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Nitrogen loading from watersheds to estuaries: Verification of the Waquoit Bay Nitrogen Loading Model

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Abstract. World-wide eutrophication of estuaries has made accurate estimation of land-derived nitrogen loads an important priority. In this paper we verify predictions of nitrogen loads made by the Waquoit Bay Nitrogen Loading Model (NLM). NLM is appropriate for watersheds with mixes of forested, agricultural, and residential land uses, and underlain by coarse unconsolidated sediments. NLM tracks the fate of nitrogen inputs by atmospheric deposition, fertilizer use, and wastewater disposal, and assigns losses of nitrogen from each source as the nitrogen is transported through the land use mosaic on the watershed surface, then through the underlying soils, vadose zones, and aquifers.

We verified predictions of nitrogen loads by NLM in two independent ways. First, we compared NLM predictions to measured nitrogen loads in different subestuaries in the Waquoit Bay estuarine system. Nitrogen loads predicted by NLM were statistically indistinguishable from field-measured nitrogen loading rates. The fit of model predictions to measurements remained good across the wide range of nitrogen loads, and across a broad range in size (10–10,000 ha) of land parcels. NLM predictions were most precise when specific parcels were larger than 200 ha, and within factors of 2 for smaller parcels.

Second, we used NLM to predict the percentage of nitrogen loads to estuaries contributed by wastewater, and compared this prediction to the $\delta^{15}N$ signature distinguishable from N derived from atmospheric or fertilizer sources. The greater the contribution of wastewater, the heavier the $\delta^{15}N$ value in groundwater. The significant linear relation between NLM predictions of percent wastewater contributions and stable isotopic signature corroborated the conclusion that model outputs provide a good match to empirical measurements. The good agreement obtained in both verification exercises suggests that NLM is an useful tool to address basic and applied questions about how land use patterns alter the fate of nitrogen traversing land ecosystems, and that NLM provides verified estimates of the land-derived nitrogen exports that transform receiving aquatic ecosystems.

Introduction

Increased delivery of nitrogen from coastal watersheds to receiving estuaries is arguably the greatest agent of ecological change altering coastal ecosystems (GESAMP 1990; NRC 1994; Goldberg 1995). The critical role of nitrogen loadings from land to coastal waters derives from two basic facts. First, rates of loading of anthropogenic nitrogen to estuaries has been increasing across most of the shorelines of the world (GESAMP 1990; NRC 1994; Cole et al. 1993; Caraco & Cole 1999). Second, supply of nitrogen limits growth of most primary producers in most coastal waters, at least in the short term (Howarth 1988; Valiela 1995).

The importance of nitrogen supplies to coastal waters has prompted efforts to measure and evaluate nitrogen loads (Nixon et al. 1986; Howarth 1988), and to relate these loadings to land use patterns on the watersheds draining onto the receiving estuaries (Cole et al. 1993; Valiela et al. 1997). As part of long term studies of nitrogen loading in a series of subwatersheds and adjoining estuaries within the Waquoit Bay estuarine complex (Figure 1 left), we developed the Waquoit Bay Land Margin Ecosystems Research (WBLMER) Nitrogen Loading Model (NLM thereafter), which was described in detail in Valiela et al. (1997). NLM was developed from a multi-year effort by several researchers, and is based on comprehensive data obtained during the WBLMER work, as well as an extended review of the literature on atmospheric-, fertilizer-, and wastewater-derived nitrogen and its dynamics in watersheds.

This paper contains new material that supplements Valiela et al. (1997), by presenting results of two independent verifications of NLM predictions of nitrogen loading estimates. First, we compare NLM predictions to field-measured estimates of nitrogen loading. To assess the reliability of NLM predictions across a range of different spatial scales, we further compare NLM predictions of nitrogen loads versus measured loads, for the whole Waquoit Bay watershed, for seven subwatersheds of Waquoit Bay, and for smaller recharge areas within each of the subwatersheds.

Second, we use stable nitrogen isotopic data (McClelland & Valiela 1997; McClelland et al. 1997) to verify NLM predictions. Stable isotopic signatures of nitrate in groundwater are influenced by the sources of nitrogen to the watershed above the watertable. Groundwater contaminated by wastewater typically has δ^{15}N values of nitrate between 10‰ and 20‰ (Table 1), while groundwater receiving inputs predominantly from atmospheric deposition or fertilizer use shows lower nitrate δ^{15}N values (Table 1). We should note that nitrogen in animal waste itself has values that are 3 (for cattle, Fourqurean et al. 1997) to 5 (our own measurements of septic tank contents) ‰. These δ^{15}N values are altered by various geochemical processes, such as denitrific-

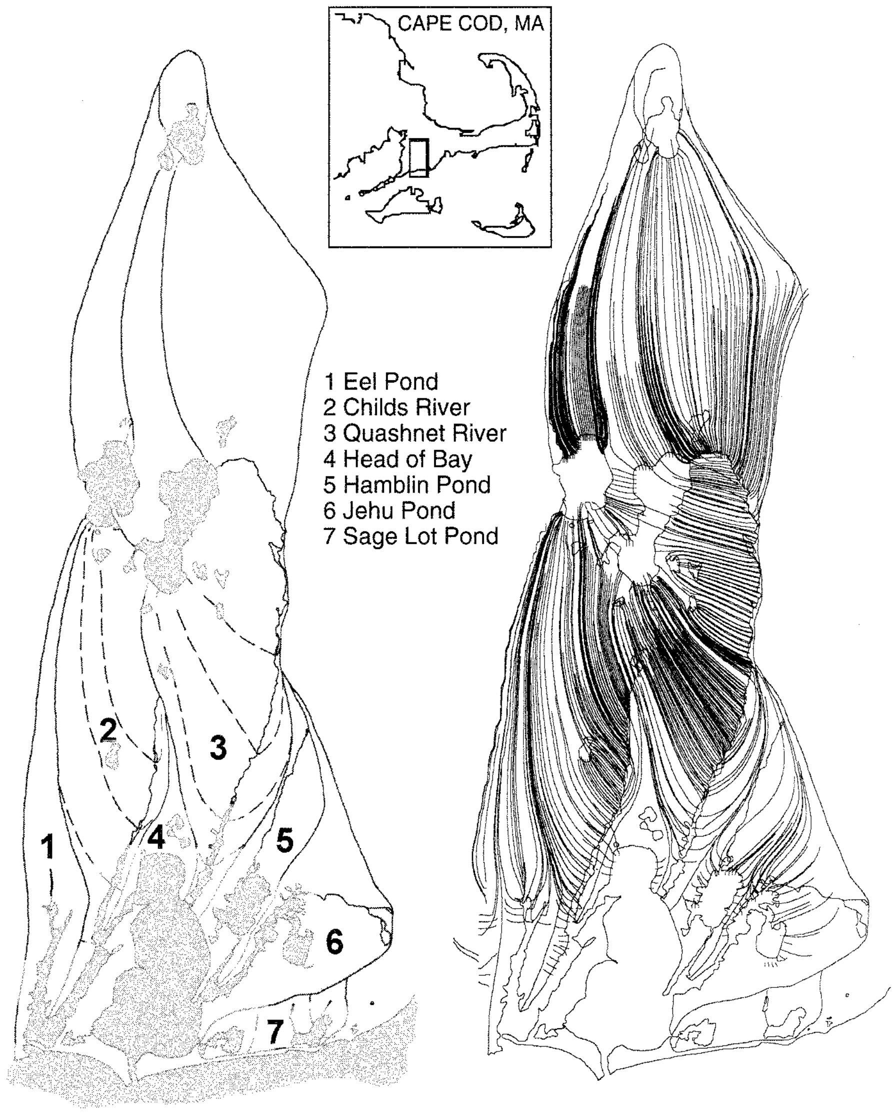


Figure 1. Left: Delineation of the watershed of Waquoit Bay. Subwatersheds draining into the seven estuaries of the Waquoit estuarine system (indicated by numbers); recharge areas within subwatersheds are indicated by dashed lines within subwatersheds. Right: Tracks of paths of water "parcels" simulated with MODFLOW (McDonald & Harbaugh 1988), using local data on water table contours, hydraulic conductivity, and effective porosity (J. Brawley, WBLMER, unpublished results). Model was run backwards from shore, and this output was used to make the delineations shown on map on left of this figure. Top: Inset showing position of Waquoit watershed in Cape Cod, MA.

Table 1. $\delta^{15}N$ values for nitrate in groundwater receiving nitrogen inputs predominantly from animal wastes, atmospheric deposition, or fertilizer.

Source	$\delta^{15}N$(‰) of nitrate in groundwater	References
Wastewater[1]	10 to 20	Kreitler 1975; Kreitler and Jones 1975; Kreitler et al. 1978; Gormly and Spalding 1979; Aravena et al. 1993
Atmospheric deposition	2 to 8	Kreitler 1975; Kreitler and Jones 1975; Gromly and Spalding 1979; Macko and Ostrom 1994
Fertilizer	−3 to 3	Kohl et al. 1973; Freyer and Aly 1974; Mariotti and Lètolle 1977; Macko and Ostrom 1994

[1] Includes nitrate derived from both human and animal waste

ation, so that freshwater moving away from the source bears N with heavier signatures (Table 1).

Wastewater, atmospheric, and fertilizer N all contribute to the nitrogen pool in groundwater within the Waquoit Bay watershed, and differences in the relative proportions of these N sources result in differences in the stable isotopic signature of groundwater nitrate under each specific watershed (McClelland & Valiela 1997). We predict that as the proportion of wastewater nitrogen in the total nitrogen load increases, the $\delta^{15}N$ signal will become heavier, from a low value up to near 20‰.

In this paper we compare the NLM prediction of the percentage of nitrogen loads from land to estuaries that is derived from wastewater to the stable isotopic measurements of nitrogen in groundwater about to enter the estuaries. These comparisons of NLM predictions to measured loads and to stable isotope data are two critical and independent tests of the ability of the model to predict specific features of interest to managers and policy-makers, as well as to researchers.

Methods

The Waquoit Bay Nitrogen Loading Model

Details and rationale of NLM were discussed in our earlier paper (Valiela et al. 1997). The components of NLM were empirically defined based on our own work on the Waquoit Bay watershed, as well as an extensive review of published material. NLM was designed for application in watersheds with rural to suburban land covers, and where groundwater bears most of the nitrogen flow to receiving estuaries. Major aspects of the model are summarized in the diagram of Figure 2. Users of NLM have to provide (1) locally appropriate rates of delivery of atmospheric nitrogen and fertilizer nitrogen to the watershed surfaces; (2) areas of different types of land covers (natural vegetation, turf, impervious surfaces, agricultural) on the watershed; (3) number of residences and occupancy rates per dwelling. From the input data on deposition and fertilizer use, NLM calculates the amount of nitrogen from fertilizers and atmospheric deposition that pass through the watershed surface, enter the vadose zone, and course through the aquifer, at rates of loss as indicated by the numbers in the various components of Figure 2. From the human occupancy data, NLM estimates the amount of wastewater nitrogen that travels from septic systems into the vadose zone beneath, through the plume of the septic system, and through the aquifer. NLM (Figure 2) includes runoff from impervious surfaces such as runoff from roads, driveways, and roofs (Valiela et al. 1997). NLM does not include surface runoff and stream inputs because of the coarse nature of the underlying glacial sediments on Cape Cod (Oldale 1992) strongly favors percolation over runoff of precipitation.

As examples of NLM calculations, we can consider the fates of wastewater nitrogen and of atmospheric nitrogen delivered to forested areas as illustrated in Figure 2. To estimate loads of wastewater nitrogen to the seepage face of estuaries, NLM estimates nitrogen inputs from human occupancy data that are entered by the user; then (cf. Figure 2, left side) NLM considers that 6% of the inputs are lost in the septic tank itself, then that a further 35% of the nitrogen that leaves the septic tank is lost in the leaching field, and that 34% of the nitrogen leaving the leaching field is lost within the plume of the septic system. Lastly, as the surviving wastewater-derived nitrogen travels beyond the plume (beyond 200 m from the septic system), NLM considers that there is a further loss of 35% of the by now small amount of wastewater nitrogen. To estimate the losses of nitrogen delivered to forested areas, NLM takes inputs of atmospheric nitrogen provided by the user, considers that 65% of the inputs are lost during passage through vegetation and soils, that 61% of the atmospheric nitrogen that leaves the soil is lost in the unsaturated vadose zone, and that 35% of the atmospheric nitrogen that crosses the water table is lost within the aquifer before seeping out to the estuary.

As shown in Figure 2, NLM makes similar calculations for the fate of nitrogen delivered to other land use types. Then NLM adds the amounts of nitrogen from all sources that manage to traverse the aquifer. The sum of these terms is what we report as the nitrogen loading to the receiving estuary

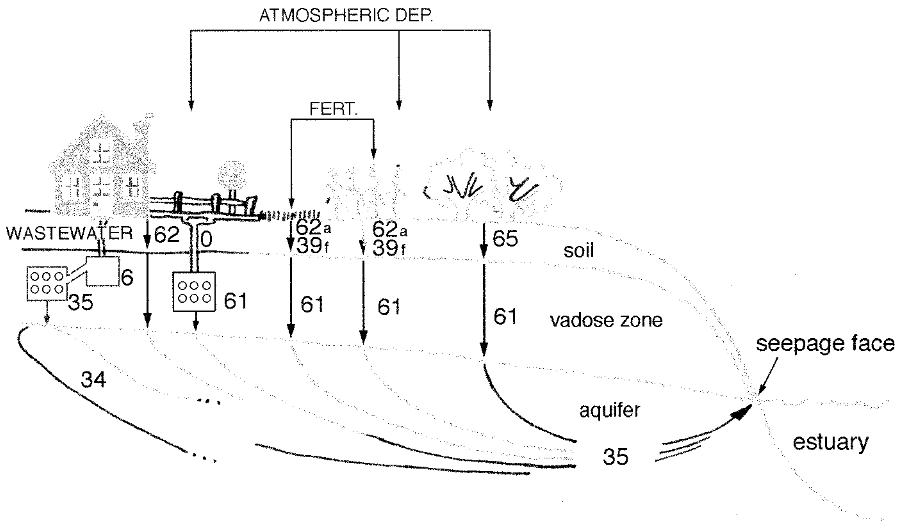


Figure 2. Schematic of NLM, showing inputs of wastewater-, fertilizer-, and atmospheric-derived nitrogen to the watershed, and % losses (shown as numbers) as the nitrogen from the three sources is inserted by septic sytsems, or falls on impervious surfaces, turf, agricultural parcels, or vegetated parcels, and then traverses soils, vadose zone, aquifer, and seepage face on its way to receiving estuaries. As the diagram shows, waterwater first enters a septic tank and then moves to a leaching tank, with different losses as shown; the wastewater nitrogen then moves down-gradient in a septic system plume, where further losses accrue, and beyond 200 m, the plume cannot be detected, and the surviving nitrogen moves in the mass flow of groundwater, with corresponding losses. Turf and agricultural fields receive both atomspheric (a) and fertilizer (f) nitrogen, and these two suffer different losses. Further details and explanation of NLM were given in Valiela et al. (1997).

estimated by the model. The model estimates total nitrogen loads, and does not distinguish any subcomponent such as nitrate, ammonium, or dissolved organic nitrogen. Through error propagation and bootstrap methods, we estimated that the standard error of NLM estimate ranged from 12 to 14% of the estimate, and the standard deviation between 37 to 38% of the estimate. This is but a brief sketch of the workings of NLM, included here to make this paper self-contained. The many further details of NLM are included in Valiela et al. (1997).

Measurement of nitrogen loading rates

To obtain actual measured rates of nitrogen loads from watersheds to estuaries to compare to the NLM estimates, we first measured nitrogen concentrations in groundwater at the seepage face. Then we multiplied the measured concentrations by the annual recharge of water to the aquifer for the catchment area upgradient from the site where the groundwater was sampled.

We measured nitrate (NO_3), ammonium (NH_4), and dissolved organic nitrogen (DON) contents in samples of groundwater. We did not look at nitrite (NO_2) independently because, as is common in most waters, concentrations of nitrite were one to two orders of magnitude lower than those of the other nitrogen species. In addition, the method for NO_3 (+NO_2) determination includes any NO_2 present in the sample. Concentrations of NO_3 were determined on the Lachat Autoanalyzer by cadmium column reduction of NO_3 to NO_2 (QuickChem® method 31-107-04-1-C). DON was measured identically to the method described for nitrate except there is an initial persulfate digestion (modified from D'Elia et al. 1977) step prior to the cadmium reduction step. Concentrations of NH_4 were measured at 630 nm on the Lachat Autoanalyzer using a standard alkaline phenol method (QuickChem® method 31-107-06-1-C) for color determination. NLM calculates loadings in terms of total nitrogen, so for the comparisons to loadings estimated by NLM we summed the three nitrogen species measured in groundwater samples.

Groundwater about to enter the estuary was sampled by driving piezometers below the water table at sites just above the high tide mark at the seepage face, and pumping water out of the aquifer. We repeated this sampling at stations all around the periphery of the estuaries so that no significant groundwater flows went unsampled. The number of samples varied depending on the dimensions of the shoreline of the estuary (Table 2, column 3). The spacing between sampling stations varied between 1 m to 50 m; examination of the data did not show evident differences in the distribution of concentrations taken from the different spatial distributions, so we treated measurements from all the piezometer samples alike.

To prevent differences in groundwater flow, number of stations, or other differences from one place to another from biasing our estimates of nitrogen loads, we subdivided the watersheds into recharge areas (Figure 1 left). We assumed recharge areas had the same groundwater flow along the discharge face for that specific recharge area. We delineated the recharge areas based on land surface features and groundwater flow lines obtained from hydrological modeling (Figure 1 right), using the MODFLOW (McDonald & Harbaugh 1988) groundwater transport model. Hydraulic conductivities, porosities, and watertable contours of this part of Cape Cod are well defined (LeBlanc et al. 1991; Solomon et al. 1995; Portniaguine & Solomon 1998), so that we could run MODFLOW to delineate particle tracks and the watersheds (J. Brawley & C. H. Sham, unpublished WBLMER data).

We then estimated measured nitrogen loads from a given recharge area by multiplying the average nitrogen content of groundwater (Table 2, column 4) by the annual water recharge to groundwater under recharge areas. Recharge was calculated from average annual precipitation data obtained for the

Table 2. Variables used in comparisons of modeled vs measured nitrogen loads. Values shown for the whole watershed of Waquoit Bay, subwatersheds, and recharge areas within the subwatersheds (see Figure 1).

Land parcel	Land area (ha)	No. of ground-water samples	Mean conc. of TDN (μM)	N load (kg N yr^{-1})	
				Modeled	Measured (x $\pm$ s.e.)
WB watershed	3788	1059	85	22000	26781 $\pm$ 9.6
Childs River	866	386	313	5536	8116 $\pm$ 22.4
C1	52	263	398	994	1677 $\pm$ 29.6
C2	280	74	153	1499	3614 $\pm$ 23.1
C3	225	27	93	1102	1837 $\pm$ 26.7
C4	239	22	416	1942	988 $\pm$ 319.3
Quashnet River	2055	232	60	8406	9879 $\pm$ 11.0
Q1	31	136	61	118	141 $\pm$ 31.2
Q2	165	30	77	719	1192 $\pm$ 14.0
Q3	294	26	92	912	2296 $\pm$ 7.2
Q4	214	24	22	643	442 $\pm$ 2.9
Eel Pond	354	89	164	3029	4502 $\pm$ 20.4
E1	15	9	158	209	180 $\pm$ 55.0
E2E	19	11	137	371	214 $\pm$ 36.0
E2W	17	13	93	126	119 $\pm$ 12.0
E3E	29	17	148	731	353 $\pm$ 69.9
E3W	34	8	57	270	361 $\pm$ 80.2
E4	248	31	221	1411	3275 $\pm$ 62.5
Hamblin Pond	260	46	44	1661	893 $\pm$ 5.6
H1	32	5	128	575	197 $\pm$ 16.2
H2	34	19	34	249	86 $\pm$ 6.1
H3	184	22	45	955	610 $\pm$ 9.4
Jehu Pond	422	78	62	2709	1968 $\pm$ 9.4
J2	56	12	91	496	422 $\pm$ 36.1
J4	176	31	66	504	848 $\pm$ 26.6
J5	163	35	48	1509	589 $\pm$ 9.8
Sage Lot Pond	119	191	90	361	990 $\pm$ 8.8
SP	104	161	112	147	846 $\pm$ 13.2
FP	15	30	79	213	145 $\pm$ 12.1
Head of the Bay	92	37	60	532	433 $\pm$ 6.7

western Cape Cod area (Valiela et al. 1997; Valiela & Costa 1988). We used regional estimates of evapo-transpirative losses of precipitation (55% of annual precipitation) to estimate the volume of freshwater that, on average, flows through the aquifers to the estuaries. This calculation assumes that the aquifer is sufficiently uniform so that flow rates from the various recharge areas was similar. The unconsolidated sands underlying the recharge areas differ to a minor degree in Cape Cod (Oldale 1992). We checked the flow vs actual flows in the various streams (Valiela et al. 1992) emanating via groundwater flow from the different watersheds. These volumes of freshwater recharge were comparable to measurements of actual discharge from the streams that convey much of the groundwater to the estuaries (Valiela et al. 1992), and amount to 91% of the groundwater flow (unpubl.).

To evaluate the effect of spatial scales on NLM predictions, we made use of the nested layout of the recharge areas, subwatersheds, and entire Waquoit Bay watershed. We compared estimates of nitrogen loads for the recharge areas, estimates of nitrogen loads to the subwatersheds obtained by aggregating the recharge areas within each subwatershed (Figure 1 left), and lastly, estimates for the entire Waquoit Bay watershed obtained by aggregating recharge areas for all subwatersheds.

Measurements of stable isotopic ratios in groundwater

Details of the sampling and analytic procedures for the measurements of stable nitrogen isotopes in groundwater about to enter the estuaries are given in McClelland and Valiela (1997). In brief, samples of groundwater were collected from the margin of recharge areas in the estuaries; the number of samples per recharge area were proportional to the area of the recharge area, so as to obtain representative values of the isotope ratio of the nitrate (the main nitrogen form in groundwater) entering the estuary in groundwater. Nitrate was isolated from groundwater by the method of Sigman et al. (1997), modified for use in freshwater, and ammonium was separated by the method of Holmes et al. (1998). The ratio of the two isotopes of nitrogen were determined in the Boston University Stable Isotope Laboratory by a mass spectrometer coupled to an elemental analyzer.

Results

Model predictions vs measurements of N loads

Nitrogen loading rates predicted by NLM for different parcels of landscape are similar to measured estimates of nitrogen loading (Figure 3). Figure 3 shows the results for the whole of Waquoit Bay's watershed and for the smaller, spatially-nested subwatersheds and recharge areas.

There is variation associated with our measurements, owing to differences in nitrogen concentrations in groundwater samples, and to a smaller error in the water recharge estimate. We estimate that, on average, the error of measured values, based on the variation among concentrations of nitrogen in samples of groundwater, was about 20%. These errors are somewhat larger than the calculated standard error for the NLM predictions (12–14%, Valiela et al. 1997). “Error terms” associated with the measured estimates of nitrogen load are not shown in Figure 3 because these measurements are pseudoreplicates, in Hurlbert’s (1984) sense. The measurements come from *within* rather than *among* estuaries subject to the same treatment combination, and are therefore unsuitable for inter-estuary comparisons. Instead, we analyzed the data using a regression approach, where we treat each mean as an observation, and examine variation among the observations by regression. The data are shown in Figure 3 are shown on a log log scale because the values span three orders of magnitude.

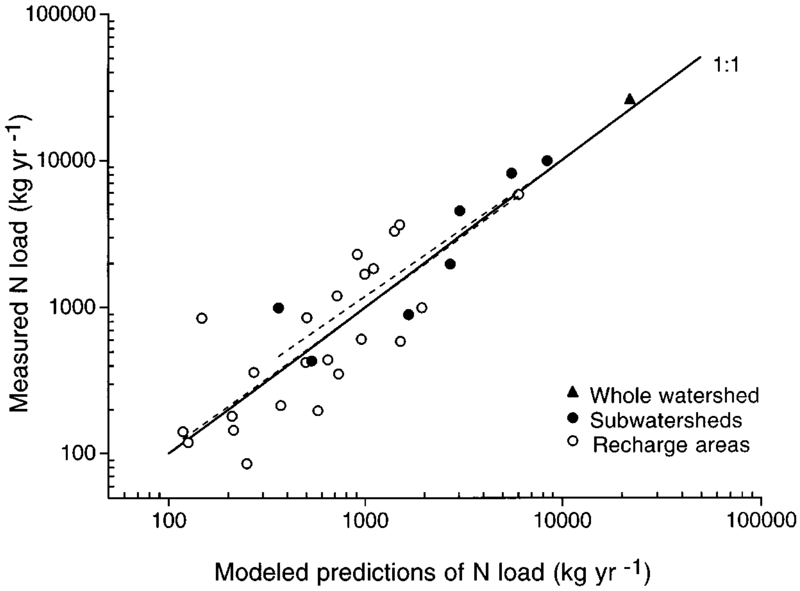
We examined statistical significance of the comparisons in two tiers of tests: first we asked, how good were the linear regressions between measured and modeled estimates for the subwatersheds, and for the recharge areas? Second, we asked how far from the 1:1 line indicating a perfect fit did the results fall for the subwatersheds and for the recharge areas? No regressions were run for loads to the entire watershed, because we only had one value.

Regressions for subwatersheds and recharge areas both have highly significant slopes (equations given in Figure 3, P for both regression $F <$ 0.01), and account for most of the variation detected. Values along the horizontal axis were calculated by the model as specific values, so the data of Figure 3 fit the Berkson case, which meant that we could use Model I regression methods (Sokal & Rohlf 1995). We conclude from this first tier of tests that, for both the subwatershed and recharge area results, there was a significant linear relationship between model predictions and measured estimates of nitrogen loads, with only a modest scatter of points about the lines.

For the second tier of tests, we checked whether the relationships between measured and predicted nitrogen loads approximated a perfect fit, by using t tests to compare the slope of the two calculated regression lines to the 1:1 slope (Steel & Torrie 1960; Zar 1984; Sokal & Rohlf 1995). The slopes of the regressions for subwatersheds and recharge areas were both indistinguishable from the 1:1 line, judging from the nonsignificant values of the t tests (Figure 3). We conclude that the model predictions compared quite reliably to measured estimates.

Match of model vs measurement estimates at different spatial scales

Plots of modeled vs. measured values for nitrogen loads fall around the 1:1 line of Figure 3. There are, however, hints of somewhat larger departures from the 1:1 lines as land parcels become smaller; for example, the coefficient of determination (R^2) for recharge areas was smaller than that calculated for the subwatersheds. To see if area of the land parcel alters the match between model and measured estimates, we first calculated residuals for each data



Subwatersheds: $y = 0.93x - 0.28$, $r^2 = 0.79^{**}$, $t = 0.05$ ns

Recharge area: $y = 0.96x + 0.10$, $r^2 = 0.63^{**}$, $t = 0.51$ ns

Figure 3. Comparison of measured nitrogen loads vs loads modeled using NLM. Values shown for the whole of the Waquoit Bay watershed, for the seven subwatersheds of Waquoit Bay, and for recharge areas within the subwatersheds. Statistical analysis of the fit of the points to linear regression lines (equation and R^2 values, $P < 0.01$ for F for mean squares for regression) and comparisons of the fitted regression slopes to the slope of the 1:1 line of perfect fit (t values, both not significant) are included at foot of figure.

point from the 1:1 line, and normalized the residuals relative to the magnitude of the measured values. Then we plotted the normalized residuals vs the area of the land parcels (data from Table 2) (Figure 4).

The residual analysis shows an excellent match between modeled and measured loading rates when we deal with land parcels of more than 200 or so hectares (Figure 4): departures from perfect fit indicated by the normalized residuals remain within factors of about 1 when we deal with parcels of more than a few hundred hectares. The residuals do, however, splay out to as much as a factor of 2 as parcel area becomes smaller. We should note that the regression adequately defines the overall relationship across most of the range of parcel sizes, but that it just does so with less accuracy for smaller land parcels. We remind the reader that that the horizontal axis is in a log scale, which makes it somewhat hard to perceive that the model performs well across more than 99% of the range of parcel sizes. As parcel

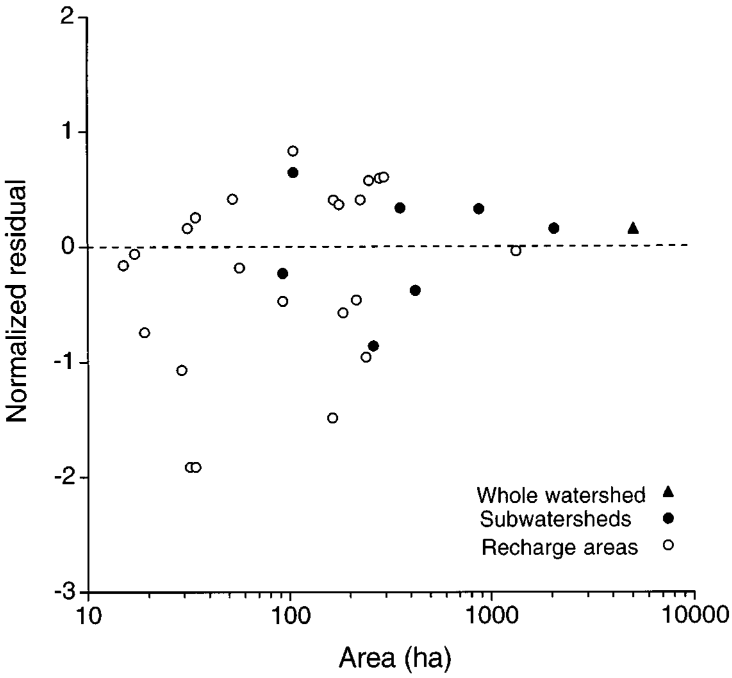


Figure 4. Normalized residuals from the 1:1 line of perfect fit (Figure 3), vs the area of the parcel for which a prediction was made by NLM. The units in the vertical axis are factors.

area becomes smaller than 200 ha or so, there is a slight bias towards negative departures in predictions about individual points, as well as tendency for a few of the model predictions to underestimate nitrogen loads by factors of up to 2. Model predictions by NLM therefore seem quite reliable for data sets taken on aggregate, or for specific predictions about larger parcels of coastal landscape, somewhat less so for small land parcels.

Model predictions vs stable isotopic measurements in groundwater

We have shown elsewhere (Sham et al. 1995; Valiela et al. 1997) that wastewater furnishes 48%, fertilizer use provides 16%, and atmospheric deposition 29% of the increasing nitrogen load to Waquoit Bay estuaries. Wastewater is such a prominent source of land-derived nitrogen to Waquoit estuaries, that there is a positive relationship between the stable isotopic value of groundwater nitrogen and the proportion of groundwater nitrogen coming from wastewater (McClelland et al. 1997). In fact, the δ^{15}N value of nitrate increases linearly as the relative contribution of wastewater to nitrogen loading to estuaries increases (Figure 5). We interpret this as an independent

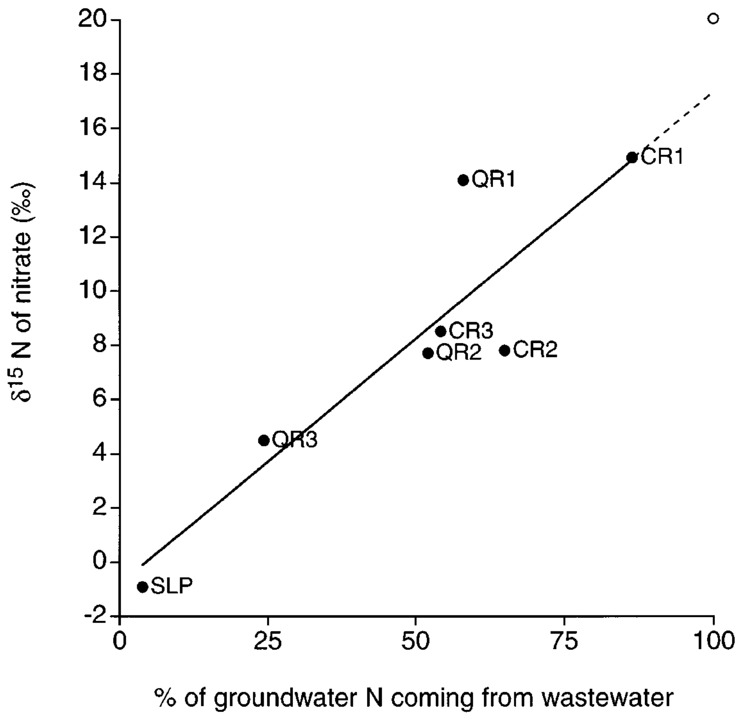


Figure 5. Values of $\delta^{15}N$ of nitrate measured in groundwater from different areas of the Waquoit Bay watershed, vs the percentage of groundwater nitrogen predicted by NLM to have been contributed by wastewater. Codes as in Table 2. Open circle is upper value provided by literature (McClelland and Valiela 1997) for $\delta^{15}N$ of wastewater-derived nitrogen. Dashed line shows extrapolation for data from Waquoit Bay watersheds, which predicts value of 17.3‰ at 100% wastewater. Solid line shows regression through solid points ($y = 0.181x - 0.784$, $F = 22.6^{**}$, $r = 0.91$).

confirmation of our supposition that the model reflects the actual situation in Waquoit estuaries.

The relationship of Figure 5 can be used for a further comparison. The range of values for wastewater-derived nitrate is 10 to 20‰ (Table 1). In Figure 5 we show the position of the upper literature value (20‰) by a open point. Extrapolation to 100% wastewater contribution from our own regression line (dashed line in Figure 5) suggests a value of 17.3, which approximates the published upper limit. These results suggest that the lower values in the range of published values might have actually have resulted from different relative amounts of wastewater-derived nitrate in groundwater sampled in the published reports, rather than inherently from variability in the isotopic signature of wastewater-derived nitrate.

Discussion

The comparisons reported here provide some confidence that the nitrogen loading rates estimated by NLM bear a reasonable semblance to actual conditions in the field. The accuracy of NLM is best at land parcels greater than 200 ha, but even with the smallest parcels the residuals were at most off by a factor of 2. In this paper we did not test the applicability of NLM to even smaller (few ha or less) spatial units, such as would be involved in assessing the loading from specific buildings or developments, but we surmise that such applications would be less desirable than use for larger landscape parcels.

The different accuracy of NLM predictions at different spatial scales might be caused by the minimal degree of spatial information required by NLM. In larger parcels, the complex land use mosaics might cancel out effects of distance from shore of, for example, housing developments or forest tracts, and hence improve prediction of total loads. The effects of specific location may be proportionally more important in small parcels. It would be useful for management purposes, however, to add spatial resolution to NLM so it could be more freely applied to the many cases requiring decisions regarding smaller land parcels.

In regions underlain by unconsolidated coarse sediments, such as Cape Cod, the nitrate in groundwater will be transported into the receiving estuaries. There is much evidence that increased deliveries of wastewater nitrate are responsible for the increasing eutrophication of these coastal waters (Valiela et al. 1992; Valiela et al. 1998), so that monitoring of nitrogen entry to receiving waters has become increasingly needed. The evident linear relationship of δ^{15}N of groundwater nitrate and relative contribution of wastewater nitrogen provides a novel way to assess the increased delivery of wastewater nitrate to receiving estuaries. Annual N loads to coastal lagoons such as Waquoit Bay derive largely from increases in wastewater (McClelland et al. 1997; McClelland & Valiela 1998; Valiela et al. 1997; Valiela et al. 1998). The regression of Figure 5 seems sensitive enough to detect even low contributions of wastewater nitrate, and hence seems appropriate for monitoring of incipient eutrophication of receiving estuaries. Most biological indicators are *post-facto*; the isotope approach offers an exciting new approach for early detection of eutrophication.

The development of NLM, and the verification of its predictions by the results reported in this paper, provide new possibilities to do basic work as well as answer applied questions. Exploration of the model, by sensitivity and other model analysis, can eventually raise questions about our basic understanding of how land use patterns may alter the nitrogen cycle in coupled land/sea ecosystems. We know that there are key couplings that link terrestrial and aquatic coastal ecosystems, and nitrogen transport is among the major mechanisms that are changing these ecosystems (Cole et al. 1993). NLM affords a way to quantitatively assess such transport in some of these changing coastal environments.

Land near the sea is also being developed at a dizzying pace on most shorelines, with consequent increases in nitrogen loads from land to sea. It is a certainty that managers, decision makers, and stakeholders in general will need to know more about nitrogen loads to their estuaries in decades to come, and NLM should be a useful tool for these purposes.

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