ELM, AN ESTUARINE NITROGEN LOADING MODEL: FORMULATION AND VERIFICATION OF PREDICTED CONCENTRATIONS OF DISSOLVED INORGANIC NITROGEN

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Abstract. ELM is an Estuarine Loading Model that calculates mean annual concentration of dissolved inorganic nitrogen (DIN) available to producers in shallow estuaries by considering how different processes modify pools of nitrogen provided by inputs (streams, groundwater flow, atmospheric deposition, N_2 fixation, and regeneration), and losses (burial and denitrification), within components of the estuarine system (bare sediments, seagrass meadows, salt marshes, water column). ELM also considers the effect of flushing rate within an estuary. Its formulation was constrained to minimize demands of data needed to run the model. In spite of simplifications such as the use of loss coefficients instead of functional formulations of processes, and uncertainties in all the terms included in ELM, predictions of mean annual DIN in water were not significantly different than field measurements done in estuaries in Cape Cod, Massachusetts, subject to different rates of nitrogen (N) loading. This verification suggests that, in spite of its simple formulation, ELM captures the functioning of nutrient dynamics within estuaries. ELM may therefore be a reasonable tool for use in basic studies in nutrient dynamics and land/estuary coupling. Because of its simplicity and comprehensiveness in inclusion of components and processes, ELM may also be useful in efforts to manage N loads to estuaries and related management issues.

Keywords: atmospheric deposition, estuaries, eutrophication, fertilizer, nitrogen, nutrient loading, wastewater, watersheds

1. Introduction

Nutrient enrichment of shallow coastal waters creates the eutrophication that is arguably the principal agent of change altering coastal ecosystems world-wide (GESAMP, 1990; National Research Council, 1994; Goldberg, 1995). As in much of the world's shorelines, the bays and lagoons of New England are increasingly subject to elevated N loads from terrestrial sources (Nixon and Pilson, 1983; Lee and Olson, 1985; Nixon *et al.*, 1986; Valiela and Costa, 1988; Culliton *et al.*, 1989; Cole *et al.*, 1993). To investigate how land-derived N loads alter conditions in the receiving waters of the estuarine system of Waquoit Bay in Cape Cod, Massachusetts (Valiela *et al.*, 1992; D'Avanzo *et al.*, 1996; Valiela *et al.*, 1997a), we first developed and subsequently verified the Waquoit Bay Nitrogen Loading Model (NLM) (Valiela *et al.*, 1997b; Heberlig *et al.*, 1997; Kroeger *et al.*, 1999; Valiela *et al.*, 2000)

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as part of the Waquoit Bay Land Margin Ecosystems Research project (WBLMER). NLM quantifies land-derived N loads to shallow estuaries underlain by unconsolidated sands, and with watersheds containing mixes of forest, rural, and suburban land uses. NLM comprehensively considers total N [including nitrate (NO_3), ammonium (NH_4), and dissolved organic nitrogen (DON)] from atmospheric deposition, fertilizer use, and residential wastewater disposal, and keeps track of the fate of N from these sources as the N traverses soils, vadose zones, and travels in aquifers on its way to receiving estuaries.

Evaluation of the effects of land-derived N loads on estuarine ecosystems requires, as a minimal first step, a translation of the N loads into some measure of N supply available to estuarine producers. To do this, we developed an Estuarine Loading Model (ELM) that estimates the average estuarine water concentration of dissolved inorganic nitrogen (DIN) by considering the fate of land-derived N in the estuaries, accounting for additional gains, and losses of N within the estuaries, and including the effect of water mixing and exchange within the estuaries.

ELM is comprehensive in that it includes the major input and output terms, as well as key transformations within the estuary, but its formulation was constrained by two features. First, there was insufficient information on which to base functional expressions for many of the processes affecting N transformations. Second, we wanted to produce a model that could readily be applied by different users to many estuaries. This required that we develop a model that made relatively modest demands for user inputs. To satisfy both constraints we used simple loss coefficients for processes throughout the model. These coefficients might be considered general default expressions that could be replaced, at the user's convenience, with local values if available, and later, in more developed versions of ELM, by functional expressions as they may become available.

To verify the performance of ELM as a model, we statistically compared the calculated mean DIN concentrations to observed DIN concentrations obtained from multi-year data collected from the water column of seven Cape Cod estuaries subject to different N loads from their watersheds. The measured values were taken from information obtained during WBLMER and subsequent work.

2. Methods

2.1. Model formulation

ELM focuses on major features that drive transport and transformations within linked elements of the land/estuary system (Figure 1). The concept is that N derived from watersheds is transported to streams within freshwater reaches of the system, and directly to the estuary itself. Once in the stream, certain losses occur and the remaining N is transported to the saline portions of the system. There, further inputs by direct atmospheric deposition and N fixation take place. Losses by burial

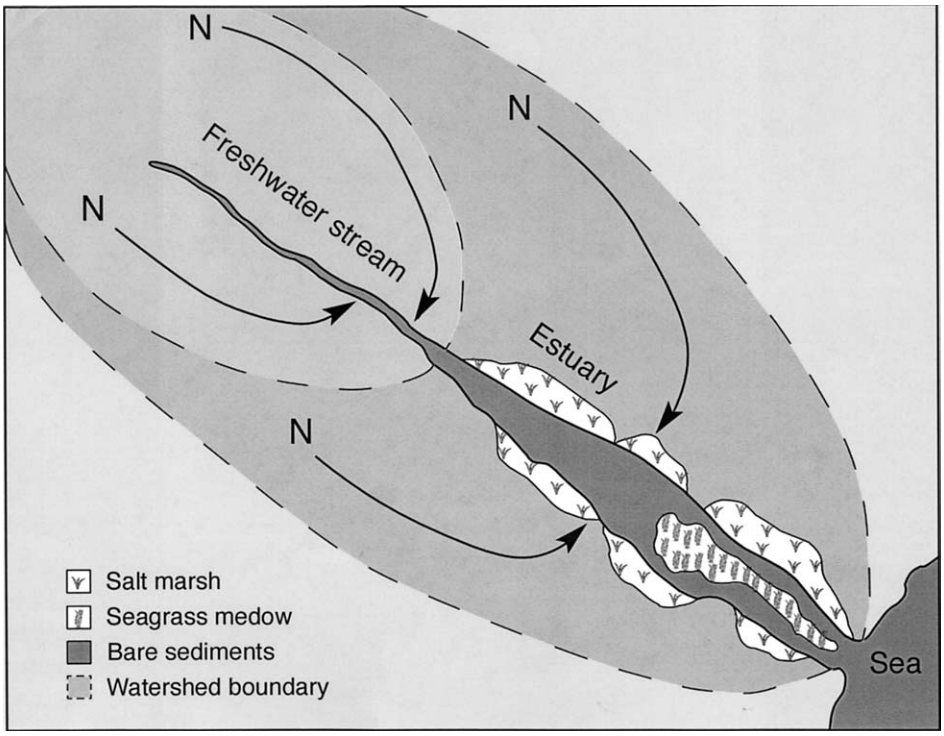

Figure 1. Diagrammatic plan view of a watershed/stream/estuary system such as modeled by ELM. The dashed lines indicate the watershed boundaries for stream and for estuary. 'N' shows nitrogen from land transported to stream and estuary via groundwater flow. The estuarine area is divided into salt marsh, seagrass meadows, and bare sediments.

and denitrification, and other transformations also take place in each of the major habitats within the estuary (bare sediments, seagrass meadows, salt marshes, water column). The pool of DIN that is the net result of these various processes is further affected by the rate of water renewal within the estuary. Below, we discuss each of these processes and components in more detail, and we use a sketch of ELM (Figure 2) to convey the main features of the structure of the model.

2.1.1. *Land-Derived Nitrogen Loads*

ELM requires an input term that describes the magnitude of N entering the receiving water from land to both stream and estuary (Figure 2). We used NLM to furnish these inputs, but loads calculated by any other model or measured data would be suitable. To calculate N loads, NLM requires that the user enter data on locally applicable atmospheric deposition, fertilizer use, and human population, or accepts defaults provided in NLM (Valiela *et al.*, 1997b). From these inputs NLM calculates the amounts of total N from atmospheric, fertilizer, and wastewater sources that are transported through the watershed surface, enter the water table, and course through the aquifer.

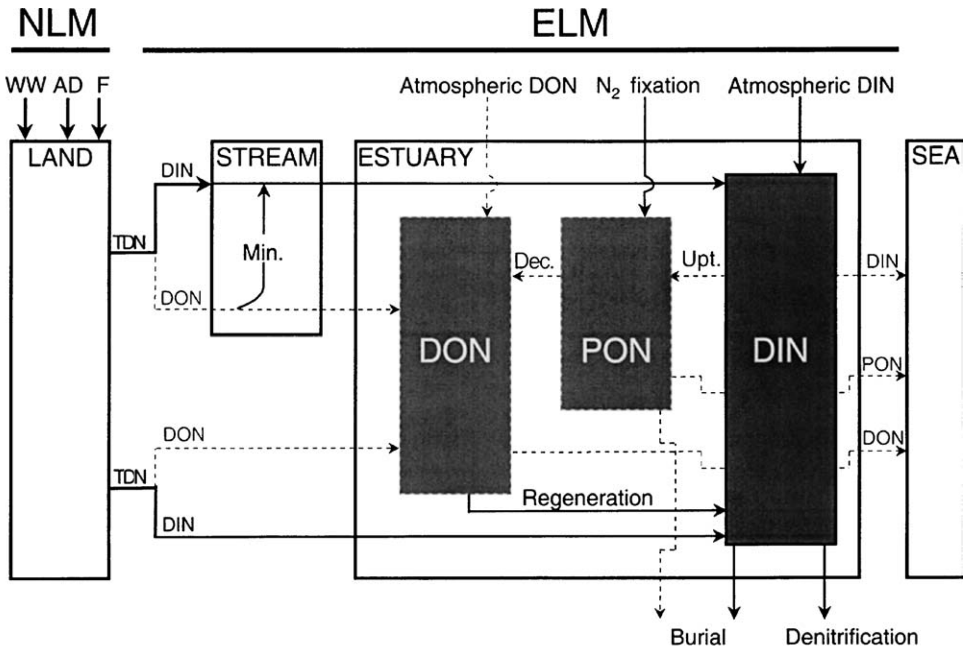

Figure 2. Summary diagram of the structure of ELM. NLM (or other model) supplies the land-derived total dissolved nitrogen (TDN) load to ELM, from wastewater (WW), atmospheric deposition (AD), and use of fertilizers (F). Some of the N in groundwater flows by seeping into freshwater stream reaches of the hydrological system, and some flows directly into the estuarine reaches; both of these flows include some dissolved inorganic nitrogen (DIN), and some dissolved organic nitrogen (DON). ELM partitions the inputs into DIN and DON, and does not track DON or particulate organic nitrogen (PON), or uptake by producers (Upt) and decomposition (Dec), so we show these pools as light gray boxes, and these process pathways as dashed grey lines. This is in contrast to the DIN pool (black) and processes (black) considered by ELM. Part of the DON delivered to streams is mineralized (Min), and ELM treats that portion of DON as an additional source of available DIN. Additional N enters estuaries by N_2 fixation and by direct atmospheric deposition of DIN and DON. Losses of N from the estuaries take place by denitrification and burial in sediments. N within estuaries is actively regenerated, and made newly and repeatedly available as DIN. DIN discharges to sea, and the rates of water renewal are determined in ELM by water residence times and by tidal exchange return. The net N supply within estuaries is expressed as the mean DIN concentration.

Land-derived N entering streams and estuaries consists of NO_3, NH_4, and DON. The fate of these forms of N varies because these compounds differ in biological lability and use. Only a fraction of DON is likely to be labile, and inorganic N forms are much more available for uptake by producers. In addition, there is much more information on the NO_3 and NH_4 dynamics than on DON. In ELM we, therefore, opted to follow the fate of DIN as the form most likely to be of biological significance. This required that in ELM we translate the total N loads from NLM into DIN. To do so, we applied a two-step process to both the stream and estuary N loads (Figure 2).

First, ELM determines the percentage of total dissolved nitrogen (TDN) as DON, in groundwater, by using a relationship determined from surveys of groundwater N concentrations collected from Cape Cod watersheds (Kroeger, 2003; Kroeger *et al.*, submitted). The relationship links the percent of TDN that is DON as a function of population density and flow path lengths (% DON = 236.685–64.519*$\log_{10}$ aquifer path length) -4.698*people per ha^{-1}, $R^2 = 0.81$, $F = 14.597^{**}$ (Kroeger *et al.*, unpublished). ELM uses this expression to estimate the percentage of the land-derived N entering the receiving stream or estuary that is DON, and by difference, estimates the DIN load.

Second, some fraction of the DON is labile, and could therefore be converted to DIN. This fraction of the DON that becomes DIN, therefore, needs to be added to the DIN load calculated in our first step. To estimate the labile fraction, we made use of data from incubation experiments (Kroeger *et al.*, unpublished.) in which fresh groundwater containing N was incubated to measure the loss of DON across time (Figure 3). The results of these incubations provided a relationship from which ELM calculates how much of the DON that is furnished by the external sources might be converted to DIN within the streams and estuaries across the time of

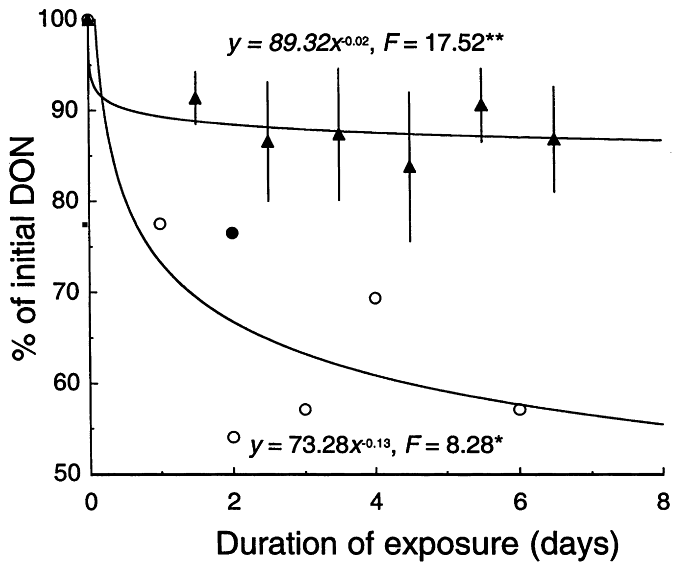

Figure 3. Percentage of initial DON remaining in water during the course of incubation experiments in which groundwater (top line) and atmospheric DON (bottom line) were exposed to degradation by bacterial and phytoplankton communities in estuarine water. Triangles indicate data from groundwater incubation studies of three Cape Cod watersheds (Kroeger *et al.*, unpublished). Circles indicate atmospheric DON incubation data from Seitzinger and Sanders (1999) (open circles) and Peierls and Pearl (1997) (black circle). Our value for day 0 was taken from Seitzinger and Sanders (1999) day 1 data, to account for a lag in microbiological activity at the start of incubations (Seitzinger, pers. comm.).

exposure. This portion of DIN is added here because it is an external contribution to the N supply within the aquatic system. ELM uses the flushing time of the stream or estuary (discussed below) as a way to set the duration of exposure within the water body during which DON is degraded. This requires that the user provide an estimate of flushing time for the specific receiving water body.

2.1.2. *Losses of Nitrogen in Upstream Freshwater Reaches of Estuaries*

Part of the N load from land flows through seepage faces into the freshwater reaches of streams up-gradient from estuaries (Figure 1, Figure 2, 'LAND' component). Travel downstream exposes the land-derived N to losses, and hence we needed to add terms describing this loss in ELM (Figure 1, Figure 2, 'STREAM' component). There is a large literature on nutrient spiraling in streams during travel. Many factors – substrate type, land use, travel time or length of stream, depth, stream order – affect loss of nutrients during downstream transport (Meyer *et al.*, 1981; Richey *et al.*, 1985; Grimm, 1987; Triska *et al.*, 1989; Mulholland *et al.*, 2000; Alexander *et al.*, 2000; Peterson *et al.*, 2002, Seitzinger *et al.*, 2002), and published values for in-stream losses of N vary accordingly.

Rather than delve into the complex in-stream hydro- and nutrient dynamics, we sought a simple way to include in-stream losses in ELM. We compiled published estimates of % loss of N inputs (Table I) for mostly headwater or first-order streams.

TABLE I

Percentage of N inputs that were intercepted by streams in various sites, most of which were small first order streams

River	% N removed	Sources
Neversink, NY, USA	11	Burns (1998)
Neversink, NY, USA	12	Burns (1998)
Gelbaek, Denmark	1	Christensen and Sorensen (1988), Christensen *et al.* (1990)
River Dorn, UK	15	Cooke and White (1987)
Hamilton, New Zealand	21	Cooper (1990)
Purukohukohu, New Zealand	14	Cooper and Cooke (1984)
Purukohukohu, New Zealand	17	Cooper and Cooke (1984)
Sycamore Creek, AZ	5	Grimm (1987)
Duffin Creek, Canada	6	Hill (1983)
Nottawasaga River, Canada	14	Hill (1983)
Raan, Sweden	6	Jansson *et al.* (1994)
Bear Brook, NH US	8	Meyer *et al.* (1981)
Swifts Brook, Canada	20	Robinson *et al.* (1979), Kaushik and Robinson (1976)
Andrews Exp. Forest, OR	27	Triska *et al.* (1984)
Mean ± std. dev.	13 ± 7.2	

We focused on small, first-order streams because first, streams in the Waquoit watershed were small and first order. Second, it is in such water courses where the largest interception of land-derived N inputs take place; higher-order streams would show lower losses (Seitzinger *et al.*, 2002). Length of stream or reach also alters interception (Seitzinger *et al.*, 2002). We examined the possible influence of stream length on N loss and found no discernible pattern within the data available for streams in the Cape Cod watersheds. We therefore concluded that, for simplicity, ELM could use the mean % loss from Table I to calculate in-stream losses of N during transit.

2.1.3. *Direct Nitrogen Deposition on Estuary Surface*

Direct deposition of atmospheric N onto estuaries (Figure 2, 'ESTUARY' component) can be significant (Correll and Ford, 1982; Fisher and Oppenheimer, 1991; Scudlark and Church, 1993; Paerl, 1995; Russell *et al.*, 1998). Much sophisticated theoretical and field work is being done to quantify direct deposition onto water surfaces (Voldner *et al.*, 1986; Owens *et al.*, 1992; Jakeman and Hornberger, 1993; Michaels *et al.*, 1993; Hu *et al.*, 1998).

Because there were insufficient data to support complex general expressions that could produce a model that is widely transportable, we used a simplified expression of direct deposition onto the estuary in ELM. We converted estimates of wet DIN deposition to total DIN deposition by simple extrapolation. For example, for Cape Cod, Lajtha *et al.* (1995) estimated a wet deposition of 4.2 kg DIN ha^{-1} y^{-1}. Bowen and Valiela (2001) estimated a similar value, 4.7 kg DIN ha^{-1} y^{-1}, for DIN deposition toward the end of the 20th century. This latter estimate was derived from an extensive compilation of data on wet deposition to the northeast United States and Maritime provinces of Canada (Bowen and Valiela, 2001). Sheeder *et al.* (2002) report ratios of dry to wet deposition of 0.35–0.67 from U.S. national surveys. We used extensive data reviewed in Valigura *et al.* (1996) to calculate that dry DIN deposition equals 44% of wet deposition, so that wet plus dry deposition of DIN reaches 6.7 kg DIN ha^{-1} y^{-1} as a maximum value. The calculation for dry deposition probably overestimates actual values, since the relatively flat water surface is less likely to have the same capacity for uptake of atmospheric particles and aerosols evident for land surfaces. Nevertheless, we opted for our simple approach because wet deposition data are available for most areas of the world, so that use of this extrapolation makes it possible to apply ELM to a broad geographic range of sites. To allow ELM to quantify direct deposition of atmospheric DIN onto the surface of estuaries, users therefore need to provide locally relevant estimates of wet deposition, or use the default value available in ELM (4.7 kg DIN ha^{-1} y^{-1}).

So far, we have dealt with deposition of DIN; atmospheric deposition also includes DON, a labile fraction of which may be mineralized to NH_4 (Peierls and Pearl, 1997; Seitzinger and Sanders, 1999). To estimate the DIN released from atmospheric DON, we first needed to determine the quantity of DON, and then assess the fraction of DON that might be mineralizable to DIN. The proportion of

DON relative to TDN from atmospheric deposition on Cape Cod is 51.3% (Valiela *et al.*, 1978; Valiela and Teal, 1979). Cornell *et al.* (1995) found that, for several coastal locations around the world, DON varied from 21–84% of TDN, with a mean of 40%. In ELM we considered that deposition of DON was half the deposition of TDN (6.7 kg DON ha^{-1} y^{-1}).

To estimate the fraction of atmospheric DON likely to be mineralized within a given time of exposure in the water of the estuary, ELM uses the same procedure applied to the case of groundwater DON (Figure 3). ELM requires input of an estimate of flushing times in the estuary of concern, from which it estimates the labile atmospheric DON, then adds the resulting mineralized DIN to the amount of N deposited directly as DIN.

So far we have defined how ELM estimates delivery of direct DIN deposition to estuary surfaces on a per unit area basis. To estimate the total per-estuary load from direct atmospheric deposition of N, the user needs to input the surface area of the estuary at mean tide height. From this information ELM then calculates the total DIN from atmospheric sources delivered directly to the estuary surface. Streams usually have much smaller areas than estuaries, and hence we ignored deposition on streams in ELM.

2.1.4. *Denitrification*

Losses of NO_3 via denitrification may occur in most environments. In ELM we included losses by denitrification in wetlands and subtidal sediments, which we suspect constitute the two largest NO_3 loss terms within estuaries (Figure 2, 'ESTUARY' component). We lacked data with which to estimate water column denitrification in the estuaries, so to some extent ELM underestimates losses via denitrification.

Methods to measure denitrification have been discussed extensively, and published rates differ markedly. For the compilations discussed below we included estimates made by several methods. Our review of published rates indicated that the spatial variation in denitrification rates was large enough that biases based on differences in methods were not detectable (Table II). For ELM, we therefore opted to simply include all data we found and calculated an overall mean for denitrification in salt marshes and in subtidal sediments.

2.1.4.1. *Denitrification in Salt Marshes.* Many shallow estuaries and lagoons in temperate latitudes include a fringe of salt marsh between land and open water, and denitrification rates are high in these marshes (Valiela and Teal, 1979; Seitzinger, 1988). Significant portions of the land-derived N loads are intercepted within fringing salt marshes (Valiela and Cole, 2002), particularly since much of the land-derived N is in the form of NO_3. We supposed that denitrification in salt marshes did not depend on land-derived N loading rates from watersheds, because denitrification rates did not differ among salt marsh plots enriched with different doses of N fertilizer (Kaplan, 1977).

TABLE II

Compilation of published rates of denitrification in subtidal sediments of many coastal sites, done by different methods

Method	Estuary	Denitrification rate (kg N ha^{-1} y^{-1})	References
^{15}N	Norsminde Fjord, Denmark	29.0	Nielsen *et al.* (1995)
^{15}N	Thames Est., UK	219.5	Trimmer *et al.* (2000)
^{15}N	Patuxent River, MD	38.8	Twilley and Kemp (1987), Boynton *et al.* (1995)
	Mean ± se for ^{15}N:	95.8 ± 61.9	
Acetylene	Chesapeake Bay, MD	49.4	Kemp *et al.* (1990), Boynton *et al.* (1995)
Acetylene	Narragansett Bay, RI	54.6	Nixon *et al.* (1995), Nixon (1996)
Acetylene	Delaware Bay, DE	123.0	Seitzinger (1988), Nixon (1996)
Acetylene	Great Bay, NY	13.5	Slater and Capone (1987), Seitzinger (1988)
Acetylene	Choptank River, MD	38.4	Twilley and Kemp 1987, Boynton *et al.* (1995)
	Mean ± se for acetylene reduction:	55.8 ± 18.2	
N flux	Guadalupe Est., TX	44.8	Longley (1994), Nixon (1996)
N flux	Columbia River, WA	49.5	Devol and Christensen (1993)
N flux	Boston Harbor, MA	127.4	Giblin *et al.* (1993), Nixon (1996)
N flux	Waquoit Bay, MA	135.0	LaMontange and Valiela (1995)
N flux	Boston Harbor, MA	75.4	Nowicki (1994)
N flux	Nauset Marsh Est., MA	28.0	Nowicki *et al.* (1999)
N flux	Ochlockonee Bay, FL	90.8	Seitzinger (1987), Seitzinger (1988)
N flux	Narragansett Bay, RI	72.4	Seitzinger *et al.* (1984), Seitzinger (1988)
N flux	Vilhelmsborg, Denmark	45.0	Seitzinger *et al.* (1993)
N flux	Guadalupe Est., TX	49.0	Yoon and Benner (1992)
N flux	Neuces Est., TX	64.0	Yoon and Benner (1992)
N flux	Trinity-San Jacinto Est., TX	45.0	Zimmerman and Benner (1994)
	Mean ± se for N flux:	68.9. ± 9.7	
	Mean for all methods ± se:	69.6 ± 10.9	

To include in ELM an estimate of loss of nitrate by denitrification in salt marshes, we compiled measurements of denitrification done in different locations (Valiela and Cole, 2002); those values were largely obtained from sediments supporting stands of salt marsh vegetation. The mean rate of denitrification in these vegetated sediments was 57.1 kg N ha^{-1} y^{-1}, with a range of 9.5 to 120 kg N ha^{-1} y^{-1}. Coastal wetlands include habitats other than vegetated areas (algal mats,

TABLE III

Measured mean annual dissolved inorganic nitrogen concentrations (± s.e.) for several estuaries in Cape Cod, Massachusetts (WBLMER, unpublished data)

Estuary	DIN (μM)
Childs River	12.1 ± 2.4
Quashnet River	5.3 ± 2.6
Jehu Pond	3.0 ± 1.1
Hamblin Pond	2.2 ± 0.1
Sage Lot Pond	1.9 ± 1.3
West Falmouth Harbor	4.5 ± 0.4
Green Pond	4.5 ± 0.2

mud and sand flats, intertidal creeks and creek banks), and these need inclusion. Valiela and Teal (1979) reported that denitrification for the entire Great Sippewissett salt marsh ecosystem, including diverse habitats, was 90 kg N ha^{-1} y^{-1}, which we used as an overall value for denitrification for salt marsh areas in ELM.

2.1.4.2. *Denitrification in Subtidal Estuarine Sediments.* Measured rates of denitrification in subtidal sediments vary greatly (Table II), and the rates may or may not be influenced by the N load entering the systems. Measurements of denitrification rates in bare sediments of Waquoit estuaries showed no notable differences among estuaries that received widely different land-derived N loads (LaMontagne and Valiela, 1995). We used 70 kg N ha^{-1} y^{-1} (the mean value from Table II) as the annual denitrification rate in ELM, if local values are not available, users of ELM may use this as a default value.

2.1.5. *Nitrogen Fixation*

Nitrogen fixation in estuaries (Figure 2, 'ESTUARY' component) may take place in fringing salt marshes, within vegetated and bare estuarine sediments, and in the water column. We estimated rates of fixation in each of these environments from published values, and had ELM apply the literature values to each estuary by multiplying the rates by the area of each of these environments within each estuary. Gains of fixed N are added by ELM to the annual amount of total N entering the estuarine volume. ELM works on annual time steps; at this scale, we assume that there is, on average, no accumulation or net storage of fixed N. With this supposition we allow ELM to convert the annually fixed N into NH_4, which is the form of N released by the fixers. Below we describe how we formulated ELM to include N fixation in each of the subsystems.

2.1.5.1. *Nitrogen Fixation in Salt Marshes.* Nitrogen fixation is quite active in salt marshes. In Great Sippewissett salt marsh Valiela and Teal (1979) reported an average of 67.8 kg N fixed ha^{-1} y^{-1}. We used this value as the default in ELM; it is within the high part of the range reported for salt marsh sites in Nova Scotia, Southern England, and Long Island, NY (cf. Table II in Carpenter *et al.*, 1978). Users of ELM need to supply area of salt marsh habitat for the estuary of concern.

2.1.5.2. *Nitrogen Fixation in Subtidal Sediments.* Howarth (1988) compiled estimates of N fixation rates in bare estuarine sediments within many coastal sites. The average of the 15 values for bare sediments was 2.8 kg N fixed ha^{-1} y^{-1}. Average N fixation in four temperate sites with eelgrass vegetated sediments were higher (12 kg N fixed ha^{-1} y^{-1}; McGlathery *et al.*, 1998). ELM uses these values, and calculates total inputs of fixed N by multiplying the rates by the area of bare sediments or eelgrass beds. Information on areas of seagrass beds and bare sediments for the estuary under consideration has to be provided by the user as an input for ELM.

2.1.5.3. *Nitrogen Fixation in Water Columns.* Howarth (1988) compiled values of planktonic N fixation rates in estuarine water columns in four temperate coastal estuaries. The average rate for these sites was 6.6 kg N fixed ha^{-1} y^{-1}; we used this mean as the default value for ELM.

2.1.6. *Burial*

Burial of DIN may take place within estuaries (Figure 2, 'ESTUARY' component), and rates differ between different estuarine habitats. Below we review data on burial of N in salt marshes and subtidal sediments.

2.1.6.1. *Burial in Salt Marsh Sediments.* Some of the land-derived and estuarine N is buried within aggrading sediments of fringing salt marshes. Results from ^{15}N tracer experiments done in Cape Cod suggested that about 39 kg N ha^{-1} y^{-1} were buried in salt marsh sediments (White and Howes, 1994b). Valiela and Teal (1979) provided data from which Valiela and Cole (2002) calculated a burial rate of 41 kg N ha^{-1} y^{-1}. These values are smaller than the 60–230 kg N ha^{-1} y^{-1} measured in sediments of marshes in the Gulf of Mexico (Smith *et al.*, 1985). We used a value of 40 kg N ha^{-1} y^{-1} as an estimate for burial of N in ELM, but locally applicable accretion data should be used, if available, for application to other estuaries. Users need to furnish areas of salt marsh so that ELM can convert per-unit area rates to whole-estuary burial estimates.

Nitrogen burial in marsh sediments may occur as different forms of N (NH_4, DON or particulate N) (Smith *et al.*, 1985; White and Howes, 1994a). Nitrate is unlikely to make much of a contribution to the buried N pool in anaerobic sediments. The variety of forms of buried nitrogen imposes an additional problem for the calculation of concentrations of DIN in the water above. White and Howes (1994a) reported that 10% of injected $^{15}NH_4$ was detected as NH_4, presumably at long-term steady state, buried at depth in salt marsh sediments. ELM calculations, therefore, assume that only 10% of the N buried in salt marsh sediments is DIN, and hence only 10% is removed from the pool of DIN in water overlying marsh sediments.

2.1.6.2. *Burial in Subtidal Sediments.* The rates at which N is buried in subtidal sediments vary greatly among estuaries. Burial rates depend on local differences in sedimentary accretion as well as the amount of organic matter buried. We lacked estimates from many sites with which to generate an overall burial rate. Instead, we calculated burial rates of nitrogen in estuarine subtidal sediments of Waquoit estuaries from vertical profiles of % nitrogen in sediment sections, and sediment accretion data (Legra *et al.*, 1998; Safran *et al.*, 1998). The average % nitrogen in each cm of the top 10 cm of dry sediments was multiplied by an accretion rate (0.46–0.55 cm y^{-1}) and and the product converted to kg N ha^{-1} y^{-1}. Resulting N burial rates for three different estuaries of the Waquoit estuarine system were 46.0, 47.4, and 46.5 kg N ha^{-1} y^{-1}, respectively, and the mean burial rate (47 kg N ha^{-1} y^{-1}) was used in ELM. These rates of burial were applied to the entire subtidal estuary area, including bare sediment and eelgrass meadows. The ELM calculation also considers that 20% of the N buried in sediments is likely to be DIN, as was the case in Potomac River estuary sediments (Simon and Kennedy, 1987).

For application of ELM to other estuaries it may be best to use local burial rates if available, because the default values used in ELM may differ widely from those in other systems. Smith *et al.* (1985), for example, calculated N burial rates of 61–112 kg N ha^{-1} y^{-1} in Atchafalaya sediments, rates considerably larger than those of the Waquoit estuaries.

ELM calculates burial of N in salt marsh and estuary sediments, multiplies the per area unit rates by the area of salt marsh and subtidal sediments (supplied by the user) within the estuary in question, adds losses in the two sediment types, and subtracts the sum from the annual inputs of DIN into the estuary.

2.1.7. *Regeneration*

Inclusion of regeneration (Figure 2, 'ESTUARY' component) in a model that focuses on inputs and outputs might be thought unusual. For most other processes included in ELM, we have a reasonable data set to estimate rates at annual time steps, and we can safely assume that across a year, the uptake is nearly the same as the losses [which is why in ELM we did not consider plant uptake and release of N (Figure 2, light gray boxes and dashed lines)]. The cycle of re-use of 'old' N taken up by producers and consumers occurs at time scales considerably shorter than annual time steps. Regeneration thus repeatedly furnishes available DIN for uptake into the food web throughout the annual time step; this forces inclusion of regenerated DIN as part of the pool of available N. The amounts of DIN thus made newly available are large enough to make it necessary to consider regeneration as an 'input' of available DIN, in spite of the logical quandary this represents. An additional complication is that empirical measurements of regeneration in part include the DIN released through decay of N acquired via N fixation, which we treat separately in ELM. To some extent, we are double accounting here, but the data available are simply inadequate to make such fine distinctions.

In ELM we assumed that regeneration provides NH_4. Decay of organic matter releases NH_4 and DON and, as already noted, part of the DON is mineralized to NH_4. Both DON and NH_4 are then released to overlying waters. We concentrated on release of NH_4 because much more is known about this process than on releases of DON. In the few instances where both were measured, DON release was considerably smaller than NH_4 release. Burdige and Zheng (1998) measured release rates that amounted to −1 to 14.5% DON relative to DIN, and Hopkinson (1987), Nixon and Pilson (1983), and Burdige and Zheng (1998) reported that DON made up only 3–13% of TDN flux. One study (Enoksson, 1993) reported a value of about 40%, which seems out of line with the bulk of the data. We therefore assumed in ELM that DON release would be low compared to regeneration of NH_4. Regeneration of DIN from organic N occurs everywhere in ecosystems, but in ELM we focus on the regeneration that takes place in salt marshes, subtidal sediments, and in the water column.

2.1.7.1. *Regeneration in Salt Marshes.* Release of DIN from salt marsh sediments was about 2 g N m^{-2} y^{-1} in a Cape Cod salt marsh (20 kg N ha^{-1} y^{-1}; White and Howes, 1994a). ELM uses this Cape Cod estimate as a default, and multiplies this rate of DIN regenerated from sediments by the area of salt marsh in each estuary (provided by the user).

2.1.7.2. *Regeneration in Subtidal Sediments.* There are many studies that evaluate rates of regeneration in subtidal shallow sediments. We compiled values of regeneration of DIN from sediments in various shallow estuaries from the literature, and found an evident seasonal pattern (Figure 4). From this seasonal description we calculated an average annual value for regeneration of NH_4 from sediments (Figure 4), a value that translates into 114 kg N ha^{-1} y^{-1}, which ELM applies to the total subtidal sediment area (supplied by the user) in each estuary.

For ELM we did not make the rate of regeneration of NH_4 depend on land-derived nitrogen loads for two reasons. First, measurements of NH_4 release from the sediments of different Waquoit estuaries did not differ significantly, in spite of clearly different land-derived loads entering these estuaries (LaMontagne, 1996). Second, in spite of the different loads to these estuaries, the concentrations of NH_4 in the water column did not differ accordingly (Valiela *et al.*, 2000).

2.1.7.3. *Regeneration in the Water Column.* Rates of regeneration of DIN in water columns of shallow estuaries are likely to be significant, but data are few. Regeneration of N in the water column of Narragansett Bay amounted to approximately 40% of the regeneration carried out within sediments (Nixon, 1981; Nixon *et al.*, 1986;

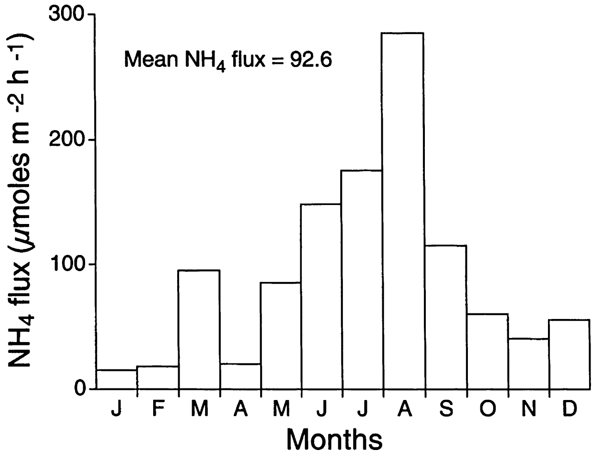

Figure 4. Measured rates of regeneration (as ammonium flux) from sediments compiled from published papers. Data from Blackburn (1979), Short (1983), Seitzinger (1988), Valiela (1995), LaMontagne (1996), Rysgaard *et al.* (1996) and Twilley *et al.* (1999).

Nixon *et al.*, 1996). For ELM we considered as a default value, that regeneration in the water column was equivalent to 40% of regeneration in sediments. There are so few data on this aspect that changing this input may not be feasible for most estuaries.

2.1.8. *Flushing Times, Water Volumes, and Exchanges*

The rate of water turnover within estuaries can influence biogeochemical transformations (Nielsen *et al.*, 1995), as well as the availability of N to producers. To determine the concentration of nutrients in the water column, ELM distributes the net annual DIN load to the estuary into the net volume of water that passes through the estuary within the span of a year. ELM calculates this volume from the water volume at mean high tide, and flushing time of water within the estuary (T_f, see below). The user must furnish both of these values.

As already noted, flushing times are also used by ELM in calculation of the fraction of DON that might be mineralized (discussed in Sections 2.1.1. and 2.1.3). It is also used to estimate water volumes exchanged (Section 2.1.3); below we detail this latter application of T_f in ELM.

2.1.8.1. *Flushing Time Calculation.* The transit of water through estuaries is a topic that has received considerable discussion; it is a topic that appears initially simple, but becomes increasingly complicated under further examination. The concept has been variously referred to as residence, retention, transit, and turnover times (Ketchum, 1951; Dyer, 1973; Zimmerman, 1976; Isaji *et al.*, 1985; Geyer and Signell, 1992; Asselin and Spaulding, 1993; Hearn, 1995; Vallino and Hopkinson, 1998), and definitions and clarifications of these terms, and their application, have been added by Oliveira and Baptista (1997), Lukatina (1998), Geyer *et al.* (2000), and Monsen *et al.* (2002).

Residence time is the time it takes for a water parcel that has entered a water body at a specific location, to leave that water body (Dronkers and Zimmerman, 1988; Monsen *et al.*, 2002). Each parcel of water can be said to have a specific age determined from the time of entry to the water body. Residence times and water parcel ages thus may differ at different places within the water body, depending on the point of entry, where in the water body a measurement is made, and where the release point may be (Monsen *et al.*, 2002).

More relevant for our purposes is flushing time (Sanford *et al.*, 1992; Geyer *et al.*, 2000; Monsen *et al.*, 2002), which refers to the exchange of water out of an entire defined water body. The classic approach to estimate flushing time (T_f, in days) is the tidal prism method, $T_f = (V + P)/P$, where P is the intertidal volume (tidal prism) and V is the low tide volume (In ELM the units of volume are set in liters, but can be easily changed as can any other units in the calculation). This calculation assumes that the estuary is completely mixed, that freshwater flow into the estuary is small relative to tidal exchange, that the coastal water body receiving export from the estuary is large, and that the estuary is in steady state relative to the tidal regime. Violations of these assumptions might lead to under- and overestimations of T_f (Pilson, 1985; Lukatina, 1998; Monsen *et al.*, 2002).

The tidal prism method ignores that portion of the tidal volume that exits at each ebb tide and reenters the estuary in the following flood (Dyer, 1973; Callaway, 1981), even though up to 50% (Sanford *et al.*, 1992) of ebbing water may return to an estuary after the tide turns. To the extent that the return flow takes place, nutrients and biota in that return flow volume have a longer time in which to take part in biogeochemical transformations within the estuary. A tidal return of 0.5 of the ebb volume has been suggested as a default value in the absence of local data (US EPA, 1985); this value seems rather high as a mean, considering other estimates (Lukatina, 1998; Sanford *et al.*, 1992).

More sophisticated methods to estimate T_f involve considerably more demanding models, such as finite element two- and three-dimension hydrodynamic and scalar transport models (Isaji *et al.*, 1985; Asselin and Spaulding, 1993; Casulli and Catana, 1994; Gross *et al.*, 1999). These models require complex computations, expertise, and resources unavailable in the vast majority of settings in which ELM may be used. To retain a simple approach and keep ELM broadly applicable, we included the simple tidal prism method in ELM. As a precaution, however, we compared flushing times estimated by the tidal prism method with estimates obtained by a more complicated hydrodynamic model. Furthermore, we assessed the implications of tidal water return for the T_f calculations based on the simple tidal prism formulation in ELM.

2.1.8.2. *Tidal Prism Calculation of T_f.* For ELM we used a version of the tidal prism method derived from Sanford *et al.* (1992), $T_f = [V_{HT}/((V_{HT} - V_{LT})*$

$(1-b))]T_{TP}$, where V_{HT} is the estuary volume at high tide, V_{LT} is the estuary volume at low tide, b is the tidal water return, and T_{TP} is the area of open water multiplied by the tidal range. We selected this version because it includes possible effects of tidal water return. Since we lacked data on tidal water return for the Cape Cod estuaries, we assessed the influence of return flows on T_f by simulations in which flushing times for Waquoit estuaries were assumed to be 0, 10, 20, 30, 40, and 50% of tidal flow returns.

To calculate volumes for each estuary in the Waquoit Bay system we used data on areas of each estuary obtained from aerial photos. Water volumes for each estuary were calculated from hypsometric curves obtained from extensive bathymetric surveys (WBLMER unpublished data).

2.1.8.3. *Hydrodynamic Model Calculation.* To assess the appropriateness of the simple tidal prism estimates of T_f, we obtained T_f values using a simplified version of a finite difference, vertically integrated two-dimensional hydrodynamic model developed for WBLMER. This model subdivided the estuaries into many finite spatial elements (defined in two or three dimensions), and used inputs of local bathymetric and tidal data to calculate the motion of water from cell to cell on the basis of fluid mechanics equations that describe the hydrodynamics of the system. Such a two-dimensional finite difference model was developed for Waquoit Bay by Tatsu Isaji of Applied Science Associates, Narragansett, RI (unpublished, WBLMER). This hydrodynamic model is similar in structure to models developed by M. Spaulding and colleagues at the University of Rhode Island (Isaji *et al.*, 1985; Asselin and Spaulding, 1993). James N. Kremer of the University of Connecticut, Avery Point, simplified the Isaji model by aggregating the many small elements of the version into fewer and larger boxes. Comparisons of model runs showed that the exchanges among boxes in the Kremer modification closely reproduced the hydrodynamics of the estuaries as depicted by the Isaji model (J.N. Kremer, unpublished results).

We used the Kremer version of the model to simulate a dye tracing experiment, and calculated dye concentrations within each of the elements of the estuaries for successive tidal periods. We estimated the T_f for water in the estuaries as the time needed to lower the dye concentration by an exponential factor e (Van de Kreeke, 1983), based on plots of the slopes of dye concentration versus time, in each element.

2.2. Verification of ELM

To verify ELM predictions of mean annual concentrations of DIN, we compared its estimates of annually averaged DIN concentrations in estuaries to means calculated from monthly measurements of DIN in the estuaries by the WBLMER project in Waquoit Bay (Valiela *et al.*, 1992; Valiela *et al.*, 1997b; Valiela *et al.*, 2000). The large set of data collected by WBLMER include measurements of nitrate, ammonium, and DON in surface and near-bottom samples in five stations within each estuary of Waquoit Bay, repeated monthly for four years (Valiela *et al.*, 2000). We used annual averages (Table III) to estimate mean DIN concentrations for each estuary.

Measured and modeled values were in all respects independently obtained. None of the Waquoit watershed and bay data used in the formulation of ELM were used to calculate the measured DIN concentrations. Comparison of modeled versus measured DIN concentrations were assessed by regression methods.

3. Results and Discussion

3.1. Verification

Estimates of mean annual DIN concentrations calculated by ELM were statistically indistinguishable from values measured in Waquoit estuaries (Figure 5). A linear regression fitted to the points was highly significant, and did not differ significantly from the 1:1 line of perfect fit (Figure 5), as determined by a t-test of the slopes (Sokal and Rohlf, 1995). Estimates of DIN concentrations produced by ELM seem to sufficiently capture the dynamics of nitrogen in these watershed/estuary systems. Thus ELM may be a useful tool for research and management, since it can link land use on watersheds to resulting concentrations of DIN in the waters of receiving estuaries.

To get the results of Figure 5, we used the modified tidal prism method, and assumed no tidal return, to estimate flushing times. We made this decision after comparing the tidal prism-based values versus values obtained from the

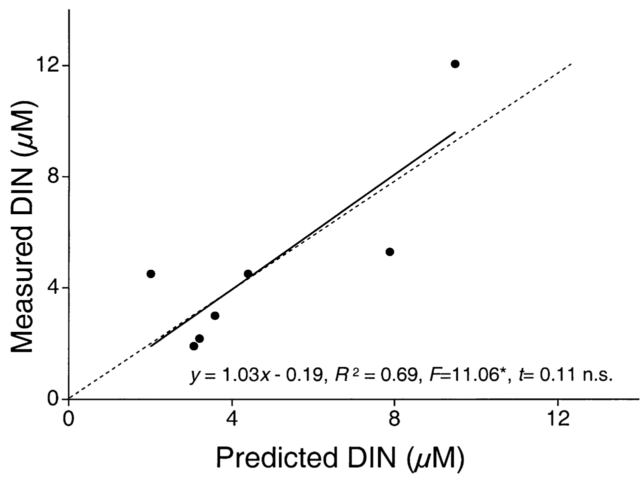

Figure 5. Comparison of mean annual concentrations of DIN predicted by ELM and measured DIN concentrations in the water column of seven Cape Cod estuaries.

hydrodynamic calculations (Figure 6). The simulations in which we set tidal water return at 0, 10, or 20%, showed no significant differences in the regression fit to the points versus the 1:1 line of perfect fit (Table IV). When we set tidal return at 30, 40, and 50% of the volume of the tidal prism, the regressions were significantly different from the line of perfect fit (Table IV). Mean annual DIN concentration calculated using returns of 0, 10, and 20% did not therefore differ significantly from the 1:1 line of perfect fit. These results suggested that if tidal returns were relatively small, the simpler tidal prism estimates with no tidal return would be adequate. Unfortunately, there are too few data to evaluate tidal returns for virtually all estuaries; as a default, we therefore used 0% return in ELM, and applied the tidal prism method as needed. This ancillary result suggests that the simple tidal prism method may be a suitable approach in estuaries where tidal return is a minor feature.

ELM predictions of mean annual concentrations of DIN in the Waquoit Bay estuaries consistently increased, as NLM-predicted modeled annual land-derived N load entering the different estuaries increased (Figure 7). This consistent relationship fits well with earlier demonstrations that ^{15}N of groundwater, estuary water, and estuarine producers and consumers unambiguously showed a direct relationship between N delivered by the specific land use mosaic on each watershed and the N in the estuaries (McClelland *et al.*, 1997; McClelland and Valiela, 1998a; McClelland and Valiela, 1998b; Valiela *et al.*, 2000).

The comparison between modeled and measured concentrations, and the demonstrated relationship of land-derived loads to in-estuary DIN concentrations supports the argument that ELM provides a useful tool to assess how watershed land use affects water quality in receiving estuaries.

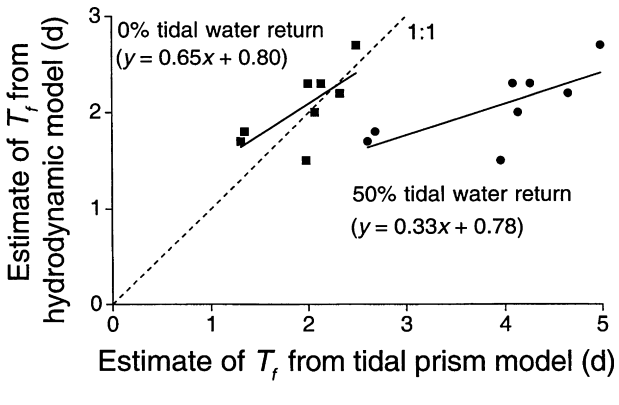

Figure 6. Relationship of flushing times for eight Cape Cod estuaries estimated by the tidal excursion and by a hydrodynamic model, for simulations in which we allowed 0 and 50% of the tidal water exported to return into the estuaries during the next tide. The regressions for other % returns were intermediate between the two extremes, and are not shown. The F and t values for all the regressions in the simulation are shown in Table IV.

TABLE IV

F values calculated for the regression tidal prism and hydrodynamic model estimates of flushing time for eight Cape Cod estuaries assuming different % tidal returns. The *t* value refers to comparisons of the slope to the 1:1 line of perfect fit. Points of tidal return of 0 and 50% are shown in Figure 6

% Tidal water return	*F* value	*t* value
0	6.36*	1.34 n.s.
10	6.36*	1.77 n.s.
20	6.36*	2.31 n.s.
30	6.36*	3.00*
40	6.36*	3.92**
50	6.36*	5.21**

3.2. Uncertainty of estimates of DIN

ELM furnished a reasonable fit to actual measurements, in spite of the simplified expressions, the many terms with associated uncertainties, and the many untested assumptions regarding various inputs, losses, and pools of N, and about how these features articulate together in the estuaries. Uncertainty characterized all the steps

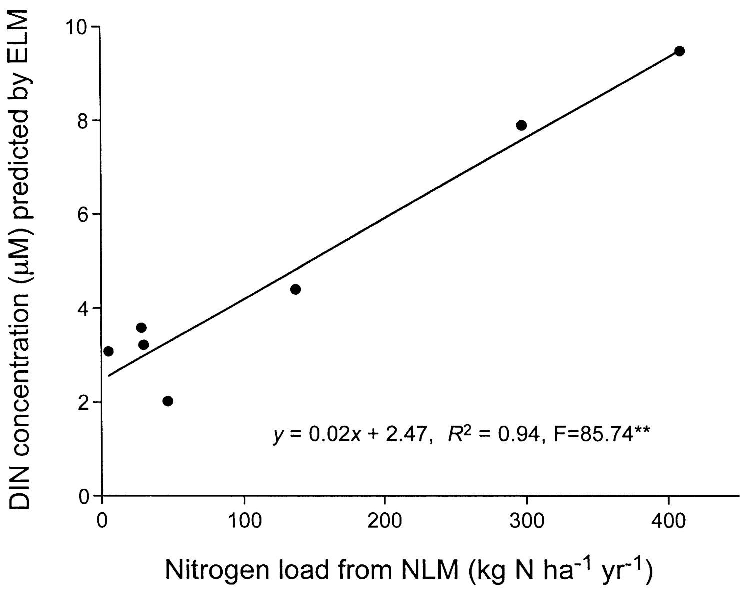

Figure 7. Comparison of mean annual DIN concentrations in the water column of seven estuaries of Cape Cod predicted by ELM, and mean annual nitrogen load to the estuaries, predicted by NLM.

taken to construct ELM; at every stage we made simplifications, best guesses, and reasonable assumptions.

The relative uncertainty in estimates of water column DIN concentrations estimated by ELM was relatively small (Table V). ELM estimated mean DIN concentrations with an associated uncertainty of less than 10 or 30 %, on the basis of the standard error or standard deviation relative to the mean. We estimated the uncertainty on the basis of information available on variations in 17 out of 22 terms within ELM. The uncertainties associated with ELM estimates are likely higher, because we lacked uncertainty measures for five terms within ELM (Table V), and because in any application to other estuaries, the user will provide values for 16 input terms, each of which would have some error. These errors would be present in any other approach; here we have furnished estimates of uncertainty within the model whenever possible. Users of ELM will have to consider their results in the context of both the estimates of Table V as well as the error inherent in the input data applied.

3.3. Requirements for use of ELM

The first requirement to use ELM is an estimate of nitrogen loading from the watershed. Use of NLM for that purpose requires a delineation of the watershed of the particular water body of interest, and a description of the land use mosaic on the watershed, including a few general types of land covers (natural vegetation, turf, impervious surfaces, agriculture, number of residences, occupancy rates per dwelling, and knowledge of the number of on-site septic systems). NLM required other input data, which users may either enter as local data for the specific site of application, or opt to allow NLM to use default values for these variables (Valiela *et al.*, 1997b).

Users of ELM will also need to provide areas of open water, salt marsh, and eelgrass meadows within the estuaries of interest. In addition, average depth and tidal range will be needed for a calculation of flushing time by ELM.

TABLE V

Number of terms required as inputs to ELM, number of terms within ELM, and coefficients of variation propagated from terms within ELM. The uncertainty of the estimates are expressed as standard deviation (sd) or standard error (se) as a % of mean DIN concentrations

	Input terms to ELM	Terms within ELM	Based on (sd/mean) × 100	Based on (se/mean) × 100
Total number of terms in ELM	16	22	–	–
No. of terms with available estimates of uncertainty	–	17	29.8%	8.3%
No. of terms with no estimates of uncertainty	–	5	–	–

The good match between modeled and measured estimates of concentrations of DIN (Figure 5), the relatively modest uncertainties (Table V) as well as the relative simplicity of the requirements for input data make a case for the ready use of ELM for many management applications. The predicted DIN concentrations could further be readily related to responses of phytoplankton, macroalgae, seagrasses, as well as other food web components. The combination of NLM and ELM could also be used to carry out simulations to predict the consequences of remediation of land-derived loads by implementation of management options. Finally, ELM may also be used to assess the relative importance of the various processes that mediate the fate of anthropogenic nitrogen in shallow, near-shore estuaries with known inputs of external loads.

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