

A review of land–sea coupling by groundwater discharge of nitrogen to New England estuaries: Mechanisms and effects

J.L. Bowen¹, K.D. Kroeger², G. Tomasky, W.J. Pabich³, M.L. Cole⁴,
R.H. Carmichael⁵, I. Valiela^{*}

Boston University Marine Program, Marine Biological Laboratory, Woods Hole, MA 02543, USA

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Abstract

Hydrologists have long been concerned with the interface of groundwater flow into estuaries, but not until the end of the last century did other disciplines realize the major role played by groundwater transport of nutrients to estuaries. Mass balance and stable isotopic data suggest that land-derived NO₃, NH₄, and dissolved organic N do enter estuaries in amounts likely to affect the function of the receiving ecosystem. Because of increasing human occupancy of the coastal zone, the nutrient loads borne by groundwater have increased in recent decades, in spite of substantial interception of nutrients within the land and aquifer components of watersheds. Groundwater-borne nutrient loads have increased the N content of receiving estuaries, increased phytoplankton and macroalgal production and biomass, decreased the area of seagrasses, and created a cascade of associated ecological changes. This linkage between land use and eutrophication of estuaries occurs in spite of mechanisms, including uptake of land-derived N by riparian vegetation and fringing wetlands, “unloading” by rapid water removal, and direct N inputs to estuaries, that tend to uncouple the effects of land use on receiving estuaries. It can be expected that as human activity on coastal watersheds continues to increase, the role of groundwater-borne nutrients to the receiving estuary will also increase.

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1. Background

Awareness of the importance of transport of materials by freshwater flow through rivers and streams to receiving coastal waters has existed as long as the history of natural science, but knowledge about the role of subsurface flows has a more recent history. Interest in the interaction of groundwater and coastal waters emerged early. Key features of flow through aquifers were identified in pioneering work by Darcy (1856), and by Baden Ghijben (1888–1889) and Herzberg (1901), who interpreted

^{*} Corresponding author. Tel.: +1 508 289 7515; fax: +1 508 289 7949.

E-mail address: valiela@bu.edu (I. Valiela).

¹ Present address: The Ecosystems Center, Marine Biological Laboratory, Woods Hole, MA 02543, USA.

² Present address: US Geological Survey, Woods Hole Science Center, Woods Hole, MA 02543, USA.

³ Present address: P.O. Box 3814, Hailey, ID 83333, USA.

⁴ Present address: Save The Bay, Narragansett Bay, Providence, RI 02908, USA.

⁵ Present address: Dauphin Island Sea Lab, 101 Bienville Blvd., Dauphin Island, AL 36528, USA.

vertical profiles of salinity in near-shore wells as indications that as groundwater flowing through an aquifer approached a coastal water body, the flow lines converge, and curve upward, forcing discharge through a relatively narrow zone of seepage. Hubbert (1940) developed a broad theory of groundwater motion, and proposed mechanisms to account for flow of freshwater over salty underlying aquifer water, and extensively discussed seepage of fresh groundwater directly through the sediment/water boundary into coastal waters. Glover (1959) further concluded that the width of the discharge zone was proportional to the volume of water flow, and Lock and John (1978), and Lee et al. (1980) made measurements that corroborated earlier predictions. McBride and Pfannkuch (1975) found similar patterns for discharge of groundwater onto lakebeds; their explanation of the upward curve of flow lines was based on release from head pressures as groundwater reached the shores; these results suggested that changes in pressure, as well as density-related mechanisms might be involved in the near-shore dynamics of groundwater flow (Pfannkuch and Winter, 1984/1985).

Many other researchers have investigated groundwater flow, but the work of the few cited above are representative. Indeed, groundwater discharges into estuaries and coastal waters, and most of the flow out of aquifers is likely to occur through a near-shore zone of seepage. That being so, it seemed evident that whatever substances are present in groundwater would be transported to receiving coastal waters. Knowledge of this possibility dovetailed with increased concern about eutrophication of receiving waters.

By the mid-20th century there was growing awareness that human activities in the near-shore were creating changes in the adjoining estuaries, and headlines such as “The fringe of the ocean—Under siege from land” (*Science*, 13 April 1990, p. 163), or “Agriculture kills marine fish in the 1980s. Who is responsible for fish kills in the year 2000?” (*Ambio*, 18:347–350) were not unusual. Analyses of accumulating data led to the conclusion that eutrophication by land- and atmospheric-derived nutrient loadings is a major agent of change altering coastal waters world-wide (GESAMP, 1990; NRC, 1993, 2000; Goldberg, 1995; Howarth et al., 2000). In the USA, for example, two thirds of coastal water bodies are moderately to severely degraded as a result of N enrichment (NRC, 2000).

Along many coasts of the world, the increases in nutrient loads follow the inexorable expansion of urban sprawl (Cohen et al., 1997; Correll, 1998; Wickham et al., 2002). A measure of the intensification of urbanization is provided by data on 51 watersheds from Eastern USA (Fig. 1). These watersheds feed major rivers in 11 states, ranging from Wisconsin to Alabama to New York. Residential land cover in these large watersheds varies broadly, with modal frequency of 3.2–6.2% of the area covered by residential areas. More worrisome is that many watersheds already show urban covers of 12.5–100% (Fig. 1), and that population density increased in 63% of these watersheds in recent decades. These data suggest a surprisingly advanced state of urbanization in many watersheds, and that the aquatic environmental degradation associated with urbanization of the East coast of the US (and elsewhere) will clearly intensify in the future.

The issue of urbanization, and the consequent eutrophication of estuaries, has been of particular concern in Cape Cod, the fastest-growing county in the conterminous Massachusetts, where development has pervaded the landscape since the 1960s. Since 1970 the population of Cape Cod has increased 130%, more than 10 times the mean for the rest of the state. Nitrogen loading associated with sprawl has threatened many of the estuaries that link this peninsula to the sea. Nitrogen loads to Cape Cod estuaries (mainly from wastewater) have more than doubled in the last 4 decades (Bowen and Valiela, 2001a). For the entire USA, N loads have doubled over this time period (Howarth et al., 2002).

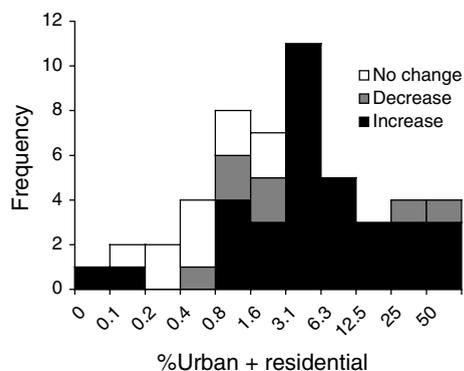


Fig. 1. Frequency distribution of percent of area in 51 watersheds on the East of the US covered by urban or residential land uses. Also shown is whether the population density in these watersheds increased, remained unchanged, or decreased between 1980 and 1990. Data from Dow and DeWalle (2000).

During the 1960s–1970s those working on ecological and biogeochemical controls of coastal systems and related human-derived perturbations were focused on the surface transport of materials, and on other agents of change, such as the role of point source nutrient additions. In many cases, these studies eventually led to the realization that there was a need to understand the role of groundwater transport.

For an example, a study of salt marsh ecosystems that began in 1970 in Great Sippewissett Marsh on Cape Cod, Massachusetts can be used. This work was designed to understand how natural and human-derived nutrient supply—particularly of N, the principal nutrient limiting producers in coastal waters (Howarth, 1988; Nixon, 1992; Valiela, 1995)—might control the producers (marsh grasses, benthic microalgae, etc.), and hence, the rest of the food web dependant on the producers. Some time later, in compiling the N budget for the entire salt marsh ecosystem (Valiela et al., 1978; Valiela and Teal, 1979), it was revealed that, given the concentrations and volume flows of groundwater into this salt marsh ecosystem, the contribution of groundwater-borne N was of considerable magnitude. Similar studies of N inputs into coastal lagoons in Rhode Island concluded that groundwater transported 71–94% of the N entering these shallow estuaries (Lee and Olson, 1985). Johannes (1980) after reviewing the authors' and others' data, concluded "Discharge of groundwater into the sea is widespread. Overlooking it may lead to serious misinterpretations of ecological data in studies of coastal pollution, of... productivity, and of the flux of dissolved substances (to receiving) water."

Below the authors first examine evidence underlying why groundwater transport of solutes might be large. Second, how nutrient transport depends on human land uses on watersheds is discussed. Third, the effects of these human-enhanced nutrient loads on different aspects of estuarine ecosystems is reviewed. A variety of sources of evidence is used but the authors' concentrate on information gathered in their work on coastal systems of Cape Cod, Massachusetts.

2. Nutrient transport by groundwater

The magnitude of land-derived nutrient transport by groundwater is set by the concentrations of nutrients near-shore, attenuation processes along flowpaths, and by groundwater flow rates. Of

course, to some extent the impact of these exports are mediated by the ambient concentrations in the receiving waters, but in general, groundwater holds considerably higher concentrations of solutes than receiving estuaries. Here the forms of N dissolved in groundwater are focussed on because N is the principal element limiting producer growth in most coastal systems, and because aquifers retain particulate forms of N.

2.1. Concentrations of N in groundwater

Nitrate is nearly ubiquitous in oxic groundwater, is frequently the dominant form of N, and travels through aquifers with minimal physical retention (Korom, 1992; Keeney, 1986; Egboka, 1984; Capone and Bautista, 1985). Concentrations of NO_3 in groundwater span large ranges (Table 1). Nitrate concentrations also differ among geographical locales (Table 1). Even within one site there can be 3 orders of magnitude differences in concentrations at spatial scales of tens of meters (Fig. 2, top), and the authors have additional data showing similar heterogeneity at meter scales. Concentrations of groundwater NO_3 therefore vary widely over several orders of magnitude at multiple spatial scales.

Ammonium concentrations are as variable as those of NO_3 (Fig. 2, bottom), and groundwater concentrations of NH_4 can also be high (Table 2), but in general, there is less NH_4 in groundwater, in part owing to the action of nitrifiers. Ammonium, unlike NO_3 , suffers some adsorptive losses during passage through sediments. Ammonium, however, is regenerated in groundwater as a result of decomposition of sedimentary and dissolved organic N (DON).

Most discussions of groundwater nutrients have centered on NO_3 (Korom, 1992; Keeney, 1986). Little has been said about groundwater DON, although there are large concentrations of DON in groundwater about to enter estuaries (Table 2, Kroeger et al., 1999, 2006a,b). Here the authors give what might be a disproportionately large amount of attention to DON, to redress the paucity of previous discussions.

DON found in surface waters and in atmospheric deposition is a complex mixture of N-containing organic compounds, consisting of perhaps 20% known compounds such as proteins, amino acids, amino sugars, amines and urea, while the remainder is a mix of chemically undescribed compounds

Table 1

Ranges of concentrations of nitrate in groundwater of coastal aquifers, in groundwater discharging into coastal waters, and in seawater

Site	Nitrate concentrations (μM)	References
<i>US groundwater</i>		
Agricultural land use	241 ^a	Nolan and Stoner (2000)
Urban land use	114 ^a	Nolan and Stoner (2000)
Major aquifers	34 ^a	Nolan and Stoner (2000)
<i>Groundwater in coastal aquifers</i>		
Orleans, MA	0–393	Gaines et al. (1983)
North Carolina	1–2250	Gilliam et al. (1974)
Falmouth, MA	0.7–693	Meade and Vaccaro (1971)
Cape Cod, MA	0–450	Frimpter and Gay (1979)
Long Island, NY	8–610	Bowman (1977), Capone and Bautista (1985)
<i>Groundwater discharging into coastal waters</i>		
Great Sippewissett Marsh, MA	10–100	Valiela et al. (1978)
Town Cove, MA	9.7–107	Giblin (1983)
Agana Bay, Guam	178	Marsh (1977)
Western Island of Hawaii	29–91	Kay et al. (1997)
Swan River, W. Australia	115–380	Johannes (1980)
Discovery Bay, Jamaica	88–250	D'Elia et al. (1981)
Wye Estuary, Maryland	710–1491	Staver and Brinsfield (1996)
<i>Seawater</i>		
Surface seawater	0–3	McCarthy (1980)
Coastal water	0–30 ^b	Valiela (1995)
Estuarine waters	0–350 ^b	Valiela (1995)

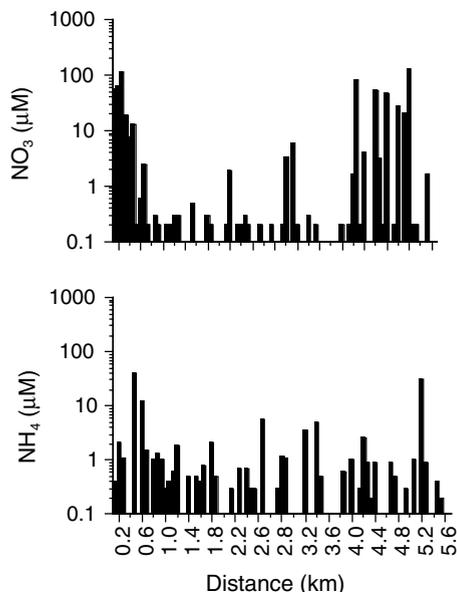
^a Median values.^b Most recorded values toward the lower end of the range (0–10 μM).

Fig. 2. Concentrations of NO_3^- (top) and NH_4^+ (bottom) measured in groundwater sampled by piezometers inserted at about 200 m intervals into the seepage face around a Cape Cod estuary. Data from Cole (2002) and Cole et al. (2006).

(Druffel et al., 1992; Hopkinson et al., 1993; Novakov and Penner, 1993; McCarthy et al., 1996, 1998).

Common wisdom has been that land-derived DON does not contribute to eutrophication because it was assumed to be humus-like dissolved organic matter largely refractory to microbial attack (Beck et al., 1974; Gardner and Stephens, 1978). More recently, terrestrially-derived DOC and DON (Meyer et al., 1987; Qualls and Haines, 1992; Zhu and Ehrenfeld, 1999), marsh-derived humic material (Bronk et al., 1994) and groundwater DOC (Gron et al., 1992) have been shown to be in some measure available to bacteria. DON in lakes, rivers, estuaries, and the sea (Antia et al., 1991; Bronk and Gilbert, 1993; Seitzinger and Sanders, 1997; Benner et al., 1997), and in atmospheric deposition (Peierls and Pearl, 1997; Seitzinger and Sanders, 1999) are also to some extent labile. Decomposition of labile fractions of DON may release NH_4 and hence could stimulate algal productivity (Peierls and Pearl, 1997; Seitzinger and Sanders, 1997, 1999). There may be some uptake of certain DON compounds directly by phytoplankton (Antia et al., 1991), but this path-

Table 2
Concentration of nitrate, ammonium and dissolved organic nitrogen in groundwater of various receiving water bodies

Site	Concentration (μM)			% DIN	Source
	NO_3^-	NH_4^+	DON		
Great Pond, MA	251	2	37	87	Cole et al. (2006)
Green Pond, MA	71	3	140	35	Cole et al. (2006)
Mashpee River, MA	10	2	14	46	Cole et al. (2006)
Eel Pond, MA	24	37	96	39	Kroeger et al. (2006a,b)
Childs River, MA	69	11	22	80	Kroeger et al. (2006b)
Quashnet River, MA	13	7	29	41	Kroeger et al. (2006b)
Hamblin Pond, MA	7	8	33	31	Kroeger et al. (2006b)
Jehu Pond, MA	13	8	42	33	Kroeger et al. (2006b)
Sage Lot Pond, MA	7	16	83	22	Kroeger et al. (2006b)
Coonamessett Pond, MA	33	–	–	60	Cole et al. (2005)
Gr. Sipp. Marsh, MA	4	0.5	3	57	Valiela et al. (1978)
S. Fork of Flanders Bay NY	24	71	12	89	Montlucon and Sanudo-Wilhelmy (2001)
N. Fork of Flanders Bay NY	246	65	20	94	Montlucon and Sanudo-Wilhelmy (2001)
Peconic Bay, NY	500	–	0	100	Laroche et al. (1997)
Taiga forest, AK	–	–	66	16	McLean et al. (1999)
Walker Branch, TN	25	19	57	44	Mulholland (1992)
Mean \pm SD	87 ± 140	19 ± 24	44 ± 39	55 ± 27	

way is likely of minor importance to most primary producers.

The influence of land use on the magnitude, chemical composition, or lability of DON transported by groundwater is not well defined, but because of the relatively large concentrations of DON in groundwater, even a small labile portion could make a significant difference to the amount of N available to N-limited estuaries. Many models developed to estimate land-derived N loads to estuaries focus on NO_3^- . It is evident from this brief review of knowledge about NH_4^+ and DON in groundwater that inclusion of these other forms of N is desirable in estimates of land-derived N loads.

In sum, then, groundwater in the northeastern United States tends to hold more NO_3^- than NH_4^+ , and about equal amounts of DON and DIN (Table 2, Kroeger et al., 2006b). The variation of all these N forms (Table 2), however, is so great from one site to another that it is difficult to generalize.

2.2. Volume of groundwater flow

The volumes of groundwater moving onto coastal waters have been estimated as around 10% of riverine flow (Garrels and MacKenzie, 1967), but these are likely to be underestimates. Recent development of Ra isotopic techniques have permitted new assessments of groundwater flows at regional spatial scales, and these seem to be of

considerable magnitude (Moore, 2000; Hancock et al., 2000).

The relative flow of groundwater versus surface flows varies greatly at local spatial scales: groundwater flow into specific small lakes, for example, can vary from 10% to at least 49% of total inflow, depending on geological characteristics (Shaw and Prepas, 1990). In certain estuarine situations, groundwater could contribute 17–20% of total water flow (Johannes, 1980; Bokuniewicz, 1980). The temporal and spatial patterns of longer-term, near-steady state flow of groundwater near shore are modified at shorter time scales and local spatial scales by the effects of changing tidal heights and wave effects in the coastal water body (Inouchi et al., 1990; Turner et al., 1997; Ataie-Ashtiani et al., 1999), as well as by fingers of salt resulting from unstable density profiles where salty water overlies freshwater (Bokuniewicz, 1992).

In general, the major flows of groundwater from surficial aquifers occur quite near the shore (Bokuniewicz, 1992). In shallow estuaries of Cape Cod, Massachusetts, the authors calculated that, on average, 91% of the groundwater flows through the narrow near-shore seepage zone (Valiela et al., 2002). Under certain geological circumstances, flows of groundwater out of surficial aquifers may take place via subaquatic springs, rather than mainly through seepage through unconsolidated sediments (Lee et al., 1980). In some deeper aquifers, or where there are constraining less-permeable layers, groundwater

may flow into the sea floor at considerable distances offshore (Moore, 2000; Hancock et al., 2000).

2.3. Nitrogen loads from land

Recent concern about land-derived N inputs to receiving estuaries is caused by the evident increases in loadings taking place during recent decades (Bowen and Valiela, 2001a). In response to these concerns, researchers have endeavored to quantify transfers of N from land to sea at a variety of spatial scales (Howarth et al., 2000). Many researchers have developed protocols to estimate N loads (Cole et al., 1993; Caraco and Cole, 1999; Boyer et al., 2002; Schwarz et al., 2006). The authors developed NLM (Valiela et al., 1997), a model that uses land cover data to calculate N inputs to watershed surfaces, assess losses of N within the watershed/vadose zone/aquifer system, and predict the N load about to emerge into a down-gradient receiving water body. NLM can also partition the N contributions from the major sources of N: atmospheric deposition, fertilizer use, and wastewater disposal.

NLM can be used to assess the fate of N as it travels through groundwater (and other ecosystem components) on its way from land to open water. For example, using NLM, it has been estimated that 80% of the total N load to the watershed of Waquoit Bay is intercepted within the watershed (Table 3). There are different rates of loss of N from different sources within the watershed, so that the relative importance of various sources differs. Nitrogen loads to the *watershed surface* are dominated by atmospheric deposition (56% of the load to the watershed). In contrast, because of differential loss rates (Table 3), N loads to *receiving waters* derive largely from wastewater (48% of the load to the estuary) (Table 3). Knowledge of these features is important to establish priorities for management

of waters and estuaries, as well as for understanding the fundamentals of the systems.

In general, a considerable portion of the N that enters the watershed surface is retained within the watershed. This occurs, in part, because there is significant retention and denitrification of N in the vegetation and soils of aggrading forests (Seely et al., 1998). It needs to be pointed out that if atmospheric N loads increase, as they have in various parts of the world (Bowen and Valiela, 2001b), the retention within vegetation and soils of terrestrial landscapes might sharply decrease. This N saturation (Aber et al., 1998) will need monitoring, as it might significantly increase the magnitude of land-derived N loads to estuaries.

Denitrification of NO_3 and retention of NH_4 and DON by adsorption take place in aquifers. Denitrification is the larger of these terms. The highest rates of denitrification seem restricted to the upper layers of groundwater where there are sufficient concentrations of DOC (Pabich et al., 2001); the DOC that survives passage through the vadose zone enters the aquifer, where additional large losses of DOC occur (Pabich et al., 2001). DOC concentrations are therefore strongly attenuated during passage through vadose zones and upper layers of groundwater. The lowered DOC concentrations in lower layers of groundwater could therefore restrict activity of microbial processes, including denitrification. The authors have measured marked lowering of denitrification rates with distance below the water table (Fig. 3); this lowering seems coupled to the DOC concentration gradients (Pabich et al., 2001). Similar results, reporting denitrification mainly near the water table, can be found elsewhere (Puckett and Cowdery, 2002).

The finding that denitrification takes place mainly near the top part the water table resolves a long-held paradox, and an unexplained dilemma.

Table 3

Nitrogen loads to watersheds, losses within the watersheds, and loads to estuaries of Waquoit Bay, Massachusetts, from the three major sources

Sources	N load to watershed		Loss of N within the watershed	N load to estuaries	
	kg N y ⁻¹	%		%	kg N y ⁻¹
Atmospheric deposition	64,400	56	89	6900	30
Fertilizer use	16,600	14	79	3400	15
Wastewater disposal	31,700	27	65	11,000	48
Ponds upgradient	2800	2	37	1800	7
Total	115,500	100	80	23,100	100

Adapted from Valiela et al. (1997).

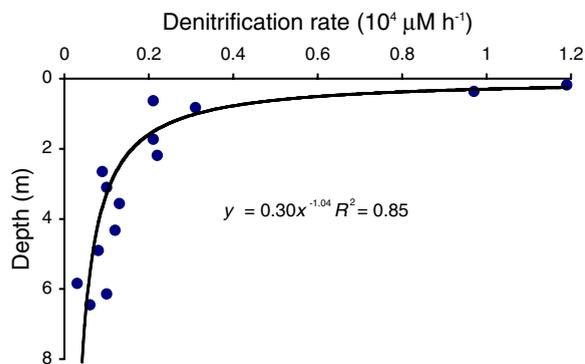


Fig. 3. Vertical profile of denitrification rates within the Cape Cod aquifer relative to depth below water table. Data from Pabich (2000).

First, some held that denitrification took place in groundwater, based on evidence of NO_3 concentrations that were attenuated beyond mere dilution during transit through aquifers; others pointed out that there was much evidence that there was insufficient DOC in groundwater to power denitrification. The problem may be that the groundwater sampling was done in such a way as to avoid placing the upper sampling port in multiple-depth sampling wells at or near the water table, since during dry times, such positioning would mean a missed sample depth. Thus groundwater from the upper layers, where we might expect to find enough DOC, and hence denitrification, went largely unsampled in most hydrological surveys.

Second, Brawley et al. (2000) ran simulations that allowed time-dependent loss rates during modeled transport of N through groundwater under watersheds of several estuaries, involving quite different travel times within the aquifer. The loads arriving at the estuary shore differed by only 10% compared to N loads modeled by simply assuming one loss rate for all the watersheds: duration of passage through the aquifer seemed to make little difference. The answer to this dilemma may be that losses within the aquifer occur mostly at the upper layers of groundwater near the water table. Regardless of the duration of travel further downgradient, the major losses of N within the aquifer had already taken place.

It should be noted that the studies described above (Pabich et al., 2001; Brawley et al., 2000) were undertaken in a watershed that had little variation in C content within the largely sand and gravel aquifer (Smith et al., 1987, 1991). Thus in these C depauperate sandy systems, the organic C that is delivered

to the aquifer from the above vadose zone is necessary for denitrification to proceed (Pabich et al., 2001). In systems that have a more varied stratigraphy, for example with layers of pyrite (Böhlke et al., 2002), reduced S compounds (as found in clayey soils; Robertson et al., 1996), or organic layers, may have higher rates of denitrification lower in the aquifer (McMahon et al., 1999).

3. Effects of land use on groundwater nutrients

3.1. Concentrations

The relative area of diverse types of land covers and biogeochemical processes that occur during groundwater transport greatly alter not only the magnitude but also the composition, or chemical form, of N loads delivered from land to receiving waters (Kroeger, 2003; Kroeger et al., 2006b). On Cape Cod (and elsewhere, Fig. 1), the primary land use change in recent decades has been conversion of forested and agricultural land to residential uses (Bowen and Valiela, 2001a). This conversion to residential land uses has resulted in increases in DIN due largely to increased wastewater disposal through on-site septic systems (Valiela et al., 1997; Kroeger et al., 1999; Bowen and Valiela, 2001a).

Forested watersheds with low population densities export relatively little N (Fig. 4), and the composition of the total load is dominated by organic N (Fig. 4b and c). Increasing human population on watersheds is accompanied by large increases in groundwater transport of DIN to receiving waters (Fig. 4a), but surprisingly, DON loads also increase (Fig. 4b). The result is that the percent of DON that comprises total groundwater dissolved N loads to receiving waters is not related to population density on watersheds (Fig. 4c).

The composition and magnitude of wastewater N loads transported from watersheds by groundwater is likely controlled by transformations and losses occurring in vadose zones and aquifers. It has been found that groundwater N exports from watersheds with short path lengths through vadose zones and through aquifers tend to be dominated by DON (a chemically reduced form), while N in groundwater leaving watersheds with long flow paths through each of these zones is dominated by NO_3 (the most oxidized form) (Kroeger, 2003; Kroeger et al., 2006b; Fig. 4d). Path lengths through vadose zones are correlated with path lengths through aquifers so with the whole watershed and correlation approach

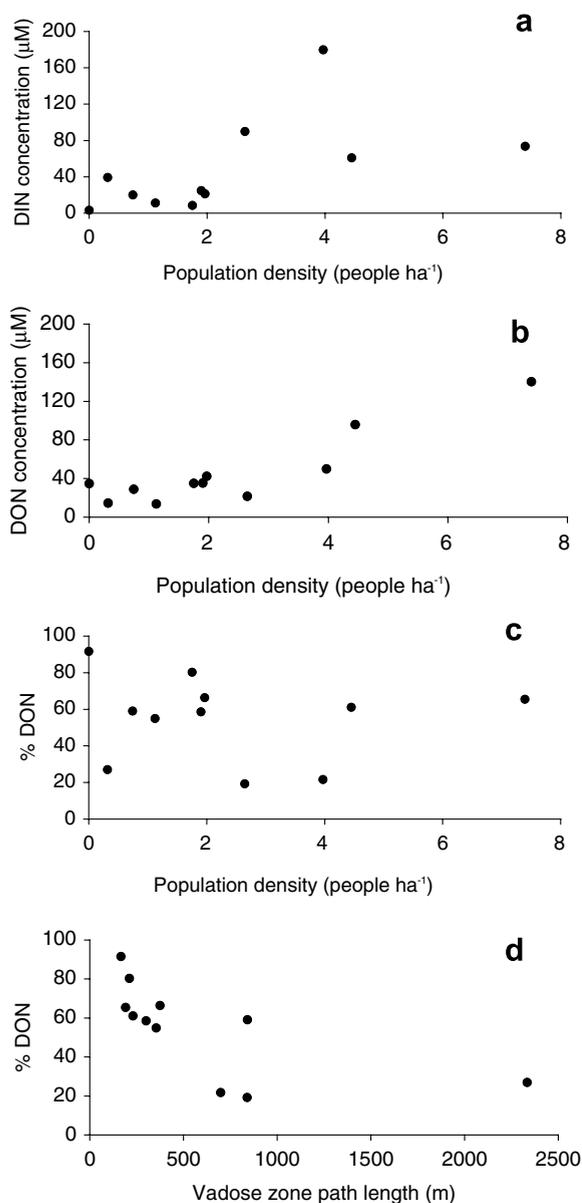


Fig. 4. Concentrations of dissolved inorganic N (a) and organic N (b) in groundwater from several Cape Cod watersheds versus population density on the watershed. Percentage of TDN concentrations that are composed of DON versus the population density on the watershed (c) and versus the average path length that the water traverses during recharge to the aquifer (d). Each data point is an average of many observations. Data from Kroeger (2003).

it is difficult to make an independent determination of the relative importance of each of these terms in controlling the form of N.

The relationship between flow path length and N form can likely be explained by the oxidation of DON and NH_4 , from wastewater and other sources,

during transport through both the vadose zone and the aquifer. Due to intense ammonification under anoxic conditions within septic tanks, wastewater N exits septic tanks primarily as NH_4 , but with typically about 30% of TDN as DON (Kroeger et al., 2006b). However, beneath properly functioning septic systems with sufficient separation from the aquifer, rapid nitrification and DON mineralization occur during transport through the vadose zone (Willhelm et al., 1994; DeSimone and Howes, 1998). The result is that septic plumes in aquifers near the source typically have 2000–3000 µM total N composed of about 90% NO_3 and 10% DON (Kroeger and Cole, unpublished; Westgate et al., 2000). Nitrate concentrations in wastewater plumes decrease during transport through the aquifer due to dilution and, when organic C or other electron donor supply is sufficient, due to loss through denitrification (Valiela et al., 1997; Aravena and Robertson, 1998; Kroeger et al., 2006b). Further DON losses might also occur during transport through the aquifer.

However, increasing DON loads to receiving water with increasing population density (Fig. 4b) suggests that substantial concentrations of wastewater-derived DON occur in groundwater (Kroeger, 2003; Kroeger et al., 2006a). Furthermore, decreasing contribution of DON to total dissolved N concentrations with increasing path length through the vadose zone (Fig. 4d) and through the aquifer suggests that in coastal watersheds with thin vadose zones and short path lengths through aquifers, the extent of both ammonification and nitrification may be limited. Thus, in watersheds with long path lengths through the vadose zone and aquifer, substantial loss of wastewater DON, and of DON from other sources appears to occur, while in watersheds with short flow paths through those zones a large proportion of total dissolved N concentrations in groundwater entering the estuaries is in the form of DON. The result is that, in some cases, even in watersheds with intermediate to high human population density, and with quite impacted receiving waters, as much as 60% of N loads may be composed of DON (Fig. 4c).

3.2. Nitrogen stable isotopic signatures

Differences in the ratio of ^{15}N to ^{14}N can be used to discriminate among the different N sources, wastewater from onsite septic systems, atmospheric deposition, and fertilizer use (Kreitler et al., 1978;

Macko and Ostrom, 1994). Groundwater NO_3 that is derived from wastewater typically has a $\delta^{15}\text{N}$ of +10 to +22‰ (Kreitler et al., 1978; Macko and Ostrom, 1994). This range is significantly higher than the $\delta^{15}\text{N}$ of groundwater N derived from atmospheric deposition (+2 to +8‰; Kreitler et al., 1978), and from fertilizers (−3 to +3‰; Kreitler et al., 1978). The ratio is expressed as $\delta^{15}\text{N}$ (‰) = $[(R_{\text{sample}} - R_{\text{reference}})/R_{\text{reference}}] \times 1000$, where R is $^{15}\text{N}/^{14}\text{N}$ and the reference is atmospheric N_2 (Peterson and Fry, 1987). The elevated ^{15}N signature of wastewater is derived from the many transformations that the wastewater-borne N undergoes as it moves through the landscape. The end result of all these N transformations is a NO_3 pool that is enriched in ^{15}N relative to ^{14}N as compared to sites without wastewater contamination.

$\delta^{15}\text{NO}_3$ values increase as the human population of the watershed and wastewater load increases (Fig. 5, top). The $\delta^{15}\text{NO}_3$ values respond logarithmically as the influence of humans increase, and are thus sensitive at the lower range of watershed urbanization. In contrast, $\delta^{15}\text{NH}_4$ values show no relationship to either watershed population or wastewater load (Fig. 5, bottom), although they have the same range of values as those of NO_3 .

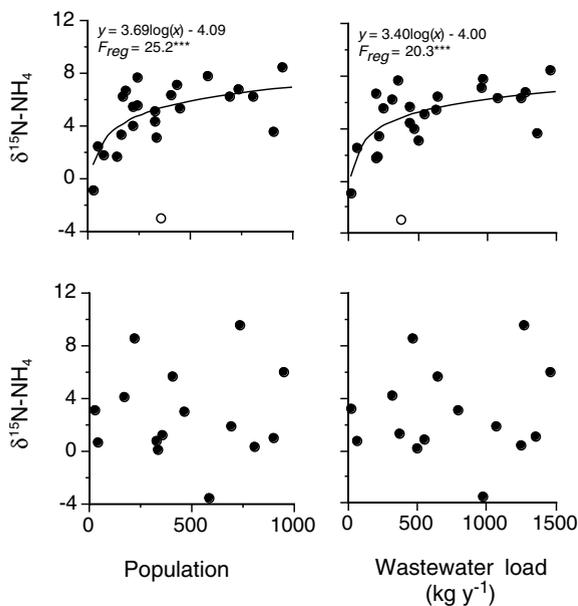


Fig. 5. $\delta^{15}\text{N}$ of NO_3 (top panel) and NH_4 (bottom panel) as a function of human population on watersheds (left column), and on total load attributed to wastewater disposal on those watersheds (right column). Data from Cole (2002) and Cole et al. (2005). The open circles are outliers that are not included in the regression.

Nearly all NH_4 in wastewater is lost to volatilization or nitrification before entering the aquifer. Although these processes enrich the remaining NH_4 in ^{15}N , the concentration of wastewater-generated NH_4 in groundwater is low in relation to other NH_4 sources. Spatially different mixes of the other NH_4 sources (atmospheric deposition and fertilizer use) irregularly dominate the groundwater NH_4 pool. $\delta^{15}\text{NO}_3$ in groundwater is thus more indicative of urbanization on watersheds than $\delta^{15}\text{NH}_4$.

4. Effects of land-derived nitrogen loads on estuaries

4.1. Effects on nitrogen concentrations in water of receiving estuaries

Nitrogen concentrations in receiving estuaries are directly related to both groundwater N concentration and within-estuary processing in the Waquoit Bay estuaries (Valiela et al., 2000a). Groundwater, the predominant transport mechanism in the Waquoit Bay system, delivers N-rich water to the receiving estuaries (Fig. 6, solid points). The composition of N compounds in groundwater depends on land use mosaics on the watersheds.

Nitrate is the dominant form of N in groundwater entering Childs River (CR), the estuary with the most urbanized watershed (Fig. 6, left column, black circles). Nitrate concentrations in groundwater decrease in Quashnet River (QR), and in Sage Lot Pond (SLP), where urbanization is less marked. Nitrate concentrations in water columns tend to be highest at the fresh end of the Waquoit estuaries, and decrease down estuary (Fig. 6). The lowered concentrations of NO_3 along the salinity gradient (Fig. 6, left most column) are greater than expected from conservative mixing (Fig. 6, dashed lines). A significant proportion of NO_3 is lost at the seepage face (point of groundwater entry) and at freshwater reaches of the rivers (Valiela et al., 2000b). The significant loss of NO_3 down-estuary is most likely due to biological uptake and export, and to denitrification.

Ammonium and DON concentrations in groundwater about to enter estuaries are higher in the estuary with the most forest cover (Sage Lot Pond, Fig. 6, bottom panels, black circles). Ammonium concentrations within the estuaries do not follow salinity gradients (Fig. 6, center and right columns), and may most likely be affected by within-estuary regeneration.

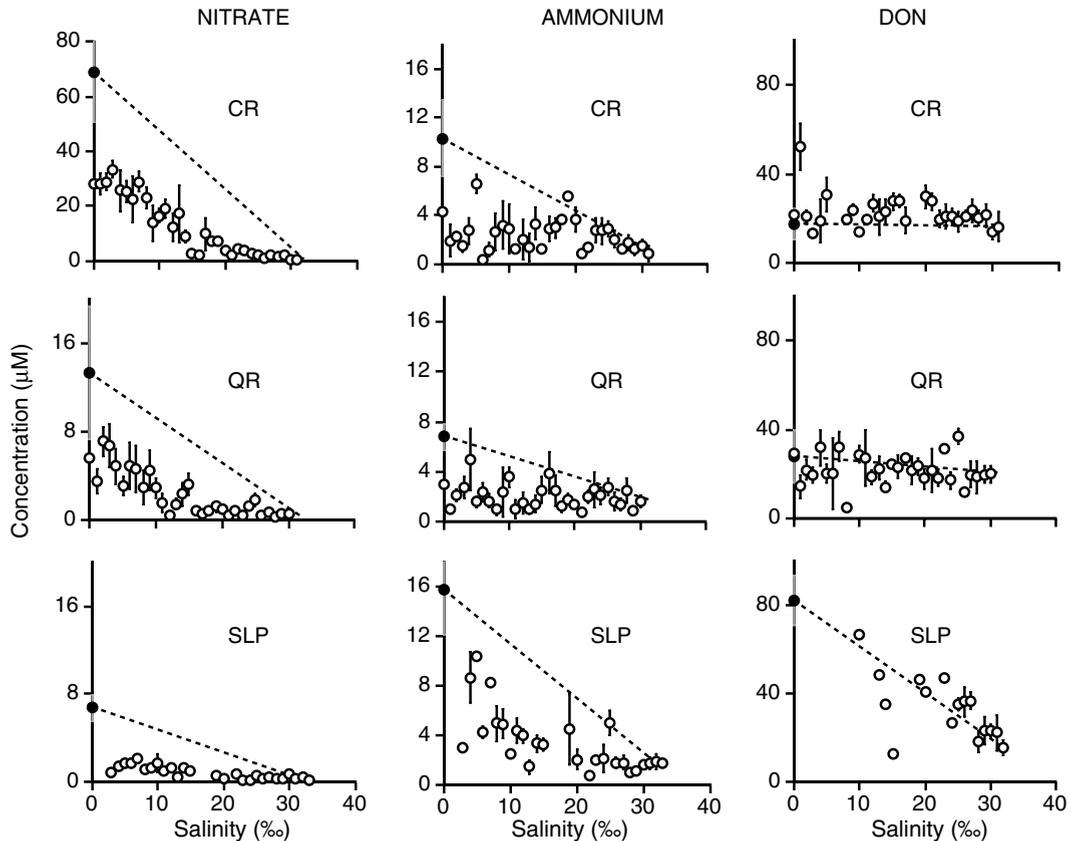


Fig. 6. Mean (\pm SE) concentrations of NO_3 , NH_4 and DON in groundwater (\bullet) and in estuary water at different salinities (\circ) in 3 estuaries of Waquoit Bay, Massachusetts. Dashed lines indicate conservative mixing between groundwater and coastal water (from Valiela et al., 2000a). CR = Childs River, QR = Quashnet River, and SLP = Sage Lot Pond.

The data of Fig. 6 suggest that there is a clear effect of groundwater-borne loads on the nutrient content of the receiving waters, but that the coupling is modified to an extent by within-estuary transformations.

4.2. Effects on estuarine biota

The coupling between land and estuarine ecosystems is mediated by the transport of land-derived N to the estuaries by flow of ground- and surface waters. Unambiguous evidence of the linkage, in the case of groundwater, is furnished by stable isotopic analyses of the producers within the estuaries. As discussed earlier, land use mosaics on watersheds impress characteristic isotopic signatures onto groundwater. These identifiable signatures are incorporated into the estuarine producers (phytoplankton and macrophytes) that use the land-derived N (McClelland et al., 1997; McClelland

and Valiela, 1998). $\delta^{15}\text{N}$ values in macrophytes, for example, increase as N load or DIN concentrations in the water column increase (McClelland et al., 1997; McClelland and Valiela, 1998), and as the percent contribution of wastewater N increases (Fig. 7). These significant relationships demonstrate that it is the specific molecules of N transported from specific land parcels by groundwater to specific estuaries that is taken up by the estuarine producers and then moves up throughout the estuarine food webs (McClelland and Valiela, 1998).

Increases in land-derived N loading rates, and subsequent increases in estuarine N concentration, cause increases in biomass and production of phytoplankton and macroalgae (Fig. 8, top and middle). These producers are N-limited, and additional N inputs force blooms. In contrast, seagrasses such as eelgrass (*Zostera marina*) decrease with increased N concentrations (Fig. 8, bottom). Eelgrass is not limited by nutrients, but is instead limited by light

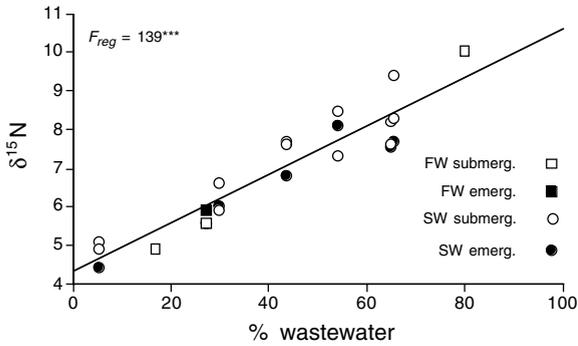


Fig. 7. Relationship of $\delta^{15}\text{N}$ in different estuarine (SW) and freshwater (FW) macroalgae and plants (both emergent and submerged) relative to percent of land-derived N load from wastewater entering estuaries or ponds ($R^2 = 0.84$). Each point refers to a different water body on Cape Cod MA. Data from Cole et al. (2005).

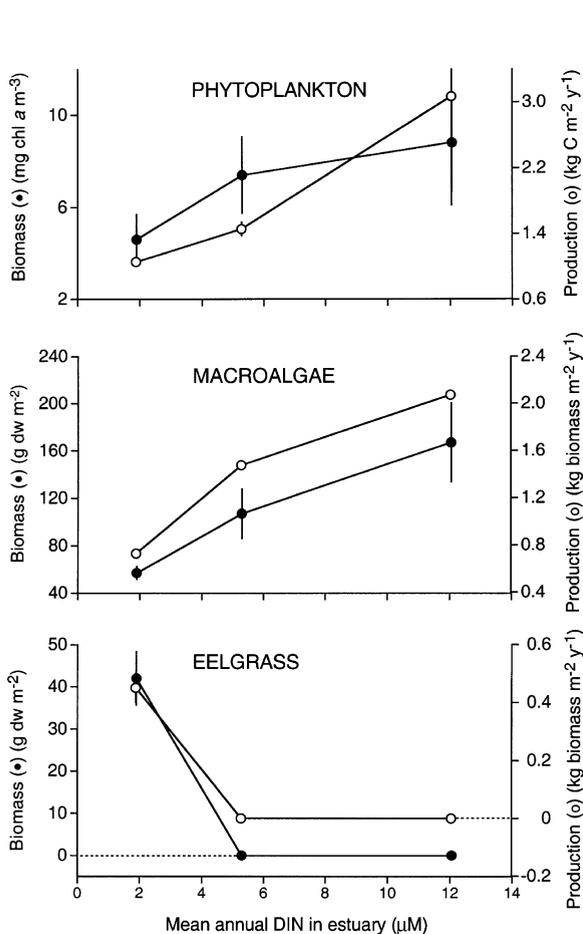


Fig. 8. Effects of N loading on biomass (left axes, closed circles) and primary production (right axes, open circles) of phytoplankton (top), macroalgae (middle), and eelgrass (bottom) in 3 Waquoit estuaries (Sage Lot Pond, Quashnet River, and Childs River in that order). From Valiela et al. (2000a).

availability (Hauxwell et al., 2001). As ambient N increases, the increases in biomass of phytoplankton and macroalgae (Fig. 8) reduce light penetration to the eelgrass below, which prompts decreases in the biomass and production of eelgrass. Primary production in estuaries exposed to low land-derived N loads may be mainly carried out by seagrasses: as loads increase, there is a shift towards greater proportions of production by macroalgae, and by phytoplankton (Fig. 9, top).

The changes depicted in Fig. 9 cascade throughout the food webs of the affected estuaries. Phytoplankton, for example, are a major food source for bivalves (Abraham and Dillon, 1986), and hence it is not surprising that growth of softshell clams, *Mya arenaria*, increase (Fig. 10) as phytoplankton biomass (measured as chlorophyll concentrations)

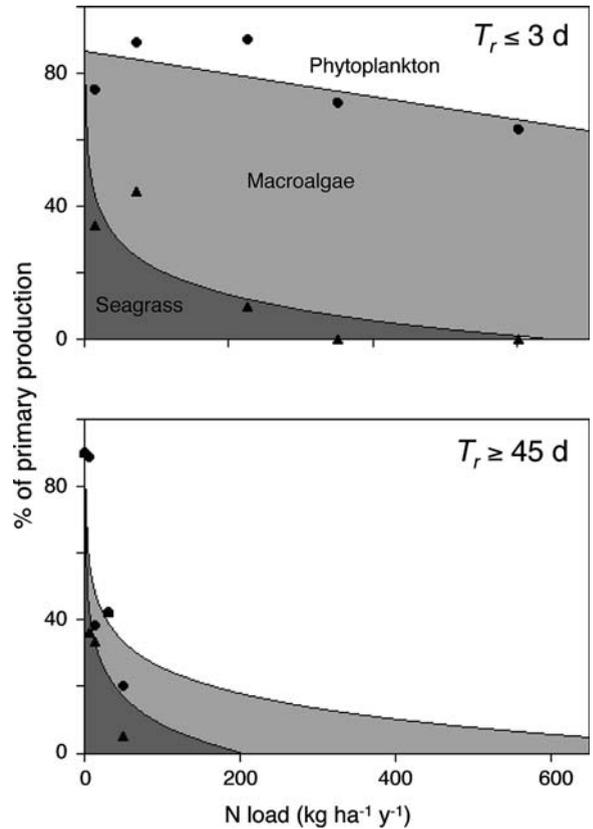


Fig. 9. Partition of total primary production in shallow estuaries into contributions by phytoplankton, macroalgae, and seagrasses plotted against measured annual N load. The top panel includes data for estuaries with a residence time less than 3 days, and the bottom panel includes estuaries with residence times longer than 45 days. From Valiela et al. (2000a). Circles represent the percent of primary production that is accounted for by phytoplankton, and the triangles represent the total primary production from seagrasses.

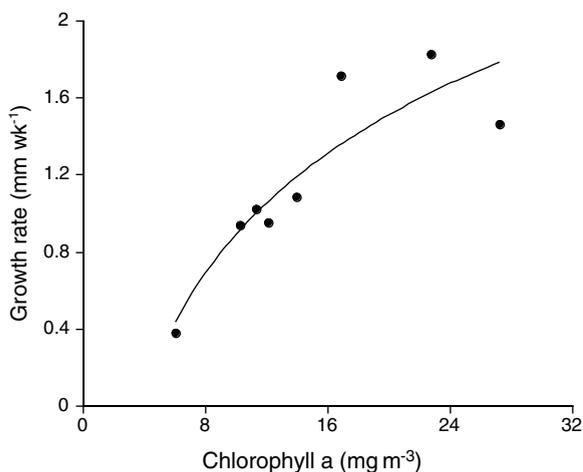


Fig. 10. Growth rates of soft shell clam as a function of mean water column chlorophyll *a* concentrations measured in a number of Cape Cod embayments. Data from Carmichael et al. (2004).

increases (Fig. 8, top). Nitrogen load-driven increases in food supply affect a similar growth response in quahogs (Carmichael et al., 2004; Weiss, 2001) and ribbed mussels (Evgenidou and Valiela, 2002). The changes in macrophytes (Fig. 9) have similar impacts on other estuarine organisms that depend on those macrophytes (Valiela et al., 1992, 2000a).

5. Modifications to degree of coupling between land and estuary

The mass balance and isotopic evidence, and the field measurements clearly argue that there are powerful couplings between land and open waters. In specific settings, it may be that diverse mechanisms work to uncouple receiving waters from the influence of land-derived N loads. Below three of these features: riparian and wetland fringes, and water residence times, are briefly discussed.

5.1. Riparian vegetation

Fringes of riparian vegetation often occur above high tide marks of estuarine waters, and support mostly terrestrial vegetation that tolerates wet soils and some salt. The wet soils provide circumstances favoring denitrification of the NO_3 transported by shallow groundwater flow that has to traverse the riparian zones, deeper groundwater, however, could bypass this riparian zone (Puckett et al., 2002). The occurrence of denitrification is supported by mass balance measurements (Jordan et al., 1993), as well

as by fractionation to heavier $\delta^{15}\text{N}$ values in the groundwater-borne NO_3 that occurs as the NO_3 traverses the riparian zone before entering the receiving estuary (Mengis et al., 1999). Interception of NO_3 in the riparian zone is not complete, so that some of the terrestrial NO_3 borne in the groundwater does move into receiving waters (Nelson et al., 1995; Willems et al., 1997).

5.2. Fringing wetlands

Fringing wetlands interposed between land and estuary may intercept enough groundwater-borne N to uncouple receiving estuaries from their watersheds (Valiela and Cole, 2002). For example, as already noted, seagrass meadows are highly sensitive to increased N inputs from land. The rates of denitrification and burial of land-derived N in salt marshes and mangroves may be high enough to protect the sensitive seagrass meadows located seaward of the wetlands. The protection furnished by wetlands, however, appears limited to situations where the land-derived N loads are lower than 20–100 $\text{kg N ha}^{-1} \text{a}^{-1}$ (Valiela and Cole, 2002); above these loads, the uncoupling role of wetlands is overwhelmed.

5.3. Estuarine water residence times

The coupling of land and estuary that forces the shift in primary producers—from systems dominated by eelgrass to systems dominated by phytoplankton and macroalgae—is to a degree moderated by the residence time (T_r) of water in the receiving estuary (Valiela et al., 2000a). In many shallow estuaries such as Waquoit Bay, T_r is relatively short (Fig. 9, top). In these instances, the responses of macroalgae, for instance, to increased groundwater-borne N loads is relatively clear (Fig. 9). In such systems, water may be renewed at roughly the same rate as phytoplankton cell division (Tomasky and Valiela, unpublished data), and hence phytoplankton blooms might be curtailed. In estuaries with longer T_r phytoplankton cell division may more effectively increase phytoplankton cell density, thereby lowering light attenuation, and limiting the growth of both macroalgae and seagrasses; in estuaries with longer T_r , therefore, the phytoplankton may make it difficult for other producers to respond to increasing N loads. To a degree, longer T_r therefore may modify, if not uncouple, the land/estuary linkage to producers.

The effect of water residence time is also likely to be felt by consumers that depend on the producers. Copepods, for instance, feed on phytoplankton in the Waquoit estuaries. Female *Acartia tonsa* collected in the Waquoit estuaries produce eggs at rates proportional to the concentration of chlorophyll in the estuaries (Cubbage et al., 1999). Yet, densities of these copepods bear no relationship to groundwater-borne N loading rate (Lawrence et al., 2004; Valiela et al., 2001). Pace et al. (1992) pointed out that water residence times can be considerably shorter than the generation times of the major grazers of phytoplankton. The potential for control of phytoplankton by grazers (Kerfoot and Sih, 1987; Metaxas and Scheibling, 1996) may thus be weakened by short water residence times, since the stock of the grazers would not be able to “grow into” the available food supply, but rather would be uncoupled from its food source.

5.4. Other direct nitrogen inputs

The degree of coupling between watershed and estuary may be weakened if the magnitude of the other direct N inputs or losses to the estuary are sufficiently large. In particular, atmospheric deposition has been mentioned as a potentially large N source (Hinga et al., 1991; Paerl et al., 1999). It is estimated that between 10% and 40% of the N inputs to shallow coastal waters might be by direct atmospheric deposition.

In estuaries whose watersheds are relatively unaffected by human activities the significant input of direct atmospheric deposition may be so dominant as to uncouple the links between land and estuary. For example, the relative magnitude of direct atmospheric deposition of N to estuaries of Waquoit Bay decreased to about 20% as density of people on the contributing watershed increases (Valiela and Bowen, 2002). This suggests that the relative importance of direct atmospheric inputs is greatest in near-pristine watersheds. In these types of watersheds, direct atmospheric deposition might uncouple the links between land and estuary. As watersheds become developed, groundwater inputs become considerably larger than direct atmospheric inputs, and hence we have a tighter linkage between land uses on watersheds and the enrichment of receiving estuaries.

Although in this last section factors have been mentioned that might, under certain circumstances, uncouple linkages between land and receiving water

bodies, it should be evident from the overall thrust of this review that in most cases what happens on land matters fundamentally to the functioning of the receiving aquatic ecosystem. In many cases, the transport of the land-derived materials occurs via groundwater. As knowledge is developed, it will no doubt be found that groundwater transport of terrigenous materials plays a greater-than expected role in understanding the major changes affecting receiving waters world-wide.

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