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Title: Effects of watershed land use on nitrogen concentrations and δ^{15}Nitrogen in groundwater

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Abstract

Eutrophication is a major agent of change affecting freshwater, estuarine, and marine systems. It is largely driven by transportation of nitrogen from natural and anthropogenic sources. Research is needed to quantify this nitrogen delivery and to link the delivery to specific land-derived sources. In this study we measured nitrogen concentrations and $\delta^{15}N$ values in seepage water entering three freshwater ponds and six estuaries on Cape Cod, Massachusetts and assessed how they varied with different types of land use. Nitrate concentrations and $\delta^{15}N$ values in groundwater reflected land use in developed and pristine watersheds. In particular, watersheds with larger populations delivered larger nitrate loads with higher $\delta^{15}N$ values to receiving waters. The enriched $\delta^{15}N$ values confirmed nitrogen loading model results identifying wastewater contributions from septic tanks as the major N source. Furthermore, it was apparent that N coastal sources had a relatively larger impact on the N loads and isotopic signatures than did inland N sources further upstream in the watersheds. This finding suggests that management priorities could focus on coastal sources as a first course of action. This would require management constraints on a much smaller population.

Introduction

Eutrophication is a major agent of change affecting freshwater, estuarine, and marine systems. Increased N delivery stimulates production of phytoplankton and macrophytes, which can lead to a loss of important habitats such as seagrass meadows (Morand & Briand 1996; Hauxwell et al. 2001). Loss of habitat has contributed to decreased commercially important fin and shellfish stocks (Baden et al. 1990). Degradation of water quality also affects land owners directly by decreasing the aesthetic value of coastal property. Eutrophied estuaries also suffer from hypoxia and anoxia (Zimmerman and Canuel 2000), which can result in major fish kills in embayments such as Narragansett Bay, Rhode Island (RIDEM 2003). As populations grow along coastal areas, there is an increasing need to understand how urbanization and associated nitrogen dynamics impact adjacent bodies of water.

Groundwater transports nitrogen from natural and anthropogenic sources to many freshwater (LaBaugh et al. 1995; Hagerthey & Kerfoot 1998) and estuarine systems (Capone & Slater 1990; Valiela et al. 1990). N loads transported from watersheds to receiving waters are markedly affected by the distribution of land use on contributing watersheds (Valiela et al. 1990; 1997), leading to spatial heterogeneity in land-derived N loads. There may also be temporal variation in delivery of nitrogen to receiving waters at tidal (Ataie-Ashtiani et al. 2001) and seasonal time scales (Gobler & Sanudo-Wilhelmy 2001; Kemp & Dodds 2001).

Differences in land use on coastal watersheds can affect nitrogen delivery by changing the form and quantity of N entering groundwater via atmospheric deposition, fertilizer use, and wastewater (Cole et al. 1993; Valiela et al. 1997). In particular, wastewater delivery to Cape Cod estuaries from nearby septic systems has increased over the last few decades (Bowen & Valiela 2001), as human populations have increased along the Cape Cod coast (Bowen &

Valiela 2001). Loads from atmospherically deposited N have also increased over the last hundred years (8%, Bowen & Valiela 2001), but this increase is minor compared to increases in wastewater N loads (93%, Bowen & Valiela 2001). This is of particular concern because populations closer to the coast (i.e., <200 m) are believed to contribute more N to receiving waters than populations located more inland (Valiela et al. 1997; Corbett et al. 2002).

Estimates of N loads as well as stable isotopes can be used to determine how land use affects nitrogen loading to adjacent bodies of water. Magnitude of N loads to water bodies can be calculated from the product of measured nutrient concentrations in groundwater and annual groundwater discharge (Kroeger et al. 1999; Valiela et al. 2000). Different sources of nitrogen can be identified using nitrogen stable isotopes, but only when the sources have distinctive isotope signatures, particularly wastewater (McClelland et al. 1997; Kendall 1998). In untreated sewage, ammonium typically has a $\delta^{15}N$ of +5 to +9 ‰ (Aravena et al. 1993; Waldron et al. 2001), and volatilization, nitrification, and subsequent denitrification within the septic system or wastewater treatment plant can enrich remaining nitrate in ^{15}N relative to ^{14}N. As a result, nitrate in groundwater from septic system wastewater can become enriched, with $\delta^{15}N$ values ranging from +10 to +20 ‰ (Kendall 1998). This range is significantly higher than the $\delta^{15}N$ of groundwater nitrate derived from atmospheric deposition (-4 to +6 ‰, Kendall 1998), and from fertilizers (-4 to +4 ‰, Kendall 1998).

In this study, we used estimates of N loading and stable isotopes to examine linkages between land use and land-derived N loads, DIN in groundwater, and $\delta^{15}N$ of nitrate in groundwater. To do this we first examined the distribution of N concentrations and isotopes at the seepage face (where fresh groundwater was entering receiving waters) of several freshwater ponds and estuaries. We related these distributions of N concentrations and isotopes to land

use in a series of watersheds where land use differed substantially. We then evaluated how proximity of land uses to the shoreline affected these relationships. To verify our results we compared measured groundwater $\delta^{15}N\text{-}NO_3$ values to those predicted by a three member mixing model.

Methods

Site description

The sites sampled in this study included recharge zones around three estuarine watersheds (Mashpee River, Great Pond, and Green Pond) and three freshwater pond watersheds in southwestern Cape Cod (Coonamessett Pond, and Ashumet Pond) and on Nantucket, MA (Miacomet Pond) (Fig. 1). We also included previously published data for the different recharge zones of Sage Lot Pond, Quashnet River, and Childs River, (McClelland et al. 1997; McClelland & Valiela 1998). All of the recharge zones are underlain by sandy, unconsolidated sediments and have an average groundwater travel time of 146 m per year (LeBlanc et al. 1991). To obtain a description of the land use mosaics in each contributing watershed and to obtain data with which to relate differences in land use to concentrations of NO_3 load and $\delta^{15}N\text{-}NO_3$ in groundwater, we identified watershed boundaries using water table contours (Savoie 1995), then subdivided each of the larger watersheds into several smaller recharge zones (Fig. 1).

Groundwater collection

To assess the linkage of watershed land use patterns to NO_3 concentrations (μM) in groundwater to land derived NO_3 loads (kg N y^{-1}), and to groundwater isotopic signatures of

NO_3, we measured concentrations and $\delta^{15}N\text{-}NO_3$ of the samples of groundwater collected from where each recharge zone entered the pond or estuary (i.e, the seepage face). We sampled groundwater during summer, fall, and winter of 1998-2000. 250 mL of groundwater were collected every 50 meters along the seepage face of the pond or estuary for each of the nine watersheds, using drive point piezometers (Valiela et al. 2000). We composited four groundwater samples, each composite thus representing approximately 200 m of shoreline. In Cape Cod, freshwater ponds commonly receive flowing groundwater on the up-gradient side, and discharge pond water into the aquifer on their down-gradient side (Strahler 1966). Groundwater was therefore only sampled along the up-gradient portion of a pond margin. After collection, water samples were filtered through 0.7 μm ashed glass fiber filters (Whatman GF/F) and either acidified and stored at 4°C (summer) or frozen (fall and winter). We analyzed nutrient concentrations in each 200 m composite sample. For stable isotope analysis, we combined two adjacent 200 m composites, so that each isotope value represented about 400 m of shoreline.

Nutrient analyses

Concentrations of NO_3 were measured in each sample composite of groundwater. Nitrate concentrations were measured colorimetrically after cadmium reduction to NO_2 using either a manual method (Jones 1984) or a Lachat autoanalyzer. Values presented in this paper are NO_3 plus NO_2. Sample values were averaged to represent each recharge zone within each watershed.

Stable isotopic analyses

Nitrate was isolated from composited groundwater samples for $\delta^{15}N\text{-}NO_3$ analysis following the methods of Sigman et al. (1997). Samples were boiled to concentrate NO_3 and to remove NH_3 by volatilization. Devarda's alloy was then added to the samples to convert NO_3 and remove NH_3, NH_3 was then trapped on an acidified filter. Samples were shaken for one week at 40˚C to allow the diffusion to reach completion. Sample analysis was conducted by the UC Davis Stable Isotope Laboratory. $\delta^{15}N\text{-}NO_3$ values were measured by continuous flow isotope ratio mass spectrometry (20-20 PDZEuropa, Norwich, UK) after sample combustion to N^2 at 1000 C° in an online elemental analyzer (PDZEuropa ANCA-GSL). Isotopic values are expressed as $\delta^{15}N$ (‰) = $[(R_{sample} - R_{reference})/ R_{reference}] * 1000$, where R is $^{15}N/^{14}N$ and the reference is atmospheric N_2 (Peterson & Fry 1987). Only samples with 90 to 100% recovery were used. Standard deviation of replicates was less than 0.1 per mille. Replicates of a known working standard of ammonium sulfate (initially calibrated against the IAEA standard N1) were inserted every 12 samples. Final sample isotopic values were adjusted based on the working standard. Working standards were periodically calibrated against international isotope standards.

To obtain an average $\delta^{15}N\text{-}NO_3$ value for each of the nine watersheds, we first calculated values for each recharge zone. Simply taking the mean of all sample values for a whole watershed would not take into account sample concentration or recharge volume. Therefore the isotopic values were normalized for concentration and volume. For each recharge zone, to calculate the $\delta^{15}N\text{-}NO_3$ value of the incoming nitrate load, we weighted the average value (from 400m composites) by the concentration of nitrate (from 200m composites) for each sample. For all samples the product of concentration and $\delta^{15}N\text{-}NO_3$ value were summed, then divided again by the sum of the concentrations. This calculation yields a

weighted average value by the concentration in each sample. Thus, samples with high concentration carry more weight than samples with low concentrations. Since the product of concentration and $\delta^{15}N\text{-}NO_3$ value is a non-sensical value, we divided by the sum of the concentrations to remove concentration from the result to yield an average for each recharge zone. A similar calculation was used to derive an average $\delta^{15}N\text{-}NO_3$ value for the whole watershed, weighted by the nitrate load. For all recharge zones, the product of nitrate load (kg y^{-1}) and the weighted $\delta^{15}N\text{-}NO_3$ value were summed, then divided by the sum of all recharge zone nitrate loads.

NO_3 load calculations

To calculate NO_3 loads from recharge zones of Mashpee River, Great Pond, Green Pond, Miacomet Pond, Coonamessett Pond, and Ashumet Pond, we multiplied the mean concentration of NO_3 for each recharge zone by the annual recharge volume of groundwater from each recharge zone. Recharge volume was calculated by multiplying annual average rainfall minus evapotranspiration by the area of each recharge zone; this is the volume of groundwater that will discharge into the water body annually. In our study area, average annual rainfall is 1130 mm (Lajtha et al. 1995), and approximately 55% of the precipitation is evapotranspired (Running et al. 1988; Eichner & Cambareri 1992). The resulting recharge estimate of 51 cm per year is very similar to the 53 cm per year estimate from LeBlanc (1984) and Barlow and Hess (1993). When we multiply average nitrate concentrations in groundwater from a given recharge zone by the groundwater recharge volume, we arrive at the total nitrate load (kg y^{-1}) from that recharge zone to the receiving waters. In the calculation in question, we divided that total annual load for each recharge zone by the surface area of the recharge zone to

arrive at a normalized loading rate in units of kg per hectare per year. That calculation allows comparison of loading from many recharge zones of different sizes.

Wastewater load and land use calculations

While measurements of N load provide information on the different species of N, by themselves they cannot serve to partition the N load into the different sources (atmospheric deposition, fertilizer, wastewater). To obtain such a partition, we needed to use a nitrogen loading model (NLM), a land use based model that allows calculation of total nitrogen loads from various sources (Valiela et al. 1997, 2000). NLM calculates the contribution of wastewater total N using an average input per person (4.8 kg N y^{-1}) to septic systems, average losses in septic systems and leaching fields (40%), and losses of DIN and DON as they travel through groundwater (35%, Valiela et al. 1997). The number of persons per household (1.8 people) was estimated based on 1990 census data for the Waquoit Bay watershed. Number of houses was determined by aerial photos. We obtained for each recharge zone of each waterbody a NLM estimate of land-derived N loads to the receiving water body from wastewater, and estimated the contribution of wastewater relative to the total N load. NLM requires land use information on watersheds of the receiving waters to calculate a nitrogen load based on land use. We collected land use data from aerial photographs and GIS databases from the Towns of Falmouth and Nantucket, MA, to quantify areas of land cover types and the number of buildings within the watershed boundaries. Land uses included residential, freshwater ponds and bogs, agricultural land, golf courses, impervious surfaces, and forested land (Table 1). NLM also calculates area of natural vegetation, based on land use inputs.

Coefficients for nitrogen inputs to the watersheds from three sources (wastewater disposal, atmospheric deposition, and to a lesser extent, fertilizer application) and losses of N during transport through the watersheds modeled in NLM were based on compilations from the literature and on measurements specifically for model development (Valiela et al. 1997). The model used previous measurements of total atmospheric N deposition for Cape Cod (Valiela & Teal 1979; Lajtha et al. 1995) to estimate deposition rates to the watersheds. Fertilizer application rates were based on average literature values for common local crops, 136 kg N ha^{-1} y^{-1}, (Howes & Teal 1995; Valiela et al 1997), for residential areas, 104 kg N ha^{-1} y^{-1}, and for golf courses, 115 kg N ha^{-1} y^{-1}, (Nelson et al. 1988; Eichner & Cambareri 1992). The coefficients for atmospheric deposition and fertilizer use were multiplied by the area of land receiving those inputs (atmospheric deposition – all land uses, fertilizer use – residential, golf courses, and agriculture including cranberry bogs). The standard error and standard deviation of modeled N load, calculated by bootstrapping and by error propagation methods of all the contributions of uncertainty to the model, range from 12 to 14% and 37 to 38%, respectively (Valiela et al. 1997). Modeled wastewater loads and % wastewater have previously been published for the recharge zones of Childs River, Quashnet River, and Sage Lot Pond (Valiela et al. 1997; 2000).

To ascertain whether coastal land use (both residential and natural) might have a more important effect on nitrogen dynamics than land use farther inland, land use in each recharge zone was calculated for both a buffer area within 200 m of the pond or estuary seepage face, and the area beyond 200 m. Valiela et al. (1997) chose a distance of 200 m based on the maximum horizontal distance at which a septic plume may be identifiable in aquifers based on solute concentration data from Robertson et al. (1991) (Valiela et al. 1997).

Mixing model

To predict groundwater $\delta^{15}N$ based on land use, we used a three member mixing model. We used average literature values for groundwater $\delta^{15}N\text{-}NO_3$ derived from wastewater (13 ‰), atmospheric deposition (3 ‰), and fertilizer (1 ‰) (Kendall 1998). The value for wastewater agrees well with values reported by Kroeger et al. (In press). We included all three sources as endmembers due to their high variability between watersheds. We used a simple mixing model described by Owens (1987) which uses the relative amount of each N source. In our case we applied land-derived N loads calculated for each of the nine watersheds multiplied by average literature values of $\delta^{15}N\text{-}NO_3$ for all three N sources. Most isotopic mixing models use two members, but this model allows more precise isotopic estimates. The mixing model formula was $\delta^{15}N\text{-}NO_{3\ P}$ (‰) = $(N\ load_{WW}/Nload_T * \delta^{15}N\text{-}NO_{3\ WW}) + (N\ load_{AD}/Nload_T * \delta^{15}N\text{-}NO_{3\ AD}) + (N\ load_{FE}/Nload_T * \delta^{15}N\text{-}NO_{3\ FE})$, where P is the predicted $\delta^{15}N\text{-}NO_3$ value in groundwater, N load (in kg N y^{-1}) is the land-derived NLM calculate N load to the pond or estuary, WW is wastewater, T is total, AD is atmospheric deposition, and FE is fertilizer application. WW, AD, and FE calculated using NLM.

Results and Discussion

We first discuss N concentrations and isotopic values at the scale of individual groundwater samples. To link land use to groundwater N loads and isotopes, we then discuss concentrations and isotopes at the scale of recharge zones for all nine watersheds.

Nutrient concentrations and $\delta^{15}N$ values

In general, concentrations of NO_3 of groundwater in the aquifer along the seepage face were variable. In all nine watersheds, differences of as much as three orders of magnitude were found in concentrations of NO_3 among adjoining samples 50-200 m apart. As examples of such variation, data from Mashpee River are shown in Fig. 2a. Mashpee River was selected for this example because it displayed a range of N concentrations and isotopic values similar to the other eight watersheds, and it clearly depicted differences in both concentrations and isotopic values in the different recharge areas. Data on nitrate concentrations and isotope values from all recharge zones measured for this study are presented in Table 2.

The heterogeneity of N concentrations in seepage water is may be due to location of different land uses on the watershed (Takatert et al. 1999; Kemp & Dodds 2001). The large differences in distribution of N concentrations in our estuaries are also probably related to differences in watershed land uses. Other factors affecting N concentrations in groundwater are hydrology, aquifer biogeochemistry, and groundwater oxygen concentrations. Denitrification may also play a large role in grounwater N concentrations. In Fig 2a, the horizontal bars across the top of the figure represent the shoreline of recharge zones delineated in Fig 1. The NO_3 concentrations, while highly variable, do not seem to be randomly spaced. High NO_3 concentrations are found in recharge zones 1, 4 and 5, while recharge zones 2 and 3 contain low concentrations. Recharge zones 1, 4, and 5 have moderate to high density residential areas, while recharge zones 2 and 3 are covered mainly by forested conservation lands. This relationship suggests a strong land use and N concentration linkage.

$\delta^{15}N\text{-}NO_3$ values in groundwater were also spatially heterogeneous along the shoreline, varying from -6 to +10 ‰ (Fig. 2b). The distribution of $\delta^{15}N\text{-}NO_3$ were similar to the NO_3 concentrations, higher values in developed recharge zones, lower values in forested recharge

zones. Beyond Mashpee River, an analysis of the relationship between NO_3 concentrations and $\delta^{15}N$ values for all 9 watersheds recharge zones shows a significant logarithmic relationship, $R^2 = 0.46$*** (*** = $P < 0.001$, ** = $P < 0.01$, * = $P < 0.05$). This suggests a linkage between $\delta^{15}N$-NO_3 values and land use.

Linkage of land use to NO_3 loads

The mix of land uses in most watersheds is complex; for simplicity, we focused on two of the major representative features, the human population, and the area of natural vegetation. These not only subsume many of the major features of land use, but also represent the major changes that are taking place on watersheds world wide, the conversion of vegetated land to residential uses (Bowen & Valiela 2001). For these results, we use data from all recharge zones within each of the nine watersheds of this study. Recharge zone land use varied greatly. Wastewater as a percentage of the total modeled nitrogen load, ranged from 5% to 86%. Natural open space covered 44% to 100% of the recharge zone areas.

NO_3 loads to all nine receiving waters per hectare of recharge zone increased with wastewater load (Fig. 3a). In many cases, NO_3 is a much larger component of septic system effluent than ammonium or dissolved organic nitrogen (Wilhelm et al. 1994), due to nitrification in the oxic portions of the leaching field. Conversely, NO_3 loads were inversely related to area of natural vegetation (Fig. 3b). Nitrate loads from areas of natural vegetation are generally lower than residential land uses, and much of the nitrate is likely denitrified in the vadose zone before it reaches the water table. These results show that urbanization of watersheds, in general, increases nitrate in the groundwater, and thus land-derived N loads to

receiving waters. These results also suggest that preservation of undeveloped open space may be one way to maintain lower rates of N loading to receiving waters.

Linkage of land use to $\delta^{15}N$ in nitrate

The $\delta^{15}N$ of NO_3 increased as human population, represented by wastewater load, increased on watersheds (Fig. 4a). As more of the total nitrogen load is composed of wastewater, the $\delta^{15}N$-NO_3 values of groundwater will be become dominated by the wastewater isotopic signal. The shape of the relationship differs from the exponential curves of Fig. 3. The slope of the response of $\delta^{15}N$ values decreased logarithmically as the influence of humans increased. As wastewater load increases, an equilibrium is reached where $\delta^{15}N$-NO_3 values do not change with subsequent increases in wastewater (Fig. 4a). Nitrate loads were relatively more sensitive at the higher range of anthropogenic effects (Fig. 3a), but the response of $\delta^{15}N$ values were more sensitive at the lower ranges. At the lower range of wastewater inputs, there is a mix of N sources with similar concentrations of nitrate. At the higher end of the range, wastewater NO_3 concentrations are so much larger than the other sources, that the wastewater isotopic signature overpowers other sources isotopic signatures. Mayer et al. (2002) found a similar relationship of $\delta^{15}N$-NO_3 values and wastewater and manure inputs for 16 large river catchments in the northeast US. Although Mayer et al. (2002) applied a 2^{nd} degree polynomial regression, the shape of the curve was very similar to that in Figure 4a. $\delta^{15}N$-NO_3 values were not significantly related to the area of the watershed covered by natural vegetation, although a trend of lower $\delta^{15}N$-NO_3 values with increasing area of natural vegetation exists (Fig. 4b). Many factors may cloud this relationship, for example, size of the watershed, proximity of areas of natural vegetation to the seepage face, or population size.

A model was developed to predict groundwater $\delta^{15}N$ values based on shifts in major N sources, because nitrogen isotope values were affected by changes in anthropogenic land uses. To verify our results, we compared predicted $\delta^{15}N\text{-}NO_3$ values to measured values. The relationship of measured versus predicted $\delta^{15}N\text{-}NO_3$ values was significant (solid line in Fig. 5). We then compared the regression fitted to the points to the 1:1 line of perfect fit using a *t* test (Sokal & Rohlf 1995). Neither the slope nor the intercept of the fitted line differed significantly from the 1:1 line. The predicted values of $\delta^{15}N\text{-}NO_3$ therefore are a reasonable approximation of the actual values. This model allows for predictions of how changes in watershed land use will affect changes in $\delta^{15}N\text{-}NO_3$ values by adjusting the N source percentages to model watershed urbanization. It also allows the user to change the isotopic values of the end members depending on the N source. For example, we used 1‰ to represent fertilizer application because in our study sites, manmade inorganic fertilizer is most commonly used. If organic manure fertilizers were commonly used, the fertilizer end member would be heavier (Kendall 1998). In locations where raw sewage is a problem, the wastewater end member would have to be considerably lighter than that used in this study.

Relationship of N to spatial distribution of land use

On the whole, coastal land uses within 200 m of the shore of receiving water bodies were more closely associated with nitrate load per watershed area and $\delta^{15}N\text{-}NO_3$ in groundwater than land uses beyond 200 m (Table 3). $\delta^{15}N\text{-}NO_3$ values increased with % wastewater only within 200 m of the shore (Figure 6). These results are similar to those of Lake et al. (2001), who found that coastal land use was more closely linked to $\delta^{15}N$ in groundwater than inland land use more than 90 m from shore.

Denitrification may account for the lack of correlation between inland land use and nitrate loads, concentrations, and isotope values at the seepage face. Pabich et al. (2001) found that dissolved organic carbon (DOC), a source of electrons for denitrification, was lower in concentration in water tables underlying thick vadose zones (inland) than thin vadose zones (coastal). This is likely due to denitrification in the vadose zone and in the upper aquifer. Thick vadose zones allow more time for denitrification before DOC and nitrate enter the groundwater. Therefore, less nitrate from coastal areas may be denitrified and thus the potential for degradation of the isotope signatures of the N sources is lower. Pabich et al. (2001) suggest that the upper aquifer is a biogeochemically active zone. Travel time then, along with vadose zone depth, may be important in determining the concentration of nitrate and it's stable isotopic value at the seepage face. Longer travel times within both the vadose zone and aquifer mean more opportunities for denitrification and N removal. Additional parameter measurements may help clarify these issues. Measurement of $\delta^{18}O\text{-}NO_3$ values and dissolved O_2 concentrations in conjunction with $\delta^{15}N\text{-}NO_3$ values may further elucidate the role of denitrification in the removal of NO_3 (Bottcher et al. 1990). Mayer et al. (2002) found that $\delta^{15}N\text{-}NO_3$ values differed between different land use sources of NO_3.

The comparisons of Table 3 suggest at least two notable aspects. First, the parts of the watersheds farther from shore are relatively uncoupled from the nitrogen inputs to receiving waters from watersheds, which can be taken to mean that some process diminishes the impact of nitrogen sources up-gradient. Second, if this is so, management measures might most effectively be applied to coastal areas, rather than to entire watersheds. This might furnish far more feasible opportunities for management of nitrogen loads.

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Table 1. Land use inputs used for a Nitrogen Loading Model for the 6 ponds and estuaries sampled for this paper. All data collected from aerial photos unless otherwise noted.

Inputs	units	Ashumet Pond	Coonamessett Pond	Miacomet Pond[a]	Great Pond	Green Pond	Mashpee River
Drainage area	ha	459	745	513	2809	852	2944
Houses	#	149	124	955	3347	1176	1458
Houses w/i 200 m	#	44	37	27	847	523	110
Sewered houses	#	0	0	357	0	0	0
Wetlands (including ponds)	ha	3	0	2	0	15	3
Cranberry bogs	ha	0	0	0	29	14	2
Other agriculture	ha	0	0	0	17	12	0
Golf courses	ha	0	19	30	48	29	6
Other turf	ha	151	171	2	285	105	83
Commercial/industrial impervious surfaces	ha	38	35	0	69	31	27

[a] land use taken from GIS data

Table 2. Mean and standard error of NO_3 concentrations and $\delta^{15}N\text{-}NO_3$ values for all recharge zones (Rech. zone) of the 6 ponds and estuaries sampled for this study.

	Rech. zone	NO_3 (µM) Mean	NO_3 (µM) SE	$\delta^{15}N\text{-}NO_3$ Mean	$\delta^{15}N\text{-}NO_3$ SE
Ashumet Pond	1	35	18	8.5	7.1
Coonamessett Pond	1	30	8	4	1.7
Miacomet Pond	1	29	12	4.4	0.1
	2	319	159	5.4	0.3
	3	29	18	3.4	2.2
	4	10	8	1.7	11.8
Great Pond	1	261	40	3.6	1.6
	2	248	47	6.3	1.7
	3	137	38	6.3	1.3
	4	269	85	5.1	4.4
	5	45	27	6.4	4.4
	6	43	7		
Green Pond	1	24	8	5.5	1.6
	2	78	51	5.6	4.4
	3	62	41	-4.0	
	4	40	23	6.7	
	5	15	9	1.8	
	6	208	110	7.1	1.2
	7	10	5		
	8	47	32		
Mashpee River	1	31	13	6.2	2.5
	2	0	0	-3.0	1.2
	3	14	1	6.8	
	4	0	0	2.5	2.4
	5	18	7	3.1	1.7

Table 3. R^2 values and *F* values for NO_3 load and $\delta^{15}N\text{-}NO_3$ values versus recharge zone watershed land use (wastewater load, % of total that is wastewater, % cover of natural vegetation) within 200 m of shore and outside of 200 m of shore. *** = $P < 0.001$, ** = $P < 0.01$, * = $P < 0.05$, and ns = $P > 0.05$.

		Within 200 m		Outside 200 m	
y	*x*	r^2	*F*	r^2	*F*
NO_3 load (kg N ha_{ws}^{-1} y^{-1})	Wastewater load (kg N y^{-1})	0.40	26.3***	0.38	4.2ns
	% wastewater	0.37	31.6***	0.21	3.4ns
	% area of natural vegetation	0.27	10.4**	0.31	8.8**
$\delta^{15}N\text{-}NO_3$ (‰)	Wastewater load (kg N y^{-1})	0.53	25.4***	0.05	1.1ns
	% wastewater	0.55	20.3***	0.06	1.4ns
	% area of natural vegetation	0.26	8.2**	0.11	2.2ns

Figure Legends

Figure 1. Map of upper Cape Cod showing study sites including 6 water bodies of present study (Ashumet Pond, AP; Coonamessett Pond, CP; Miacomet Pond, MP; Green Pond, GnP; Great Pond, GtP; Mashpee River, MR) and 3 of McClelland et al. (1997) and McClelland and Valiela (1998) (Childs River, CR; Quashnet River, QR; Sage Lot Pond, SLP). Also shown is an example watershed and five recharge zones (sub-watersheds) delineated for one of the study sites, Mashpee River. These five recharge zones correspond to those in Figure 2.

Figure 2. Example of variation of NO_3 concentrations (a) and isotope values (b) in seepage face water of an estuary of this study, Mashpee River. Concentrations for each 200 m composite were averaged across all seasons collected (summer, fall, winter). Numbered horizontal lines across top represent recharge zones delineated in Fig. 1, and each line covers samples collected within that recharge zone. Distance along the x-axis is measured in a counter clock-wise direction from the eastern side of the river mouth to the western side of the river mouth. Stream water samples collected upstream of the tidal range represent Recharge Zone 3.

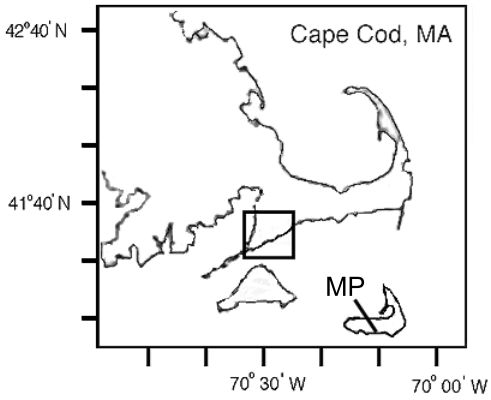
Figure 3. Mean NO_3 load to all nine receiving waters (kg N per hectare of watershed y^{-1}) for each recharge zone vs. (a) recharge zone wastewater N load (kg N y^{-1}) and (b) natural vegetation cover as a percent of total land area. *** = $P< 0.001$, ** = $P < 0.01$, * = $P < 0.05$. Open circles are statistically determined outliers not included in regressions.

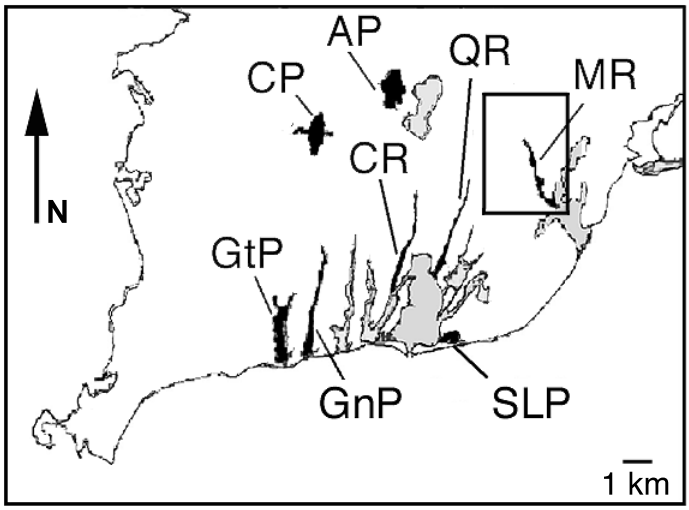
Figure 4. Mean $\delta^{15}N\text{-}NO_3$ for each recharge zone for all nine receiving waters vs. recharge zone wastewater load (a) and % cover of natural vegetation (b). Open circles are statistically determined outliers not included in regressions.

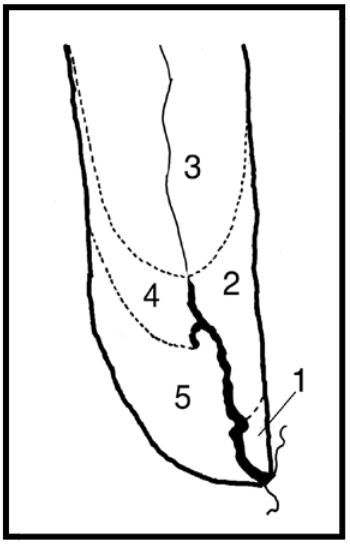
Figure 5. Predicted seepage face groundwater $\delta^{15}N\text{-}NO_3$ vs. measured groundwater $\delta^{15}N\text{-}NO_3$ for all nine watersheds. Dotted line is 1 to 1 line of perfect fit. Solid line is fit to data.

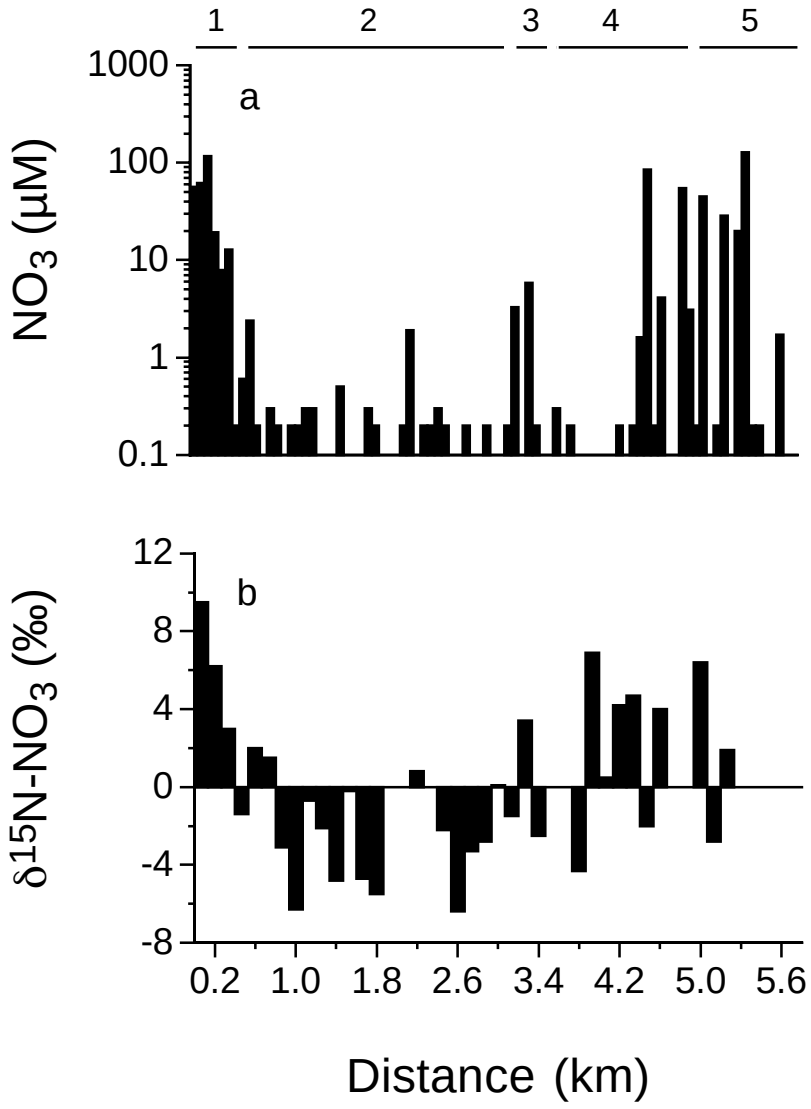
Figure 6. Mean $\delta^{15}N\text{-}NO_3$ for each recharge zone vs. recharge zone wastewater load as a percent of the total load. (a) data for the watershed within 200 m of shore, and (b) data for the watershed greater than 200 m from shore.

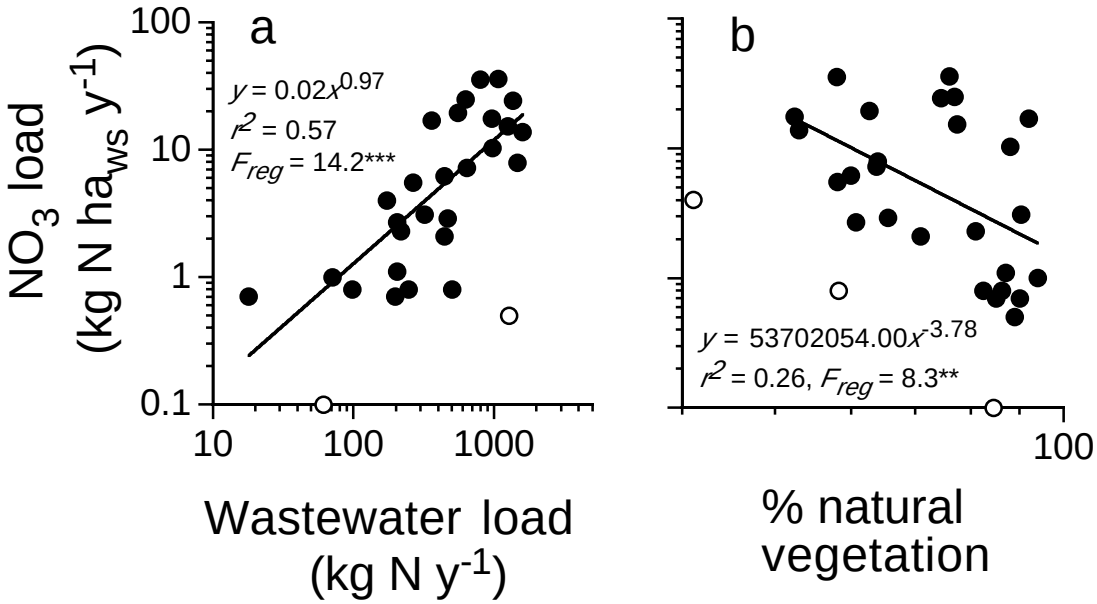
Cole Fig 1

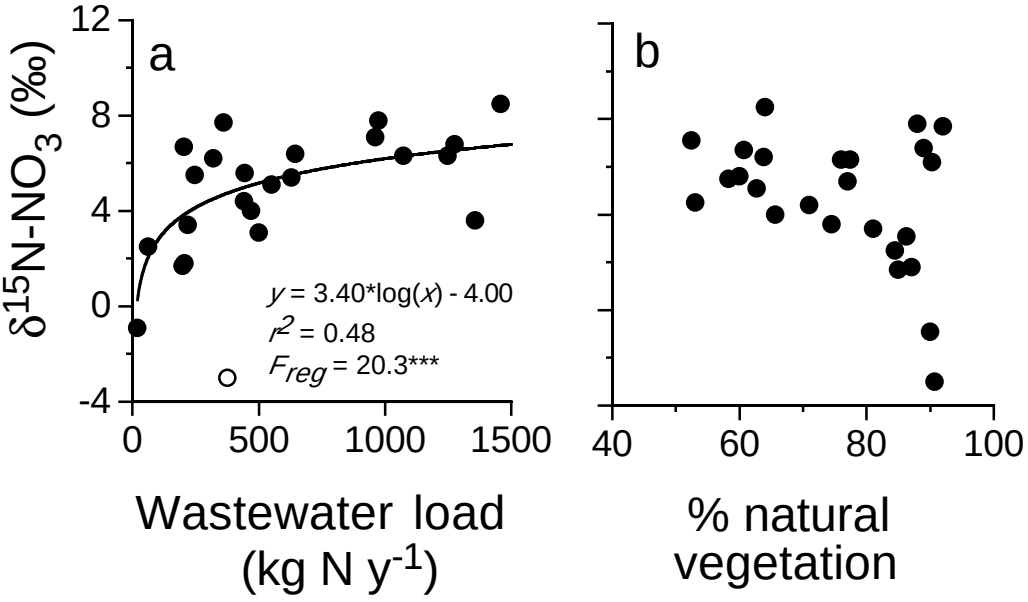

42°40' N
41°40' N
Cape Cod, MA
MP
70° 30' W
70° 00' W

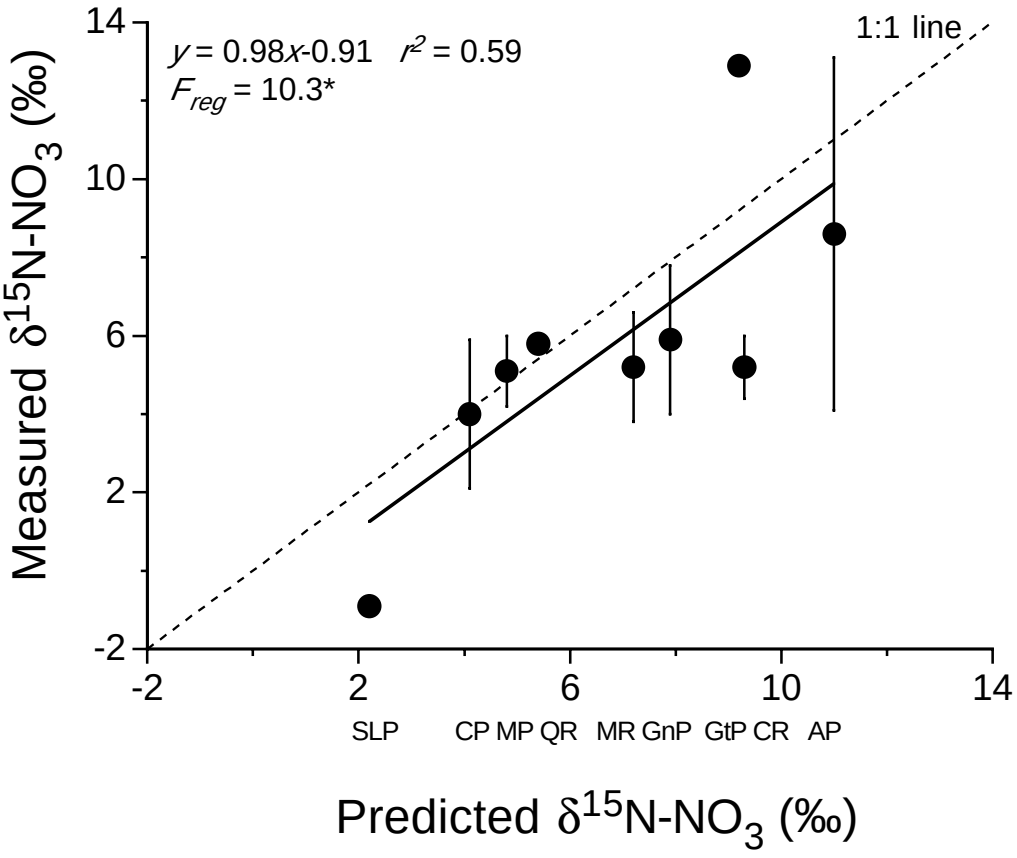

AP
QR
CP
MR
CR
N
GtP
GnP
SLP
1 km

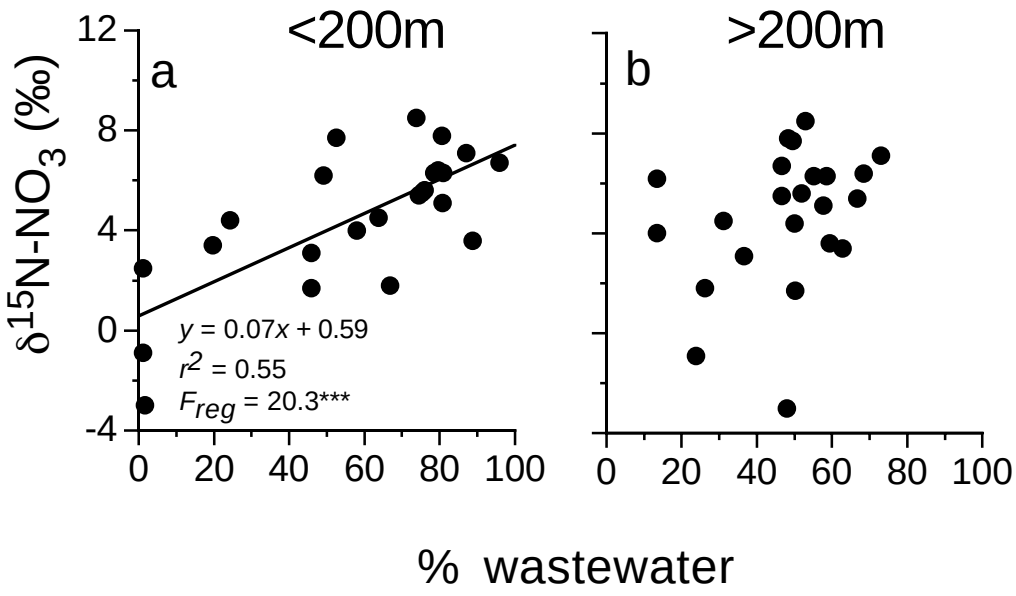

3
4
2
5
1


1
2
3
4
5
1000
100
10
1
0.1
a
NO_3 (µM)
12
8
4
0
-4
-8
b
$\delta^{15}N$-NO_3 (‰)
0.2
1.0
1.8
2.6
3.4
4.2
5.0
5.6
Distance (km)


a
b
100
10
1
0.1
10
100
1000
NO_3 load
(kg N ha_{ws} y^{-1})
$y = 0.02x^{0.97}$
$r^2 = 0.57$
$F_{reg} = 14.2$***
Wastewater load
(kg N y^{-1})
$y = 53702054.00x^{-3.78}$
$r^2 = 0.26$, $F_{reg} = 8.3$**
100
% natural
vegetation


a
b
δ^{15}N-NO$_3$ (‰)
12
8
4
0
-4
0
500
1000
1500
40
60
80
100
y = 3.40*log(x) - 4.00
r^2 = 0.48
F_{reg} = 20.3***
Wastewater load
(kg N y^{-1})
% natural
vegetation


y = 0.98x-0.91 r² = 0.59
F_reg = 10.3*
1:1 line
Measured δ15N-NO3 (‰)
Predicted δ15N-NO3 (‰)
14
10
6
2
-2
-2
2
6
10
14
SLP
CP MP QR
MR GnP
GtP CR
AP


12
8
4
0
-4
δ15N-NO3 (‰)
a
<200m
y = 0.07x + 0.59
r2 = 0.55
Freg = 20.3***
0
20
40
60
80
100
b
>200m
0
20
40
60
80
100
% wastewater