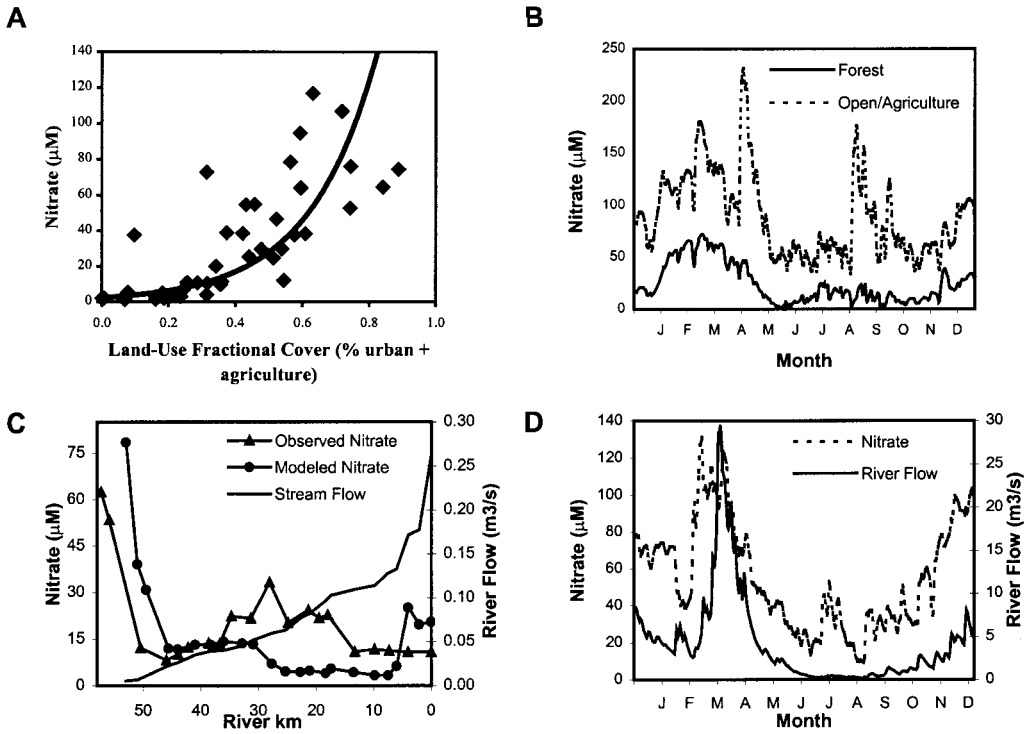

Figure 1. *(A) An empirical relationship between the forest cover in a catchment and the nitrate concentration in streams draining the catchment. (B) Modeled nitrate concentration timeseries in first-order streams with all forest and all open plus agriculture contributing land area. (C) Modeled nitrate concentration and stream flow transect along the main stem of the Ipswich River in July 1993, and observed nitrate data from July 1998. (D) Modeled nitrate concentration and river flow at the mouth of the Ipswich River over the course of 1993.*

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Solute Dynamics in Storm Flow of the Ipswich River Basin: Effects of Land Use

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The Ipswich River in northeastern Massachusetts has supplied surrounding suburban communities with water since the 1800s. With current projections of increased urbanization in the watershed (1), solute fluxes from developed areas may have an impact on the ecology of the Ipswich River. Solute fluxes from storm flow are particularly important since storms commonly flush solutes from storage reservoirs, thereby increasing the mass transfer of solutes to the aquatic system (2). The objectives of this study were to observe solute dynamics in storm flow in three first-order catchments of the Ipswich River basin to infer how increased development will affect the aquatic system.

The three catchments were selected to represent the end-members of different land-use areas commonly found in the Ipswich River basin. The catchments represent predominately urban (URB), agricultural (AG) and forested (FOR) areas. The baseline discharges were 100, 0.4 and 10 l/s at the URB, AG and FOR sites, respectively. Rain volume at each site was measured using manual rain gauges, and samples for chemical analyses were collected.

Baseline samples of stream water were collected before and after a storm that occurred 15–16 June, 2000. Each hour during the storm, filtered and unfiltered samples of stream water were collected and stage measurements were taken. Discharge was estimated from stage measurements. Stream water and rain samples were filtered immediately with glass-fiber filters, stored on ice in the field, and refrigerated at the laboratory until analysis. All filtered samples were analyzed for NH_4 colorimetrically, for Cl, NO_3, and SO_4 using ion chromatography, and for Na, K, Ca, and Mg by atomic absorption. Unfiltered samples were analyzed for acid neutralizing capacity (ANC) and pH.

Total rainfall at the sites ranged from 19 to 46 mm. Maximum stage observed was 25, 12, and 3 cm above base flow at the URB, AG and FOR sites, respectively; maximum discharges were 400, 140, and 70 l/s. Solute concentrations in rain were similar among all sites and much lower than those found in stream water. Base flow values for all solutes were lower at the FOR site than at the other, more developed sites. Sodium and Cl concentrations were high at the URB site, probably because of salting roadways in winter months. Calcium concentrations were high in the AG site, perhaps due to the addition of lime to agricultural fields. During the storm, solute concentrations in stream water of the FOR site were relatively invariant compared to the URB and AG sites (Fig. 1a–c). Concentrations of NH_4 and NO_3 increased at the beginning of the storm, and trends were similar at the AG and URB sites (Fig. 1a). Concentrations of other solutes at the URB and AG sites decreased with the onset of the storm (Figs. 1b, c). After the storm, solute concentrations at the AG site increased rapidly toward base flow values (Figs. 1b, c). Stream water discharge from the URB site was the highest of the three catchments, as was the net flux of solutes measured (Fig. 1d).

The variations in solute concentrations observed are primarily due to site-specific differences in the relative proportions of groundwater and overland flow inputs to the stream. The proportion of these inputs is commonly regulated by the type and amount of ground cover in a particular catchment. The lack of forest cover in agricultural areas and impermeable surfaces in urban settings increase overland flow inputs to streams during storms (3). In forested catchments, runoff is typically smaller than in more developed catchments because soil and vegetation allow much of the precipitation to percolate slowly to the groundwater table. In contrast, soils in predominately agricultural catchments can become quickly saturated during storms, causing larger inputs of water to enter a stream in the form of overland flow and diluting solute concentrations. As a storm subsides, solute concentrations in stream water will typically return to base flow levels as the ratio of groundwater inputs to overland flow increases. Urban settings characteristically have large amounts of impervious ground cover preventing rain from percolating to groundwater reservoirs, thereby increasing the proportion of overland flow (urban runoff) to the stream. Hence, the large decreases in solute concentrations observed at the AG and URB sites during a storm are probably due to a larger overland flow component in these catchment streams. In contrast, the increases of NH_4 and NO_3 concentrations at these sites must be due to strong sources of nitrogen in overland flow and groundwater at the beginning of a storm that may be linked to the application of fertilizers in developed settings.

Our results show that there are marked differences in the solute dynamics of storm flow among streams in areas characterized by different land uses. Because anthropogenic inputs of nitrogen are associated with the eutrophication of receiving waters, further study is required to determine the impact of increased NH_4 and NO_3 export from urban and agricultural catchments on the aquatic ecology of the Ipswich River.

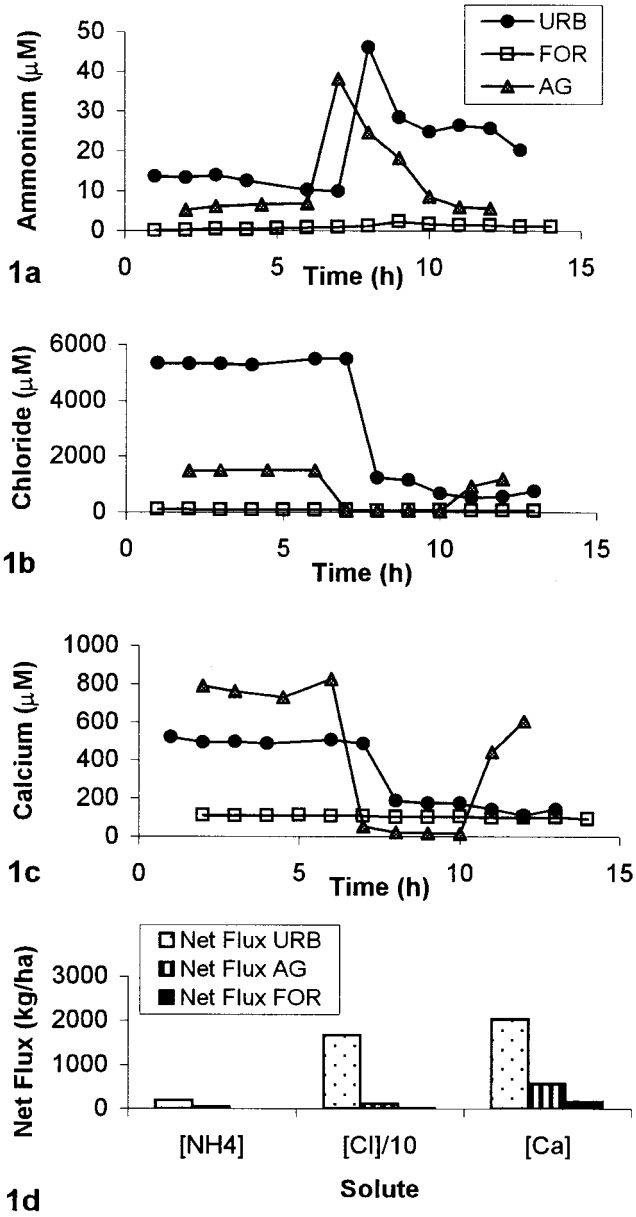

Figure 1. *Concentrations of ammonium (A), chloride (B), and calcium (C) plotted against time. Relative fluxes of ammonium, chloride (divided by 10) and calcium at the three study sites (D).*

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Fate of Anthropogenic Nitrogen in a Nearshore Cape Cod Aquifer

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Nitrogen loading from land is a principal cause of eutrophication of shallow estuaries (1, 2, 3). In regions such as Cape Cod, Massachusetts, which are underlain by unconsolidated sands, the major mechanism that transports nitrogen to estuaries is groundwater flow, and the major nitrogen source (primarily in the form of nitrate, NO_3) is often wastewater from septic systems (1, 2, 3). Wastewater nitrate concentrations decrease during travel in groundwater due to dilution with clean groundwater and to loss by denitrification (4). The loss of nitrogen during flow between a septic tank and receiving estuary can be calculated by determining the reduction in concentration of dissolved inorganic nitrogen relative to the change in concentration of a passive tracer that accounts for dilution.

We investigated losses of nitrate for a domestic septic system in the watershed of Quashnet River, Cape Cod. Effluent from septic systems moves downgradient within plumes containing high concentrations of nitrate. In addition, the study area has plumes derived from fertilized turf or fields. To sort out the different plumes, we measured boron (B, a passive tracer derived from laundry detergents and associated with wastewater sources [5, 6, 7]) and potassium (K, associated with both wastewater and fertilizer sources [8, 9]) in the samples of groundwater.

To calculate loss of nitrate along the plumes, we collected samples from nine wells downgradient from the septic system. Each well was furnished with 14 ports that allowed us to sample groundwater at intervals of 1–2 m. We collected 300 ml of water from 129 ports during June and July 2000 and measured concentrations of nitrate ($NO_3 + NO_2$) and ammonium (NH_4) using colorimetric and fluorometric techniques, respectively. We selected samples with nitrate concentrations above 8 μM and conductivities less than 4,000 μS/cm for measurements of B and K. These samples were analyzed by Ward Laboratories (Kearney, NE).

Examination of vertical and horizontal profiles of nitrate and ammonium suggested that there were three distinct plumes within our well field (Fig. 1). The upper plume moved along near the surface of the water table and contained the highest nitrate concentration of the three plumes; at nearly 3000 μM, it was similar to literature values (8) for septic effluent that has just left the leaching field. The nitrate, B, and K concentrations in this plume differed considerably from those of the other plumes (Fig. 2, A and B).

In contrast, the lower plume showed no increase in nitrate relative to increase in B (Fig. 2, A). It did, however, show a positive relationship to K, and at a given K concentration had a much higher nitrate concentration than did the upper plume (Fig. 2, B). This evidence suggests that the lower plume might be due to fertilizer use upgradient of our septic system.

The middle plume had no significant relationships between nitrate and B or K, perhaps because of the small number of samples and the low concentrations. The concentrations of nitrate, B, and K from the middle plume do, however, fit on the lower portions of the curves for the upper plume (Fig. 2, A and B). These circumstances lead us to think that the middle plume was probably the leading edge of a plume from a septic system located farther upgradient from our septic system. We therefore used data for the upper and middle plumes in our examination of the fate of septic system nitrogen in this watershed.

Concentrations of nitrate and B diminished as water parcels aged (age, Fig. 2, C and D, calculated from Vogel equations [10] that predict time since recharge as a function of depth in aquifer). To allow for dilution, we normalized the data by expressing concentrations as NO_3/B (Fig. 2, E). We estimated the NO_3/B in the effluent that had just left the septic system (age 0) by using a literature value (8) (Fig. 2, E, upper dashed line). The NO_3/B values we used came from a Cape Cod site near our study area, and the data dated from 1992, only a 7–8 year difference from our date of collection. We presume that differences in B were therefore a reasonable proxy for those in our study system. We calculated losses of NO_3 as the difference between the age 0 nitrate concentration, allowing for dilution, and the measured nitrate concentration.

Losses of nitrate in excess of dilution were quite rapid, with rates reaching 50% loss at 0.2 years (Fig. 2, F). The loss rates diminished with time, which suggests that, if these data are representative of losses elsewhere, N losses by denitrification and retention take place primarily near the septic system source. Extrapolating the curve of Figure 2 (F), we find that near-complete losses may be reached at 4.8 years, which is equivalent to 480–730 m from the septic system, assuming a travel rate of 100–150 m per year (11).

As a minimum estimate of loss, we also calculated loss relative to our highest measured NO_3/B ratio (Fig. 2, E, lower dashed line). If our initial NO_3/B ratio were closer to this measured value, our estimate of time to 50% NO_3 loss would increase to 0.6 years; but the estimate of time to 100% loss was not affected. The extrapolation to 100% loss assumes that the relationship between percent loss NO_3 and age continues to hold beyond our oldest sample. This would not be the case if the availability of labile organic carbon were to limit NO_3 loss before 100% loss is achieved.

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