RELATIONSHIPS OF LAND USE AND STREAM SOLUTE CONCENTRATIONS IN THE IPSWICH RIVER BASIN, NORTHEASTERN MASSACHUSETTS

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Abstract. The relationships of land use/land cover (LULC) on major solute concentrations in stream water were investigated for the Ipswich River basin (404 km^2) in northeastern Massachusetts. Stream water was sampled seven times during base flow in 43 first-order catchments and four times in 28 second- and third-order catchments. Regression analysis of the first-order catchment data indicates that NO_3^-, acid neutralizing capacity (ANC), Cl^-, SO_4^{2-}, and the base cations had positive, mostly exponential relationships with the increasing extent of urban + agricultural area ($P < 0.05$), whereas dissolved organic nitrogen (DON) and dissolved organic carbon (DOC) had positive, exponential relationships with the increasing extent of wetland + open water ($P < 0.05$). Solute sources responsible for many of these relationships are human-derived constituents found in septic effluent, fertilizers, and road salts. In contrast to more conservative solutes, concentrations of NO_3^- in the first-order streams were commonly higher than in those of second- and third-order streams with similar proportions of urban + agricultural land use. Using LULC subclasses (e.g., high density residential), as well as the proportions of LULC in 50, 100, and 200 m concentric zones bordering streams, generally decreased the relationships (r^2) determined above. Hence, the disturbed area of the entire subbasin was the best descriptor of streamwater solute concentrations. Potassium concentrations in stream water had stronger relationships than any other ion, yet these explained <60% of the variability, indicating that there are a number of important ancillary factors that affect streamwater solute composition in the Ipswich River basin.

Keywords: land cover, land use, solute concentrations, urbanization, watershed

1. Introduction

Stream water quality can be dramatically affected by land use changes. Forest conversion to either agricultural or urban land use generally increases nutrient loading to the aquatic environment in both tropical and temperate systems (Osborne and Wiley, 1988; Peierls *et al.*, 1991; Jordan *et al.*, 1997; Williams and Melack, 1997; Liu *et al.*, 2000; Williams *et al.*, 2001a, 2004a; Filoso *et al.*, 2003). Moreover, the influx of nutrients and pollutants from urban and agricultural areas typically results in poor water quality in many estuarine and coastal areas (Omernick *et al.*,

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1981; Correll *et al*., 1992; Staver *et al*., 1996; Jordan *et al*., 1997). Nutrient enrichment from upland runoff is directly linked to the eutrophication of receiving waters, which can result in excessive algal blooms, loss of submerged aquatic vegetation, increased duration and magnitude of hypoxia and anoxia, and shifts in species composition (Officer *et al*., 1984; Howarth *et al*., 1996, 2000; Boesch *et al*., 2001).

In heavily agricultural watersheds, riparian buffers commonly reduce the flux of nutrients and sediments to receiving waters (Peterjohn and Correll, 1984; Staver and Brinsfield, 1990; 1996; 1998; Staver *et al*., 1996; Jordan *et al*., 1997; Norton and Fisher, 2000). Nevertheless, agricultural land use in upland areas away from streams can have similar effects on water quality as that in areas immediately adjacent to streams (Omernick *et al*., 1981). Thus, from a management perspective, it is valuable to determine the hydrochemical importance of different sizes and configurations of contributing areas bordering streams and their effectiveness as predictors of streamwater solute concentrations (Gergel *et al*., 1999).

Defining the relationship between land use and solute concentrations in large urban and agricultural watersheds is confounded by landscape complexity that often combines a large variety of human activities, land cover types, topography, geology, soils, and vegetation (Herlihy *et al*., 1998; Norton and Fisher, 2000). Moreover, in-stream processes such as denitrification or water withdrawals can change solute concentrations in larger streams and rivers, thereby confounding relationships between land use and stream water quality (Liu *et al*., 2000). In contrast, determining land use/solute concentration relationships at smaller spatial scales reduces the complexity of these confounding factors, thereby facilitating extrapolations to larger scales and the development of accurate hydrochemical models and effective watershed management strategies.

This is one in a series of papers dealing with the hydrochemical effects of increasing development in the Ipswich River basin in northeastern Massachusetts. The Ipswich River basin is largest of three basins that form the watershed drainage of the Plum Island Sound estuary, a long-term ecological research (LTER) site. The other papers in this series address issues pertaining to (1) watershed-scale N budgets and aquatic uptake (Williams *et al*., 2004a) and (2) the relative importance of various solute inputs from human sources in the Ipswich River basin (Williams *et al*., 2004b). In the former paper, we developed a detailed N budget and calculated N losses within the aquatic environment using the land use and water quality relationships developed fully in the current article. In the latter paper, we extended the budget analyses to all the major solutes measured in these studies in order to quantify human-derived inputs of these solutes from atmospheric deposition, sewage, fertilizers, and road deicers.

Here we use a hydrochemical characterization of an entire river network to determine the influence of land use quantity, location, and watershed size on the concentrations of major solutes in stream water of the Ipswich River watershed. Geographical data on land use from 1999 and wetlands from 1991 were compiled to determine the relationships of various land use types and solute concentrations in stream water in first-order, and second- and third-order subbasins. Moreover, we discuss the importance of land use/land cover (LULC) in different sized concentric zones bordering streams in regulating streamwater chemistry, the major solute sources responsible for land use/solute concentration relationships, and some alternative factors that influence the spatial and temporal variability of our data.

2. Study Site Description

The Ipswich River basin (404 km^2; Figure 1) lies entirely within the Seaboard Lowland section of the New England physiographic province (Fenneman, 1938). Air temperature varies annually between an average winter minimum of −7 °C and an average summer maximum of about 28 °C (Sammel, 1967), and the average growing season is 180 days between mid-April and mid-October. Geology of the basin is primarily igneous and metasedimentary Paleozoic and Precambrian bedrock with surficial deposits of till, gravel and sand formed during the last ice age (Carlozzi *et al*., 1975).

The main stem of the Ipswich River is a low gradient, meandering system with its highest point at about 24 m above mean sea level (a.m.s.l.); the highest point

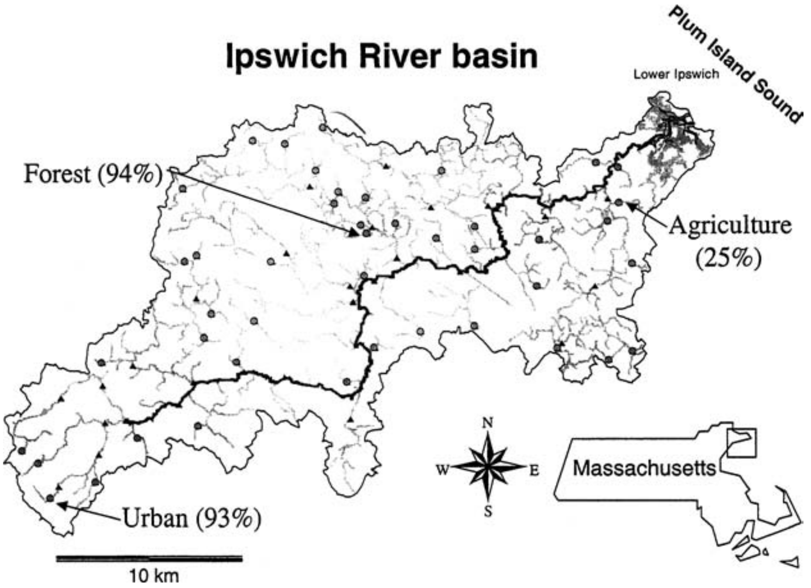

Figure 1. The Ipswich River basin in northeastern Massachusetts (404 km^2). First-order catchments are designated by circles, and second- and third-order catchments by triangles. Locations of the urban (92%), forest (94%) and agriculture (25%) subbasins used as quasi end-members in our analysis are indicated.

in the watershed is 126 m a.m.s.l. Long-term precipitation averages 1180 mm yr^{-1} and is evenly distributed throughout the year (Williams *et al.*, 2004a). Average precipitation in the Ipswich River basin over the sampling period from 1999 to 2002 was 1134 mm. Runoff is seasonal, with discharge typically low in the summer and fall when evapotranspiration and municipal water withdrawals exceed rainfall, and greatest during early spring snowmelt. Average discharge is about $656(10)^3$ m^3 d^{-1} of which $175(10)^3$ m^3 d^{-1} are withdrawn for municipal consumption, about 60% of which is outside the watershed boundary. Discharge in 43 first-order streams was estimated during the high- and low-flow samplings of September 2000 and April 2002 and ranged from 0 to 80 L s^{-1}, but was commonly around 20 to 30 L s^{-1} in most subbasins in April 2002.

Almost 25% of the Ipswich watershed is conservation land, and Boston bedroom communities have been encroaching along the southern portion of the watershed for several decades. Population growth accelerated in the 1990s to rates common in the 1950s and 1960s (over 4000 new inhabitants per year), with total population of the Ipswich River basin estimated at about 130 000 in 2001 (322 individuals km^{-2}).

3. Methods

3.1. WATER SAMPLES

All water samples collected in this study were base flow and these were immediately stored on ice during transport to the laboratory. Samples were analyzed for ammonium (NH_4^+), nitrate ($NO_3^- = NO_2^- + NO_3^-$), phosphate (PO_4^{3-}), total dissolved N and P (TDN and TDP, respectively), total N and P (TN and TP, respectively), dissolved organic carbon (DOC), chloride (Cl^-), sulfate (SO_4^{2-}), sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), acid neutralizing capacity (ANC), pH, and silicate (SiO_4^{3-}). Samples were frozen if NH_4^+ or PO_4^{3-} could not be processed within 2 to 3 days after collection. Refrigerated samples were stored at about 4 °C until analysis. Using a paired *t*-test, there were no significant differences in NH_4^+ and NO_3^- concentrations between frozen and refrigerated samples ($n = 12$, $P < 0.01$). Streamwater samples were collected in a plastic bucket and immediately filtered into acid-washed polyethylene vials using Whatman GF/F glass-fiber filters (nominal pore size of 0.7 μm), plastic filter holders, and syringes. Streamwater samples used to determine SiO_4^{3-} were filtered using Nuclepore polycarbonate filters (0.4 μm), and samples for TN and TP were unfiltered.

Ammonium, NO_3^- ($NO_2^- + NO_3^-$), PO_4^{3-}, TDN, TDP, TN, TP, and SiO_4^{3-} concentrations were determined using standard colorimetric methods described in Williams and Melack (1997), using a spectrophotometer. Concentrations of NO_2^- were negligible (<0.2 μM), and sample aliquots were run on a Dionex ion chromatograph to determine NO_3^-, SO_4^{2-}, and Cl^-. Using a paired *t*-test, there were no significant differences in NO_3^- concentrations between methods ($n = 100$, $P < 0.001$). Persulfate oxidation followed by NO_3^- and PO_4^{3-} analysis was done to quantify TDN, TDP, TN and TP (Valderrama, 1981). Dissolved organic N and P (DON and DOP) were calculated as the difference between TDN and DIN, and TDP and PO_4^{3-}, respectively. Unfiltered aliquots were analyzed for pH and acid neutralizing capacity (Gran, 1950, 1952). DOC samples were refrigerated in acid-washed, glass bottles with teflon liners and 100 μL of H_3PO_4 (pH < 2). Base cations were analyzed on a Perkin Elmer atomic absorption spectrometer, SiO_4^{3-} on an AlpChem flow injection analyzer, and DOC by high temperature combustion (Hopkinson *et al.*, 1998). pH and ANC titrations were done using an Orion pH meter with plexiglass probe and a micrometer burette.

3.2. SUBBASIN AND LAND USE CHARACTERIZATION

A vector-based, geographic information system (GIS) database was compiled for the Ipswich River basin. Data layers included those of LULC, streams, wetlands, and watershed and subbasin boundaries; ArcInfo was used to manipulate and manage the GIS data layers. Relationships between land use and the concentrations of major solutes in the stream water of 43 first-order (0.6 to 5.3 km^2) catchments of the Ipswich River watershed were determined from seven samplings across the seasons between April 1999 and April 2002. The subbasins 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.

LULC in the Ipswich River watershed and subbasins was determined from 1:25 000 aerial photography (land use coverage, MassGIS, www.state.ma.us/mgis/massgis.htm). Different land use categories of the MassGIS database were binned into the more general categories of forest (MassGIS code 3), urban (codes 5–20), agriculture (codes 1, 2, and 21), and wetland (codes 4 and 20). Additional subcategories, such as the sum of residential and commercial areas (codes 10–13, 15, and 16), were used in our land use/solute concentration relationship analysis.

A stream coverage was obtained from the United States Geological Survey (USGS) and stream order was visually interpreted and confirmed by ground surveys. Watershed and subbasin boundaries were manually interpreted from topographic map contours and digitized using ArcInfo.

Wetlands were visually interpreted from stereo, 1:12 000-scale, color-infrared photographs of the Ipswich River basin from 1991 (MassGIS). Major categories in the wetland coverage include upland (76%), deciduous wooded swamp (12%), and a combination of wooded swamp (mixed-tree), shrub swamp, shallow marsh, deep marsh, and open water (12%). The MassGIS categorization in our 43, first-order catchments was 84% upland and 16% wetland, the latter including a mixture of the wetland categories listed above. Merging the wetlands cover with the 1999 land use cover (MassGIS) increased the percentage of wetland area from 9 to 12% of the total basin, largely at the expense of forested area.

Landscape proximity analysis was conducted by delineating concentric zones around the stream within each subbasin. Zone widths of 0–50, 0–100, and 0–200 m from streams were selected since larger zone sizes tended to exceed the subbasin boundary.

3.3. SOLUTE SOURCES ANALYSES

We used two approaches to examine the relative importance and seasonal influence of different source areas (i.e., predominately urban or forested areas) on the Ipswich River. The two analyses were: (1) the ratio of individual ion concentrations to the sum of base cations (SBC) and (2) individual ion concentrations altered by a silicate modification factor (SMF). The premise of the former analysis is that if there were relatively constant sources of individual ions to the aquatic system throughout the year, the individual ion: SBC ratios would be invariant. Hence, the extent to which mechanisms, such as cation exchange or strong seasonal or external inputs, influence river water solute concentrations would be reflected in the deviations of individual ion concentrations from linearity. In the latter analysis, the SiO_4^{3-} factor is calculated by dividing each SiO_4^{3-} concentration by the largest concentration of SiO_4^{3-} in a series; the concentration of each sample divided by the SiO_4^{3-}:maximum SiO_4^{3-} ratio calculated above creates a linear reference against which other solutes can be compared because it reduces the effect of dilution. Assuming that SiO_4^{3-} is derived solely from mineral weathering, then the ion: SiO_4^{3-} ratios with a predominant weathering source would tend to be invariant (Williams *et al.*, 2001b). We used intensive measurements of stream chemistry from an end-member urban subbasin of the Ipswich basin (Figure 1) with those of Ipswich River runoff over the period from May 2000 through April 2001 ($n = 31$ and 62 for the urban subbasin stream and the mouth of the Ipswich River, respectively) in these analyses.

4. Results

4.1. LAND USE/SOLUTE CONCENTRATION RELATIONSHIPS

LULC in the Ipswich River basin in 1999 was approximately 35, 49, 9, and 7% urban, forest, wetland, and agriculture in 1999, respectively. Cumulative LULC in the 43 first-order subbasins (0.5 to 4 km^2) using these binned categories was 51% forest, 40% urban, 5% wetland, and 5% agricultural, which are 104, 114, 180, and 71% of the percentages of these categories for the entire basin mentioned above (i.e., the percent of forested land in the entire Ipswich River watershed is 104% of the cumulative percent of forest in the subbasins).

Goodness-of-fit tests of the chemical variables indicated that they were generally log-normally distributed. Not all solutes were analyzed on each sampling. For instance, relationships of pH, ANC, and TN were determined from one sampling only (April 2002), and those of SiO_4^{3-} and DOC from two samplings (September 2000 and April 2002).

Solute concentrations were strongly related by land use in the Ipswich subbasins. Concentrations of Cl^-, SO_4^{2-}, NO_3^-, the base cations, and ANC in stream water had significant, positive relationships with the percentage of urban + agricultural land use in the 43, first-order catchments (Figure 2; Tables I and II). There were no discernable, positive relationships with the other measured solutes and urban + agriculture land use, albeit there were significant, positive relationships of DON and DOC to the increasing proportion of wetland area (wetlands cover) in the first-order catchments. Coefficients of determination (r^2) from our land use/solute concentration relationships were generally highest using the binned categories of urban + agricultural land use. Commonly, the relationships were less robust using subcategories (e.g., high density residential + commercial) of the binned land use categories described above to characterize the first-order catchments. For instance, using a residential category instead of the urban + agricultural category decreased the r^2 of NO_3^- from a mean of 0.47 to 0.35. Similarly, the r^2 values of most solutes tended to decrease from the land use configuration of the entire subbasin to those of smaller zone-widths bordering the streams (i.e., r^2 of land use within 50, 100 and 200 m wide zones adjacent to the stream; Table II).

Generally, strong land use/solute concentration relationships were observed in larger second- and third-order catchments (Figure 3, $n = 28$). Although the relationships were similar between first- and higher-order catchments for most individual solutes, solute concentrations of NO_3^- were commonly higher in first-order catchment streams than in streams of the higher-order catchments with proportionally similar LULC (Figure 3).

4.2. SOLUTE SOURCES

The patterns of individual cations in the sum of base cations (SBC) analysis were generally similar between the outflow of the urban subbasin and that of the entire watershed for Na^+ and Mg^{2+} throughout the year, but differed in the fall and winter for K^+ and spring and summer for Ca^{2+} (Figure 4). Sodium in the SBC analysis increased in the winter months, whereas other cations decreased as a result of the Na^+ increase. The patterns of individual cations in the silicate modification factor (SMF) analysis differed between the outflow of the urban subbasin and that of the entire watershed for most solutes for at least part of the year (Figure 5). Silicate in water is mostly a product of relatively slow, geochemical weathering reactions. Hence, the dramatic increase observed in March through May indicates that SiO_4^{3-} was strongly diluted by snowmelt runoff, and the exhaustion of SiO_4^{3-} was more pronounced than that of the other solutes that have a large weathering component (i.e., Ca^{2+} and Mg^{2+}). In contrast to patterns observed in Ipswich River runoff, SiO_4^{3-} in the stream water of the urban subbasin was not dramatically diluted

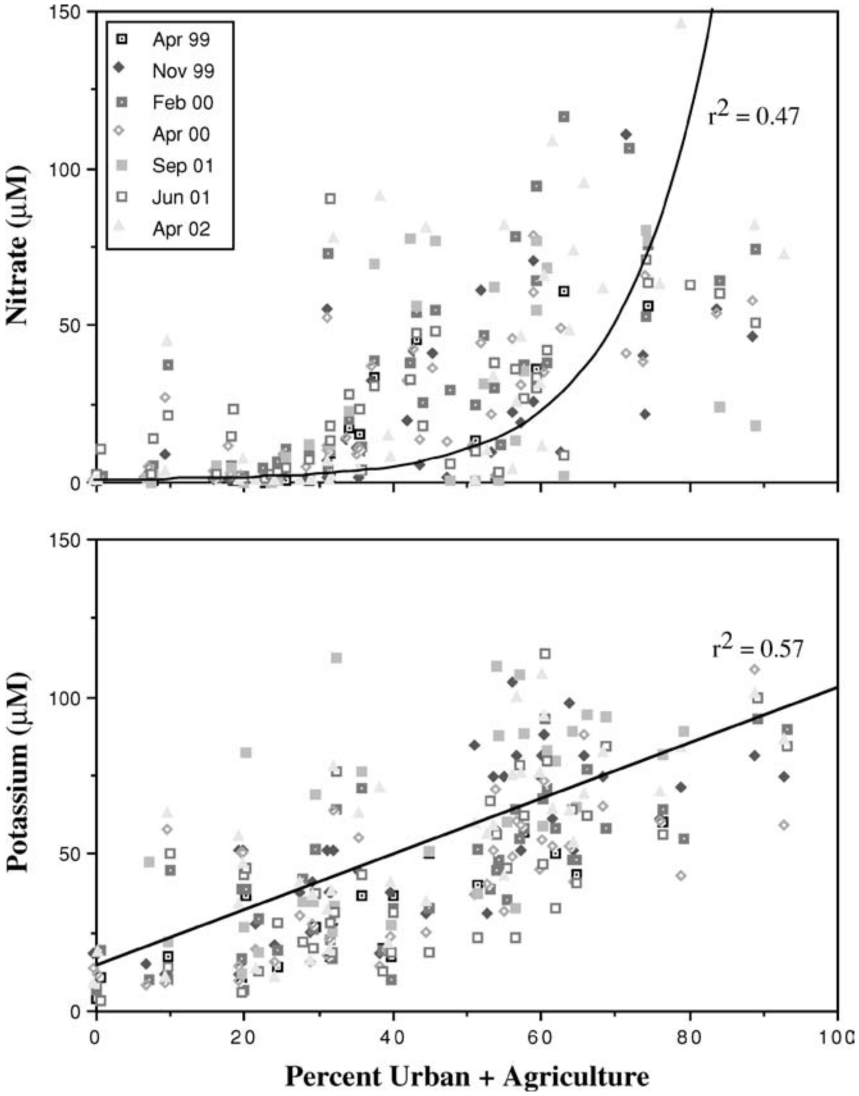

Figure 2. The percentage of combined urban land + agriculture land use versus NO_3^- (top panel) and K^+ (bottom panel) concentrations in the catchments of 43 first-order streams throughout the Ipswich River basin. Relationships are significant ($P < 0.05$). The coefficients of determination (r^2) for each sampling are listed in Table I.

during the snowmelt runoff period. In both the SMF and SBC analyses, there was a noticeable summertime increase in K^+ (Figures 4 and 5).

The time series of $NO_3{}^-$ concentrations over the period from May 2000 through April 2001 in the stream water of two highly urban (93%) and forested (94%) subbasins indicated that, though the seasonal patterns were similar, $NO_3{}^-$ concentrations were consistently at least a factor of three times higher in the urban subbasin

TABLE I

Relationships of urban + agricultural (Urb + Agr) land use and solute concentrations in the stream water of 43 first-order catchments during a total of seven samplings that were done to span the seasons from April 1999 to April 2002

	Urban + Agriculture						
Solute	April 99 ($n = 23$)	Nov 99 ($n = 43$)	Feb 00 ($n = 43$)	April 00 ($n = 43$)	Sep 00 ($n = 34$)	Jun 01 ($n = 39$)	April 02 ($n = 40$)
Cl^-	0.52 E	0.46 E	0.50 E	0.50 E	0.45 E	0.45 E	0.44 E
NO_3^-	0.59 E	0.46 E	0.55 E	0.60 E	0.30 E	0.33 E	0.48 E
SO_4^{2-}	0.63 E	0.41 E	0.66 E	0.59 E	0.47 E	0.56 L	0.09 E
PO_4^{3-}	0.22 E	0.06 L	0.14 E	0.11 E	0.04 L	na	0.06 L
ANC	na	na	na	na	na	na	0.46 E
NH_4^+	0.16 L	0.32 E	0.26 E	0.28 E	0.03 L	0.27 E	0.04 L
Na^+	0.42 E	0.46 E	0.49 E	0.51 E	0.41 E	0.45 E	0.46 E
K^+	0.73 L	0.61 E	0.59 L	0.52 E	0.53 E	0.49 E	0.55 L
Ca^{2+}	0.51 E	0.41 E	0.44 E	0.59 E	0.37 E	0.28 E	0.42 E
Mg^{2+}	0.70 L	0.42 E	0.49 E	0.56 E	0.40 E	0.37 E	0.43 E
H^+	na	na	na	na	na	na	0.15 E
DON	0.19 E	0.23 L	0.001 E	0.06 E	0.026 L	na	0.01 L
TN	na	na	na	na	na	na	0.34 E
DOP	0.002 E	0.01 E	0.01 E	0.004 L	0.09 L	na	na
TP	na	na	na	na	na	na	0.10 E
DOC	na	na	na	na	0.23 E	na	0.24 L
SiO_4^{3-}	na	na	na	na	na	0.06 L	0.15 L

Urban + agricultural land use and solute concentration relationships were determined using MacIntosh Cricket Graph software and typically represent the strongest relationship derived from any land use class or combination of classes in the MassGIS data set. DON, DOP and DOC relationships are negative. Abbreviations: E = exponential; L = linear. The means of the relationships above are presented in Table II.

than in the forested subbasin (Figure 6). The largest increases in NO_3^- occured during the fall and snowmelt runoff periods, and SO_4^{2-} had a similar pattern to that of NO_3^- (SO_4^{2-} data not shown).

In addition to the concentration differences observed in the base flow of our first-order catchments, stormflow hydrographs had distinct signatures. For example, during a relatively large stormflow event (46 mm of rain) on July 14th–15th, 2000, inorganic N initially increased in relation to background concentrations in our most urban (93%) and one of our most agricultural (25%) subbasins, whereas the concentrations of other solutes decreased as a result of dilution (Figure 7; Perring *et al.*, 2000). In contrast, there was a delayed and small increase in NO_3^- concentrations in the predominately forested subbasin (94% forest), while the other solutes remained relatively invariant throughout the storm event.

TABLE II

Volume-weighted mean (VWM) solute concentrations of the Ipswich River (mouth) for the period of May 2000 through April 2001 and average coefficients of determination (r^2) for land use/streamwater solute concentration relationships (mean of all samplings in Table I)

	VWM	Urban	Urb + Agr	Urb (200 m Zone)	Urb + Agr (200 m Zone)	(P or N) (E or L)	Wetland	(P or N) (E or L)
Precipitation (mm)	1134							
Runoff (mm)	511							
Solute	μEq L^{-1}	r^2	r^2	r^2	r^2		r^2	
Cl^-	1245	0.45	**0.47**	0.30	0.36	PE	0.09	NE
NO_3^-	21.7	0.42	**0.47**	0.30	0.45	PE	0.29	NE
SO_4^{2-}	182.6	0.38	**0.49**	0.23	0.38	PE	0.20	NE
PO_4^{3-}	0.15	0.08	0.11	0.06	0.10	PE	0.06	NE
ANC	450.9	0.42	**0.46**	0.27	0.34	PE	0.11	NE
NH_4^+	1.5	**0.22**	0.19	0.15	0.15	PE	0.10	NE
Na^+	1002	0.44	**0.46**	0.29	0.33	PE	0.10	NE
K^+	32.2	0.51	**0.57**	0.32	0.41	PE	0.16	NL
Ca^{2+}	692.4	0.34	**0.43**	0.17	0.29	PE	0.13	NE
Mg^{2+}	230.8	0.32	**0.48**	0.18	0.32	PE	0.09	NE
H^+	0.2	0.13	0.15	0.06	0.11	PE	0.07	NE
DON	30.5	0.14	0.11	0.14	0.11	NE	**0.17**	NE
TN	60.8	0.22	**0.34**	0.11	0.23	PE	0.08	NL
DOP	0.46	0.08	0.02	0.07	0.11	PE	0.06	NE
TP	0.82	0.05	0.10	0.06	0.09	PE	0.05	NE
SiO_4^{3-}	105.1	0.11	0.11	0.11	0.11	PL	0.09	NL
DOC	761.2	0.22	0.24	0.19	0.28	NE	**0.32**	PE

Ion concentrations are expressed in μEq L^{-1}; all other solutes are in μM. Land use categories are urban, urban + agriculture, urban area and urban + agricultural area in a 200 m zone bordering the streams, and the MassGIS wetlands cover (Wetland). Only the most common relationships observed for each solute during the period of study (1999 through 2002) are indicated , and are either positive or negative and exponential or linear (P, N, E, or L, respectively). Significant relationships ($P < 0.05$) are indicated by bold type. Average precipitation and runoff are for the period from 1999 through 2001 with 121 mm added to runoff to account for water withdrawals.

5. Discussion

5.1. COMPARISONS WITH OTHER STUDIES

Many of the relationships we observed in our study are similar to those in streams of other eastern US regions, but there are important differences that are related to the use of broad LULC categories. For instance, a study by Herlihy *et al.* (1998) in the mid-Atlantic had 70, 20, 1 and <1% of the study area as forest, agriculture,

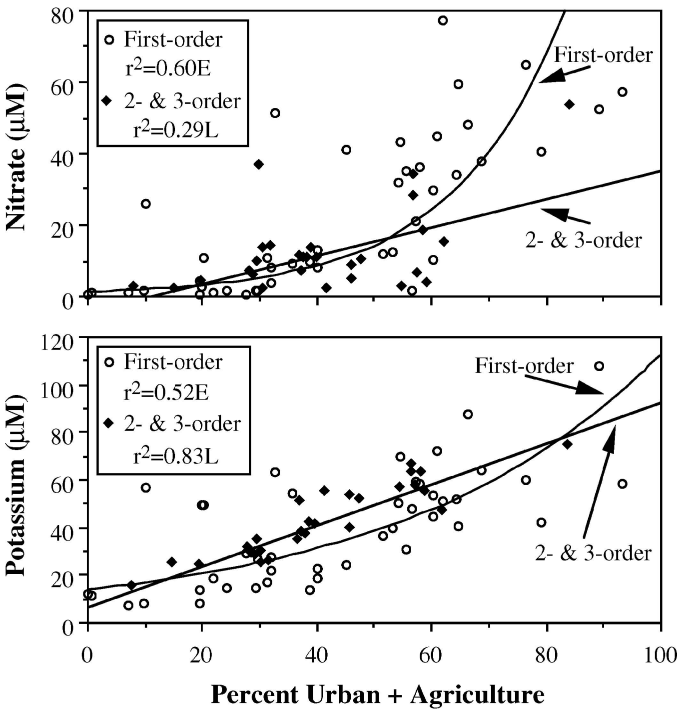

Figure 3. The percentage of combined urban land + agriculture land use versus NO_3^- and K^+ concentrations in the catchments of 43 first-order and 28 second- and third-order streams (Figure 1) throughout the Ipswich River basin. Relationships are positive and significant ($P < 0.05$), and commonly exponential for NO_3^- and linear for K^+. The coefficients of determination (r^2) for each sampling in the first-order catchments versus the second- and third-order catchments for NO_3^- are: February 2000, $r^2 = 0.55$ vs. 0.28; April 2000, $r^2 = 0.60$ vs. 0.29; September 2000, $r^2 = 0.30$ vs. 0.01; April 2002, $r^2 = 0.48$ vs. 0.20. The coefficients of determination (r^2) for each sampling in the first-order catchments versus the second- and third-order catchments for K^+ are: February 2000, $r^2 = 0.59$ vs. 0.61; April 2000, $r^2 = 0.52$ vs. 0.83; September 2000, $r^2 = 0.53$ vs. 0.64; April 2002, $r^2 = 0.55$ vs. 0.50. Note that the first-order catchments commonly have higher concentrations of NO_3^- than second- and third-order subbasins with similar proportions of urban + agricultural land use, likely because of aquatic N loss, retention, and dilution as water flows from lower- to higher-order streams.

urban and wetland, respectively, whereas our study was more dominated by urban areas and less by forest (49, 7, 35, and 9%, respectively). Herlihy *et al.* (1998) observed that Cl^-, base cations, NO_3^-, ANC and TP decreased significantly with increasing proportion of forest cover and increased significantly with increasing proportion of agricultural area. Major differences in the solute concentration/land use relationships between our study and that of Herlihy *et al.* (1998) are that there is a strong relationship with SO_4^{2-} and urban + agricultural use, but not with TP. These differences could be explained by the large contribution of SO_4^{2-} derived from septic effluent (Williams *et al.*, 2004b) and the larger particulate and

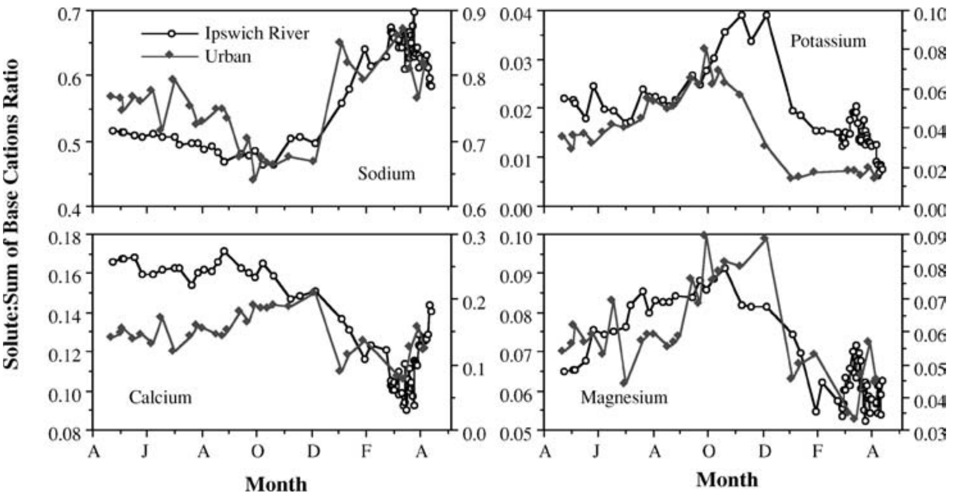

Figure 4. Comparison of the ratio of selected ion concentrations versus the sum of base cations (SBC) for samples collected from the mouth of the Ipswich River and an urban end-member subbasin (93% urban; Figure 1) over the period from May 2000 through April 2001 ($n = 62$ and 31, respectively).

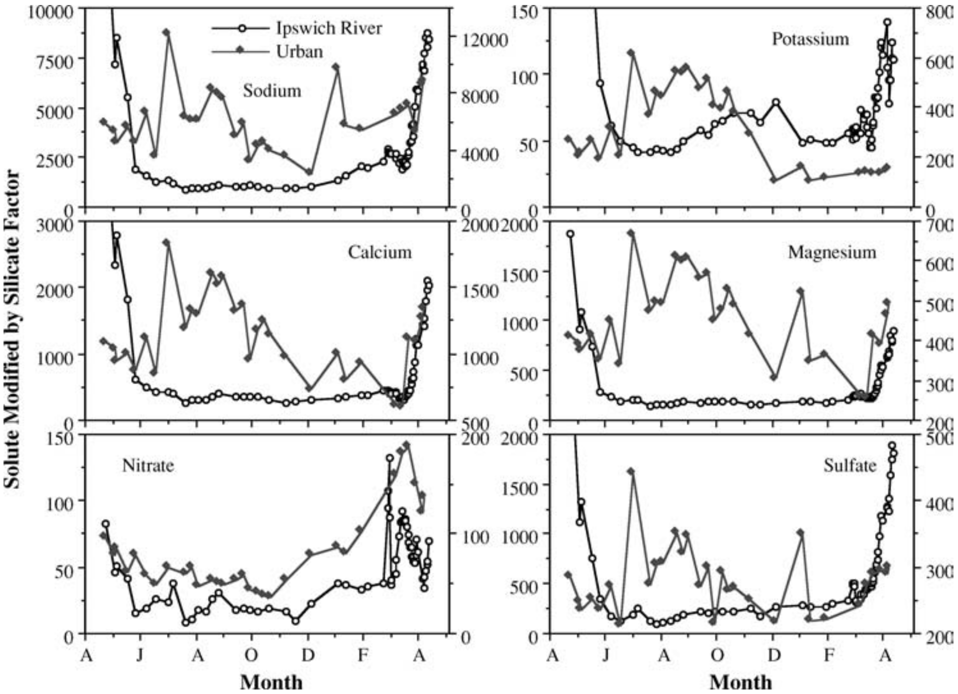

Figure 5. Comparison of selected ion concentrations altered by a silicate modification factor (SMF) for samples collected from the mouth of the Ipswich River and an urban end-member subbasin (same as Figure 4) over the period from May 2000 through April 2001 ($n = 62$ and 31, respectively).

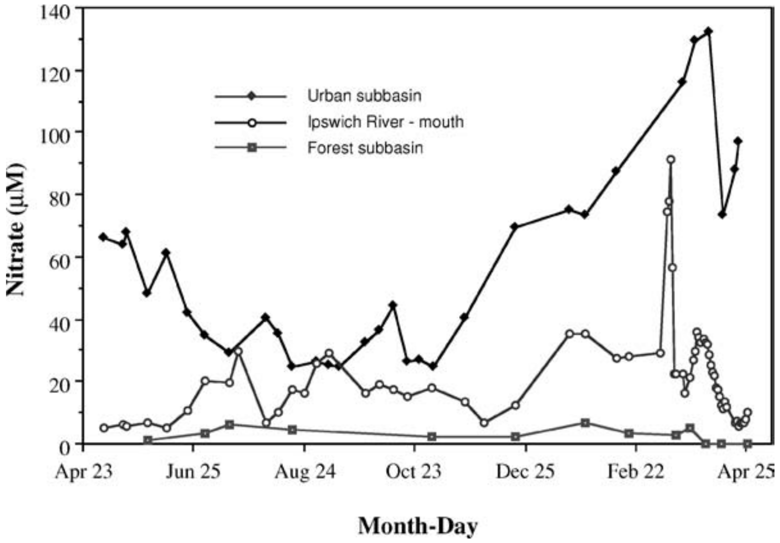

Figure 6. Time series of solute concentrations in the stream water of predominately urban (93%) and forest (94%) subbasins, and the mouth of the Ipswich River (May 2000 through April 2001).

associated P export that would be influential in mid-Atlantic watersheds where there are more intensive crop production and larger agricultural areas than in the Ipswich basin (Correll *et al.*, 1999a, b). Herlihy *et al.* (1998) and Liegle *et al.* (1991) also observed significant, positive relationships between urban and agricultural land use versus ANC and base cation concentrations, albeit the relationships in the latter study were derived from lakes and their catchment areas in the northeastern U.S.A.

In another study including the Chesapeake Bay drainage, Langland *et al.* (1995) observed that nutrient yields from predominantly urban subbasins were less than those from predominantly agricultural land. This finding is in contrast to those of our study and is, as mentioned above, a reflection of different types and the extent of agriculture. For instance, compared to the Ipswich River basin, the Chesapeake Bay watershed has proportionally less extensive (pasture) than intensive (crop production) agriculture. Moreover, there is a relatively small area of agricultural (5%) compared with urban land use (40%) in the first-order Ipswich catchments sampled, as well as the entire Ipswich River watershed (7% versus 35%, respectively).

Most studies addressing the effects of land use on solute concentrations focus on N and/or P only. For example, Jordan *et al.* (1997) observed significant effects of agricultural land use on N but not P in coastal plain catchments of the mid-Atlantic. Norton and Fisher (2000) found that forest was important in regulating N and P concentrations in the Choptank River basin in the coastal plain of Maryland, whereas forest in the adjacent Chester River basin had no effect and N and P in stream water were regulated by soil hydrologic properties.

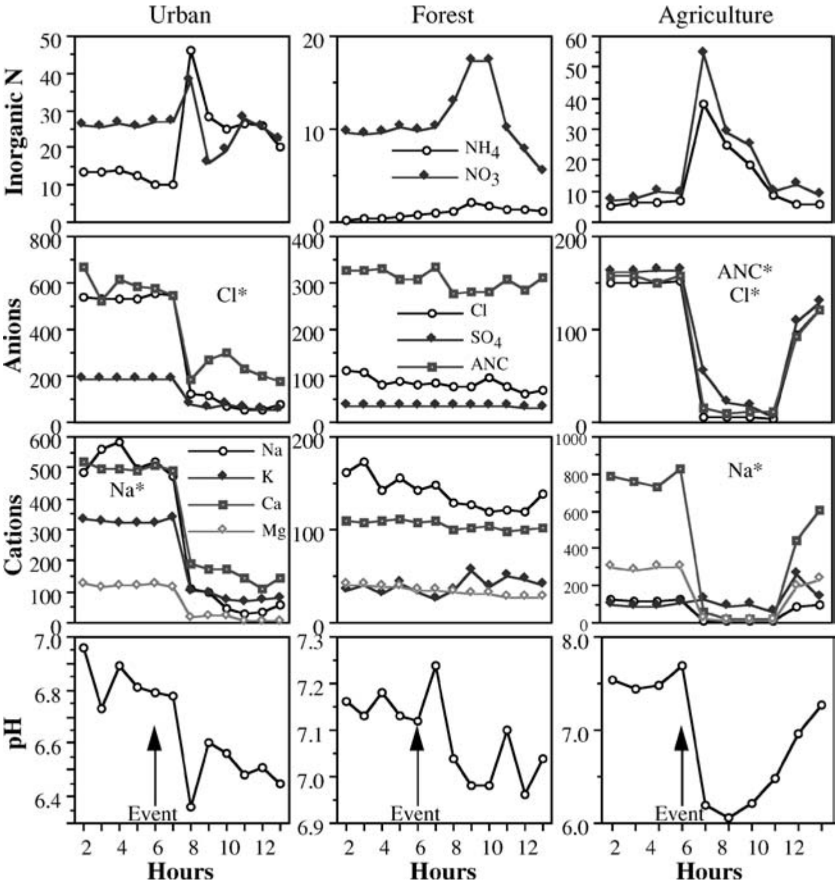

Figure 7. Time series of individual solutes in the storm flow of the urban, forest, and agricultural quasi end-member subbasins in this study. The storm event ranged from 19 (urban subbasin) to 46 mm (agricultural subbasin) and occurred on July 14th and 15th, 2000. For scaling purposes, individual ions marked by asterisks indicate that their concentrations were decreased by a factor of 10 times.

Although some researchers suggest that Cl^- is the best indicator of general human disturbance in a watershed (Herlihy *et al*., 1998), our study indicates that K^+ is a better indicator. Therefore, urban and agricultural land use explain more of the variability in K^+ concentrations in stream water than with Cl^-. Potassium is a highly mobile ion, is easily leached from soils and live and decomposing vegetative tissues, and is a strong signal of land disturbance in other studies (Likens *et al*., 1994; Williams *et al*., 1997; Filoso *et al*., 1999; Biggs *et al*., 2002). In the Ipswich River watershed study, the largest source of K^+ is from food inputs (i.e., septic sewage = 66% of total human-derived inputs; Williams *et al*., 2004b), suggesting that septic leachates are one of the dominant factors regulating the solute concentrations of stream water in urban areas.

5.2. MAJOR SOURCES OF SOLUTE INPUTS TO THE IPSWICH RIVER BASIN

Solute inputs to urban and agricultural areas include those from atmospheric deposition, fertilizers (for N, P, and K), and the importation of food (i.e., resulting in septic effluent that contributes many solutes to groundwater). In a companion study where solute budgets were constructed for the Ipswich River basin, Williams *et al.* (2004b) found that food imports (i.e., foodstuffs imported to the watershed for human consumption) were the largest sources of N, P, K^+ and $SO_4{}^{2-}$, whereas geochemical weathering was the largest source of Ca^{2+}, Mg^{2+}, and $SiO_4{}^{3-}$, and liming in agricultural areas contributed more ANC than any other source. Moreover, of the major solutes measured, new (i.e., human derived) inputs of N and P were mostly retained and lost, whereas Cl^-, $SO_4{}^{2-}$, Na^+, and ANC were near steady-state (i.e., new inputs equaled fluvial outputs); new inputs were small in comparison to fluvial export for the remainder of the solutes (Williams *et al.*, 2004b).

As shown in our LULC versus streamwater solute concentration relationships, new inputs of chemical constituents in urban and agricultural areas result in elevated streamwater solute concentrations in these areas. We determined the relative importance and seasonal influence of different source areas (i.e., predominately urban areas) on the Ipswich River using our SBC and SMF analyses. The patterns of individual cations in the SBC analysis were similar between the outflow of the urban subbasin and that of the entire watershed (Figure 4). Sodium ratios in the SBC analysis increase in the winter months, whereas other cations decrease as a result of the Na^+ increase. The increase in Na^+ is undoubtedly linked to the large quantities of road salts applied to the watershed in the winter months (Williams *et al.*, 2004b), and this pattern is well correlated with that of Cl^- ($r = 0.85$, $P < 0.05$).

The patterns of individual cations in the SMF analysis differ between the outflow of the urban subbasin and that of the entire watershed (Figure 5). In contrast to patterns observed in Ipswich River runoff, SiO_4^{3-} in the stream water of the urban subbasin is not dramatically diluted during the snowmelt runoff period. This observation indicates that there is a substantial source of $SiO_4{}^{3-}$ in runoff from more urban subbasins and this source is likely linked to the application of road sands for deicing purposes (Williams *et al.*, 2004b).

In the SMF and SBC analyses, there is a noticeable summertime increase in K^+. However, whereas the increase of K^+ in the urban subbasin extended through October, the increase in the Ipswich River extended through December, indicating that there was a distinct source of K^+ during the period of October through December that was not linked to geochemical weathering and that K^+ had different source contributors than the other base cations (Figures 4 and 5). We surmise that this source of K^+ was from the mineralization of organic matter and leaching of senescing leaves during the fall. Moreover, in most basins, the root zone reconnects with the saturated zone in the fall (rain < ET in summer, rain > ET in the winter; Staver and Brinsfield, 1998). In first-order streams with shallow unconfined aquifiers, base flow or shallow throughflow could be influenced by higher K^+ in the root zone.

There were some similarities in the patterns of negatively charged solutes to those of the base cations (data not shown). For instance, as expected, Cl^- had a similar pattern to that of Na^+ because of road salting. ANC had a similar pattern to that of Ca^{2+}, perhaps a result of $CaCO_3$ application (lime) to agricultural areas or the dissolution of concrete in urban and commercial areas. SBC and SMF analyses of $NO_3{}^-$ and $SO_4{}^{2-}$ were more difficult to interpret. Variability in $NO_3{}^-$ concentrations is likely in part a result of fertilizer applications and stormflow runoff from fertilized areas. The largest increases in $NO_3{}^-$ occur during the fall and snowmelt runoff periods, likely because of the flushing of mineralized organic matter and overwintering products, respectively. Sulfate had a similar pattern to that of $NO_3{}^-$ ($SO_4{}^{2-}$ data not shown). High concentrations in the spring were probably a result of relatively high concentrations in snowmelt runoff (there is considerable $SO_4{}^{2-}$ in wet and dry deposition; Williams *et al.*, 2004b) in conjunction with the flushing of overwintering products.

5.3. FACTORS THAT INFLUENCE LAND USE/WATER QUALITY RELATIONSHIPS

The biggest source of variation in the water chemistry of our data set is spatial, as opposed to temporal. For example, $NO_3{}^-$ concentrations in the urban end-member catchment were higher than those in the forested end-member catchment by up to a factor of 25, whereas the temporal differences in these subbasins varied by factors of 5 to 10 (Figure 6). Nevertheless, temporal variability was also responsible for the differences apparent in the land use/solute concentration relationships (Figure 2; Table I). For instance, these relationships tended to be slightly higher in the high runoff months (i.e., February and April) than in the low runoff months (i.e., September and June) (Table II), but similar despite wetter- (1370 mm in 2000) and drier-than-average (1080 mm in 1999) water years.

Some spatial and temporal variability in nutrient concentrations is likely a result of biological processing. For instance, the generally lower concentrations of $NO_3{}^-$ in second- and third-order than in first-order streams with a similar proportion of urban + agricultural land use indicate that solute removal processes (i.e., uptake, transformation, or water withdrawal) are responsible for some N removal (i.e., uptake or loss via denitrification) in the streams of this system (Figure 3). Previous research in the Ipswich River basin indicates that a combination of lateral (i.e., wetlands and riparian zones) and in-stream processes are responsible for N processing in the aquatic system (Filoso *et al.*, 2004), albeit there is strong evidence in support of more lateral than in-stream processing. This finding is supported by a number of nutrient addition experiments where NO_3^- uptake was below detection in both the main stem and upland tributaries (Williams *et al.*, 2004a). Moreover, there is likely less lateral processing in first-order than in larger-order streams because the former drain subbasins that commonly have higher elevations and downhill gradients that do not support the development of larger wetland areas, in contrast to second- and third- order streams that are flatter and have well-developed wetlands.

Consequently, N processing in the wetland buffers of larger-order catchments would be responsible for inputs of water low in N concentrations to the river, and these inputs would tend to alter the strong land use/water quality relationships observed in the first-order catchments. In contrast, the differences in K^+ concentrations between the first- and the second- and third-order streams is likely because, once out of the rooted zone, K^+ tends to be less affected by biological processing than NO_3^-.

Although LULC in our first-order catchments explains up to 73% of the variability in streamwater solute concentrations, r^2 values are typically much lower. Moreover, relationships of the LULC configuration in concentric zones of varying widths from the streams against streamwater solute concentrations in our first-order catchments always had lower r^2 values than those for the entire catchment. However, there were several instances where the r^2 values in these zones approximated those of the entire catchment. For instance, the relationship described above for NO_3^- in entire catchment was similar to that in the 200 m zone ($r^2 = 0.47$ vs. 0.45; Table II). Likewise, several other constituents that tended to have similar r^2 values for the entire catchment and the 200 m zone bordering the stream were those with a strong organic component (i.e., DON, DOP, TP and DOC) and SiO_4^{3-}. Because wetland areas are commonly net producers of organic constituents, similar relationships (i.e., r^2 values) are likely a result of the proportionally larger wetland area in the 200 m zone than that of the entire catchment and the wetland's influence regulating these constituents in stream water. For instance, DON and DOC had positive, exponential relationships with the increasing extent of wetland + open water in the fall (e.g., $r^2 = 0.35$ for DON in the composite of November 1999 and September 2000).

Other than land use, there are likely a number of factors that regulate streamwater solute concentrations at the subbasin scale. For instance, factors such as flow routing via storm drains, soil type, stream slope, septic density and efficiency, the proximity of strong source areas to the stream, and the orientation of different land use categories in relation to the stream that cannot be generalized by different stream buffer distances may also partially regulate solute concentrations in stream water.

Moreover, we have shown that there are distinct differences in the solute concentrations of base and storm flow from subbasins with predominately urban, forest, or agriculture land use (Figure 7). Pre-event baseflow indicates that the concentrations of most solutes in the urban and agricultural subbasin streams are higher than those of the forested subbasin. Storm events result in a combination of solute pulses (e.g., inorganic N) and dilution effects (base cations), and the dynamics of these solutes vary both spatially and temporally. For instance, solute signatures from stormflow events in these subbasin streams will depend on the magnitude, duration, and frequency of storm activity in the area sampled and the period of time elapsed since an event. Hence, stormflow activity can affect baseflow solute concentrations if the baseflow sampling occurs on the receding limb of a stormflow hydrograph and there has been insufficient time for the solutes to recover to their pre-event baseline concentrations. This may have occurred on one of our spring samplings that was preceded by a storm event. Hence, stormflow was also responsible for the array of chemical signatures observed in the baseflow streamwater of our first to third-order catchments.

The relative importance of the factors identified above responsible for regulating streamwater chemistry is site-specific. For example, the Cl^- relationship with urban + agricultural land use has a r^2 of 0.47, indicating that on average only 47% of the variance can be explained by these land use categories. However, an analysis of individual subbasins indicates that some moderately developed subbasins have the highest Na^+ and Cl^- concentrations. In one of these subbasins, a major highway traversing the subbasin was a strong source of NaCl from road salting, thereby slightly confounding the land use/solute concentration relationship. Another example is that some of the most urban subbasins have the highest proportions of sewered houses. Because septic waste is a strong source of many solutes to the aquatic system (Williams *et al.*, 2004b), the stream water in more urban but predominately sewered areas would probably have lower solute concentrations than urban areas predominately using septic systems. These examples are likely applicable to a number of different solutes where site-specific sources are strong regulators of solute concentrations in the streams draining their subbasins.

The large quantities of different elements imported to the Ipswich River basin emphasizes the importance of urban and agricultural land use as factors responsible for large human-derived inputs of these solutes to the Ipswich River watershed. For instance, though the study watershed is predominately forested (49%), our land use/solute concentration relationships indicate that shifts in land use to include even relatively small percentages of agricultural or urban land increase the solute concentrations of most solutes in stream water, and this is particularly true for solutes that have multiple inputs affected by anthropogenic activities. Moreover, our study indicates that land use in the entire subbasin commonly explains a higher amount of the variability in the land use/solute concentrations relationships than the land use in concentric areas at various distances from the stream. Nevertheless, land use commonly explains about 50% of the variability in the solute concentrations of stream water, indicating that these are regulated also by a number of important ancillary factors that cannot be generalized by land use classification. In some basins, identifying site-specific source areas such as highways and septic systems and integrating hydrological, geological, and soil properties with land use would likely improve land use/streamwater solute concentration relationships.

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