	76	1	7	190
Quashnet River whole watershed	15	75	3	7	70
1	13	87	0	0	270
2 West	13	83	2	2	160
2 East	13	87	0	0	280
3 West	8	88	0	4	100
4 West	10	88	0	2	60
5	17	69	5	9	60
Hamblin Pond whole watershed	13	82	5	0	180
1	8	92	0	0	320
2	14	80	6	0	150
Jehu Pond whole watershed	14	84	1	1	200
1	21	79	0	0	470
2	8	92	0	0	50
3	18	77	2	3	260
Sage Lot Pond whole watershed	0	100	0	0	0
Coonamessett Pond whole watershed	11	89	0	0	30

\* Natural vegetation includes forest, wooded areas within residential land uses, and shrub and grasslands. Residential includes lawns, roads, and other impervious surfaces, golf courses, and commercial land uses. See Figs. 1 and 2 for watershed delineations. Whole watersheds are the aggregate of the watershed segments listed below them. Statistics at the top of the table are for watershed segments.

Table 2. Watershed area and areally averaged aquifer path length and vadose-zone thickness.

	Aquifer path length (m)	Vadose zone (m)	Watershed area (km <sup>2</sup> )
Average	472	7.4	1.81
Standard deviation	473	3.3	2.54
Median	258	7.0	0.99
Range	109–2,334	1.4–18.3	0.08–13.62
Green Pond whole watershed	191	5.7	2.21
1	185	6.0	0.45
2	194	6.9	0.45
3	139	5.5	0.16
4	217	7.6	0.2
5	183	4.4	0.3
6	235	6.3	0.38
7	191	2.4	0.14
8	168	2.2	0.13
Great Pond whole watershed	699	7.4	8.37
1	1,756	7.3	2.86
2	772	7.2	2.29
3	675	8.1	2.14
4	261	7.3	0.57
5	249	5.6	0.5
Mashpee River whole watershed	355	8.8	8.55
1	109	5.1	1.11
2	409	11.6	2.19
4	635	6.6	2.01
5	593	9.6	3.24
Eel Pond whole watershed	230	7.7	3.79
1	109	3.5	0.16
2 East	144	4.1	0.25
2 West	125	5.3	0.29
3 East	120	5.3	0.3
3 West	155	6.7	0.3
4	429	8.9	2.5
Childs River whole watershed	839	9.7	7.97
1 West	258	6.9	0.6
2 West	1,260	9.8	2.94
3 West	1,100	9.6	2.45
4 West	759	10.4	1.98
Head of Waquoit Bay (segment)	300	7.8	0.99
Quashnet River whole watershed	840	12.7	20.43
1	115	4.9	0.08
2 West	914	10.6	1.75
2 East	239	8.8	0.54
3 West	807	10.4	2.09
4 West	612	9.0	2.36
5	929	14.0	13.62
Hamblin Pond whole watershed	212	nd	2.17
1	160	nd	0.34
2	222	nd	1.84
Jehu Pond whole watershed	375	nd	3.95
1	294	nd	0.56
2	320	nd	1.63
3	497	nd	1.76
Sage Lot Pond whole watershed	166	1.4	1.04
Coonamessett. Pond whole watershed	2,334	18.3	7.45

See Figs. 1 and 2 for watershed delineations. Whole watersheds are the aggregate of the watershed segments listed below them. Statistics at the top of table are for watershed segments.

vadose zone and aquifer. Percent DON was negatively correlated with path lengths through vadose zone and aquifer but was not related to population density.

To examine the significance and relative importance of the three watershed variables (population density and

lengths of flow paths through vadose zone and aquifer) that were correlated with both groundwater DON concentrations and %DON, we performed multiple linear regressions (MLRs) (Tables 4, 5). Log transformation of vadose-zone path length and aquifer path length improved

Table 3. Average concentrations in groundwater of total-dissolved N, dissolved organic N, nitrate, and ammonium.

	TDN ( $\mu\text{mol L}^{-1}$ )	DON ( $\mu\text{mol L}^{-1}$ )	$\text{NO}_3^-$ ( $\mu\text{mol L}^{-1}$ )	$\text{NH}_4^+$ ( $\mu\text{mol L}^{-1}$ )	%DON	Number of samples
Average	116	61	47	8	60	
Standard deviation	80	45	63	13	24	
Median	99	44	20	4	62	
Range	5-293	5-182	5-236	0-58	10-93	
Green Pond whole watershed	214	140	71	3	66	
1	110	94	11	4	86	21
2	210	124	82	4	59	23
3	252	182	67	3	72	9
4	171	137	34	1	80	9
5	135	117	15	3	87	15
6	207	128	78	1	62	14
7	127	114	10	3	90	9
8	214	165	47	2	77	9
Great Pond whole watershed	230	50	178	2	22	
1	289	51	236	2	18	8
2	293	71	220	2	24	6
3	111	25	85	2	22	6
4	235	63	163	9	27	8
5	127	44	82	2	34	16
Mashpee River whole watershed	25	14	10	2	55	
1	93	41	42	10	44	8
2	15	14	0	1	93	14
4	5	5	0	0	93	8
5	21	10	10	1	47	18
Eel Pond whole watershed	157	96	24	37	61	
1	158	96	4	58	61	9
2 East	137	92	33	13	67	11
2 West	93	79	9	5	85	13
3 East	148	94	46	8	64	17
3 West	141	88	2	51	62	8
4	166	99	25	42	60	31
Childs River whole watershed	112	22	79	11	19	
1 West	268	27	228	13	12	28
2 West	153	37	109	7	25	74
3 West	93	9	80	4	10	27
4 West	34	14	2	18	41	22
Head of Waquoit Bay (segment)	60	35	20	5	59	37
Quashnet River whole watershed	49	29	13	7	59	
1	61	52	6	3	85	136
2 West	77	56	17	4	73	30
2 East	12	9	3	1	72	12
3 West	92	38	49	5	41	26
4 West	22	16	2	3	76	24
5	44	26	9	9	60	18
Hamblin Pond whole watershed	44	35	4	5	80	
1	34	27	1	6	80	19
2	45	36	4	5	80	22
Jehu Pond whole watershed	64	42	13	8	66	
1	99	61	32	6	61	12
2	66	43	12	11	65	31
3	48	35	7	6	73	35
Sage Lot Pond whole watershed	38	35	1	3	92	13
Coonamessett Pond whole watershed	54	15	39	0	27	14

Also presented are percent of TDN as DON and number of samples collected from each watershed. See Figs. 1 and 2 for watershed delineations. Whole watersheds are the aggregate, weighted for the annual volume of groundwater discharge, of the watershed segments listed below them. Statistics at the top of table are for watershed segments. Data sources are groundwater collections conducted for this study and for the Waquoit Bay Land Margin Ecosystem Research project (WBLMER).

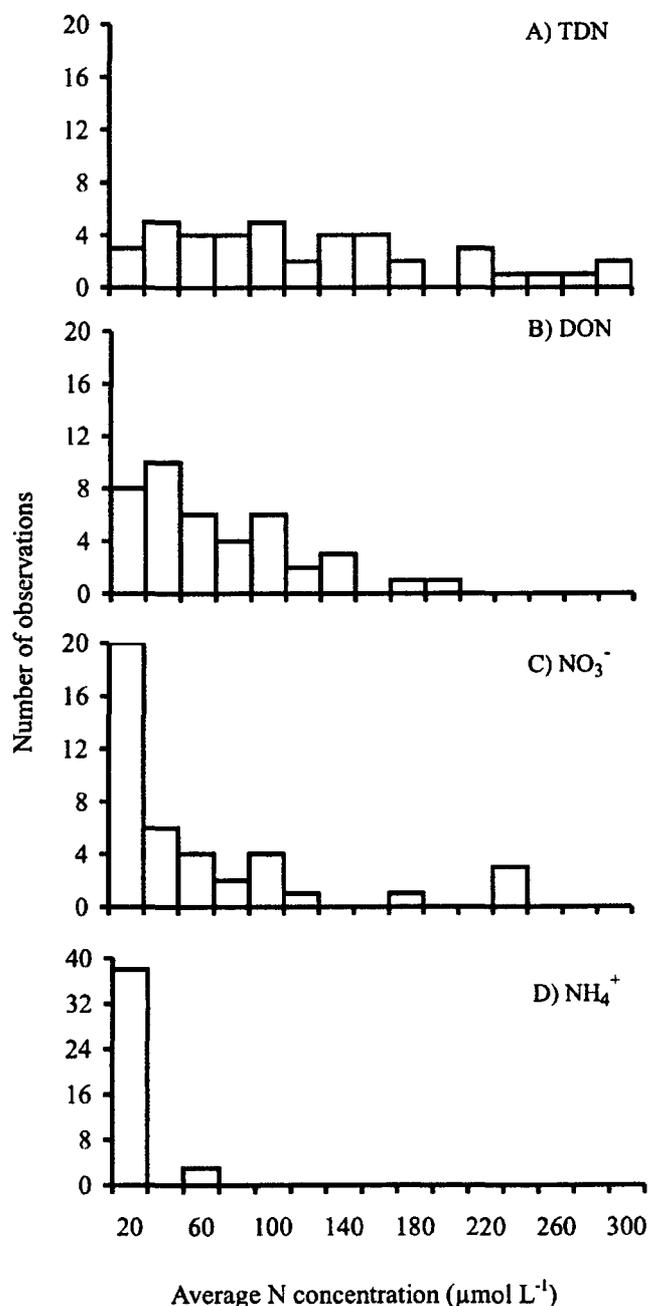


Fig. 3. Frequency histograms for average concentrations of (A) TDN, (B) DON, (C)  $\text{NO}_3^-$ , and (D)  $\text{NH}_4^+$  in groundwater samples collected at the land-sea margin from each of the 41 watershed segments. Note change in y-axis scale for  $\text{NH}_4^+$ .

homogeneity of variances in the MLRs. VIFs (Tables 4, 5) were low in the multiple regressions, which indicates that correlations between independent variables were weak, and, therefore, independent examinations were possible of the relations between  $y$  and each of the independent variables (Neter et al. 1996).

The coefficient of multiple determination,  $R^2$ , was calculated as a measure of the proportion of the total

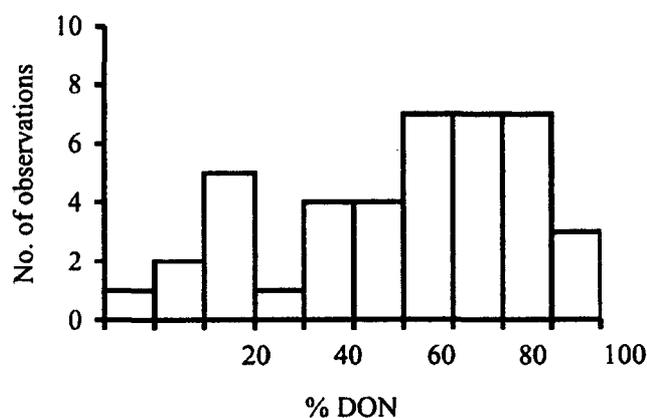


Fig. 4. Frequency histogram for percent of TDN as DON in groundwater samples collected at the land-sea margin from each of the 41 watershed segments.

variability in  $y$  that could be explained by all of the three independent variables. For each combination of independent and dependent variable, we calculated the partial correlation coefficient ( $r$ ) as a measure of the strength of the correlation between the two variables when the effects of other variables were held constant. The significance of each  $r$  was tested by application of a  $t$ -test. The coefficient of partial determination ( $r^2$ ) was calculated as a measure of the proportion of the remaining variability in the dependent variable that can be explained by each independent variable after all other independent variables have explained as much as they can of the total variability.

The overall MLR for DON concentration was highly significant ( $p < 0.0001$ ) (Table 4), but, of the three independent variables, only population density was significantly related to DON concentration in groundwater. Furthermore, the  $R^2$  for the MLR (0.59) (Table 4) was only slightly higher than the  $R^2$  for the simple linear regression between DON concentration in groundwater and watershed population density ( $R^2 = 0.53$ ) (Fig. 5). The partial correlation coefficient ( $r$ ) (Table 4), a measure of the strength of the correlation between DON concentration and each of the independent variables when other variables were held constant at their mean, indicated a strong positive relation for population density and weak negative relation for path lengths through vadose zone and aquifer. The coefficient of partial determination ( $r^2$ ) (Table 4) indicated that path lengths through vadose zone and aquifer explained a much smaller proportion of the variability in DON concentration than did population density.

The overall MLR for %DON was also highly significant ( $p = 0.002$ ) (Table 5), but only 36% of the variability in %DON could be explained by the three independent variables. Coefficients for all three independent variables were negative, but only aquifer path length was significantly related to %DON in groundwater (Table 5). The partial correlation coefficients and coefficients of partial determination again indicated that %DON was most closely related to aquifer path length.

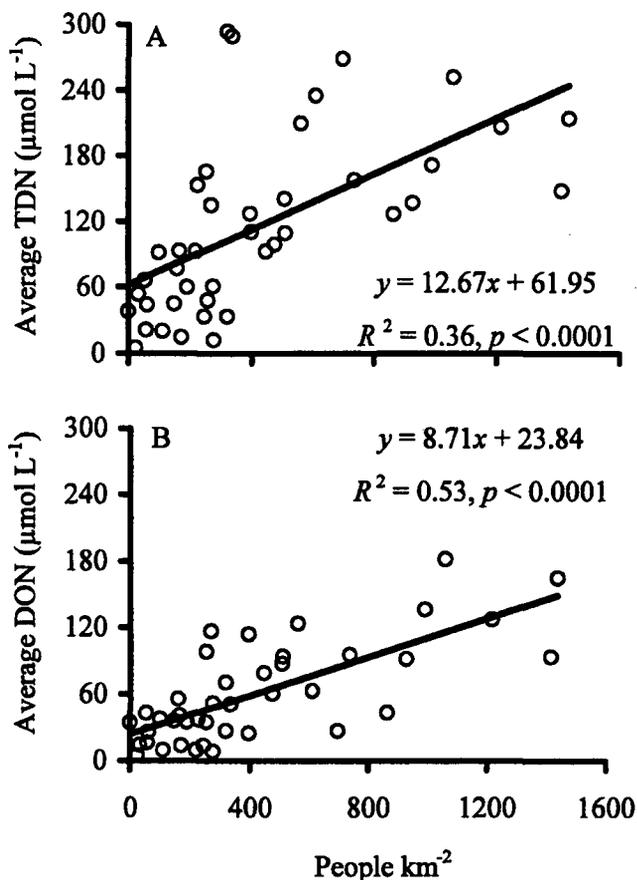


Fig. 5. Simple linear regressions for average groundwater (A) TDN concentration and (B) DON concentration for each watershed segment versus population density on the watersheds.

## Discussion

In this study, significant relations found were (1) positive relations between population density on watersheds and concentrations in groundwater of both TDN and DON and (2) negative relations between aquifer path length in watersheds and percent of TDN as DON in groundwater. The relation between population density and %DON was nonsignificant. Those results may suggest that in general, TDN and DON concentrations were related to magnitude

of the anthropogenic N load to the watersheds (population density), whereas the *chemical form* of watershed N exports was most closely related to opportunity for N *transformations* during transport from source to receiving water (path length through watersheds). The reason why %DON should be more closely related to path length through aquifers than to path lengths through vadose zones (Tables 4, 5) is not clear, and the separate roles of transport through each of those zones may be unresolved. However, in these watersheds, %DON was significantly greater in N exports from watersheds with shorter path lengths (Fig. 6A) and %DON was not significantly related to population density (Fig. 6B)

Relations between land use and TDN or DIN exports from watersheds have been shown and examined in past studies (e.g., Galloway 1998; Valiela et al. 2000). In many of the watersheds included in the present study, correlations have been shown between measured TDN exports and measures of residential development. Modeling and N stable-isotopic evidence suggest that at low population density, N exports are dominated by atmospheric deposition to the watersheds, but with increased residential development on the watersheds, on-site wastewater disposal becomes the dominant N source in groundwater and receiving surface waters (Valiela et al. 1997).

In the present study, N concentration in groundwater from the forested Sage Lot Pond watershed was low and was dominated by DON (92% of TDN) (Table 3). In portions of the same watersheds examined in the present study, Lajtha et al. (1995) found that N flux to lysimeters 15 cm beneath forested soil surfaces were also dominated by DON. The soils examined in that study included fine sand, coarse sand, and loamy sand and were representative of soils throughout the Waquoit Bay and adjacent watersheds. Predominantly DON export from forested watersheds has been reported previously. Perakis and Hedin (2002) found that in pristine, temperate South American forests with little atmospheric deposition of anthropogenic N, N in streams leaving the forests occurred largely as DON. With greater atmospheric N deposition, old-growth temperate forests in some cases export primarily nitrate, but aggrading forests may still export primarily DON (Campbell et al. 2000) because of N demands associated with accumulating living and detrital biomass (Likens and Bormann 1995).

Increased DON exports with increased population density and greater than 50% DON at higher population

Table 4. Multiple linear regression for average groundwater DON concentration versus watershed aquifer path length (m), vadose-zone path length (m), and population density (people km<sup>-2</sup>).

	F	df	p	R <sup>2</sup>	Coefficient	Partial correlation coefficient (r)	Coefficient of partial determination (r <sup>2</sup> )
Regression	15.1	32	<0.0001	0.59			
Intercept			0.04		102.9		
Aquifer path length			0.46		-16.4	-0.131	0.017
Vadose-zone path length			0.29		-36.3	-0.186	0.035
Population density			0.0001		0.071	0.613	0.376

Aquifer and vadose-zone path lengths are log transformed.

Table 5. Multiple linear regression for percent of TDN as DON versus watershed aquifer path length (m), vadose-zone path length (m), and population density (people km<sup>-2</sup>).

	<i>F</i>	<i>df</i>	<i>p</i>	<i>R</i> <sup>2</sup>	Coefficient	Partial correlation coefficient ( <i>r</i> )	Coefficient of partial determination ( <i>r</i> <sup>2</sup> )
Regression	6.03	32	0.002	0.36			
Intercept			<0.0001		183.5		
Aquifer path length			0.008		-41.2	-0.448	0.201
Vadose-zone path length			0.508		-15.1	-0.117	0.014
Population density			0.067		-0.02	0.318	0.101

Aquifer and vadose-zone path lengths are log transformed.

densities were more unexpected. Addition of wastewater and fertilizer associated with human habitation of watersheds is generally thought to increase exports of inorganic N (Peierls et al. 1991; Nolan and Stoner 2000). In an examination of watershed N exports to major world rivers, Caraco and Cole (2001) found that as human population increased on watersheds, DIN export increased, whereas DON export remained unchanged, so that a shift occurred from dominance by DON exports to dominance by DIN exports. Thus, the general conception on the basis of the current literature seems to be that DON exported from watersheds is from natural sources and that anthropogenic N is exported from watersheds as nitrate (Gildea et al. 1986; Caraco and Cole 1999, 2001).

Increased DON concentration with increased population density observed in the present study suggests that some portion of the anthropogenic N added to the watersheds, through fertilizer applications or through wastewater disposal, may be exported in organic form. Applications of inorganic N fertilizer to watersheds, after assimilation into vegetation and soil organic matter, may be a source of DON to the subsurface of watersheds. For instance, applications of fertilizer over a period of several years to plots in Harvard Forest increased DON flux below the soil (Magill et al. 2000). In addition, Kalbitz et al. (2000) found lighter  $\delta^{15}\text{N}$  in fulvic acid in groundwater from fertilized plots than in unfertilized plots, which likely indicated plant

incorporation of fertilizer N followed by release as DON to groundwater. However, insufficient data are available to estimate fertilizer contributions to DON exports on a watershed scale.

To investigate whether DON from wastewater could be responsible for increased DON exports with increased population density, we compiled literature and made our own measurements (Kroeger 2003) of DON content in wastewater effluent from on-site systems (Table 6) and estimated wastewater DON loads to watersheds (Fig. 7). Approximately 90% of N entering septic tanks is in the form of urea and other organic N, but within septic tanks, intense microbial processing under anaerobic conditions ammonifies much of the organic N so that effluent is generally dominated by  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  is negligible, and DON content is variable (Wilhelm et al. 1994). Percent of TN as DON in effluent ranged between 15 and 82 in the compiled data set, with an average of 30 (Table 6). Much of the variability among the observations may be caused by variation in extent of ammonification as determined by residence time of wastewater within tanks. Given typical total N excretion per capita of 4.82 kg N yr<sup>-1</sup> (Valiela et al. 1997), and assuming that, on average, 30% of that N leaves septic systems as DON, wastewater DON loads to the watersheds examined in this study are similar to and often larger than total DON exports from the watersheds (Fig. 7).

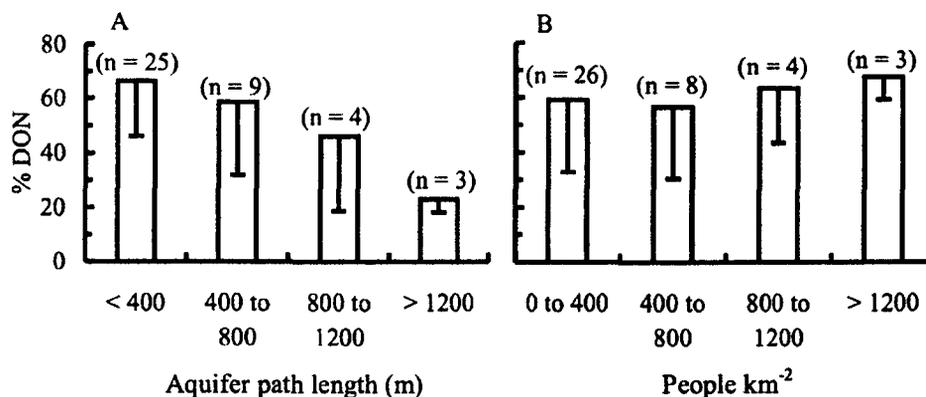


Fig. 6. Average percent of TDN as DON in groundwater samples for each of the 41 watershed segments versus (A) watershed average groundwater path length through aquifers ( $R^2 = 0.30$ ,  $p = 0.0002$ ) and (B) watershed population density ( $p = 0.90$ ).

Table 6. Percent of total N in septic-tank effluent that is DON.

%DON	Observations	Source
30	99	Harman et al. 1996
15	1	Kroeger 2003
39	1	Kroeger 2003
35	1	Kroeger 2003
82	3	Corbett et al. 2002
32	2	Corbett et al. 2002
22	1	Brown et al. 1984
25	1	Walker et al. 1973
16	4	Weiskel and Howes 1992
27	2	Wilhelm et al. 1996
31		Weighted mean
	115	Total number of observations

Mean values are weighted for number of observations.

Strong evidence suggests loss (retention or mineralization) of dissolved organic matter in vadose zones and aquifers, on the basis of studies of DOM both from atmospheric sources (Cronan and Aiken 1985; Pabich et al. 2001) and from wastewater sources (LeBlanc et al. 1991; Robertson and Cherry 1992; DeSimone et al. 1996). Therefore, we clearly should not expect that all of wastewater DON added to the watersheds is exported from the watersheds. However, information on rate or extent of DON loss is lacking, because few studies have been concerned with transport of DON traversing substantial path lengths through vadose zones or aquifers. Studies on N cycling in forests do frequently quantify DON flux through soils but generally track its fate to only ~1 m into the mineral soil (Lajtha et al. 1995; Magill et al. 2000). Studies on wastewater disposal to watershed surfaces and subsurface more commonly track materials over longer path lengths through vadose zones and aquifers, but most are concerned with DIN and reporting of DON concentrations are uncommon (Reneau et al. 1989; Wilhelm et al. 1994). Examination of the few data that are available on loss of dissolved organic matter in the subsurface of watersheds (e.g., DeSimone et al. 1996; Pabich et al. 2001) suggests that the process is initially rapid in both vadose zones and aquifers, followed by a more gradual loss in the deeper portions of those zones, and that some portion of DON loads to watersheds might survive transport through vadose zones and aquifers.

A number of factors may contribute to the large groundwater DON concentrations observed in this study and to export of wastewater DON from watersheds. First, the soils in these glacial outwash-plain watersheds are coarse and organic poor, so that percolation is rapid of rainwater and soil organic matter from the watershed surface (Lajtha et al. 1995). Second, survival of wastewater DOM during transport may occur because of short flow paths through watersheds. Oxidation of septic effluent in vadose zones may be limited if the separation distance between location of discharge and the water table is too small, if the effluent is dispersed over a small enough area that saturated flow occurs to the aquifer, or if oxygen diffusion into the vadose zone is restricted (Reneau et al.

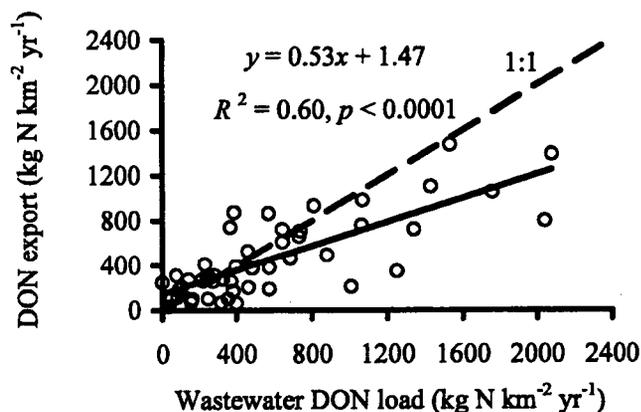


Fig. 7. Total annual groundwater-transported DON export  $\text{km}^{-2}$  of watershed versus annual wastewater DON load to the watershed. Dashed line is line of equal mass ( $y = x$ ). Solid line is regression line.

1989; Wilhelm et al. 1994). Under such conditions,  $\text{NH}_4^+$  and DON move through the vadose zone as a front (Brown et al. 1984). In the watersheds examined in the current study, median path lengths through vadose zone and aquifer were 7 m and 258 m, respectively (Table 2). Given typical burial on Cape Cod of on-site wastewater disposal systems at ~2.46 m below the watershed surface (S. Rask, Barnstable County Dept. of Health, pers. comm.), generally greater population density in near-shore portions of watersheds (Kroeger 2003), and thinner vadose zones near shore (Kroeger 2003), flow paths for many wastewater plumes may be much shorter than the average water flow paths through entire watersheds. Typical groundwater-flow rates in these watersheds are 110 to  $365 \text{ m yr}^{-1}$  (LeBlanc et al. 1988; LeBlanc et al. 1991), and, therefore, a large proportion of the wastewater plumes must be less than 1 year old at the time of discharge to surface waters.

*Comparison with literature*—To our knowledge, no past study has comprehensively investigated factors that control the chemical form of groundwater N exports from watersheds, and indeed, little is known regarding controls on the chemical form of watershed N exports on the basis of analysis of streams or rivers.

To view our results in a broader context, we compared TN exports, DON exports, and %DON in relation to watershed population density in the present study to results of the Scientific Committee on Problems of the Environment (SCOPE) study of N exports in streams and rivers from 16 large catchments that comprised a substantial portion of the Atlantic coast of the United States from Maine to Virginia (Alexander et al. 2002) (Fig. 8). The distributions of points in plots of N exports versus population density on the watersheds were remarkably similar in the two studies, despite large differences in scale ( $0.08$  to  $13.6 \text{ km}^2$  in our study;  $500$  to  $70,000 \text{ km}^2$  in the SCOPE study), and despite sample collections from groundwater in our watersheds versus sample collections from streams and rivers in the SCOPE study. In the SCOPE study, all three relations shown in Fig. 8 were

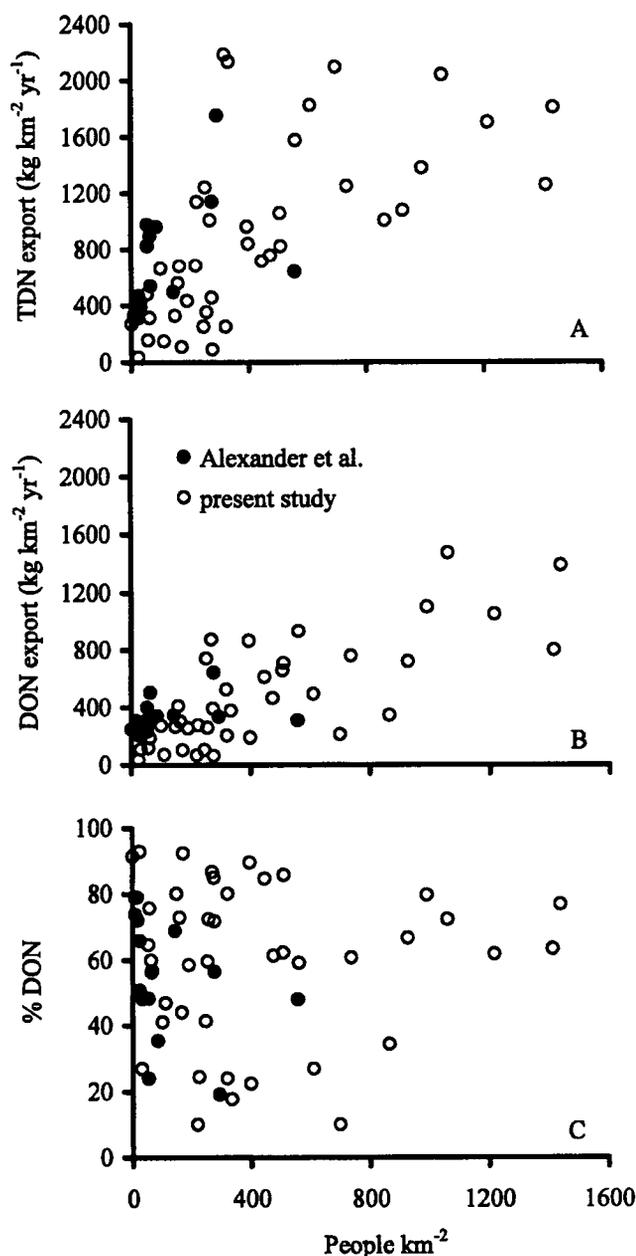


Fig. 8. Comparison of (A) TDN exports, (B) DON exports, and (C) %DON in the present study to N exports in streams and rivers from 16 large catchments on the Atlantic coast of the United States (Alexander et al. 2002). In data from the Alexander et al. (2002) study, all three relations were nonsignificant on the basis of simple linear regression (TN export  $p = 0.072$ ; DON export  $p = 0.189$ ; %DON  $p = 0.174$ ).

nonsignificant on the basis of simple linear regression (TN export  $p = 0.072$ ; DON export  $p = 0.189$ ; %DON  $p = 0.174$ ). Those nonsignificant relations may be in part caused by a narrower range of watershed population density in the SCOPE study. In addition, the watersheds examined in the SCOPE study had a wider range of land

uses, including substantial agriculture in some cases, and wastewater disposal both through on-site systems and through centralized wastewater treatment plants. Still, the two sets of watersheds had similar ranges of TDN and DON exports at a given population density, and in both sets, no significant relation occurred between %DON and population density. Forty-eight percent of the N exported from the SCOPE watershed with greatest population density was as DON (Fig. 8).

On the basis of an examination of N exports from a large number of watersheds in northeastern Massachusetts and compiled literature for watersheds in the northeastern United States (including the SCOPE study), Pellerin et al. (2004) found that DON concentration and DON/TDN in streams and rivers increased with increased proportion of watersheds that is composed of wetland. Their analysis suggested that wetlands were the primary source for DON in streams and that increasing the proportion of watersheds as developed land had a minor effect on DON concentrations in streams. Two factors may account for the differences in results of the present study and the Pellerin et al. (2004) study. First, in the watersheds included in the present study, percent cover by wetlands was small (range = 0% to 9% and average = 2%) (Table 2). In the Pellerin et al. (2004) study, watershed cover by wetlands spanned a much greater range (0% to >30%). The second factor that may account for the difference in results may be related to differences in information recorded in groundwater and in stream water. In the present study, because fringing wetlands at the land-aquatic margin are sometimes flooded and are in direct communication with receiving waters, we considered fringing wetlands to be a part of the receiving water, and we sampled groundwater landward of those wetlands so that we could examine relations between N concentrations and watershed land uses. Many of the watersheds in the Ipswich River, the primary site of the Pellerin et al. (2004) study, do have abundant fringing wetland with direct communication with stream waters, and those wetlands appear to be a dominant feature that influences N concentrations in the streams. Therefore, the conclusions to be drawn from both studies may be that anthropogenic DON appears to be an important component of N exported from watersheds through groundwater discharge, but fringing wetlands may be a major source for DON exported through stream discharge to downstream segments in the aquatic cascade from land to sea.

DON was often the dominant form of N exported from the watersheds studied here, even at high population densities. The results presented here suggest that natural sources may not be entirely responsible for organic N exports from watersheds, but, instead, a substantial portion of anthropogenic N introduced to watersheds is exported as DON. This finding is in contrast to previous results that suggest anthropogenic N is exported from watersheds largely as  $\text{NO}_3^-$  (Gildea et al. 1986; Peierls et al. 1991; Caraco and Cole 2001), and DON exported from watersheds is from natural sources (Perakis and Hedin 2002). Furthermore, because bioavailability of anthropogenic DON may be greater than that of wetland or forest-derived DON (Seitzinger et al. 2002), anthropogenic DON

exported to sea may play a role in eutrophication of coastal waters. Because (1) DON exports are large, (2) anthropogenic N may occur in any of the fixed forms, and (3) some proportion of the DON may be bioavailable, we must consider all forms of N in examinations of watershed N exports and loads to receiving waters.

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