

## N budgets and aquatic uptake in the Ipswich River basin, northeastern Massachusetts

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[1] We calculated N budgets and conducted nutrient uptake experiments to evaluate the fate of N in the aquatic environment of the Ipswich River basin, northeastern Massachusetts. A mass balance indicates that the basin retains about 50% of gross N inputs, mostly in terrestrial components of the landscape, and the loss and retention of total nitrogen (TN) in the aquatic environment was about 9% of stream loading. Uptake lengths of PO<sub>4</sub> and NH<sub>4</sub> were measurable in headwater streams, but NO<sub>3</sub> uptake was below detection (minimum detection limit = 0.05 μM). Retention or loss of NO<sub>3</sub> was observed in a main stem reach bordered by wetland habitat. Nitrate removal in urban headwater tributaries was because of water withdrawals and denitrification during hypoxic events and in ponded wetlands with long water residence times. A mass balance using an entire river network indicates that basin-wide losses due to aquatic denitrification are considerably lower than estimates from several recent studies and range from 4 to 16% of TDN in stream loading. Withdrawals for domestic use restrict the runoff of headwater catchments from reaching the main stem during low base flow periods, thereby contributing to the spatial and temporal regulation of N export from headwater tributaries. **INDEX TERMS:** 1871 Hydrology: Surface water quality; 1803 Hydrology: Anthropogenic effects; 1860 Hydrology: Runoff and streamflow; 1806 Hydrology: Chemistry of fresh water; **KEYWORDS:** anthropogenic, land use, uptake, nitrogen, water quality

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### 1. Introduction

[2] Human activities have greatly altered the nitrogen (N) cycle by increasing the amount of synthetically fixed N to levels far greater than that fixed naturally in the terrestrial environment [Galloway, 1998]. The fate and accumulation rate of this N in the environment are still poorly known. In temperate watersheds of the North Atlantic, about 60 to 80% of N inputs to watersheds is retained and/or denitrified [Howarth *et al.*, 1996; Boyer *et al.*, 2002], while the remainder is exported as fluvial outputs to estuaries and oceans.

[3] Nitrogen inputs from fertilizer applications, sewage discharges, atmospheric deposition and fixation by leguminous crops tend to increase N export from watersheds [Likens *et al.*, 1977; Vitousek *et al.*, 1997; Caraco and Cole, 1999]. Nonpoint sources typically dominate riverine fluxes in temperate systems [Howarth *et al.*, 1996], and fertilizer applications, human and animal waste production, and atmospheric deposition account for most of the inputs [Jordan *et al.*, 1997]. Increasing N inputs are causing eutrophication of aquatic ecosystems with symptoms ranging from increased primary productivity, decreased species

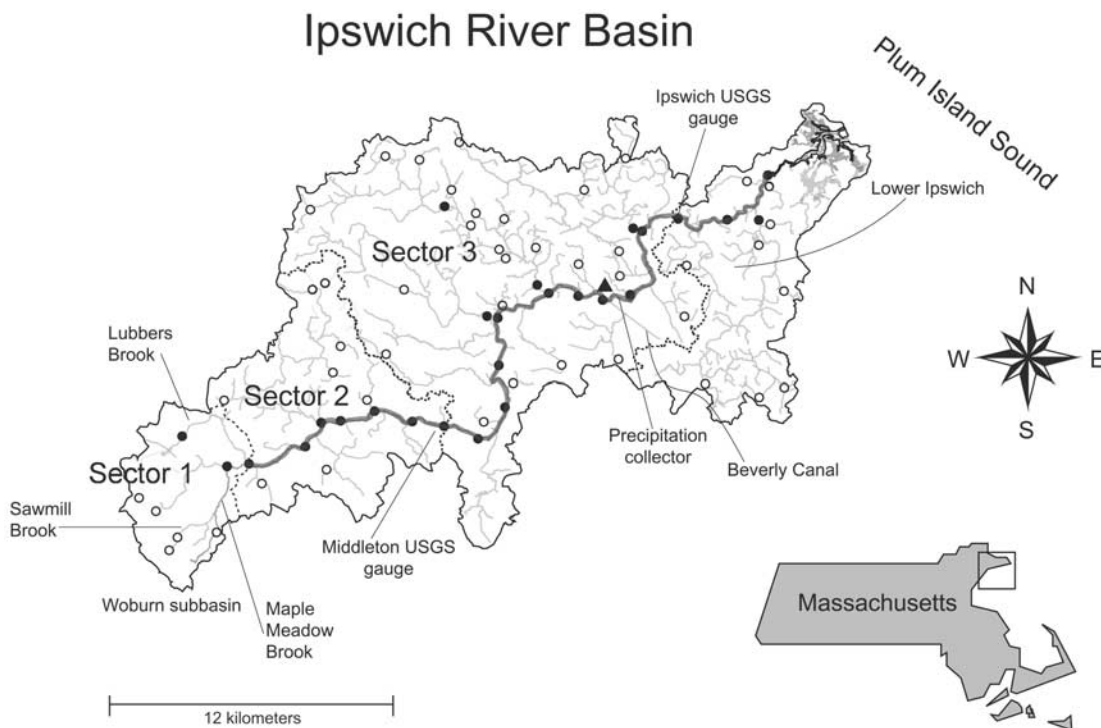
diversity, changes in food web structure, and the increased frequency and extent of aquatic hypoxia and anoxia [Turner and Rabalais, 1991].

[4] Important controls on N transport within streams have been identified recently [Alexander *et al.*, 2000; Peterson *et al.*, 2001]. For instance, mass balance analyses for the Mississippi River watershed showed that large quantities of total N and NO<sub>3</sub> are lost as water travels through its tributary streams and rivers. Loss rates are as high as 50% per day in stream channels of <50-cm depth but decline rapidly to only 0.5% per day in channels of several meters depth. Such mass balance results are consistent with <sup>15</sup>N-NH<sub>4</sub> isotope enrichment experiments, which indicate that stream uptake lengths of NH<sub>4</sub> increase logarithmically with increasing discharge and depth [Hamilton *et al.*, 2001; Mulholland *et al.*, 2000].

[5] Despite advances in our understanding of aquatic controls on N processing, estimates of aquatic N losses and storage on a basin scale have large uncertainties. Current estimates of watershed N losses in the aquatic environment have only been done indirectly. For instance, some studies use edge-of-field concentrations [Billen *et al.*, 1991] to estimate loading to streams, an approach which does not incorporate losses that occur in riparian zones. However, these N losses are substantial [Peterjohn and Correll, 1984], and by overestimating inputs, aquatic losses are thereby overestimated. Moreover, recent publications indicate that there is rapid recycling and processing of N in the aquatic environment [Mulholland *et al.*, 2000; Tank *et al.*, 2000].

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**Figure 1.** The Ipswich River basin in northeastern Massachusetts ( $404 \text{ km}^2$ ). Subbasins are designated as sectors 1, 2, and 3 and correspond to Woburn, Middleton (USGS gauging station), and Ipswich (USGS gauging station), respectively. The mouth of the river is about 7.5 km downriver from the Ipswich gauging station. Sampling sites of first-order catchment streams (open circles), major tributaries, and of the main stem (solid circles), and the location of the precipitation collector (triangle) are designated.

Consequently, although these studies did not measure N losses, they suggest that aquatic N losses are quite large. Therefore using edge-of-field estimates as inputs to streams may have inadvertently resulted in a tendency to inflate the importance of these losses. There are also large errors associated with extrapolating point estimates of denitrification or loss estimates from stream reaches (100 m to several km) to the overall aquatic network of a basin. These errors are often compounded by seasonally restricted measurements that do not incorporate lower loss rates during colder months when discharge is often highest. Hence more rigorous estimates of N losses in streams are needed to develop a better understanding of their importance in watershed budgets.

[6] Here we use a comprehensive hydrochemical characterization of a river network to determine N budgets for the Ipswich River. The basin of this river is representative of those with a large human presence responsible for large nutrient inputs to coastal receiving waters. Information on watershed land use, mass balances, and nutrient processing in the aquatic environment were compiled to address the implications of increasing urbanization on N loading to the Ipswich River system and export to the Plum Island Estuary. We include a mass balance developed to quantify N losses in the river network of an entire watershed and specifically address the mechanisms of N losses in the aquatic system and their relative importance.

## 2. Study Area

[7] The Ipswich River watershed ( $404 \text{ km}^2$ ) is one of three watersheds (Figure 1) comprising the drainage basin

of the Plum Island Sound estuary. The Parker, Rowley and Ipswich river watersheds have a combined drainage basin size of  $585 \text{ km}^2$  and lie entirely within the Seaboard Lowland section of the New England physiographic province [Fenneman, 1938]. Geology of the basin is primarily igneous and metasedimentary Paleozoic and Precambrian bedrock, and shallow soils, glacial till and bedrock outcrops are dominant geological features formed during the last ice age [Carlozzi *et al.*, 1975]. Wetlands underlain by glaciofluvial deposits are the largest natural water storage areas of the basin.

[8] The Ipswich basin has a north temperate climate [Sammel, 1967]. Precipitation averages  $1180 \text{ mm yr}^{-1}$  and is evenly distributed throughout the year. Air temperature fluctuates between an average winter minimum of  $-7^\circ\text{C}$  and an average summer maximum of about  $28^\circ\text{C}$  with an average growing season of 180 days between mid-April and mid-October. River flow is greatest during early spring snowmelt and low in the summer and fall when evapotranspiration and municipal water withdrawals exceed rainfall [Zarriello and Ries, 2000]. The Ipswich River basin has three main stem dams (at USGS gauging stations and the mouth of the Ipswich River) and several water treatment plants scattered throughout. The USGS monitors discharge at Middleton ( $115 \text{ km}^2$ ) and Ipswich ( $324 \text{ km}^2$ ) (Figure 1). The main stem of the Ipswich River is a low gradient, meandering system with its highest point at about 24 m; the highest point in the watershed is 126 m above mean sea level.

[9] Boston bedroom communities have been encroaching along the southern portion of the watershed for several

decades and population growth accelerated in the 1990s to rates common in the 1950s and 1960s (over 4000 new inhabitants per year). The total population of the Ipswich River basin was estimated at about 130,000 in 2001 (322 people km<sup>-2</sup>).

### 3. Materials and Methods

#### 3.1. Precipitation

[10] We collected event and cumulative atmospheric wet deposition on a weekly to biweekly basis from an open field at a wildlife refuge (Figure 1) for one year (May 2000 through April 2001). Deposition was collected with an Aerochem Metrics precipitation collector. A total of 42 wet events and cumulative deposition (i.e., multiple storms combined) samples were collected and analyzed for N fractions as described below. Wet deposition in this study was filtered immediately upon collection using 47 mm Nuclepore polycarbonate filters (0.4 μm) held in plastic filter holders, and filtered with 120 cc syringes under manual pressure. No deposition samples were frozen prior to analysis.

#### 3.2. Small-Catchment Stream Sampling and Land Use

[11] Stream chemistry in 43 first-order (0.5 to 3.5 km<sup>2</sup>) catchments of the Ipswich River basin were determined from synoptic surveys done on six dates between April 1999 and June 2001. Most stream water samples (80%) were frozen prior to analysis.

[12] Land use in the Ipswich drainage basin was obtained from a MassGIS <http://www.state.ma.us/mgis/massgis.htm> land use coverage for 1999 (derived from 1:25,000 aerial photography). Forest, urban, wetland, and agricultural areas represent approximately 49, 35, 9, and 7% of the basin, respectively and almost 25% of the watershed is conservation land. The 43 catchments that were sampled for stream chemistry were selected to span the range of areal extents of the various land uses within the watershed and cumulatively to approximate average land use for the entire basin. Cumulative land use in the small catchments was 43% forest, 32% urban, 19% wetland, and 6% agricultural. Stream water and land use data were used to calculate stream loading to the aquatic network of the entire Ipswich River basin.

#### 3.3. Main Stem and Tributary Sampling

[13] River water samples were collected at 28 locations along the length of the Ipswich River on a monthly basis from March 1999 to June 2001 in conjunction with the Ipswich River Watershed Association (IRWA). The mouth of the Ipswich River was sampled weekly to biweekly from May 2000 through mid-March 2001; in addition, daily sampling was done during the snowmelt runoff period of mid-March to mid-April 2001 (n = 64).

[14] We conducted several samplings across the width of the Ipswich River in the spring to test for lateral heterogeneity of river chemistry. These samplings included three measurements across the width of the Ipswich River at its mouth and from a bridge close to the output of sector 2. There were no significant variations in N concentrations using a paired t test (p < 0.01). Given this evidence and the fact that the Ipswich River is a relatively small system that is generally less than 10 m wide and 2 m deep at its

lower reaches and has no strong point sources, significant lateral or depth variations described above are probably uncommon.

[15] A small headwater stream, Sawmill Brook, in an urbanized catchment of the basin was also sampled weekly from May 2000 to December 2001 at up to 8 sites along a 5 km longitudinal transect. Because of the large effect of road salting in sector 1 (Figure 1) and the conservative dilution of Cl from the upper to lower reaches of the main stem, we were able to modify NO<sub>3</sub> transect data by a Cl factor [Williams *et al.*, 2001]. This factor is calculated by dividing each Cl concentration by the largest concentration of Cl in a series; the concentration of each sample divided by the ratio calculated above creates a linear reference against which other solutes can be compared because it reduces the effect of dilution. Most river samples (>90%) were frozen prior to analysis, albeit those collected during the intensive sampling period were refrigerated and analyzed within 1 to 3 days.

#### 3.4. Nutrient Uptake Experiments

[16] Nutrient uptake experiments were conducted over the course of the study to characterize uptake lengths of inorganic N and P in the main stem and upland tributaries. Slug additions of inorganic nutrients (NH<sub>4</sub>, NH<sub>4</sub> + NO<sub>3</sub>, and NH<sub>4</sub> + PO<sub>4</sub>), along with Rhodamine WT dye as a tracer, were done in third-order, main stem reaches of the Ipswich River with and without marsh and swamp wetlands in August and September 1998. Additions of NO<sub>3</sub>, NH<sub>4</sub>, and PO<sub>4</sub> concentrations ranged from 214 to 260, 209 to 368, and 27 μM, respectively. Ambient concentrations were approximately 15, 2 and 0.5 μM, respectively. Rhodamine WT was analyzed on a Turner Designs TD-700 laboratory fluorometer with temperature compensation and a Rhodamine filter pack (precision of ±2%).

[17] The methods used in our nutrient uptake experiments were derived from Newbold *et al.* [1981] and Mulholland *et al.* [1990]. Nutrients and a LiBr tracer were injected into small, first-order streams bordered by predominately urban, forest, and wetland covers with a high-precision Masterflex peristaltic pump and tubing during the fall of 2000 and spring and summer of 2001. Bromide concentrations were measured on a Dionex ion chromatograph (model 2010i) with a precision of ±1%. Nitrate, NH<sub>4</sub> and PO<sub>4</sub> were increased about 3, 1, and 2 μM above ambient concentrations, which ranged from 2 to 50, 1 to 13, and 0.5 to 2 μM, respectively.

#### 3.5. Chemical Analyses

[18] All water samples collected in this study were immediately stored on ice during transport to the laboratory. Samples were frozen if NH<sub>4</sub> or NO<sub>3</sub> could not be processed within 2 to 3 days of collection. There were no significant differences in NH<sub>4</sub> and NO<sub>3</sub> concentrations between frozen and refrigerated samples. Refrigerated samples were stored at about 4°C until analysis. Unless indicated otherwise, stream water samples were collected in a plastic bucket and immediately filtered into acid-washed polyethylene vials using Whatman 24 mm GF/F glass-fiber filters (nominal pore size of 0.7 μm), plastic filter holders, and syringes.

[19] We conducted tests to determine if there were measurable differences between 0.4 μm polycarbonate filters and Whatman glass fiber filters (0.7 μm nominal pore size)

and found no significant differences (paired *t* tests,  $p < 0.01$ ) between these filters in either rain or stream water samples of the Ipswich basin for any of the constituents of nitrogen measured in our study. Hence we are confident that the use of these different filters and sample processing techniques did not result in added uncertainties. Sample rejection was employed when duplicates were  $>10\%$  of each other.

[20] Ammonium,  $\text{NO}_3$  ( $\text{NO}_2 + \text{NO}_3$ ), total dissolved N (TDN), and particulate N (PN) were determined using standard colorimetric methods. Ammonium was determined using an indophenol method. Nitrate was usually analyzed colorimetrically following cadmium reduction on a Lachat autoanalyzer. Concentrations of  $\text{NO}_2$  were determined to be negligible ( $<0.2 \mu\text{M}$ ) and, therefore samples were also run on a Dionex ion chromatograph (model 2010i) from May 2000 through June 2001 to determine  $\text{NO}_3$ ,  $\text{SO}_4$ , and Cl. River samples from March 1999 to May 2000 were analyzed for  $\text{SO}_4$ , Cl, and  $\text{NO}_3$  using ion chromatography. Nitrate concentrations determined by the two methods were not significantly different (*t* test,  $p < 0.01$ ). Persulfate oxidation followed by  $\text{NO}_3$  analysis was done to quantify total dissolved nitrogen (TDN) using the method of *Valderrama* [1981]. Dissolved organic nitrogen (DON) was calculated as the difference between TDN and DIN ( $\text{NH}_4 + \text{NO}_2 + \text{NO}_3$ ). Particulate nitrogen (PN) was determined by filtering about 1 liter of water through precombusted 47 mm GF/F filters that were subsequently dried at  $60\text{--}80^\circ\text{C}$  and stored in a desiccator. Insignificant differences in the concentrations of PN determined using our TDN protocol and a CHN analyzer (paired *t* test,  $p < 0.05$ ) enabled us to use the TDN protocol during our intensive collection period of May 2000 through April 2001.

### 3.6. Flux Calculations

[21] Volume-weighted mean nutrient concentrations and riverine nutrient fluxes were calculated using daily discharges from the USGS gauging stations (sectors 2 and 3;  $n = 33$  and  $64$ , respectively). Annual volume-weighted means were calculated as:

$$\text{VWM} = (\sum C_i Q_i) / \sum Q_i \quad (1)$$

where  $C_i$  is the observed nutrient concentration of instantaneous river flow  $i$ ,  $Q_i$  is the discharge volume for the sample period with collection date as the midpoint of the period  $i$ , and the denominator is the annual  $\Sigma$  of discharge volume.

[22] The annual flux of N fractions ( $F_j$ ) at both USGS gauging stations was calculated as the product of the VWM concentration of each N fraction and annual discharge ( $Q_j$ ) at each station, or:

$$F_j = [\text{VWM}] [Q_j] \quad (2)$$

[23] The annual flux of N from sector 1 of the watershed was determined as the product of the VWM concentration and a total runoff volume. The VWM concentration was calculated from monthly IRWA samples and discharge estimates ( $n = 12$ ), and total runoff was determined using the runoff coefficient that was calculated for the entire basin (i.e., fraction of rain as runoff = 0.44).

[24] We estimated N loading (i.e., stream loading used in our riverine budget) to first-order streams from the sampling

data for 43 headwater streams. Nitrogen concentrations determined from these samples were used in conjunction with variable runoff coefficients of 0.44 to 0.51 (increasing proportionally with increasing urban land use) to calculate flux. Variable runoff coefficients were used to account for the increased runoff generally associated with disturbed, nonforested areas because of reduced evapotranspiration and increased runoff from impervious covers [*Dunne and Leopold*, 1978]. These coefficients were determined empirically for the intensive sampling period and correspond to those calculated for the entire Ipswich River basin, with and without water withdrawals included, respectively (i.e., 714 mm watershed export + 121 mm withdrawal = 835 mm; runoff coefficient = 0.51). Because about 89% of the total export of  $\text{NO}_3$  occurred from November 2000 to April 2001, loading estimates were weighted by seasonal discharge volume. Comparisons of the small stream loading and watershed export of conservative solutes (i.e., Cl, Na, Ca, and Mg) were used to evaluate the accuracy of the loading values for the dissolved N fractions and bracket the possible errors associated with this analysis (described below). Considerable particulate transport was observed from developed catchments during storm flow events but this was not quantified. On the basis of sampling at the mouth of the Ipswich River where PN was 13% of TDN in our N budget, herein we assume that PN in stream loading is about 25% of the dissolved fraction to account for the higher fluxes of particulates observed in the storm flow runoff of smaller catchments compared to the mouth of the Ipswich River.

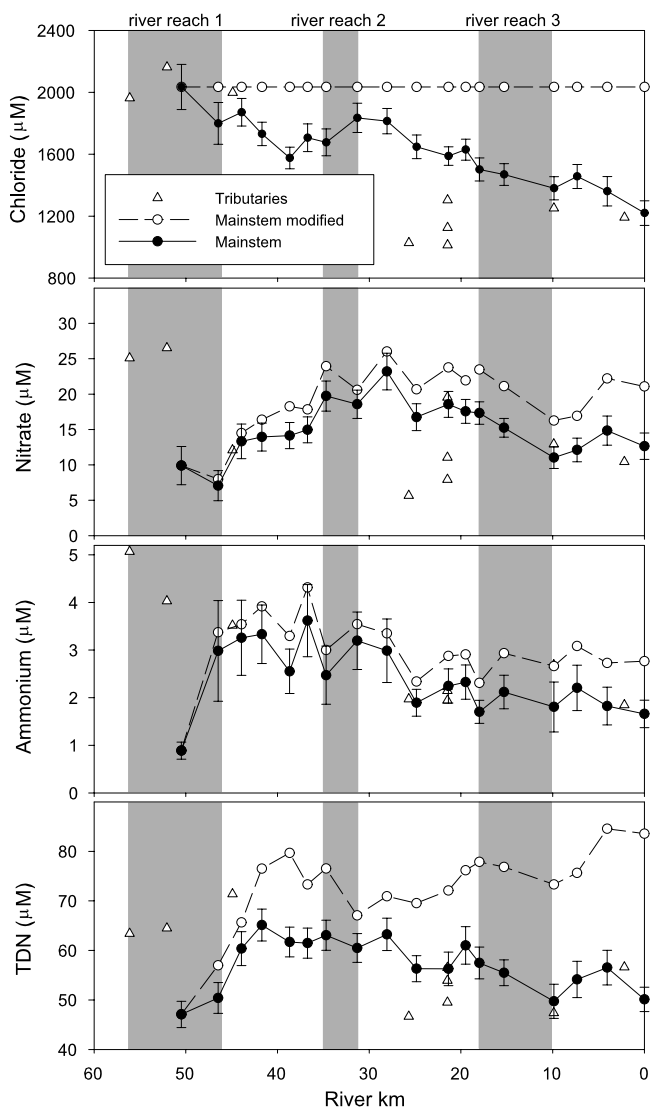
### 3.7. Solute Budgets

[25] A N balance was calculated for the entire Ipswich basin including N inputs from precipitation, fertilizer, and imported human foodstuffs, and N outputs due to municipal withdrawals and fluvial export. A riverine N balance was also constructed for 3 sectors of the Ipswich River. Sector 1 (Woburn) includes Sawmill, Maple Meadow and Lubbers brook catchments in the headwaters of the main stem of the Ipswich River, sector 2 represents the river reach and associated watershed area between the beginning of the main stem Ipswich River and the USGS gauging station at Middleton, and sector 3 represents the river reach and associated watershed area between the Middleton station and USGS gauging station at Ipswich (Figure 1). Total areas and main stem channel lengths of each of these sectors are 37 (0), 78 (14) and 209  $\text{km}^2$  (29 km), respectively.

## 4. Results

### 4.1. Main Stem Transects and Outflow Chemistry

[26] We analyzed 28 consecutive months (March 1999 to June 2001) of longitudinal transect samples from the main stem (18 sites) of the Ipswich River and its major tributaries (9 sites). A Cl modification factor was used to partially remove the effect of dilution and highlight areas of potential  $\text{NO}_3$  processing (Figure 2). There were three wetland reaches of the main stem of the Ipswich River where we observed consistent decreases in  $\text{NO}_3$  concentrations, and the largest decreases occurred in Wenham Swamp (reach 3). In contrast, Cl had relatively conservative trends and decreased from the Ipswich River headwater (km 56) to the river's mouth (Figure 2).



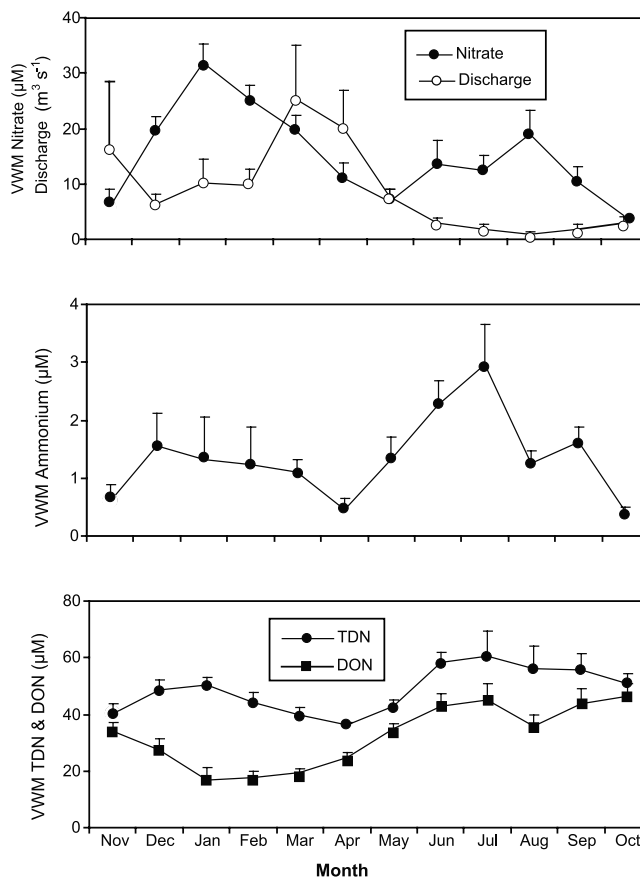
**Figure 2.** Longitudinal transects of monthly  $\text{NO}_3$ ,  $\text{NH}_4$ , TDN, and Cl concentrations (solid line, solid circles, and standard errors) and these solutes modified by a Cl factor (dashed line with open circles) along the main stem of the Ipswich River ( $n = 18$ ) and in major tributaries (open triangles;  $n = 9$ ) for the period from March 1999 to June 2001. Lubbers (56 km) and Maple Meadow (52 km) brooks are two upstream tributaries draining the most urbanized sector of the watershed. The x axis represents the distance (km) upriver from the mouth of the Ipswich River. River reaches 1, 2, and 3 represent wetland reaches that exhibit consistent decreases in  $\text{NO}_3$  concentrations. Wenham Swamp is the third river reach and is the largest contiguous wetland in the Ipswich River basin.

[27] An 8-year data set of chemistry from the outflow of the Ipswich River was collected monthly from September 1993 through August 2001 by Plum Island Estuary Long-Term Ecological Research (PIE LTER) project. All the N fractions, except DON, had annual bimodality in the 8-year average (Figure 3). There was a winter peak in N (December–January), decreasing concentrations through April or May because of increased runoff, particularly in

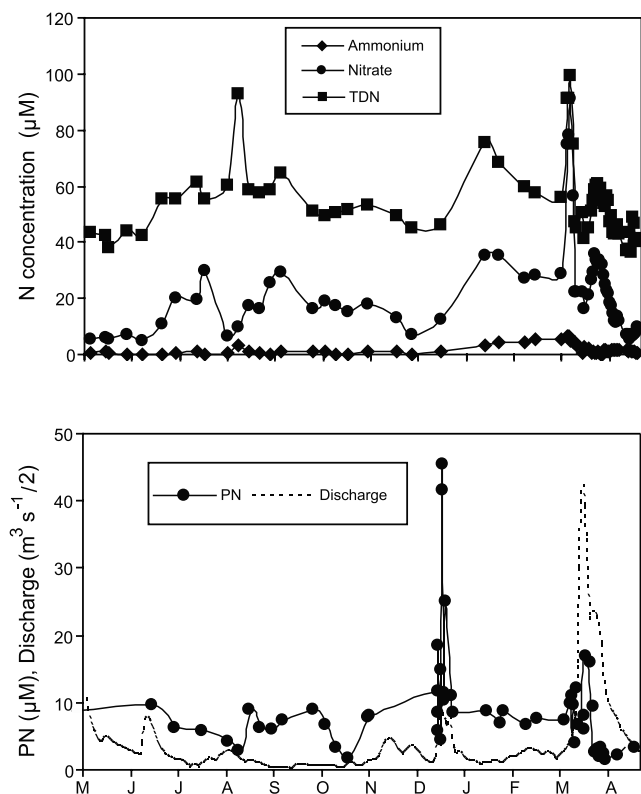
the spring snowmelt period, and a summer peak (July–August). Nitrate concentrations were highest in the winter whereas those of the other N fractions were highest in the summer.

[28] During the intensive sampling period (i.e., May 2000 through April 2001), N concentrations from the outflow of the Ipswich River varied considerably throughout the year. Nitrate and  $\text{NH}_4$  concentrations increased with the rise in discharge that occurred in December, and all solute concentrations (except PN) peaked just prior to peak runoff because of the flushing of overwintering products and snowpack elution, which was followed by a dilution effect (Figure 4). The relative importance of particulates was greatest during winter storm flow events and snowmelt runoff when live vegetative cover was least and percent runoff greatest. On a seasonal basis, the relative importance of DIN was highest during the period from February through March, and about 89 and 70% of the total export of  $\text{NO}_3$  occurred from November 2000 through April 2001 and February through April 2001, respectively.

[29] Volume-weighted mean concentrations were calculated for wet deposition and river water collected during the study period. Nitrate composed about 59% of TDN in wet



**Figure 3.** Monthly averages and standard errors of instantaneous discharge and N concentrations from September 1993 through August 2001. Data were collected and analyzed by the PIE LTER research project independently of those from the intensive sampling period from May 2000 through April 2001.



**Figure 4.** Time series of the N fractions and average daily discharge measured at the Ipswich River Dam (river km 0) during the intensive sampling period from May 2000 through April 2001.

deposition, whereas DON was only 8% of TDN (Table 1). In contrast, NO<sub>3</sub> in river water composed about 40% of TDN, whereas DON was about 58% of the TDN pool. Inputs of N from wet deposition equaled those of fluvial outputs (6.1 kg ha<sup>-1</sup> yr<sup>-1</sup>).

**4.2. Nutrient and Tracer Addition Experiments**

[30] Nutrient addition experiments along third-order reaches of the main stem with and without fringing wetlands were conducted in September and August of 1998 using a combination of NH<sub>4</sub> and NO<sub>3</sub>, NH<sub>4</sub> and PO<sub>4</sub>, and NH<sub>4</sub> with Rhodamine dye as a conservative tracer. In all experiments, NH<sub>4</sub> had insignificant deviations from the conservative tracer, whereas NO<sub>3</sub> increased slightly (data not shown).

Phosphate was the only inorganic nutrient that had measurable uptake in these reaches (uptake length (S<sub>w</sub>) = 2,365 m).

[31] Sawmill Brook, a stream draining a highly urbanized area in the headwaters of the Ipswich River basin, was extensively sampled from May to December 2000. Nutrient addition experiments using the conservative tracer LiBr were conducted in urban and forested reaches of Sawmill Brook during fall 2000 and spring 2001; uptake lengths were ranked as NO<sub>3</sub> > NH<sub>4</sub> (S<sub>w</sub> = 225 m) > PO<sub>4</sub> (S<sub>w</sub> = 124 m). Nitrate uptake was below detection because of negligible uptake and/or inputs of NO<sub>3</sub> (either lateral or regenerative) that exceeded uptake along the experimental reaches. Nutrient addition experiments conducted in a wetland reach of Lubbers Brook with low background concentrations of NO<sub>3</sub> (i.e., <2 µM) also had undetectable NO<sub>3</sub> uptake.

**4.3. Estimation of Solute Inputs and Outputs**

[32] Our N budget was calculated using data from May 2000 through April 2001 (Table 2 and Figure 5). The 3-year average deposition (1997–1999) of inorganic N (using NCDC precipitation volume for the Ipswich River basin and chemistry from NADP site MA13) was about 77% of that which occurred during our intensive study period. However, because NADP data do not include measurements of DON, we used precipitation volume and concentration data from the Ipswich River basin to estimate precipitation inputs (248 Mg). Clean Air Status and Trends Network (CASTNet) data for two sites closest to our study basin (Connecticut and Vermont) indicate that dry deposition is about 30% of total atmospheric N inputs, and we used this as our estimate of dry deposition.

[33] We also estimated bulk N inputs from imported human foodstuffs. These were estimated as the product of 4.8 kg N person<sup>-1</sup> annually [Valiela *et al.*, 1997] and a population of 130,000 (624 Mg N yr<sup>-1</sup>); net N inputs from imported human foodstuffs were estimated as the product of 4.8 kg N person<sup>-1</sup> and the number of people (81,900) living in households currently not sewered in the basin (393 Mg N yr<sup>-1</sup>). Human foodstuffs are considered to be imported N to many regions of the world [e.g., Howarth *et al.*, 1996], including the Ipswich River basin because N is almost exclusively imported from outside the region. N inputs from fertilizers were estimated as the product of a low-intensity application (14 kg N ha<sup>-1</sup> yr<sup>-1</sup>) to the total area of pervious residential areas and pastures (11,357 ha) in the basin (Table 2). The low-intensity application rate was chosen because the average application to a fertilized area in

**Table 1.** Volume-Weighted Means of Wet Deposition and River Water and Normalized Inputs and Outputs for the Ipswich River Basin From May 2000 Through April 2001<sup>a</sup>

Solute	Wet Deposition, µM	River Water, µM	Wet Deposition Input, kg ha <sup>-1</sup> yr <sup>-1</sup>	Fluvial Export, kg ha <sup>-1</sup> yr <sup>-1</sup>	Net Retention/Net Export, <sup>b</sup> kg ha <sup>-1</sup> yr <sup>-1</sup>	Wet Deposition Input, t	Fluvial Export, t
NH <sub>4</sub> -N	8.2	1.5	1.9	0.2	1.7	75.3	6.1
NO <sub>3</sub> -N	15.9	21.7	3.6	2.2	1.4	146.1	87.7
TDN	27.0	53.7	6.1	5.4	0.7	248.0	216.9
DON	2.2	30.5	0.5	3.1	-2.5	20.2	125.9
PN	0.0	7.1	0.0	0.7	-0.7	0.0	28.7

<sup>a</sup>Wet deposition volumes from the USGS gauging stations at Ipswich (1690 mm) and Middleton (1503 mm) were weighted by their respective drainage area (324 km<sup>2</sup> and 115 km<sup>2</sup>, respectively). The runoff coefficient increases from 0.44 to 0.51 if a 10-year average water withdrawal of 115 mm is added to export (714 mm).

<sup>b</sup>Positive values are net retention, and negative values are net export.

**Table 2.** Terms of the Terrestrial and Aquatic N Budgets for the Ipswich River Basin With Individual and Cumulative Errors<sup>a</sup>

	Value, Mg yr <sup>-1</sup>
<b>Inputs</b>	
Imported foodstuffs	624 ± 81
Wet deposition	248 ± 30
Dry deposition	106 ± 13
Fertilizer application	159 ± 159
Gross Inputs	1137 ± 181
<b>Runoff</b>	
Stream loading	273 ± 33
<b>Watershed Export</b>	
Fluvial export	243 ± 29
Sewage export	250 ± 25
Drinking water export	22 ± 2
<b>Mass Balances</b>	
Terrestrial	1137 - 250 - 22 - 273 = 592 ± 186 (52% retentive)
Aquatic	273 - 243 - 6 = 24 ± 44 (9% retentive)

<sup>a</sup>We assume that drinking water export is 75 and 25% groundwater and surface water withdrawal, respectively (i.e., 16 and 6 Mg N).

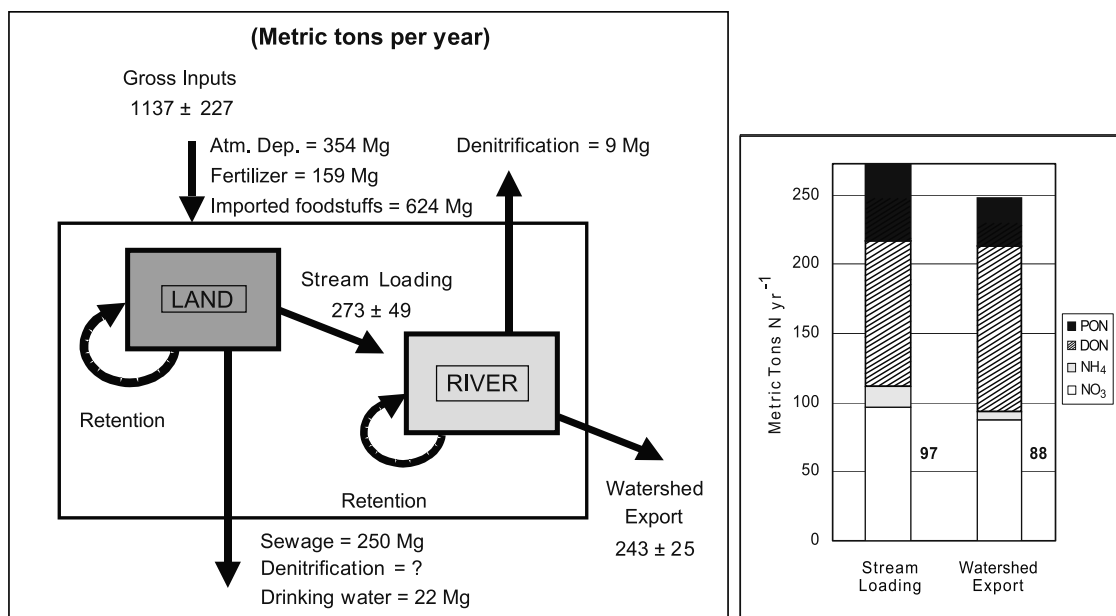
coastal Massachusetts is about 100 kg N ha<sup>-1</sup> yr<sup>-1</sup> and, of this, it is estimated that only 34% of households use fertilizers [Valiela et al., 1997]. Furthermore, many lawns and pastures are not fertilized every year (G. Porter, Massachusetts Department of Agriculture, personal communication). Estimates of low-density (8255 ha) and high-density (3102 ha) residential areas are from Zariello and Ries [2000]. Pasture, which is equated with the proportion of agricultural area in the Ipswich basin (2,828 ha), was included in the low-density estimate. The export of agricultural products from the basin was assumed to be negligible because most agricultural area is horse pasture or the small-scale farming of products that are consumed locally. The daily flux of people in and out of the basin may amount to

an overall loss or gain of N, but this could not be accurately quantified. For the sake of simplifying this budget, we assume that this net flux was negligible, as was N fixation. There are no known point source inputs.

[34] Our terrestrial budget is meant only to show the relative magnitude of N retentiveness in the Ipswich River basin and not to rigorously assess the errors associated with each input parameter. However, we estimated the maximum cumulative error associated with our terrestrial budget using calculated or assumed errors for each terrestrial input. For instance, with the maximum value of N generated per person being about 5.4 kg person<sup>-1</sup> yr<sup>-1</sup> [Valiela et al., 1997], we can use the difference compared to the value of 4.8 kg person<sup>-1</sup> yr<sup>-1</sup> in our study as a surrogate for the error associated with our imported foodstuffs term (±13%). We calculated the error of wet deposition using Tukey's jackknife method [Sokal and Rohlf, 1981] and assumed that this was the same for dry deposition (±12%). Lastly, we assumed that the error for fertilizer input could be as high as ±100%. Hence the cumulative error of our terrestrial inputs was ±16% (Table 2).

[35] Nitrogen loading to the riverine aquatic system was calculated from our first-order tributary data. The relative importance of NH<sub>4</sub>, NO<sub>3</sub>, DON, and PN export was 5, 36, 39, and 20% of TN inputs (273 Mg), respectively (Table 2). These solutes decreased by 9, 9, 28, and 26 Mg, which corresponds to a loss of 60, 9, 26, and 46% of these solutes in the riverine system (i.e., from stream loading to watershed export), respectively.

[36] On the basis of a mass balance approach, N retention and loss in the aquatic system was calculated as the difference between loading and export terms. However, the propagated error associated with this approach can be very large. For instance, with an estimated error for stream loading of ±12% (see below), a calculated error using Tukey's jackknife method [Sokal and Rohlf, 1981] of



**Figure 5.** Summary of our terrestrial and riverine N budgets for the Ipswich River basin for the period of May 2000 through April 2001. The right plot indicates the changes that occur in the riverine budget with regard to the N fractions in runoff and export.

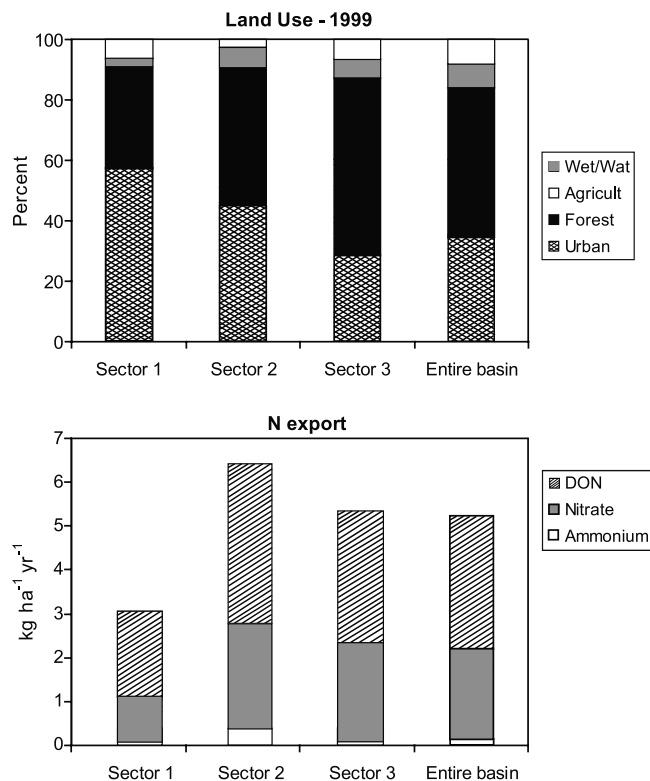
$\pm 12\%$  for watershed export, and an assumed error of  $\pm 10\%$  for surface water withdrawal, respectively, and assuming that the errors are independent of one another, the propagated error for the terms in the budget would be on the order of  $180\%$  (i.e.,  $273(\pm 33) - 243(\pm 29) - 6(\pm 0.6) = 24(\pm 44)$ ) (Table 2).

[37] To overcome this problem, we assessed retention and loss relative to conservative solutes (i.e., Na, Cl, Ca, and Mg). The stream loading of these conservative solutes (calculated using the same method as for the dissolved fractions of N) ranged from 109 to 121% of their watershed export. Assuming that storage and time delays are unimportant in the aquatic system, the stream loading of conservative solutes should equal that of watershed export, which allowed us to calibrate the N in stream loading and estimate possible errors. For example, because the stream loading for Cl was 109% of watershed export, we adjusted the N fractions in stream loading calculated in the above manner to 100% (i.e.,  $106 \text{ Mg NO}_3/1.09 = 97 \text{ Mg NO}_3$ ). We used the range of values of the conservative ions to represent the error associated with our estimates of stream loading ( $\pm 12\%$ ).

[38] Considerable particulate transport was observed from developed catchments during storm flow events, and herein we assume that this is about 25% of the dissolved fraction, or a total of  $55 \text{ Mg PN yr}^{-1}$ . Including this particulate load, total runoff was estimated as  $273 \text{ Mg N yr}^{-1}$ .

[39] We used measured fluvial export at the mouth of the Ipswich River (Table 1) and a total of 115 mm of water removal by public drinking water export (55 mm) and sewered wastewater that leaves the basin (i.e., the N in treated water before waste is added; 70 mm exported – 10 mm imported = 60 mm (L. Claessens et al., Evaluating the effect of a changing land-use and climate on the Ipswich River basin, Massachusetts, USA: Historical water budget, manuscript in preparation, 2003)) to calculate total N output from the basin. Inorganic N concentrations in treated water were obtained from the Wilmington Water and Sewer Department to estimate this N export (Table 2). Of the 85 water withdrawal sites in the Ipswich basin, there are 12 well sites that affect the main stem of the river; 8 of these are in a cluster just downriver of the headwater site at Woburn and 4 are surface withdrawal sites along the main stem, 2 in each of sectors 2 and 3. For the entire basin, net N inputs ( $1001 \text{ Mg yr}^{-1}$ ) minus outputs ( $243 \text{ Mg yr}^{-1}$ ) indicate that the basin retains about 76% of N inputs in terrestrial and aquatic compartments of the watershed (Table 2). Gross TN export was  $6.1 \text{ kg ha}^{-1} \text{ yr}^{-1}$  for the entire Ipswich River basin and storm flow was determined to be responsible for  $<5\%$  of this flux.

[40] Land use in 1999 was characterized for the entire Ipswich River basin and three subbasin areas representing different river reaches. Urban area decreases and forested area increases from sector 1 to sector 3 (i.e., SW to NE; Figure 6). Urban land use was about 58, 44 and 35% of the total basin area in sectors 1, 2 and 3 ( $37, 78$  and  $209 \text{ km}^2$ , respectively). However, the  $\text{NO}_3$  export in sector 1, that has 8 well and 1 surface withdrawal sites, was only about 80% of that in sector 2. Sector 2 had larger N export than the other sectors for all the N fractions (Figure 6). Gross TDN export was lower from sector 1 than net TDN export (i.e., sector 2 flux minus sector 1 flux) from sector 2, and net



**Figure 6.** Land use of the Ipswich River basin in 1999 and land use in 1999 and the export of dissolved N fractions for sectors 1, 2, and 3. The areal extents of sectors 1, 2, and 3 are 37, 78, and  $209 \text{ km}^2$ , respectively.

TDN export from sector 3 was lower than that of sector 2 by almost a factor of 2.

## 5. Discussion

### 5.1. N Budget

[41] Our N budget indicates that the Ipswich River basin is functioning similarly to many temperate watersheds where outputs are about 25% of inputs [Jordan et al., 1997; Howarth et al., 1996; Boyer et al., 2002]. In the Ipswich basin, gross N input via imported human foodstuffs is the dominant source to the system ( $624 \text{ Mg}$ ) and net septic sewage inputs are 63% of gross inputs. Net septic sewage inputs are higher than those from atmospheric deposition ( $393 \text{ Mg}$  versus  $354 \text{ Mg}$ , respectively). N inputs from wet deposition in our budget may be overestimated since about 30% occurs in the form of  $\text{NH}_4$ , which may be recycled  $\text{NH}_3$  volatilized from within the basin. In the regional N budgets of basins in the North Atlantic, Howarth et al. [1996] excluded  $\text{NH}_x$  deposition from the estimate of atmospheric N inputs because  $\text{NH}_3$  and  $\text{NH}_4$  do not travel far in the atmosphere before being deposited back to the ground. However, in a small coastal watershed such as the Ipswich River basin, considerable amounts of  $\text{NH}_3$  and  $\text{NH}_4$  probably originate from outside the basin boundary [Boyer et al., 2002], and we therefore include  $\text{NH}_4$  in our wet deposition estimate.

[42] The average deposition rate of N in precipitation in the Ipswich is about 70% of the  $7.9 \text{ kg ha}^{-1} \text{ yr}^{-1}$  reported



for the Chesapeake Bay [Jordan *et al.*, 1997]. In central Europe, deposition can be as high as  $59 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  [Boxman *et al.*, 1995]. In our study, imported human food-stuffs, wet + dry atmospheric deposition, and fertilizer contribute about 55, 31, 14% of gross N inputs, respectively. Fisher and Oppenheimer [1991] estimate that atmospheric deposition contributes about 40% of the N inputs in the Chesapeake Bay, followed by animal waste (31%), fertilizer (25%), and sewage (7%).

[43] Fluvial N output from the Ipswich River was  $243 \text{ t}$  ( $6.1 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ) during May 2000 to April 2001 and is similar to wet deposition inputs. Of the N exported,  $2.4 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  was in the form of DIN, ranking the Ipswich basin among those with the lowest yields of DIN in the Northeastern U.S. [Howarth *et al.*, 1996; Seitzinger and Kroeze, 1998]. This difference is likely due to low N fertilizer application and agricultural runoff and diversion of sewage from the watershed.

## 5.2. N Losses in the River System

### 5.2.1. Main Stem

[44] One of our major objectives was to determine the mechanisms responsible for the spatial and temporal variability and the removal or storage of  $\text{NO}_3$  in the Ipswich River system. Using N and conservative solute concentrations measured in longitudinal transects of the river, there were several river reaches that had consistent reductions in  $\text{NO}_3$  concentrations. Chloride had a fairly consistent dilution trend from upriver to downriver, and was therefore used to reduce some of the effects of dilution on  $\text{NO}_3$  concentrations (Figure 2). River reaches where  $\text{NO}_3$  concentrations commonly decreased were generally correlated with wetland habitats with relatively broad floodplains uninfluenced by lateral urban developments and their associated inputs from septic seepage and storm drain effluent.

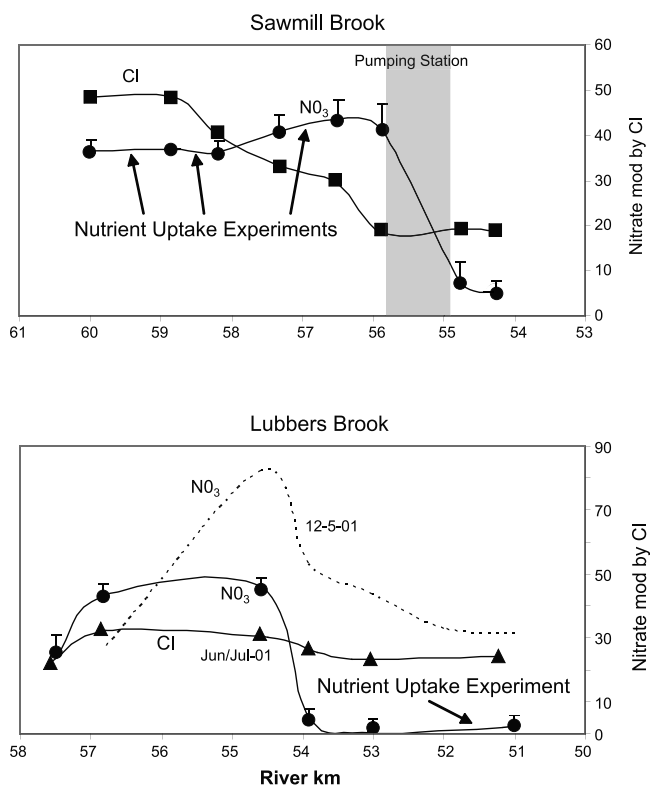
[45] In-stream denitrification could be a major factor responsible for the observed decreases in  $\text{NO}_3$  concentrations in wetland reaches. However, the vast majority of flow through these wetland reaches is channelized and does not actually flow over or through the wetlands (albeit the latter does occur during the spring runoff period). Channelized flow would likely limit rates of denitrification by keeping the surface area to volume ratio low.

[46] The results of our nutrient addition experiments indicate that  $\text{NO}_3$  removal due to denitrification or uptake is relatively unimportant in some reaches of the main stem. However, reach 3 (Wenham Swamp) is hydrologically more complex than where our nutrient addition experiments were conducted (i.e., reach 2), suggesting that there may be other mechanisms contributing to the observed concentration decrease. We identified five possible mechanisms: First, chlorophyll-a concentrations tend to increase from just above Wenham Swamp to the mouth of the river. For instance, we observed a fivefold increase in chlorophyll-a concentrations (3 to  $16 \mu\text{M}$ ) in July 1999 suggesting that phytoplankton productivity may strip some  $\text{NO}_3$  from river water along reach 3. Second, surface water is withdrawn from the Beverly Canal (Figure 1) from December to May for municipal consumption from the upper reaches of the main stem in Wenham Swamp (river km 18). Decreasing the quantity of water flowing through reach 3 would increase the importance of lateral inputs (i.e., those with low  $\text{NO}_3$

concentrations because of denitrification and plant uptake) from the wetland during low-flow periods. Third, lateral inputs of surface runoff and groundwater low in  $\text{NO}_3$  concentrations could be responsible for much of the decrease in  $\text{NO}_3$  concentrations. The fluvial geomorphology of Wenham Swamp observed in orthophotos indicates that there are numerous small tributaries along the 2 km reach where the  $\text{NO}_3$  decrease occurs (river km 13 to 11). These tributaries are a source of surface runoff during higher flows and replenish groundwater in the adjacent wetlands during low-flow periods; the latter would be replenished also by inundation of the wetlands during flooding.

[47] The flow of river water through wetland sediments (i.e., interflow) is a fourth possible mechanism of  $\text{NO}_3$  removal. However, the importance of interflow as a mechanism of  $\text{NO}_3$  removal is likely limited since  $\text{NO}_3$  concentrations decrease along only 2 km of the 10 km reach through Wenham Swamp and the hydraulic conductivities of the wetland sediments of this 2 km reach would need to be extremely high to accommodate the volume of water responsible for the observed decreases in  $\text{NO}_3$  concentrations, particularly during moderate to high-flow periods. Moreover, if interflow was an important mechanism, it is unlikely that the  $\text{NO}_3$  decrease would be restricted to 2 km of a 10 km reach having similar geomorphological and vegetation characteristics. Lastly, a dam just above the Ipswich USGS gauging station impounds water in the lower 3 km of Wenham Swamp during periods of low flow. In-stream denitrification in this ponded area appears to be influential in the summer months since concentrations can decrease to levels below detection. However, background concentrations of  $\text{NO}_3$  in the downriver reach of the wetland occur only during the lowest-flow periods ( $Q < 0.4 \text{ m}^3 \text{ s}^{-1}$ ) when water residence times in the ponded area can exceed 30 days. Hence the overall effect of in-stream denitrification or plant uptake in this reach on the annual N budget is likely to be quite small.

[48] The relative importance of lateral inputs versus in-stream processes in regulating  $\text{NO}_3$  concentrations in reach 3 is evident in estimates of the  $\text{NO}_3$  uptake potential of Wenham Swamp. Using discharge data from the USGS gauging station in Ipswich and the average of the measured decreases in  $\text{NO}_3$  concentrations along reach 3, the product of a  $6 \mu\text{M}$  average decrease in  $\text{NO}_3$  and only half of the discharge (i.e., not including the discharge that occurs during about one month straddling peak snowmelt) measured at the Ipswich USGS gauging station would amount to a total of 8.4 Mg of  $\text{NO}_3\text{-N}$  removal. This estimate accounts for 93% of the  $\text{NO}_3$  removal calculated for the entire aquatic system in our riverine budget and is unrealistically large considering that reach 3 represents at most 0.2% of the aquatic surface area of the Ipswich River network. Alternatively, estimating that the benthic surface area of the 10 km river reach through the Wenham Swamp is  $120,000 \text{ m}^2$ , a denitrification rate of over  $0.5 \text{ mmol m}^{-2} \text{ hr}^{-1}$  would be required to account for the  $8.4 \text{ Mg N yr}^{-1}$  loss in our riverine budget calculated above. Although this denitrification rate is not out of the range of reported rates, it is unlikely that rates would be this high in a river system with ambient concentrations of  $\text{NO}_3$  commonly  $< 30 \mu\text{M}$  and temperatures  $< 10^\circ\text{C}$  for the period from November through May, when about 85% of the annual discharge



**Figure 7.** Longitudinal transects of  $\text{NO}_3$  modified by a CI factor for the Sawmill ( $n = 18$ ) and Lubbers brooks ( $n = 3$ ) tributaries located in sector 1 indicate that large  $\text{NO}_3$  losses occur over relatively short distances. Chloride concentration ( $\mu\text{M}$  divided by 100) in both plots is indicated by “CI.”

occurs. These calculations in conjunction with our main stem nutrient addition experiments are good evidence that decreases in  $\text{NO}_3$  concentrations observed in the wetland reaches of the main stem are regulated more by lateral inputs of  $\text{NO}_3$  depleted groundwater (because of denitrification and uptake) than in-stream processes and therefore that the bulk of the  $\text{NO}_3$  removal in this system likely occurs in upland streams.

### 5.2.2. Upland Tributaries

[49] Our experimental work in the main stem of the Ipswich River is consistent with those of other studies [e.g., Alexander *et al.*, 2000] indicating that river corridors of greater depth and discharge are limited in their capacity to process N. We expected to measure higher retention rates in upland tributaries because our nutrient addition and tracer experiments indicate that the travel time of water along a 1 km reach is on the order of days in wetland tributaries versus hours in the main stem. Although we were unable to detect N removal in upland tributaries, there is likely great spatial variation in uptake rates with most removal occurring in hot spots that are less amenable to conducting nutrient addition experiments. The idea that most of the  $\text{NO}_3$  loss in our riverine budget occurs in upland tributaries is bolstered by (1) relationships of land use and water quality, which indicate that urban and agricultural areas are associated with higher  $\text{NO}_3$  in runoff [Williams *et al.*, 2004], and (2) our observation that sector 1, which has a combination of first and second-order streams, has the

lowest  $\text{NO}_3$  export of the three subbasins even though it is the most heavily loaded (Figure 6). Lower export from sector 1 than in the other sectors is likely due to a combination of flow routing of upland groundwater through riparian wetlands and in-stream N processing in reaches with and without fringing wetlands.

[50] We identified several important mechanisms of  $\text{NO}_3$  removal in the upland tributaries of the Ipswich River in sector 1. For example, we commonly observed fourfold to fiftyfold decreases in  $\text{NO}_3$  concentrations over relatively short distances (1 km) along several stream reaches (Figure 7) that generally had only twofold to fourfold increases in discharge. Mass balances of  $\text{NO}_3$  losses for the summer and fall indicate that these reaches are responsible for about 9% of the  $\text{NO}_3$  losses in our riverine budget. The areas where these losses occur are commonly wetland habitats that include partially inundated ponding basins, suggesting that the residence time in these ponding basins is sufficiently long to allow  $\text{NO}_3$  to diffuse into benthic sediments and algal mats where anoxia could occur before the water is flushed downstream during storm flow events and periods of higher runoff. Moreover, there is recurring hypoxia (dissolved  $\text{O}_2$  ( $\text{DO}$ )  $< 2 \text{ mg L}^{-1}$ ) in ponded areas and small headwater streams during the summer, which likely augments in-stream denitrification rates, and this assumption is supported by decreases in  $\text{NO}_3$  concentrations in headwater tributaries during hypoxic/anoxic periods. For instance,  $\text{NO}_3$  ( $\mu\text{M}$ ) and  $\text{DO}$  ( $\text{mg L}^{-1}$ ) concentrations in Lubbers Brook varied from  $25 \mu\text{M}$  ( $3 \text{ mg L}^{-1}$ ) to  $2 \mu\text{M}$  ( $1 \text{ mg L}^{-1}$ ) to  $43 \mu\text{M}$  ( $4 \text{ mg L}^{-1}$ ), respectively, over 1 month in the summer of 2001. Lastly, sites where water withdrawals are made appear to be hot spots of N loss and water withdrawals are responsible for removing about 115 mm of water annually. Slug additions of LiBr tracer upstream of one of these withdrawal sites in a wetland area of Sawmill Brook are below detection immediately downstream of the wetland. We have also observed flow reversal in drier months of the year downstream of withdrawal sites. Both observations indicate that withdrawal sites are hot spots of N loss and retention.

[51] All river reaches in close proximity to well water withdrawal sites are positively correlated with decreasing  $\text{NO}_3$  concentrations. These withdrawals have the added effect of creating a disjointed surficial hydrology in the headwater basin (sector 1) that prevents some water in these upland tributaries from reaching the main stem of the Ipswich River during moderate to low-flow conditions. For instance, there was no flow in Maple Meadow Brook from early August to late October 2000 and July to early December 2001. Seasonal variations in rainfall in conjunction with water withdrawals enhance  $\text{NO}_3$  retention in upland tributaries by contracting the contributing area and effective basin size during the summer and fall. This hydrological effect partially explains why only about 20% of  $\text{NO}_3$  export from the Ipswich River basin occurs during this period.

[52] We attempted to measure  $\text{NO}_3$  uptake in the upland tributaries of this system using nutrient addition and conservative tracer experiments. However,  $\text{NO}_3$  uptake in the upland tributaries of sector 1 was below detection in discrete stream channels with ambient concentrations of  $\text{NO}_3$  ranging from 2 to  $50 \mu\text{M}$  and discharge from 20 to  $40 \text{ L s}^{-1}$

(locations of experiments are indicated in Figure 7). Assuming a moderate denitrification rate of  $0.1 \text{ mmole N m}^{-2} \text{ hr}^{-1}$ ,  $0.14 \text{ g}$  of N would be denitrified over the  $100 \text{ m}$  experimental reach, which is only  $0.2$  to  $2\%$  of the  $\text{NO}_3$  flux in our experiments. In the urban tributaries with higher background concentrations of  $\text{NO}_3$ , rates of uptake and denitrification would need to be substantially higher than  $0.1 \text{ mmole m}^{-2} \text{ hr}^{-1}$  in order to measure uptake lengths using this experimental method. However, in the wetland tributaries where background concentrations of  $\text{NO}_3$  were  $<2 \text{ }\mu\text{M}$ , a rate as low as  $0.1 \text{ mmole m}^{-2} \text{ hr}^{-1}$  could be detected. Because  $\text{NO}_3$  removal was below detection in reaches we examined, the combined rates of uptake and denitrification were indeed low.

[53] Negligible in-stream uptake of  $\text{NO}_3$  in discrete stream channels of the Ipswich River system suggests that the major  $\text{NO}_3$  removal mechanism is denitrification that occurs along convoluted flow paths in areas of complex hydrology, such as wetlands and withdrawal sites. Furthermore, the bulk loss of  $\text{NO}_3$  in the upland tributaries of the Ipswich River is site specific (ponds, ponded wetlands, and withdrawal sites) and seasonal (anoxic events) and can be attributed to an interplay of factors, such as discharge and channel geomorphology, that dictate the flow path and residence time of water in this low-gradient system. Draw down because of municipal water withdrawals and denitrification accentuated by long water residence times in ponded wetlands (created both naturally (beaver and debris dams) [Correll *et al.*, 1999] and artificially (culverts and dams)) are the most important factors regulating  $\text{NO}_3$  export from in the most heavily urbanized sector of the Ipswich basin.

### 5.3. Total N Losses in the Aquatic Environment

[54] Recent estimates of N losses in the aquatic environment vary widely. For instance, Billen *et al.* [1991] estimate that between  $20$  and  $50\%$  of TN inputs are lost in the aquatic environment. On the basis of these and other estimates, Howarth *et al.* [1996] indicate that in-stream processes in moderately loaded systems account for the removal of about  $10$  to  $20\%$  of total N inputs and that this removal should be somewhat lower in less loaded river systems like the Ipswich basin. Caraco and Cole [1999] attribute a  $30\%$  loss of TN in the aquatic environment to denitrification and burial. In contrast, modeled N losses indicate that from  $37$  to  $76\%$  of N inputs (i.e., loading to the aquatic environment) can be removed during transport through river networks in  $16$  watersheds of the NE United States [Seitzinger *et al.*, 2002], and van Breemen *et al.* [2002] conclude that average in-stream denitrification accounts for  $11\%$  of total N storage and loss in these watersheds using the lower-end estimates of Seitzinger *et al.* [2002]. However, modeled estimates of N loading or aquatic denitrification [van Breemen *et al.*, 2002; Seitzinger *et al.*, 2002] have large uncertainties, and monthly samplings of river chemistry used in these studies may not accurately quantify fluvial outputs. Moreover, the budgets of Billen *et al.* [1991] consider only edge-of-field exports of nutrient and point discharges as inputs to the river system and do not account for potential losses that typically occur in riparian buffer zones bordering streams. There are also large errors associated with extrapolating point estimates of denitrification or loss estimates from stream reaches ( $100 \text{ m}$  to several  $\text{km}$ ) to the overall aquatic network

of a basin. These errors are often compounded by seasonally restricted measurements (i.e., spring, summer, or fall) that do not incorporate loss rates during colder months when discharge is often highest. Lastly, denitrification in the aquatic environment is commonly equated with the loss of TN, whereas decreases in  $\text{NO}_3$  or TDN reflect potential denitrification without losses from the burial of particulate N.

[55] We have reduced potential errors in our estimate of total N losses from denitrification in the aquatic environment by making a rigorous assessment of small stream loading and solute export for the entire aquatic network of the Ipswich basin. We have done this by 1) weighting our small stream loading data by seasonal discharge (i.e.,  $85\%$  of annual discharge occurs from November through May) and land use (i.e., the proportions of land covers in the  $43$  first-order catchments are similar to those of the entire Ipswich River basin, 2) using a variable runoff coefficient to account for increased loading from impervious surfaces in urban areas, 3) calculating solute export using weekly and daily samplings of river chemistry and continuous flow data (i.e.,  $15$  minute intervals), 4) comparing and adjusting estimates of stream loading and watershed export to those of several conservative solutes, and 5) equating denitrification in the aquatic environment to a decrease in  $\text{NO}_3$ .

[56] Our estimates of riverine processing for the May 2000 through April 2001 intensive study period indicate that denitrification in the aquatic system amounted to a reduction of  $9\%$   $\text{NO}_3\text{-N}$  (i.e.,  $9 \text{ t}$  of  $\text{NO}_3$  in stream loading was unaccounted for in watershed export), which is below the range of riverine N retention for moderately loaded systems indicated above. However, our intensive sampling period had an anomalously high snowmelt runoff period and may not be representative of a long-term average. A comparison of the aquatic budgets from our intensive sampling period with that from the period of September 1993 to September 2001 using monthly river sampling data indicates that the decrease in  $\text{NO}_3\text{-N}$  is larger (i.e.,  $20 \text{ Mg yr}^{-1}$ ). Hence, although additional N losses are bound to occur in the upstream reaches of our first-order catchments, potential denitrification ranges from  $4$  to  $15\%$  of TDN loading to the aquatic environment and is an average of about  $2\%$  of total N inputs to the watershed. Because uptake experiments indicate that nitrification is a relatively small source of  $\text{NO}_3$  in the aquatic environment, and considering that some  $\text{NO}_3$  losses are due to water withdrawals and conversion to DON, these values are much lower than losses attributed to aquatic denitrification in other studies [Billen *et al.*, 1991; Caraco and Cole, 1999; Seitzinger *et al.*, 2002; van Breemen *et al.*, 2002].

## 6. Summary

[57] Our study indicates that N losses in the aquatic environment are a relatively small fraction of the overall N storage and loss terms for the Ipswich River basin. Moreover, our results support the idea that rivers progressively lose smaller quantities of DIN with increasing stream order, albeit because of the effects of seasonal hypoxia and water withdrawals in this system,  $\text{NO}_3$  losses cannot be generalized by parameters of channel depth, discharge, or water residence times, as in other studies [e.g., Alexander *et al.*, 2000]. The implications of our study are that increased

urbanization will augment loading to receiving waters because of higher NO<sub>3</sub> concentrations in the stream water of urban areas and runoff from impervious surfaces. Moreover, better water management practices that return water to the groundwater reservoir will probably increase flow during drier months, thereby linking surficial flow from upland tributaries to the main stem and reducing water residence times. Since the Ipswich River main stem has a limited capacity to retain and process NO<sub>3</sub>, these inputs in conjunction with future development in close proximity to the major tributaries and main stem of this river system will likely increase the magnitude of NO<sub>3</sub> inputs to the Ipswich River and Plum Island Sound.

[58] **Acknowledgments.** We thank the Ipswich River Watershed Association for assistance with the coordination and collection of river water samples, C. Decker of the Ipswich River Wildlife Sanctuary for permission to locate our deposition collector within the confines of the Sanctuary, and J. Evans, L. Claessens, J. Goldstein, and K. Tholke for assistance with sample analysis. The USGS provided additional N data for the Middleton gauging station. This research was funded by grants DEB-9726862 and OCE-9726921 (NSF).

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