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Quantifying Dissolved Nitrogen Flux Through a Coastal Watershed

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Available nitrogen loading models, commonly used to estimate subsurface fluxes of dissolved nitrogen to coastal waters, have not been quantitatively or systematically compared; nor have they generally been field-verified at regional scales. We employed three published loading models, a site-specific model based upon water use data, and both Darcian and non-Darcian field approaches to obtain estimates of steady state, dissolved nitrogen flux through a permeable Massachusetts watershed. The two field approaches, based on independent data, yielded similar results. Results of the published loading models agreed closely with each other, but exceeded the mean of the field approaches (130 ± 12 mol N m^{-1} aquifer width yr^{-1}) by 60%, on average. The Water Use loading model agreed closely with the field results (within 4%), largely because it did not require estimates of occupancy rate, which was found to be the major source of error to the published models. The observed, median concentration of total dissolved nitrogen (TDN) in groundwater increased from 1.9 to 313 μM during transport through the subbasin, confirming loading model predictions that >99% of the TDN flux is anthropogenic. In contrast to the watershed inputs, downgradient TDN was dominantly nitrate (98%), indicating near-complete nitrification during transport. Significant transverse horizontal and vertical variations were found in the groundwater TDN distribution at scales of meters and tenths of meters, respectively, consistent with a large number of discrete nitrogen sources at the ground surface, and low transverse macrodispersivities in the aquifer. Loading models, if properly verified by field measurements at the stream tube scale, hold promise for characterizing the effects of land use on subsurface nitrogen flux through coastal watersheds.

INTRODUCTION

Surface and groundwater flow are pathways for the exchange of ecologically important constituents in many environments [*Winter*, 1978; *Valiela and Teal*, 1979; *Lewis et al.*, 1984]. Hydrologically driven fluxes of dissolved nitrogen and phosphorus are of particular interest, as their rates of transfer play key roles in structuring most aquatic ecosystems. To date, however, virtually all nutrient transport research has focused upon the surface water pathway [e.g., *Meybeck*, 1982; *D'Elia et al.*, 1986; *Malone et al.*, 1988]; groundwater nutrient transport to lakes, estuaries, and coastal embayments has rarely been directly quantified. This may lead to major misunderstandings of nutrient cycling in permeable basins in humid areas, where groundwater is potentially the dominant input pathway [*Johannes*, 1980; *Valiela et al.*, 1990].

The groundwater pathway has probably been neglected, in part, because direct measurement of groundwater nutrient transport poses a difficult field problem. Solute concentrations in shallow, unconfined aquifers often display steep vertical and transverse horizontal gradients requiring intensive sampling [*Ronen et al.*, 1987; *Robertson et al.*, 1991; *LeBlanc et al.*, 1991]. In addition, groundwater discharge is difficult to measure directly at the regional or subregional scales [*Lee*, 1977; *Cornett et al.*, 1989], and must generally be estimated using Darcian or water balance approaches. Because of these difficulties, coastal researchers typically use empirical "loading models" to estimate groundwater nutrient fluxes to receiving waters [*Teal*, 1983; *Valiela and Costa*, 1988]. Such models quantify nutrient inputs to a watershed associated with existing or anticipated land uses, and then make simple assumptions regarding the subsurface transport behavior of the nutrient in order to produce flux estimates. Unfortunately, the available models have not been systematically compared in the literature, nor, in general, have their assumptions and predictions been adequately field-verified at the subregional or regional scales.

In the present study, we evaluate a variety of methods for quantifying the flux of total dissolved nitrogen (TDN) through a coastal watershed in southeastern Massachusetts (Figure 1). Nitrogen was chosen because it is the nutrient which generally limits primary production in coastal waters [*Ryther and Dunstan*, 1971; cf. *Howarth*, 1988], and because TDN, as nitrate, is highly mobile under the oxidizing subsurface conditions of the study area [*Weiskel and Howes*, 1991]. The purposes of the study were (1) to determine the subsurface TDN flux through a watershed receiving significant nonpoint nutrient inputs, (2) to assess the horizontal and vertical scales of variation in TDN concentration, (3) to determine the accuracy and evaluate the transport assumptions of several published loading models, and (4) to propose methods appropriate to the coastal zone.

METHODS

Study Area

The Indian Heights subbasin is located at the head of Buzzards Bay in southeastern Massachusetts, in the water-

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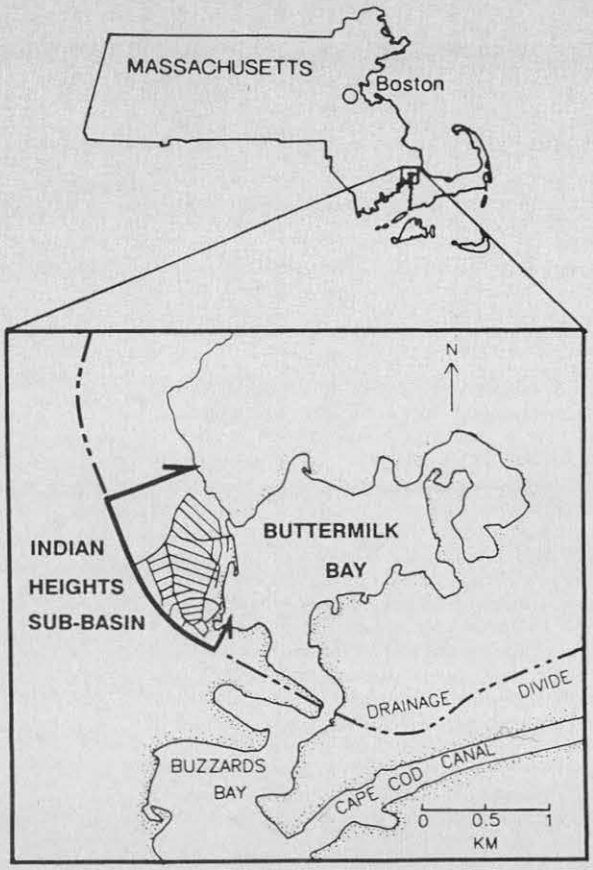

Fig. 1. Location of the Indian Heights study area.

shed of Buttermilk Bay (41°45.50′N, 70°38.00′W; Figure 1). The site was selected because (1) the area is unsewered, and receives a significant nitrogen input from nonpoint sources (e.g., septic system effluent and lawn fertilizer), (2) the area is underlain by medium-to-coarse glaciofluvial sands typical of the Cape Cod region, (3) the population (presently 1237 year-round and summer residents in a developed area of 53 ha) and housing density have remained stable for a long period (>15 years) compared to the 4-year groundwater residence time in the developed portion of the watershed, (4) water use records are available for all 524 dwellings in the watershed, and (5) a substantial upgradient area extending to a groundwater divide is overlain by an undeveloped pine/oak forest (Figure 2). Collectively, these features provide good control for the nitrogen input accounting, allow testing of loading model assumptions at the subbasin scale, and have regional application.

A flow net was constructed from mean water table elevation data and three aquifer stream tubes were selected for detailed input accounting, groundwater sampling, and flow characterization (Figure 3). The flow lines defining each stream tube are 25 m apart at the bay margin. Water table elevation data from the 1986–1988 period indicate that the stream tube positions are stable, though the magnitude of the subbasin hydraulic gradient changes seasonally. In addition, precipitation and temperature records for East Wareham, Massachusetts, over the 1980–1988 period [*National Oceanic and Atmospheric Administration*, 1988] suggest that the 1986–1988 water table data are representative of conditions prevailing over the 4-year groundwater residence time prior to 1988.

Nitrogen Loading Models

Four loading models were applied to each of the stream tubes. The models were used to determine net inputs of total dissolved nitrogen (TDN) to the saturated zone from septic effluent leachate (N_e), domestic fertilizer leachate (N_f), and natural recharge from precipitation (N_r). Storm water recharge, a significant TDN input to groundwater in some areas [*Nelson et al.*, 1988], is negligible in Indian Heights because all impervious surfaces drain directly to Buttermilk Bay via storm sewers [*Heufelder*, 1988]. Other possible TDN inputs to groundwater (agricultural fertilizer, animal feedlots, and leaking sewer lines [*Keeney*, 1986]) are absent in this subbasin.

Three of the four loading models, referred to here as the Long Island model [*Koppelman*, 1978], the Cape Cod model [*Nelson et al.*, 1988], and the U.S. Geological Survey (USGS) model [*Frimpter et al.*, 1990], have been previously published, while the fourth (the water use model) was developed for this study. The models may all be expressed as follows:

$$F_{\mathrm{TDN}} = [N_e] + [H][LA/H][F_L] + [PA][R][C_r] \qquad (1)$$

where F_{TDN} is the annual TDN flux through the stream tube (moles per year), H is the number of houses with at least 50% of their footprint within a stream tube, LA/H is the mean lawn area per house lot (square meters per house), F_L is the net lawn fertilizer loading rate to the saturated zone (moles per square meter per year), PA is the total pervious area overlying each stream tube (square meters), R is the local natural recharge rate (meters per year), and C_r is the mean TDN concentration of the natural recharge (moles N per cubic meter; see Table 1 for values of all model constants).

The models differ mainly in the way that N_e is determined. For the Cape Cod and USGS models, $N_e = [H][P/H][E/P][C_e]$, where P/H is the mean occupancy rate (persons per house), E/P is the mean effluent discharge per capita (cubic meters per person per year), and C_e is the mean TDN concentration of the effluent leachate after infiltration to the water table (moles N per cubic meter). In the Long Island model, $N_e = [H][P/H][M_{\mathrm{TDN}}/P]$, where M_{TDN}/P is the mean, per capital molar flux of effluent TDN across the water table (moles N per person per year). In the water use model, $N_e = [H][WU/H][EDF][C_e]$, where WU/H is the mean water use per house observed in the study area (cubic meters per year), and EDF is the mean fraction of water use which becomes septic effluent, according to regional data [*Massachusetts Water Resources Authority*, 1983]. Water use records, available for each of the 524 houses in the study area, were consulted to obtain WU/H (Onset Water District, unpublished data, 1989), while a site-specific value of C_e was derived from effluent samples, collected over a 6-month period from four septic systems representing the range of system types, ages, and flow rates in the study area (see *Weiskel and Howes* [1991] for sampling procedures).

Assumptions regarding subsurface TDN transport differ among the models, and among the three TDN sources. With respect to fertilizer N, all four models assume a net loading rate to groundwater (F_L, shown in Table 1), equal to the

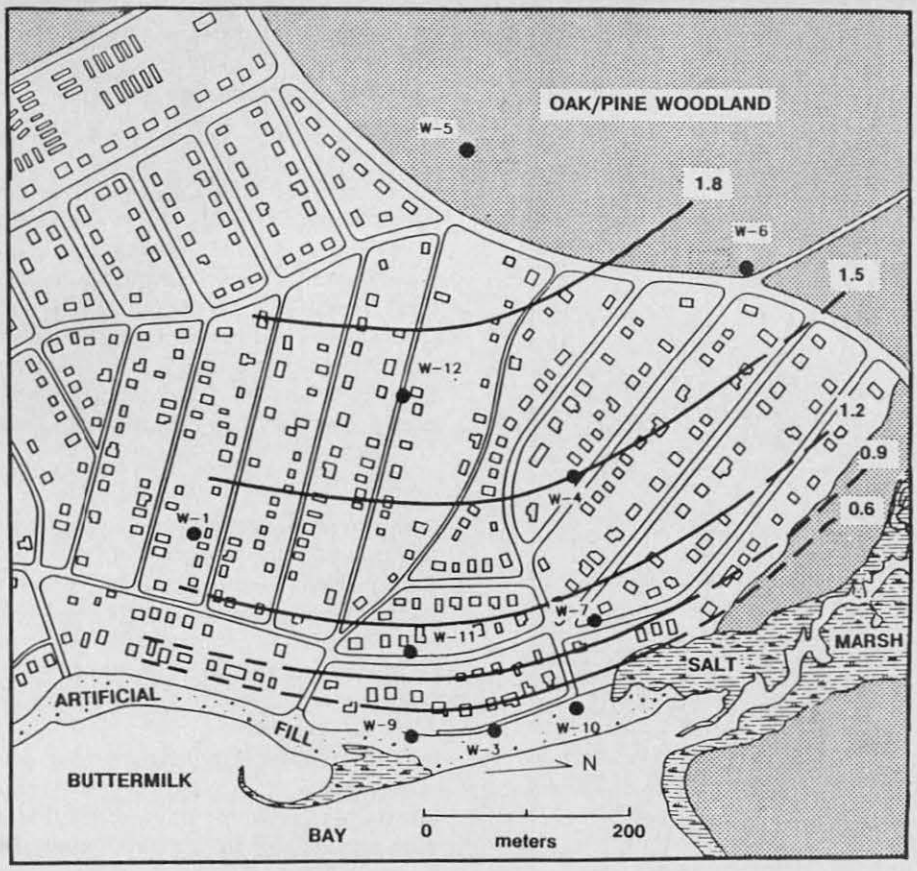

Fig. 2. Indian Heights land use/land cover, observation well network, and mean water table elevations during the period November 1986 to January 1988 (all elevations in meters above mean sea level; contour interval is 0.3 m).

product of a ground surface application rate and a leaching rate (not shown in Table 1). Fertilizer N which escapes the root zone is assumed to be transported conservatively to the water table and through the saturated zone. Likewise, conservative transport is assumed for natural recharge N after arrival at the water table (the point where C_r is determined).

With respect to effluent N, by contrast, the model authors make a variety of assumptions. In order to facilitate "worst case" loading predictions for water supply protection purposes, *Frimpter et al.* [1990] assume complete conversion of effluent TDN to nitrate during infiltration to the water table, and conservative transport thereafter. *Koppelman* [1978] assumes a net, per capita load to the water table (M_{TDN}/P, Table 1) equal to 50% of the initial per capita load from the septic systems (324 mol N person^{-1} yr^{-1}), with subsequent conservative transport. *Nelson et al.* [1988] assume a 25% reduction in mean effluent TDN concentration (with no dispersion or evapotranspiration) during vertical infiltration, from 3.23 to 2.42 mol N m^{-3}, and subsequent conservative transport. The water use model employs the 25% removal estimate of *Nelson et al.* [1988] to derive a value of C_e from effluent samples collected prior to infiltration.

Following standard practice, the number of houses overlying each stream tube was determined from large-scale air photographs, and a published occupancy rate of 2.7 persons house^{-1} [*Valiela and Costa*, 1988] was assumed in calculations of effluent TDN input. The mean lawn area per house lot was estimated and used in conjunction with the respective model F_L values, while regional values were employed for the mean rate and TDN concentration of natural recharge (except for the water use model, where a site-specific value of C_r was used; Table 1). The net, transverse dispersive flux of TDN out of each stream tube was assumed to be zero in all cases. This assumption is consistent with the central location of the stream tubes in the developed portion of the subbasin, and the relatively homogeneous areal distribution of domestic nitrogen sources.

Field Approaches

Two field approaches were used to quantify TDN flux (F_{TDN} in moles per year) at the mouths of the stream tubes. Both methods combine TDN concentration and groundwater discharge data as follows:

$$F_{TDN} = [C_N][Z_N][q][w_s] \tag{2}$$

where C_N is the mean TDN concentration (moles N per cubic meter), z_N is the mean saturated thickness of the N-contaminated zone (meters), q is the mean annual specific discharge (m^3 m^{-2} yr^{-1} or meters per year), and w_s is the stream tube width (meters); all measured at the stream tube mouths. The two methods differ in the way q is estimated. The first method is Darcian, while the second is a water balance approach which depends solely upon the aquifer geometry and the total (natural plus artificial) recharge rate.

Discharge estimation: Darcian approach. Flow through an unconfined aquifer subject to steady recharge may be

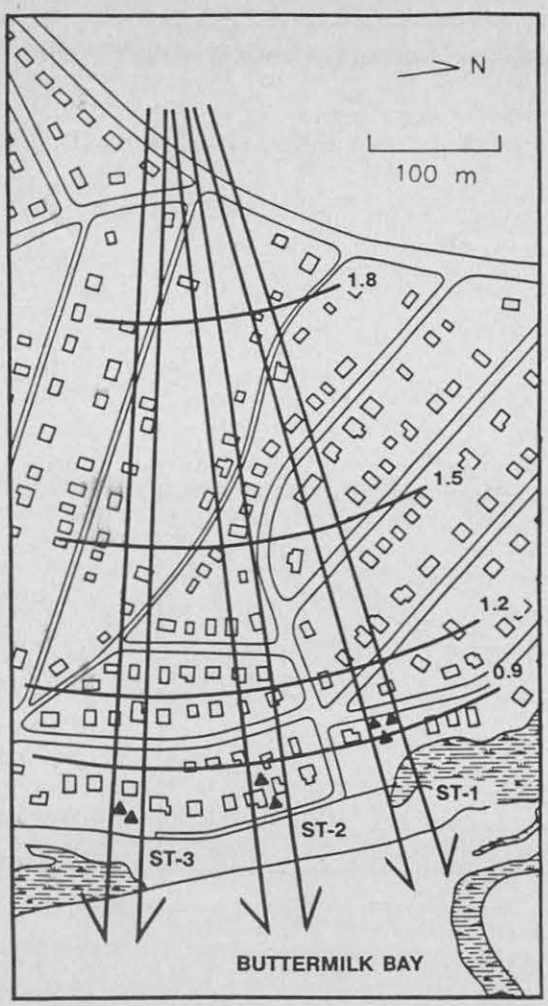

Fig. 3. Stream tubes 1, 2, and 3. Solid triangles denote multilevel samplers.

expressed with a modified form of the Dupuit equation derived by *Harr* [1962, p. 43]:

$$q'(x) = \frac{K_x(h_1^2 - h_2^2)}{2L} - w(L/2 - x) \qquad (3)$$

where $q'(x)$ is the discharge per unit aquifer width $[L^2T^{-1}]$ at some longitudinal distance x, between $x = 0$ and $x = L$; K_x is the horizontal hydraulic conductivity $[LT^{-1}]$; h_1 and h_2 are the steady state water table elevations above the aquifer base at $x = 0$ and $x = L$, respectively $[L]$; w is the average recharge rate from all sources $[LT^{-1}]$; and the Dupuit assumptions regarding horizontal flow and the equivalence of the hydraulic gradient and water table slope are in effect. At $x = L$, (3) reduces to

$$q'(L) = \frac{K_x(h_1^2 - h_2^2)}{2L} + wL/2 \qquad (4)$$

The mean subbasin water table configuration (Figures 2 and 3), obtained from biweekly observation well measurements during 1986–1988, allowed selection of values for h_1, h_2, and L near the mouths of the stream tubes for use in (4). The total recharge rate (w) was obtained from meteorological and natural recharge data for East Wareham, Massachusetts [*LeBlanc et al.*, 1986], and water use records.

The hydraulic conductivity (K) was first estimated from an empirical relationship established by *Olney* [1983] between the grain size and laboratory permeameter K values of glaciofluvial samples from the region:

$$\ln K = [2.425] \ln D_{25} - 0.538 \qquad r^2 = 0.96;\ n = 32 \qquad (5)$$

where K is the laboratory hydraulic conductivity of a repacked sample (centimeters per second at 15.6°C), and D_{25} is the 25th percentile of grain size (millimeters). In the present study, aquifer samples were collected from six to eight depths at each of four drilling locations (the stream tube mouths and one upland drilling site), and K profiles were constructed using (5). The effective horizontal hydraulic conductivity (K_x) over the N-contaminated portion of each profile was then estimated as follows:

$$K_x = (\bar{K}) \exp(\sigma_Y^2/2) \qquad (6)$$

where $\bar{K}$ is the geometric mean hydraulic conductivity over this portion, and σ_Y^2 is the variance of $Y = \ln K$ over the same portion [*Gutjahr et al.*, 1978; *Anderson*, 1989]. Finally, the resulting values of K_x were used to obtain q values with (4). Because K estimates based on grain size data are approximate, they were verified against K values from pumping tests conducted in adjacent areas of the Buttermilk basin [*Moog*, 1987].

Discharge estimation: Water balance approach. On a mean annual basis, specific discharge at the mouth of a stream tube is in approximate equilibrium with upgradient recharge to the stream tube from natural and artificial sources [*Dillon*, 1989]:

$$q(x) = wx/D \qquad (7)$$

where $q(x)$ is the mean annual specific discharge at some longitudinal distance x from a groundwater divide $[LT^{-1}]$, w is the total recharge rate $[LT^{-1}]$, and D is the saturated aquifer thickness $[L]$. Values for x and D at the stream tube mouths were obtained from drilling data and regional mapping [*Williams and Tasker*, 1974; *Moog*, 1987]. The water balance approach provides a useful check on the Darcian method, because it does not require estimates of hydraulic conductivity or gradient.

Groundwater nitrogen concentrations. In order to determine both the mean groundwater TDN concentration (C_N) and the depth of the N-contaminated zone (z_N) required by (2), two to three multilevel samplers with an average of 18 ports each were installed at the mouth of each stream tube (Figure 3). Samplers were constructed of 3.8-cm-I.D. polyvinyl chloride (PVC) casing, fitted with 0.6-cm polyethylene tubing and nylon mesh screen, and installed with a hollow stem auger [*LeBlanc et al.*, 1991]. Vertical spacing between sampler ports ranged from 25 to 100 cm, depending on preliminary measurements of the concentration gradient at each site. Horizontal spacing of samplers across each stream tube mouth ranged from 6 to 8 m.

Groundwater samples (60 mL) were drawn from each sampler port with a peristaltic pump, after purging three bore volumes. Three sampling rounds were conducted on each of the stream tubes between June 1988 and July 1989, with one additional round at stream tube 1. Samples were also collected with a PVC bailer from the 5.1-cm observation wells (Figure 2) in January and June 1988. Immediately upon collection, specific conductance was measured using a cali-

TABLE 1. Nitrogen Loading Models

Constants	Models			
	Long Island	Cape Cod	USGS	Water Use
P/H, persons house^{-1}	2.7	2.7	2.7	NA
E/P, m^3 person^{-1} yr^{-1}	NA	73.2	82.9	NA
C_e, mol N m^{-3}	NA	2.42	2.32	2.36
M_{TDN}/P, mol N person^{-1} yr^{-1}	162	NA	NA	NA
WU/H, m^3 house^{-1} yr^{-1}	NA	NA	NA	141
EDF, dimensionless	NA	NA	NA	0.89
LA/H, m^2 house^{-1}	200	200	200	200
F_L, mol N m^{-2} yr^{-1}	0.58	0.59	0.33	0.33
R, m yr^{-1}	0.54	0.54	0.54	0.54
C_r, mol N m^{-3}	0.0036	0.0036	0.0036	0.0019

See equation (1) and subsequent text for explanation of terms. Long Island values from *Koppelman* [1978], Cape Cod values from *Nelson et al.* [1988], and USGS values from *Frimpter et al.* [1990, Appendix A]. If range is given in source document, midpoint is used. Regional published values are used for P/H [*Valiela and Costa*, 1988], C_r [*Persky*, 1986], and EDF [*Massachusetts Water Resources Authority*, 1983]. Water use model value for C_e is the mean concentration of effluent samples from study area [*Weiskel and Howes*, 1991] times 0.75, in accordance with unsaturated zone removal assumptions of *Nelson et al.* [1988]. Water use model C_r is the mean concentration, upgradient samples (Table 3). WU/H is the mean water use per house in the study area during 1986–1987 (Onset Water District, unpublished data, 1989). NA denotes not applicable to model.

brated conductance meter. Parallel samples for nutrient analysis were filtered (0.45 μm Millipore), and transported to the laboratory in HCl-washed, polyethylene bottles at 4°C. Ammonium analyses were performed upon return to the laboratory by the phenol-nitroprusside technique [*Scheiner*, 1976]. Nitrate plus nitrite was determined by cadmium reduction [*Wood et al.*, 1967] with a LACHAT (r) autoanalyzer. Total dissolved nitrogen was determined in 40% of the samples by cadmium reduction with the autoanalyzer, following persulfate digestion [*D'Elia et al.*, 1977].

RESULTS

Loading Model Flux Predictions

The net TDN input to the three stream tubes averaged 4560 ± 450 mol N yr^{-1}, (mean ± standard error of the mean (SEM) of the four models; Table 2). Septic system effluent was the largest TDN source, contributing an average of 82.1% of the total input, while lawn fertilizer and recharge from precipitation provided smaller amounts (17.4% and 0.5%, on average). These findings are consistent with the high housing density (10 houses ha^{-1}) and small average lawn size (200 m^2) in this subbasin. The Cape Cod model produced the highest overall estimates (an average of 5190 mol N yr^{-1}), the water use model the lowest (3150 mol N yr^{-1}), and the Long Island and USGS models intermediate values (4810 and 5090 mol N yr^{-1}, respectively; Table 2). Stream tube 2 experienced the greatest N loading (6310 mol N yr^{-1}, on average), while stream tubes 1 and 3 had somewhat less (3170 and 4210 mol yr^{-1}, respectively).

Overall, human sources are predicted to contribute over 99% of the total stream tube flux, not including the anthropogenic component of the "natural recharge," which is strongly influenced by acidic deposition in this region [*Pack*, 1980]. The relationship between the number of houses overlying each stream tube and TDN loading is linear for all

TABLE 2. Loading Model Flux Predictions

Stream Tube	Model	H	PA, m^2	WU, m^3 yr^{-1}	N_e, mol yr^{-1}	N_f, mol yr^{-1}	N_r, mol yr^{-1}	F_{TDN}, mol yr^{-1}
1	LI	6	10,800	NA	2620	696	21	3340
1	CC	6	10,800	NA	2870	708	21	3600
1	USGS	6	10,800	NA	3116	396	21	3530
1	WU	6	10,800	847	1779	396	11	2190
2	LI	12	11,100	NA	5240	1392	22	6650
2	CC	12	11,100	NA	5739	1416	22	7180
2	USGS	12	11,100	NA	6231	792	22	7050
2	WU	12	11,100	1694	3558	792	11	4360
3	LI	8	11,000	NA	3493	928	21	4440
3	CC	8	11,000	NA	3826	944	21	4790
3	USGS	8	11,000	NA	4154	528	21	4700
3	WU	8	11,000	1130	2373	528	11	2910

LI denotes Long Island model; CC, Cape Cod model; USGS, USGS model; and WU, water use model; see Table 1 for model constants. H is the number of houses overlying each stream tube, PA is the pervious area overlying each stream tube, and WU is the product of mean water use/house in the watershed and H; see (1) and subsequent text. N_e, N_f, and N_r are net TDN input to each stream tube from effluent leachate, fertilizer leachate, and natural recharge, respectively. F_{TDN} is the model stream tube flux prediction. NA denotes not applicable to model.

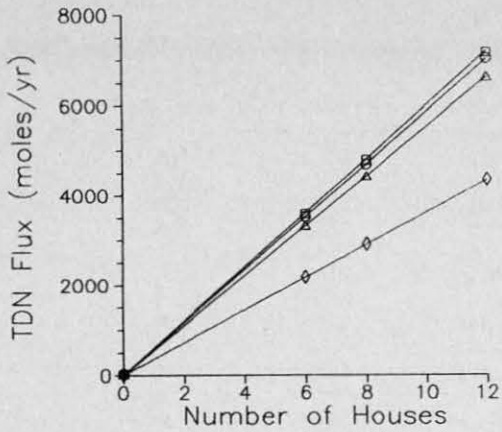

Fig. 4. Total dissolved nitrogen flux versus number of houses, stream tubes 1, 2, and 3. Triangles denote the Long Island model; squares, the Cape Cod model; circles, the USGS model; and diamonds, the water use model.

models (Figure 4), because the governing equation upon which they are based is linear with respect to H (see (1), and subsequent explanation). The slopes of the lines in Figure 4 differ in accordance with the various data sources for fertilizer and effluent TDN loading rates, while the y intercepts indicate the negligible input from natural recharge.

Field Measurements

Groundwater nitrogen concentrations. Groundwater from the undeveloped, upgradient portion of the watershed (W-5 and W-6; Table 3) contained dissolved inorganic nitrogen (DIN = $NH_4^+ + NO_2^- + NO_3^-$) at background concentrations typical of the Cape Cod region (1–4 μmol L^{-1} (μM) as N [*Persky*, 1986; *Frimpter et al.*, 1990]). Samples from the midst of the neighborhood had DIN concentrations ranging from 50 to 500 times above background; virtually all occurred as nitrate (Table 3). The larger set of downgradient samples from the stream tube mouths (n = 190) had a

TABLE 3. Specific Conductance and Dissolved N Concentrations, Observation Well and Effluent Samples, Indian Heights

Well	*SC*, μS/cm	NH_4, μM	NO_3, μM	DIN, μM	TDN, μM
		Upgradient Wells			
W-5	40	0.7	1.6	2.3	NA
W-6	34	0.7	0.8	1.5	NA
		Midgradient Wells			
W-1	270	<0.1	917	917	NA
W-4	188	0.4	1060	1060	NA
W-11	104	1.5	89	91	NA
W-12	114	0.4	186	186	NA
		Septic System Effluent			
	511	2634	7	2641	3140

See Figure 2 for location of wells. *SC* is specific conductance; NH_4, ammonium; NO_3, nitrate; DIN, dissolved inorganic nitrogen; and TDN, total dissolved nitrogen. Groundwater NO_3 samples were collected January 21, 1988; groundwater *SC* and NH_4 samples were collected January 21 and June 9, 1988, with mean values given. Mean values of Indian Heights effluent samples (n = 24) obtained from *Weiskel and Howes* [1991]. NA denotes data not available.

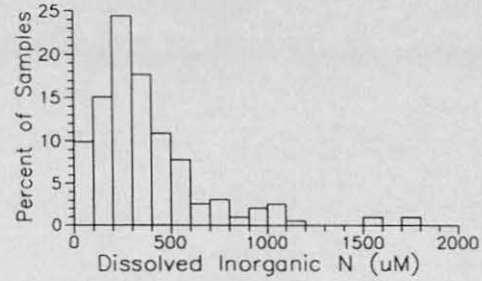

Fig. 5. Frequency distribution of dissolved inorganic N concentration, nonbackground (>4 μM), downgradient samples, stream tubes 1–3 (number of samples, 190).

median DIN concentration of 313 μM, and a skewed frequency distribution ($p < 0.05$ [*D'Agostino*, 1971]) due to a small number of high-DIN samples (Figure 5). Nitrate accounted for >99% of the DIN in all 190 downgradient samples, and 98 ± 1.6% of the TDN in a random subset of downgradient samples (mean ± SEM; n = 81). Given the dominance of ammonium and dissolved organic nitrogen (DON) in the septic effluent of the watershed (83% and 16% of effluent TDN, respectively [*Weiskel and Howes*, 1991]), it is evident that DON mineralization and nitrification of the widely distributed effluent input is both rapid and complete in this watershed. For the purposes of this study, therefore, TDN, DIN, and nitrate N concentrations were assumed to be equal at the stream tube mouths.

Mean annual TDN profiles at the mouths of stream tubes 1 and 2 displayed generally high concentrations near the water table, which declined to background levels at depths of 3–5 m (Figure 6). At stream tube 3, however, the vertical gradient was less pronounced, the base of the N-contaminated zone (z_N) was greater than 5.5 m below the water table, and the aquifer base was not well defined (Figure 6). Transverse horizontal gradients were also observed; depth-averaged TDN concentrations differed significantly ($p < 0.05$) between stream tubes, and from sampler to sampler across each stream tube mouth. In contrast to the strong spatial variations, no significant ($p < 0.05$) temporal variations in depth-averaged DIN concentration were observed between sampling dates at any of the samplers, though temporal variation at each sampling level was observed. The error bars (Figure 6) display the combined effects of transverse horizontal and temporal variation at the stream tube mouths.

Groundwater discharge estimates: Darcian approach. Medium to coarse sands dominate the stratigraphic section underlying the watershed. Depth-discrete K values predicted by (5) ranged from 0.004 to 0.11 cm s^{-1} overall (n = 28; four drilling sites), while the geometric mean hydraulic conductivity ($\bar{K}$) over the N-contaminated portion of each downgradient profile varied over a smaller range (0.027 cm s^{-1} at ST-1 to 0.043 cm s^{-1} at ST-2; Figure 7). Because the depth-discrete K estimates were lognormally distributed, and because the $\bar{K}$ values were not significantly different ($p < 0.05$), a point estimate of K_x equal to the geometric mean of the respective stream tube K_x values was determined and applied to all of the stream tubes. The resulting value of 0.034 cm s^{-1} is consistent with values obtained from pumping tests in adjacent portions of the Buttermilk Bay watershed (0.049 cm s^{-1} [*Moog*, 1987]), and regional estimates for

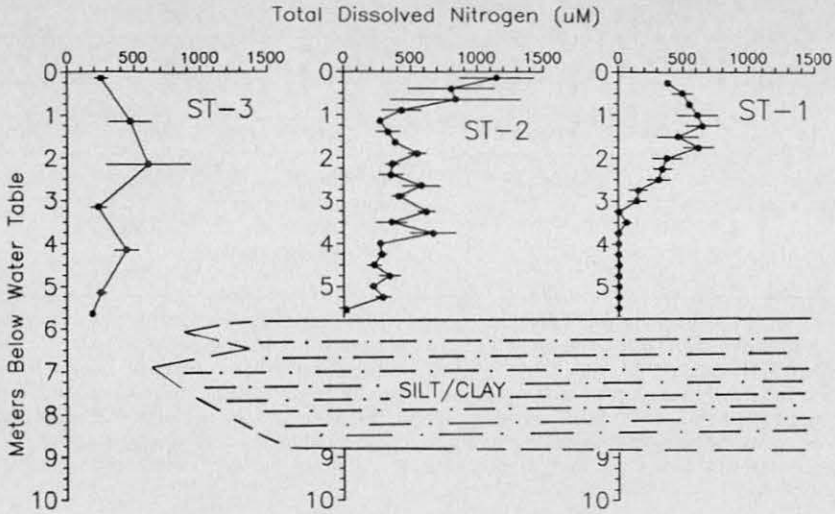

Fig. 6. Total dissolved nitrogen profiles, stream tubes 1–3 (mean ± standard error of the mean at each sampling level).

the aquifer (0.035–0.053 cm s^{-1} [*Williams and Tasker*, 1974]).

When this K_x value is substituted into (4), along with h_1, h_2, and L values of 6.1 m, 5.8 m, and 54 m, respectively (Figures 3 and 7), a mean annual specific discharge of 64 m^3 m^{-2} yr^{-1} (m yr^{-1}) is obtained for the stream tubes at the sampler locations. Because the recharge term in (4), $wL/2$, is only 4% of q in this case, the Darcian results can be considered independent of the recharge-based results presented below.

Groundwater discharge: Water balance approach. The unconfined aquifer beneath the watershed is recharged by precipitation, septic system effluent, and outdoor water use at a mean annual rate of 61 cm yr^{-1} (Table 4). Precipitation is the major source of recharge, though the 74,000 m^3 yr^{-1} imported for domestic use constitutes 10% of the total recharge, and 21% of the total recharge in the developed portion of the watershed. Substituting the total recharge rate (61 cm yr^{-1}), the estimated distance to the upgradient groundwater divide from each stream tube mouth (700 m), and the aquifer thickness at the stream tube samplers (5.8 m) into (7) yielded a mean stream tube q estimate of 74 m yr^{-1}, compared to 64 m yr^{-1} from the Darcian method. Note that both approaches overestimate q at stream tube 3, since the aquifer thickness exceeds 5.8 m by an unknown amount at this location. The good overall agreement between the Darcian and water balance q estimates supports the validity of the calculated values, since they are derived from independent data. Yet because the error associated with each method could not be directly quantified, both q estimates were used to calculate TDN flux values for each stream tube.

Stream tube nitrogen fluxes. Nitrogen flux values obtained from measured DIN concentrations and calculated groundwater discharge at the mouth of each stream tube showed the same general trend as the input estimates, with stream tube 2 > 3 > 1 (Table 5 and Figure 8). Note, also, that the stream tube 3 flux values are approximate, since q for this stream tube is overestimated and z_N is underestimated. While the water balance approach yielded 15% higher flux values than the Darcian approach due to higher q estimates, variation in TDN concentration at the stream tube mouths (SEM = ± 8–10%) causes the flux values to be similar ($p < 0.05$).

DISCUSSION

Both the loading model predictions and the field measurements indicate that large amounts of dissolved nitrogen are

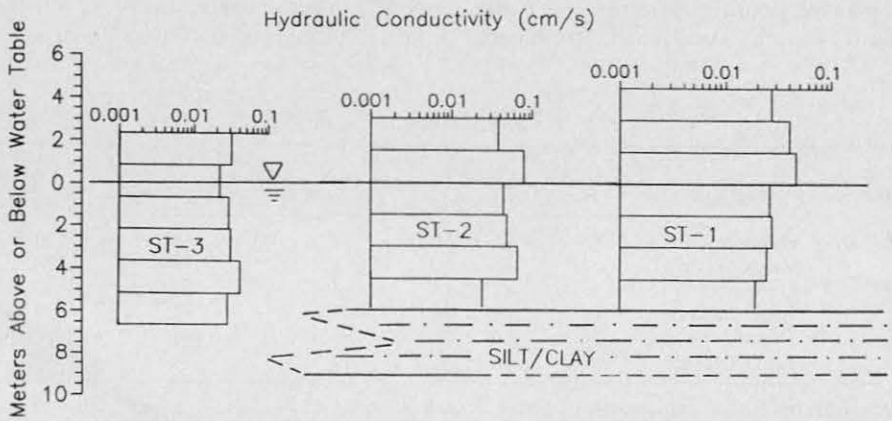

Fig. 7. Hydraulic conductivity profiles, stream tubes 1–3, estimated from grain size analyses and (5).

TABLE 4. Fate of Water Inputs to Indian Heights Subbasin

Inputs			Fate		
Type	Amount, cm yr^{-1}	Percentage	Type	Amount, cm yr^{-1}	Percentage
precipitation	118	94	street runoff	7.6	6
imported water	7.4	6	evapotranspiration	56.0	45
			aquifer recharge	60.6	48
			other surface runoff	1.2	1
Total	125.4		Total	125.4	

Mean annual precipitation for Wareham, Massachusetts, and regional estimate of evapotranspiration from *LeBlanc et al.* [1986]. Imported water from Onset Water District records (1989). Street runoff = [0.065][0.9] [Precipitation], where 0.065 is the fraction of watershed covered by impervious streets, and 0.9 is the fraction of street runoff conveyed to bay by storm sewers. Aquifer recharge is derived from precipitaiton (54.3 cm/yr [*LeBlanc et al.*, 1986]), discharge of septic effluent (5.9 cm/yr; assuming 10% loss to evapotranspiration during infiltration), and outdoor water use (0.4 cm/yr; assuming outdoor water use has same fate as precipitation). "Other surface runoff" was calculated by difference.

delivered to the subsurface and advected with flowing groundwater through this study area. The measured flux per unit aquifer width averaged 130 ± 12 mol N m^{-1} yr^{-1} (mean ± SEM). However, the loading model flux predictions vary over a considerable range at each stream tube, and generally overestimate the flux (Figure 8). We shall now assess the sources of this error, the validity of the respective model assumptions regarding TDN removal during transport, the significance of the observed variation in TDN concentration, and the implications of our findings for ecological research at the coastal land margin.

Loading Model Accuracy

Good agreement was obtained among the flux predictions of the Long Island, Cape Cod, and USGS models; the three predictions all lie within 4% of their collective mean value at each stream tube (Figure 8). However, the published models substantially overestimate, by an average of 60%, the actual TDN flux obtained with the field approaches, even when the overall uncertainty of the field measurements (±18% of the mean of the two methods) and the variations between the stream tubes are considered. The water use model, by contrast, agrees closely with the Darcian and water balance approaches (4.3% lower, on average, but within the uncertainty range noted above; Figure 8).

The poor performance of the published models can be largely attributed to the regional occupancy rate (P/H) used by the models (2.7 persons $house^{-1}$ [*Valiela and Costa*, 1988]). As is typically the case in predominantly residential watersheds of the New England coast, a substantial fraction of the houses in the study area (119 of 524, or 23%) are occupied only in the summer. Moreover, census data indicate that the mean year-round occupancy rate for the remaining 405 houses is only 2.36 persons $house^{-1}$ (Wareham Planning Department, unpublished data, 1989). The published occupancy rate is therefore 41% higher than the seasonally adjusted rate for the study area (1.91 persons $house^{-1}$).

The published model values of effluent TDN flux per capita (M_{TDN}/P for the Long Island model, or the product of E/P and C_e for the Cape Cod and USGS models; Table 1) also appear to be high for this study area; model values exceed the observed value of 155 mol N $person^{-1}$ yr^{-1} by an average of 14%. While we lack site-specific data regarding fertilizer N loading to the saturated zone, errors in F_L (Table 1) have a minor effect on overall model accuracy, because fertilizer is a relatively small TDN contributor to this study area. In agricultural and lower-density residential watersheds, however, errors in F_L play a more critical role [*Koppelman*, 1978].

Nitrogen Removal Assumptions

Modeling TDN removal at the regional scale poses a difficult problem, especially in residential areas. Dissolved nitrogen enters the subsurface in a variety of forms (as ammonium [NH_4^+] and organic N in septic effluent, as nitrate [NO_3^-] in most fertilizers, or as nitrogen oxides [NO_x] in precipitation), and may then undergo a variety of removal

TABLE 5. Stream Tube Nitrogen Fluxes

Stream Tube	Method	n	C_N, μM	Z_N, m	q, m yr^{-1}	F_{TDN}, mol N yr^{-1}
1	Darcian	55	423 ± 36	3.3	64	2230 ± 190
	water balance	55	423 ± 36	3.3	74	2820 ± 240
2	Darcian	63	433 ± 44	5.5	64	3810 ± 387
	water balance	63	433 ± 44	5.5	74	4410 ± 448
3	Darcian	70	318 ± 28	>5.5	<64	2800 ± 246
	water balance	70	318 ± 28	>5.5	<74	3240 ± 285

See equation (2) for explanation of terms; stream tube width (w_s) is 25 m; n is the number of groundwater samples collected at stream tube mouth from nitrogen-contaminated zone. Error given for C_N and F_{TDN} is the standard error of the mean.

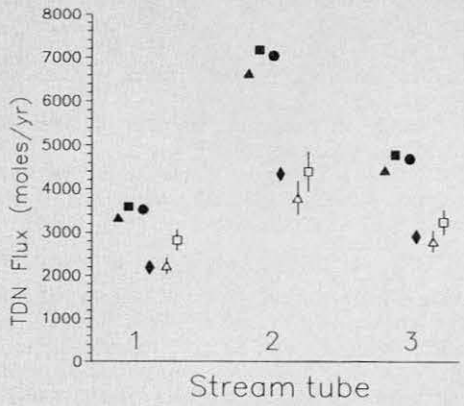

Fig. 8. Predicted and observed mean annual TDN fluxes, stream tubes 1–3. Predicted: solid triangles, Long Island model; solid squares, Cape Cod model; solid circles, USGS model; and solid diamonds, water use model. Observed: open triangles, Darcian method; and open squares, water balance method. (Error bars represent SEM of observed values).

processes, including plant uptake, volatilization of $NH_3(g)$, sorption of NH_4^+, and/or denitrification of NO_3^- to $N_2(g)$ or $N_2O(g)$ [*Fenchel and Blackburn*, 1979; *Smith et al.*, 1991]. However, because the Indian Heights watershed is in approximate steady state with respect to TDN, direct estimates of TDN removal during unsaturated/saturated zone transport can be obtained from stream tube inputs and outputs, and the respective model transport assumptions can be independently verified, within the certainty limits of the field measurements.

The water use model, using an observed mean effluent concentration (prior to infiltration) of 3.14 mol N m^{-3} [*Weiskel and Howes*, 1991], provides a measure of TDN input to the unsaturated zone overlying each stream tube, while the mean of the Darcian and water balance approaches provides a measure of stream tube output (Figure 9). Using this approach, we infer that 82 ± 7% of the input to the unsaturated zone from septic effluent, leached fertilizer, and natural recharge is transported to the stream tube mouths (mean ± standard deviation of the three stream tubes; see

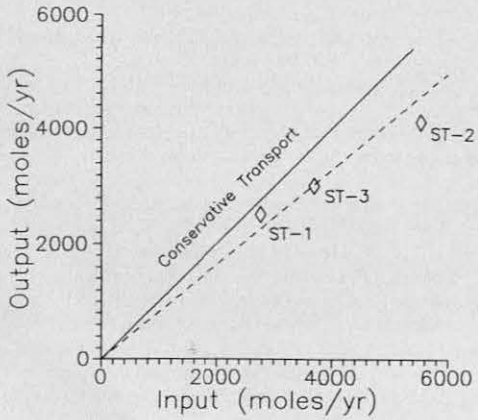

Fig. 9. TDN input to unsaturated zone overlying stream tubes (derived from the water use model) versus observed stream tube TDN output (mean of Darcian and water balance methods). Solid line represents conservative transport. Slope of dashed line equals mean fraction of TDN input to unsaturated zone which is transported to stream tube mouths.

slope of dashed line, Figure 9). This overall transport fraction corresponds to an effluent transport fraction in this study area of 79 ± 10%, assuming that effluent constitutes 85.4% of the TDN input to the unsaturated zone (water use model estimate), and that the remaining inputs (leached fertilizer and natural recharge) are transported conservatively below the root zone.

This finding is consistent with the assumptions of the Cape Cod model (i.e., 25% removal of effluent TDN during infiltration, and conservative transport thereafter) and available data from microscale studies of septic systems [*Andreoli et al.*, 1979; *Alhajjar et al.*, 1989]. By contrast, the USGS and Long Island models appear to underestimate and overestimate, respectively, TDN removal under the conditions of this study area, though the low range of values (2.14–2.50 mol N m^{-3}) cited by *Frimpter et al.* [1990] for the initial effluent TDN concentration, and the high value cited by *Koppelman et al.* [1978] for initial TDN flux per capita (324 mol N $person^{-1}$ yr^{-1}; see the methods section) tend to mask the effects of these removal assumptions.

Spatial Distribution of Groundwater TDN

As we have shown, the field approaches allow independent verification of the overall accuracy and transport assumptions of the loading models. In addition, the field data provide independent evidence concerning the relative importance of the various TDN inputs to the watershed. We observed significant variation in TDN concentration at a scale of meters in the transverse horizontal direction, and at a scale of tenths of meters in the transverse vertical direction. This downgradient TDN distribution is consistent with a large number of discrete nitrogen sources near the ground surface (septic systems and lawns), the pristine character of the ambient groundwater (which receives only trace amounts of TDN from natural recharge), and the low transverse vertical and transverse horizontal macrodispersivities typical of glaciofluvial aquifers [*Sudicky*, 1986; *Garabedian et al.*, 1991]. In particular, *Robertson et al.* [1991] have shown that nitrate plumes from individual septic systems can persist for tens to hundreds of meters in such aquifers. It is therefore likely that the TDN distribution observed in the present study is largely due the superposition of numerous individual effluent plumes near the water table. This conclusion is supported by the results of the loading models, all of which predict effluent to be the major TDN source to the saturated zone.

Implications for Coastal Research

Our findings have several implications for current efforts to understand and quantify the role of subsurface nitrogen flux through the coastal land margin.

1. Anthropogenic sources dominate the subsurface nitrogen pathway in the present case, contributing >99% of the TDN flux; median groundwater TDN concentrations increase from 1.9 to 313 μM during transport through the residential portion of the subbasin. Transport over the entire unsaturated/saturated zone pathway is moderately conservative; about 20% of the initial TDN input is removed. Virtually all (98%) of the TDN occurs as nitrate at the downgradient edge of the watershed. While the oak/pine woodland and associated soils composing the original ecosystem in this watershed are highly efficient in retaining

TDN, the subsequent residential "ecosystem" exports large quantities of TDN to the saturated zone as nitrate, which can be readily advected to adjacent coastal waters. The effects of human settlement on the nitrogen budgets of other land margin environments need further study.

2. Available loading models used to quantify TDN flux are subject to large errors because they often incorporate highly conservative assumptions with respect to human occupancy, initial loading rates, and/or TDN transport behavior. Such assumptions are appropriate for planning purposes, but may cause substantial overpredictions of actual TDN flux, especially in coastal settings. Our results show that loading model accuracy is greatly enhanced by use of site-specific, proxy data appropriate to the watershed (for example, water use records in residential areas).

3. The field approaches developed in this study, in contrast to the loading models, require no assumptions regarding the initial magnitude or subsurface transport behavior of the various nitrogen inputs. Moreover, steady state conditions need not be assumed if time series data are required, and transient increases or decreases in TDN flux due to population changes, altered agricultural practices, rerouting of storm waters, or public sewer construction can be determined empirically. Spatially intensive groundwater sampling is advisable in residential watersheds with a large number of nitrogen sources; practical considerations may therefore limit the field approaches to the stream tube or subbasin scale.

In conclusion, our results show that available nitrogen loading models should not be applied to coastal watersheds without modification. Field-based methods are necessary to verify loading model predictions; they are also less constrained by assumptions and have the potential to elucidate both short- and long-term changes in groundwater nitrogen flux through the coastal land margin.

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