

N Retention in Urbanizing Headwater Catchments

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ABSTRACT

Urbanization can potentially alter watershed nitrogen (N) retention via combined changes in N loading, water runoff, and N processing potential. We examined N export and retention for two headwater catchments (~4 km²) of contrasting land use (16% vs. 79% urban) in the Plum Island Ecosystem (PIE-LTER) watershed, MA. The study period included a dry year (2001–2002 water year) and a wet year (2002–2003 water year). We generalized results by comparing dissolved inorganic nitrogen (DIN) concentrations from 16 additional headwater catchments (0.6–4.2 km²) across a range of urbanization (6–90%). Water runoff was 25–40% higher in the urban compared to the forested catchment, corresponding with an increased proportion of impervious surfaces (25% vs. 8%). Estimated N loading was 45% higher and N flux 6.5 times higher in the urban than in the forested

catchment. N retention (1 – measured stream export / estimated loading) was 65–85% in the urban site and 93–97% in the forested site, with lower retention rates during the wetter year. The mechanisms by which N retention stays relatively high in urban systems are poorly known. We show that N retention is related to the amount of impervious surface in a catchment because of associated changes in N loading (maximized at moderate levels of imperviousness), runoff (which continues to increase with imperviousness), and biological processes that retain N. Continued declines in N retention due to urbanization have important negative implications for downstream aquatic systems including the coastal zone.

Key words: watershed; nitrogen; retention; export; loading; urban; residential; impervious.

INTRODUCTION

Nitrogen (N) export from watersheds is strongly correlated with anthropogenic N loading (Peierls and others 1991; Caraco and Cole 1999; Aber and others 2003). At the same time the proportion of N stored or denitrified in watersheds (1 – N export / N loaded, and henceforth referred to as retention) appears to be relatively constant and high (60–90%) in many large northeastern U.S. watersheds (400–

70,000 km²) experiencing a range of N loading from a variety of sources (Howarth and others 1996; Boyer and others 2002; Driscoll and others 2003). Similarly high retention has been reported for small (14–300 km²) agricultural (Jordan and others 1997) and urban catchments (Valiela and others 1997; Groffman and others 2004). A wider range of N retention (40–100%) has been reported for small forested catchments (<20 km²) experiencing a range of atmospheric N loading, but with relatively low N load compared to more anthropogenically modified watersheds (Lovett and others 2000; Aber and others 2003). One would expect urban catchments to show

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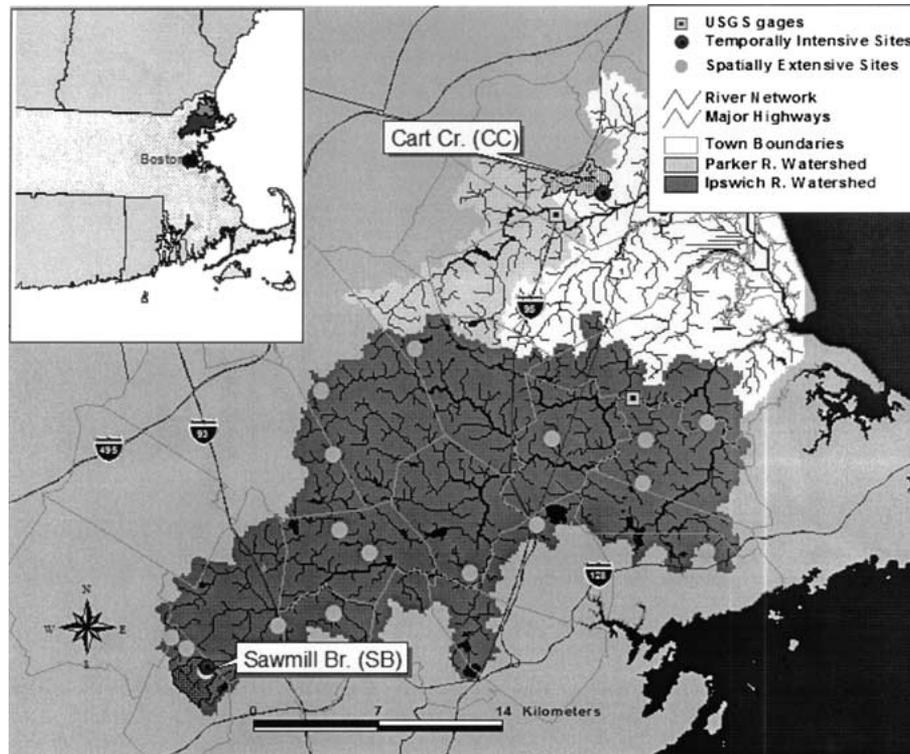


Figure 1. Map of the Plum Island Ecosystem watersheds.

at least a similar range in N retention compared with forested sites because disturbance can be severe. However, this range cannot be characterized because of the relatively few N retention studies in urban catchments (but see Valiela and others 1997; Groffman and others 2004). Moreover, although N retention appears to be relatively high in many northeastern watersheds, N retention globally can range between 0–100% as a function of hydraulic residence time, mean temperature, and preponderance of point vs. non-point source loads (Green and others 2004). There is a need to understand the factors controlling watershed N retention because small changes in retention can lead to large changes in N export (Caraco and others 2003), potentially intensifying coastal eutrophication problems associated with N enrichment.

Urbanization of watersheds invokes a wide range of consequences, both hydrological and biogeochemical. N loading to watersheds generally increases with urbanization due to human waste inputs, increased NO_x emissions and fertilizer applications to lawns (Valiela and Bowen 2002). Increased impervious surface area leads to greater water runoff along altered flow paths compared to undisturbed systems (Dunne and Leopold 1978; Schueler 1994; Arnold and Gibbons 1996; Burges and others 1998; Paul and Meyer 2001), thereby

reducing residence time of water (and N) in the system. Both runoff and residence time of water are major determinants of N export (Caraco and Cole 1999; Alexander and others 2000; Peterson and others 2001; Green and others 2004). Thus for a given amount of N loading, catchments with higher impervious surface area should show greater N export and reduced N retention. Despite these changes, the impact of urbanization on watershed N retention is poorly known.

Here we address how urbanization influences N export and retention in headwater catchments in northeastern Massachusetts. Our study focuses on the rapidly urbanizing watershed of the Plum Island Ecosystem LTER site located northeast of Boston, MA (Figure 1). There are three goals to this paper. First, we construct annual water and N budgets for two headwater catchments ($\sim 4 \text{ km}^2$) of contrasting levels of urbanization (suburban residential vs. forest) for two water years of contrasting moisture conditions (the 2001–2002 and 2002–2003 Water Years (WY01 and WY02)). Next, we evaluate the generality of the results from these two catchments by comparing them with annual DIN concentrations (for WY01) exported from a larger number of less intensively monitored headwater sites across a gradient of urbanization. Finally, we discuss the impact urbanization has on N

Table 1. Characteristics of the Study Catchments during the Study Period.

Characteristic	SawMill Br.	Cart Cr.	Other headwater sites
Size (km ²)	4.1	3.9	0.6–4.2 (2.0)
Surficial geology (%)			
Floodplain alluvium	6.1	2.9	0–33 (3.6)
Fine-grained deposits	0.0	12.8	0–15.3 (1.1)
Sand/Gravel	15.2	12.3	0–92.6 (30.8)
Till	77.2	68.2	7.3–100 (63.3)
Land Use (%)			
Forest	13.7	55.3	7.7–55.8 (29.9)
Residential	72.3	10.6	6.6–89.0 (44.3)
Agricultural/open field	4.2	7.5	0–29 (3.9)
Industrial/commercial	4.6	5.6	0–28.2 (5.7)
Wetland	4.3	18.6	1.7–25.5 (13.8)
Open water	0.0	0.2	0–20.7 (1.8)
Impervious surface area (%)	24.6	8.2	1.3–28.6 (14.8)
Population (# km ⁻²)			
Total	981	130	20–1149 (527)
Waste treatment via septic	73	122	20–1050 (231)

Range and mean shown for other headwater sites ($n = 16$).

retention, focusing on changes in water runoff, N concentrations, and N loading associated with impervious surfaces.

STUDY AREA

The headwater catchments are located in the Ipswich River and Parker River watersheds, which drain to the Plum Island Estuary in northeastern MA (Figure 1). The watersheds are located on the coastal lowland section of New England and are characterized by low to moderate relief and relatively poor drainage (Baker and others 1964). The watersheds are underlain by igneous and sedimentary Paleozoic and Precambrian bedrock and have shallow soils developed on surficial till, gravel and sand deposits (Baker and others 1964). Maximum elevation is about 150 m and mean watershed slope is 24 m km⁻¹. Mean precipitation is about 1,150 mm y⁻¹, and evenly distributed throughout the year.

Two catchments of contrasting land use were intensively studied to characterize runoff and N exports. Sawmill Brook catchment (SB) is a 4.1 km², heavily residential watershed that drains a portion of the town of Burlington, MA (Figure 1). Residential development is relatively high density, single-family lots (< 0.25 acres), with an abundance of lawns (Table 1). Cart Creek catchment (CC) is primarily forest and wetland draining 3.9 km² of the town of Newbury, MA. The forest is primarily oak that has regrown following agricul-

tural abandonment early in the 20th century. SB is roughly 25% impervious surface area, composed primarily of rooftops and roads, with several large parking lots. Although CC is primarily natural vegetation it has a major interstate (I-95) cutting through it, which results in a relatively high % impervious area (8.2%). A purely forested catchment is difficult to find in our region, but CC is on the less impacted end of the urban continuum. SB has a fairly high population density (981 km⁻²), most of whose waste is exported out of the catchment via sewer systems. In contrast, CC has a much lower population density (119 km⁻²), most of whose waste enters the catchment via septic systems. Wetlands represent 18% of CC catchment and only 4% of SB catchment. Both catchments are underlain by similar surficial geology, although CC has more fine-grained deposits (Table 1).

A number of additional headwater catchments were studied less intensively to characterize mean annual DIN concentrations. These catchments range in size from 0.6 to 4.2 km² and are distributed throughout the Ipswich watershed (Figure 1). Urban development ranges from 7 to 90% and imperviousness from 1 to 29% (Table 1). Urban development is primarily residential, but several of the catchments include a large industrial component. Population density ranges from 20 to 1,150 km⁻² and is highly correlated with percent residential area ($r^2 = 0.90$). The number of people on septic systems peaks at intermediate levels of residential development (~40–50% residential), be-

cause as development increases more communities convert from septic to sewage systems. Most of the communities on sewer systems are serviced by the Massachusetts water resources authority (MWRA) and all sewage waste is exported from the watersheds. Generally, urbanization results in co-varying changes in the headwater catchments, with % imperviousness, total population density, and % residential all showing significant positive correlations (Pellerin 2004). Wetland abundance also tends to decline as % residential increases ($r^2 = 0.28$, $P = 0.03$).

METHODS

Water and N Fluxes—Headwater End Member Sites

Depth was continuously monitored in Sawmill Brook (SB) and Cart Creek (CC) using YSI-6920 (Yellow Springs Instruments, Yellow Springs OH) or Sigma depth data loggers (American Sigma, Loveland CO). Depth vs. discharge rating curves were developed at each monitoring site. Daily runoff (mm d^{-1}) was determined from daily average discharge and watershed area. Our rating curve did not encompass the entire range of depths so we extrapolated the high end of the rating curve. As a result, discharge during storm peaks in both SB and CC is subject to uncertainty (corresponding with runoffs above 2.2 mm d^{-1} in SB and 1.8 mm d^{-1} in CC). To calculate annual runoff for WY01, some data gaps of several days to several weeks were filled by interpolating the ratio of headwater runoff to Ipswich R. runoff (USGS gage 01102000) measured at either end of the gap, and multiplying the daily ratio by the Ipswich R. runoff during the gap. Because the gaps were relatively short, this approach provided a reasonable approximation of runoff. For WY02, we used the same approach for interpolating discharge, despite the much longer data gap occurring in the winter period because of extremely cold conditions. The annual estimates for WY02 are therefore subject to greater uncertainty than for WY01. In each year, daily precipitation was based on interpolated NCDC data for stations in northeastern Massachusetts and southern New Hampshire.

Nutrients were collected at the discharge monitoring sites using both grab samples and automated samplers (American Sigma). Grab samples were collected roughly every 2 weeks, and automated samples daily during deployment periods. Automated samples were collected only for nitrate + nitrite ($\text{NO}_3\text{-N} + \text{NO}_2\text{-N}$) and preserved by adding H_2SO_4 to the bottles prior to deployment. Bottles

remained in the field for up to one month before retrieval. Upon retrieval, these samples were filtered and frozen until analysis. Grab samples were filtered through Millipore-HA $0.45 \mu\text{m}$ filters and frozen until analysis for $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$, and ammonium ($\text{NH}_4\text{-N}$) by flow injection using a Lachat QuikChem 8000 Automated Analyzer (Milwaukee, WI). Dissolved inorganic nitrogen (DIN) is the sum of $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{NH}_4\text{-N}$. Monthly samples were also analyzed for total dissolved nitrogen (TDN) using an Antek High Temperature Total Nitrogen Analyzer. Dissolved organic nitrogen (DON) was derived by subtracting DIN from TDN. PON was not measured in SB and CC during this study; we assume that PON makes a relatively small contribution to N exports from these watersheds (C.S. Hopkinson, unpublished data). There was no difference between $\text{NO}_3\text{-N}$ determined from grab or automated samplers, so data from the two methods were combined. Mean annual flow-weighted concentrations were estimated for each constituent using flow from the sample day. Annual fluxes were calculated by linearly interpolating nutrient concentrations between sample days and multiplying by daily discharge. We feel this is valid because generally N concentrations trended over time and because there was no clear relationship between concentration and flow.

Flow-Weighted DIN Concentration—Spatially Extensive Headwater Sites

Monthly nutrient samples were collected at 16 additional small headwater catchments ($0.6\text{--}4.2 \text{ km}^2$) across a gradient of land use characteristics during WY01. At least ten samples were collected at each site over the course of the water year. Additional sites were sampled less frequently and were not included in this study because the reduced frequency was inadequate to characterize annual flow-weighted N concentrations. The samples were analyzed for $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ as described above. Discharge was not measured at these sites. We calculated annual flow-weighted mean concentrations using discharge reported at the Ipswich USGS gage for the sample day to more heavily weight concentrations from seasonally higher flow periods.

GIS

Land use (1:25000) and National Wetland Inventory (NWI) wetland (1:5000) data layers were obtained from MASSGIS (<http://www.state.ma.us/mgis/massgis.htm>), and combined into a hybrid

land use/wetland coverage. Land use was aggregated to six land use features: residential, agricultural/open field, industrial/commercial, forest, wetlands, and open water. Impervious surface area was derived from estimates of percent impervious surface vs. land use type (Arnold and Gibbons 1996). Distributed population was based on Census 2000 Summary File (SF) 1 tabular data and the Topologically Integrated Geographic Encoding and Referencing system (TIGER/line) geographical database, corresponding with the block level. The percent of the population on septic systems was based on census surveys from 1990 (SF3 tables, code HO24) at the census tract level. The census tract scale is relatively coarse. However, most of the variability in waste treatment occurs at the town level (DEP 2002) and generally there are several census tracts per town. Therefore, we believe that our estimates of waste treatment of people in different catchments are reasonable. The waste treatment survey was discontinued after the 1990 survey, necessitating the assumption that the percent of people on septic systems in 1990 could be applied to the updated 2000 population.

Watershed attributes were estimated using a 120m gridded river network developed for the Plum Island Estuary from 30 m DEM's with USGS stream hydrography "burned in". All spatial data sets were aggregated to 120 m grid cells either as percentage grids (land cover), or density grids (population). Upstream average characteristics were calculated using a watershed GIS analysis program, GHAAS/River GIS (Water Systems Analysis Group, University of New Hampshire). At the 120 m grid scale, there are 70 grid cells in each square kilometer.

N Loading Estimates

The major sources of N to the Ipswich and Parker watersheds are atmospheric deposition, waste N inputs via septic systems, and fertilizer applications to lawns (Williams and others 2004). We assumed N fixation was a relatively small input and did not include it in our budgets. N inputs from leaking sewer lines and pets might be important (Baker and others 2001), but lacking information we do not include them in our budget. Sewage waste is treated outside the basin and no major point sources exist within the small headwater catchments of our study. Wet deposition was estimated using interpolated daily precipitation from NCDC and monthly precipitation-weighted N concentrations obtained from the NADP site in Lexington MA. Comparison of NADP estimates with atmospheric N

deposition collected within the watershed showed similar results for N (Williams and others 2004). For dry deposition, we assumed constant loading rates over the course of the year based on Ollinger and others (1993). Dry deposition was assumed constant for all land use types, possibly leading to overestimates of inputs to areas with reduced canopies such as urban areas.

Spatial information described above was used to estimate N inputs via septic waste and fertilizer applications to lawns. Fertilizer N inputs are difficult to quantify, especially at the small catchment scale. Because of uncertainties in the parameters used to calculate these inputs (Valiela and others 1997), we estimated a high and low N load scenario to determine how these assumptions might affect the results. For the high N load scenario, septic waste inputs were estimated using population on septic systems and a per capita N loading rate of 4.8 kg N person⁻¹ y⁻¹ (Valiela and others 1997). We estimated fertilizer N inputs to lawns from land use estimates of pervious surface areas in human dominated areas (residential + industrial/commercial + agriculture - impervious surface area). We assumed that 75% of pervious surfaces in human dominated areas are potentially fertilized (that is, are lawns), and that 34% of these areas are actually fertilized (Valiela and others 1997; Williams and others, submitted). Finally, we assumed that on average 100 kg N ha⁻¹ y⁻¹ are added to lawns that are fertilized (Valiela and others 1997) and that fertilizer inputs to agricultural areas are similar to lawns. Agriculture is generally low intensity haying and horse pasture and usually represents a small proportion of land use in our study sites (< 10%). For a low N load scenario, we changed the per capita N loading rate to 1.85 kg N person⁻¹ y⁻¹ (Caraco and others 2003), and we reduced the percent of pervious areas that is potentially fertilized to 37.5%. These changes reduce estimated waste N and fertilizer inputs by 62 and 50% respectively. The two scenarios serve to constrain N retention estimates. All N sources were summed together to estimate spatially distributed total annual N load.

Water Runoff and N Retention Coefficients—Headwater End Member Sites

Water runoff and N retention coefficients for the two intensively studied sites were determined for the period October 1, 2001 to September 30, 2002 (WY01) and October 1, 2002 to September 30, 2003 (WY02). Water runoff coefficients were determined by dividing measured stream by annual

Table 2. Summary of Water and N Budget Results for the 2001–2002 Water Year (WY01) and the 2002–2003 Water Year (WY02)

Parameter	WY01		WY02	
	SawMill Br.	Cart Cr.	SawMill Br.	Cart Cr.
Water				
Precipitation (mm y ⁻¹)	974	942	1360	1339
Total runoff (mm y ⁻¹)	272	194	449	358
Annual Runoff coefficient (%)	27.9	20.6	33.0	26.7
Total N loading (kg km ⁻² y ⁻¹)				
Wet deposition (DIN)	494	496	497	527
Dry deposition (DIN)	290	290	290	290
Net waste N	350 (135)	586 (226)	350 (135)	586 (226)
Fertilizer N	1443 (721)	395 (198)	1443 (721)	395 (198)
Sum	2578 (1641)	1767 (1209)	2581 (1644)	1798 (1240)
River N exports (kg km ⁻² y ⁻¹)				
DIN (NO ₃ + NH ₄)	333	7.5	502	15.6
DON	51.5	51.6	76.5	72.6
Sum	384.5	59.1	578.5	88.2
N retention (%)	85 (77)	97 (95)	78 (65)	95 (93)

Values in parentheses refer to a low N load scenario to test sensitivity to N loading assumptions.

precipitation. N retention was determined by dividing annual TDN export in streams by the estimated annual N load and subtracting from 1. N retention in this calculation includes storage in biomass and soils, denitrification, as well as unmeasured exports (see Discussion).

RESULTS

Water runoff

During both water years, annual runoff was higher in the urban than in the forested catchment. Precipitation was roughly 200 mm above the long-term average of 1,150 mm in WY02 and 200 mm below average in WY01 (Table 2). During WY01, annual runoff was 272 mm y⁻¹ in the urban Sawmill Br. catchment (SB) compared to 194 mm y⁻¹ in the forested Cart Cr. catchment (CC) (Table 2). During WY02, annual runoff increased to 449 mm y⁻¹ in SB and to 358 mm y⁻¹ in CC. SB had higher storm runoff especially during the growing season, and generally higher baseflows throughout the year compared with CC (Figure 2a). The annual runoff coefficient was roughly the same percentage higher in SB than in CC in both water years (28% vs. 21% in WY01 and 33 vs. 27% in WY02; Table 2).

N concentrations

Annual flow-weighted mean DIN concentrations for forested CC and urban SB were 2.8 and

65.1 µM, respectively, in WY01 and 4.3 and 72.4 µM, respectively, in WY02. In SB, DIN was dominated by NO₃-N (~90% in each year). In CC, NH₄-N was a larger component of DIN (40–60%). NO₃-N was lower through most of the year in CC compared to SB (Figure 2b). There was an apparent relationship between NO₃-N and flow in CC and a weak relationship in SB (Figure 3). In CC, NO₃-N was most variable at low runoffs (< 0.05 mm d⁻¹), ranging between 0 and 10 µM. At moderate runoff (0.05–0.5 mm d⁻¹), NO₃-N was usually higher (~10 µM), with several extremely high levels. Extremely high concentrations coincided with increasing flows at the end of the growing season. At higher runoffs (> 0.5 mm d⁻¹), NO₃-N declined (Figure 3a). In SB, NO₃-N showed little relationship with flow, although there was an increased likelihood of higher concentrations at runoffs greater than 1 mm d⁻¹ (Figure 3b). Although based on many fewer samples, there was no relationship between NH₄-N and DON with runoff in either stream. During both litter fall periods in SB (early WY01 and WY02) when flows were still low, NO₃-N briefly dropped to very low levels (Figure 2b), possibly due to immobilization by or denitrification within accumulated leaf litter from the adjacent forested area. Flow weighted mean DON concentrations were higher in CC than SB during WY01 (20.9 µM vs. 13.9 µM) but were similar in WY02 (13.5 µM vs. 12.1 µM).

DIN concentrations determined for WY01 in the less intensively monitored headwater sites showed

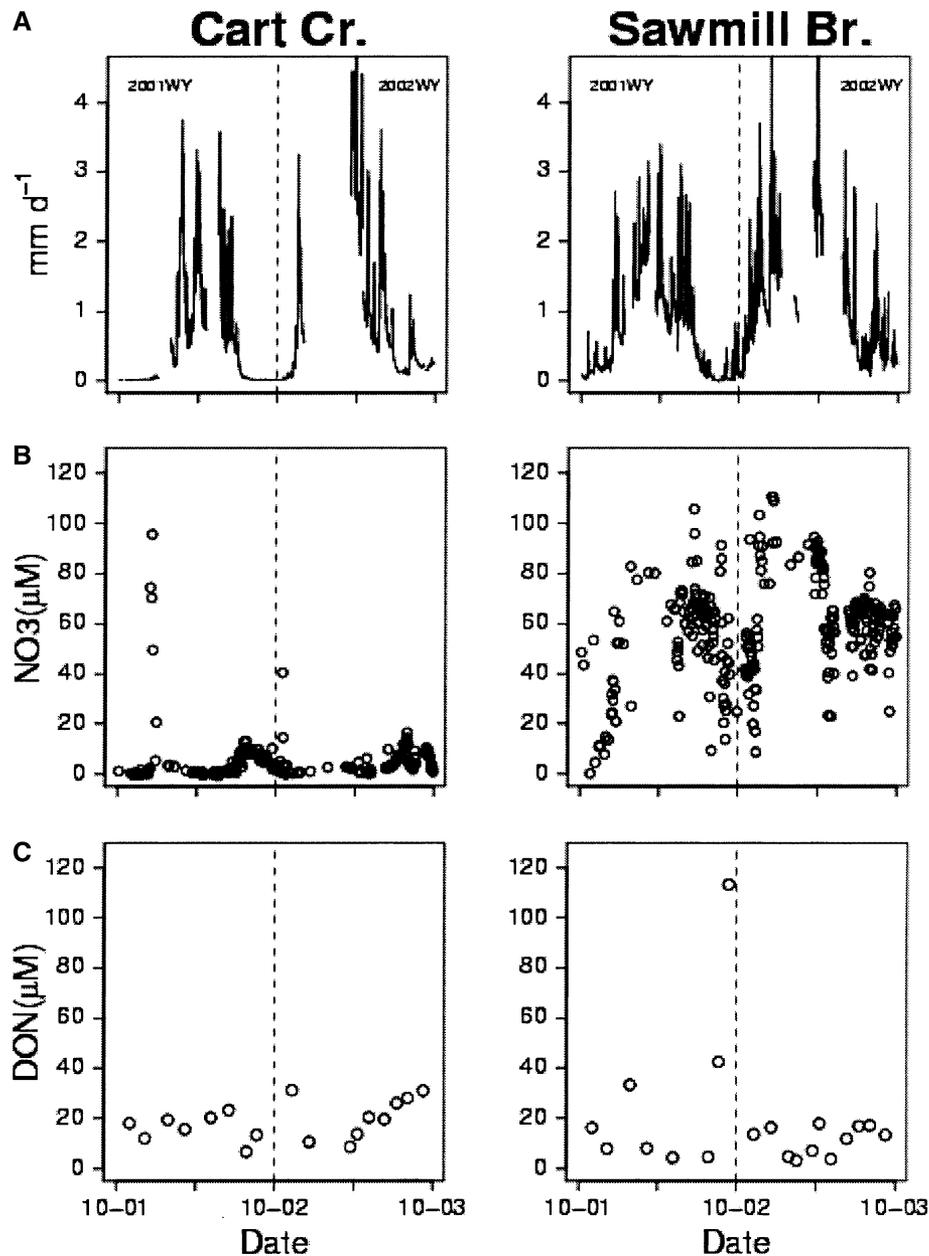


Figure 2. Measured runoff and nutrient concentrations for the intensively monitored headwater sites during the study period. **A** Runoff (mm d^{-1}), **B** $\text{NO}_3\text{-N}$ concentrations (μM), and **C** DON concentrations (μM) for Cart Cr. (forested, area = 3.9 km^2) and Sawmill Br. (residential, area = 4.1 km^2).

similar effects of urbanization. Annual flow-weighted DIN ranged from 1 to $90 \mu\text{M}$ and was highly correlated with both % residential land ($r^2 = 0.58$, $n = 16$, $P < 0.001$), and total population density ($r^2 = 0.49$, $n = 16$, $P < 0.01$) (Figure 4a,c). DIN concentrations were positively related to impervious surface area, but the relationship was not significant ($r^2 = 0.20$, $P = 0.06$) (Figure 4b). A weak relationship occurred between DIN concentration and the high N load scenario ($r^2 = 0.30$, $P = 0.02$; Figure 4d) but no significant relationship

was found with the low N load scenario ($r^2 = 0.22$, $P = 0.06$). The low r^2 's for the N load scenarios were driven in part by a single catchment with high septic N loads that lacked a corresponding increase in DIN concentrations. Multiple regressions did not improve upon the simple regression using only residential land use (based on adjusted r^2). Flow weighted estimates from the more frequently sampled SB and CC from both WY01 and WY02 corresponded well with the relationship for the less intensively studied sites (Figure 4).

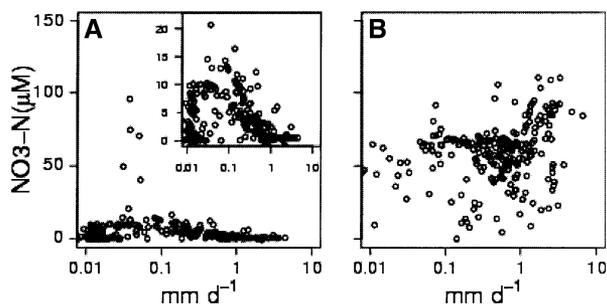


Figure 3. $\text{NO}_3\text{-N}$ concentrations (μM) vs. runoff ($\log \text{mm d}^{-1}$) for **A** Cart Cr. and **B** Sawmill Br. Inset in **A** shows the relationship in Cart Cr. at a reduced nitrate scale.

N Runoff

Total dissolved N runoff was much higher from the urbanized SB than from CC because both runoff and N concentrations were higher. In WY01, annual N runoff totaled $385 \text{ kg N km}^{-2} \text{ y}^{-1}$ in SB vs. $59.1 \text{ kg N km}^{-2} \text{ y}^{-1}$ in CC (Table 2). In WY02, annual N runoff totaled $579 \text{ kg N km}^{-2} \text{ y}^{-1}$ in SB vs. $89 \text{ kg N km}^{-2} \text{ y}^{-1}$ in CC. N runoff was dominated by DIN in the urban site, and by DON in the forested site (Table 2).

N Retention

N retention (TDN export / total N loading) was high in both intensively monitored headwater sites, but was greater in the forested catchment. Whereas the urbanized catchment exported several times more N than the forested catchment, the difference in N loading between the two catchments was relatively small (Table 2). For the high N load scenario, total N loads during WY01 were estimated at 2578 and $1767 \text{ kg N km}^{-2} \text{ y}^{-1}$ in SB and CC, respectively (Table 2). Atmospheric deposition, waste N, and fertilizer represented 30, 14, and 56% of total N loads in SB, and represented 44, 33, and 22% in CC. N loads were similar in WY02 because we assumed fertilizer and waste inputs were the same, and because N inputs via wet deposition were similar despite much higher precipitation. Concentration estimates from the NADP site suggested that a dilution of N in precipitation occurred in the wetter year.

N retention was 85% in SB and 97% in CC (Table 2) during WY01. During the wetter WY02, N retention dropped to 78% in SB and only slightly to 95% in CC. For the low N load scenario, waste N and fertilizer N were both considerably reduced (Table 2). The low N load scenario resulted in a greater decrease in N retention in the urban site (85–77% in WY01 and 78–65% in WY02), than in

the forested site (97–95% in WY01 and 95–93% in WY02). Uncertainty in N loads therefore limits our understanding of the rate at which N retention declines with development.

DISCUSSION

Effect of Urbanization on Water Runoff

Runoff coefficients increase with urbanization due to the impact of impervious surfaces. This phenomenon has long been known for individual storms (Dunne and Leopold 1978; Urbonas and Roesner 1992; Schueler 1994). Recent reports have confirmed that the increase can occur on annual time scales as well (Burges and others 1998; Grove and others 2001; Jennings and Jarnagian 2002). Burges and others (1998) found that annual stream runoff as a percentage of precipitation ranged from 12–30% in a forested catchment (0% impervious) to 44–48% in an urban catchment (30% impervious) over a 3-year period in Washington State. In the Lower Charles R. basin, which includes the city of Boston, annual runoff increased from 20 to 80% across five catchments that ranged from 11 to 86% impervious surface (Zarriello and Barlow 2002). Our estimates of annual runoff coefficient are consistent with these other studies, although the rate of increase between our forested and urban catchments was slightly slower (Figure 5).

The increased runoff from our urban catchment is due to both greater surface runoff and higher baseflows (Figure 2). In SB, hydrograph separations suggest that 4–11% (mean = 5%, $n = 12$) of rainfall enters the stream immediately as new water, presumably as direct runoff from impervious surfaces (Pellerin 2004). Although this is relatively low for an urban catchment, a much smaller percentage enters as new water in the forested CC, despite 8% impervious surfaces. Thus, a large proportion of the observed 6–7% difference in annual runoff coefficients for SB and CC (Table 2) is likely due to higher surface runoff during storm events. However, baseflow appears to be more consistent and higher in the urban site relative to the forested site, especially during the growing season (Figure 2). Because SB is 25% impervious and roughly 5% runs off via surface flowpaths, a significant fraction of rain falling on impervious surfaces likely enters pervious surfaces. Increased runoff through pervious soils can be an important factor in urban catchments (for example, Burges and others 1998). The different mechanisms leading to increased runoff (surface vs. subsurface) have different impacts on biogeochemical cycles.

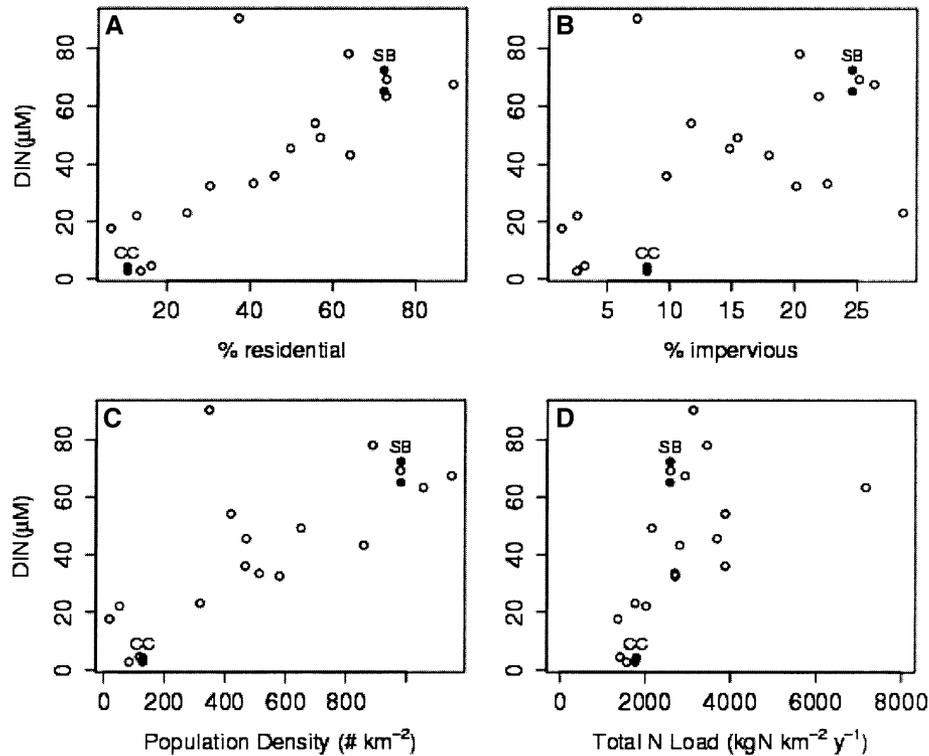


Figure 4. Annual flow-weighted DIN concentration (μM) for the headwater catchments vs. **A** residential area (%), **B** impervious area (%), **C** total population density ($\# \text{ km}^{-2}$), and **D** estimated N loading ($\text{kg N km}^{-2} \text{ y}^{-1}$, high N load scenario, Table 2). Estimates from the Cart Cr. (CC) and Sawmill Br. (SB) are shown for comparison. The two points for SB represent the estimates for each water year. CC concentrations were similar in each year so are not distinguished.

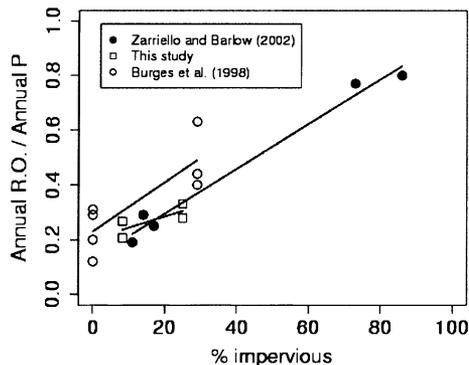


Figure 5. Proportion of annual precipitation that emerges as stream runoff vs. % impervious surface area from this and two other studies. Data from this study and Burges and others (1998) represent different water years for each level of impervious surface.

For example, surface flow paths will redirect atmospheric N inputs away from active retention sites, whereas increased runoff through pervious soils will increase flushing of accumulated N, thereby reduce residence times and the effectiveness of biological processes.

Accurately closing the water budget is difficult in small urban catchments. Both inflow and infiltration (I/I) or exfiltration could be occurring (Lerner 2002). Lawn watering imports water during summers in catchments with public water supply. These processes are difficult to quantify for small watersheds. An additional issue for closing the water budget in small headwater catchments in general is potential loss via deep groundwater flow paths that bypass gauging stations (for example, Jordan and others 1997). Zariello and Barlow (2002) found in the Charles River watershed (MA) that up to 40% of rain inputs might be lost to deep groundwater. Based on comparison of runoff coefficients for CC and the Ipswich R. watershed as a whole (both with similar proportion of impervious surfaces), losses via groundwater in our headwater catchments are potentially 10% of annual precipitation ($\sim 100 \text{ mm}$). Unmeasured groundwater export is a major challenge when studying small urban catchments, which are selected based on land use and not geological considerations that ensure all runoff exits via streams (Likens and Bormann 1995). Nevertheless, consistent rates of change in the annual runoff coefficient reported by

various studies (Figure 5) suggest that the effects of impervious surfaces outweigh other changes in urban systems.

Effect of Urbanization on Stream N Concentrations

Elevated DIN concentrations are also a common feature of urbanizing watersheds (Omernik 1976; Wahl and others 1997; Driscoll and others 2003; Groffman and others 2004; Williams and others 2004). Our intensively monitored sites suggest little inter-annual variability in concentration, despite very different runoff conditions in WY01 and WY02. Because DIN concentrations in the two intensively monitored watersheds correspond well with those from the spatially extensive data set (Figure 4), we believe that both sets of DIN results (that is, temporally intensive and spatially extensive catchments) are representative for our area.

The rate of N loading clearly contributes to elevated N concentrations. However, N loading by itself was a relatively poor predictor of DIN concentrations in our study (Figure 4). This is not entirely unexpected because N loading estimation involves many assumptions (for example, fertilizer application). In addition, we did not account for other potential inputs, such as pet waste (Baker and others 2001) or leakage from sewer systems (Lerner 2002). High variability in the $\text{NO}_3\text{-N}$ vs. N loading relationship has also been observed in forested systems (Aber and others 2003), where the estimate of N loading (via N deposition) is more certain. Factors other than N loading rates, such as the hydrology or biological processing within the catchment, likely influence variability in DIN concentrations (for example, Stoddard 1994; Lovett and others 2000; Aber and others 2003).

The pattern of nitrate vs. runoff in the forested catchment suggests that several mechanisms influence $\text{NO}_3\text{-N}$ export concentrations. In CC, $\text{NO}_3\text{-N}$ accumulates during dry periods and is flushed at moderate runoff levels (Figure 3). Flushing is a common response in forested watersheds (Creed and others 1996; Creed and Band 1998). At high runoffs, nitrate is diluted to levels ($< 3 \mu\text{M}$) much lower than expected based on $\text{NO}_3\text{-N}$ in precipitation ($> 10 \mu\text{M}$). Reasons for low NO_3 concentrations at highest discharge are not clear, although riparian zones may be important (Groffman and others 1996, 2002). In our urban catchment, high runoff events do not lead to dilution as expected based on precipitation N. In fact, concentrations in SB tend to increase with higher runoffs, suggesting flushing and/or additional N

sources become a factor [for example, fertilizer in surface runoff (Morton and others 1988), sewage leakage]. Although sewage is pumped out of the watershed, waste N may be more important than our N budget suggests. Nitrate stable isotopes ($\delta^{15}\text{NO}_3$) sampled in SB were roughly 10 per mil, within the range of wastewater N (Pellerin 2004).

DON concentrations did not differ as dramatically as NO_3 in our urban and forest streams. The higher DON concentrations in the forest compared to urban catchment in WY01 correspond with a greater abundance of wetlands, consistent with other studies on the influence of wetlands on DON (Pellerin and others 2004). During the wetter WY02, DON concentrations were similar in the two catchments. The reason for this is unclear. DON fluxes were similar in the two catchments, suggesting DON sources remain in urban areas.

Effect of Urbanization on N Export and Retention

The relatively few urban N budgets reported in the literature (Groffman and others 2004; Baker and others 2001; Valiela and others 1997) suggest that N retention remains relatively high in heavily modified urban ecosystems. At the same time, comparisons between undisturbed and urban catchments do indicate that N retention declines with urbanization. Groffman and others (2004) found that whereas N loads increased 2.3 times, N exports were an order of magnitude higher in an urban vs. forested watershed (650 vs. $52 \text{ kg N km}^{-2} \text{ y}^{-1}$) corresponding with a decline in N retention from 95 to 75%. Our catchments showed similar differences in N exports and retention during the wet year, and smaller differences during the dry year (Table 2). Because small declines in N retention lead to proportionally large increases in flux, understanding the mechanisms of N retention is important as urban areas continue to expand.

N retention can result from sequestration in soils or biomass, as well as denitrification in groundwater, wetlands, or streams. Sequestration and denitrification are likely to decline in urban systems. Changes such as increased impervious surface area (with minimal biological activity), reduced wetland abundance, reduced rooting zone depths (lawns vs. forests), increased surface runoff to streams, and increased water inputs to pervious soils (lowering residence times and increasing flushing for example Green and others 2004) should lead to reduced biological activity. Reductions in stream residence times due to increased water flow will also lower N retention in streams

(Peterson and others 2001; Wollheim and others 2001; Seitzinger and others 2002). Our urban catchment displays many of these characteristics (Table 2), some combination of which probably contributes to the decline in N retention. Nevertheless overall levels of N retention are apparently high, even in wet years.

Some factors that might be expected to cause large drops in N retention may not have a big impact. For example, in our urban watershed on average 5% of precipitation enters as new water (equivalent to 50–70 mm y^{-1}) (Pellerin 2004). This corresponds to a direct input of approximately 40 kg N $km^{-2} y^{-1}$ (5% of wet plus dry deposition), which represents 7–10% of estimated annual N flux and less than 3% of N loads in our urban catchment. Flushing of fertilizer inputs via surface flowpaths is relatively rare (Petrovic 1990; Morton and others 1998).

Interannual climate variability appears to impact N export and retention in urban systems much more so than in forested systems. The influence of runoff on N fluxes is well known (for example, Alexander and others 1996; Jaworski and others 1992; Donner and others 2002). The 2 water years of our study are near the opposite end of the precipitation range in our area. Because N export concentrations were similar in the 2 years, the higher flux in the wet year is due primarily to increased runoff (Table 2). But because flux was so low to begin with in the forested catchment, the change in absolute terms was relatively small and N retention declined little.

The high apparent rates of N retention in the urban watershed could result from unquantified components of the N budget. Although we did not measure PON exports as part of this study, past measurements of PON concentrations (12 μM in SB and 4 μM in CC; C.S. Hopkinson, unpublished data) suggest that retention would decline only slightly (2–4%) under the high and low N load scenarios. N export via groundwater flow paths could also be important. N in this water is not truly retained, and is likely to reenter the river network further downstream. If 100 mm of water is exported via groundwater with N concentrations similar to streams, then N retention would decline in SB by 4–5% using the high N load scenario and 7–8% using the low N load scenario.

Several other factors may be important but are difficult to quantify in complex urban watersheds. As mentioned above, infiltration/inflow could lead to unmeasured exports from the basin (Lerner 2002). Other non-hydrologic vectors (volatilization, export of garden waste) might also be

important (Baker and others 2001). During wetter years, it is likely that a greater proportion of fertilizer inputs are washed out prior to incorporation into lawn biomass, contributing to the higher exports. In addition, sewer leaks and pet waste could contribute N inputs to urban catchments (Baker and others 2001; Groffman and others 2004), leading to underestimation of N retention. Despite uncertainties in our N budget, however, the net effect of urbanization appears to be increased N exports in surface waters and reduced N retention.

Impervious Surfaces as Controls on N Retention—A Hypothesis

Although the mechanisms by which N is retained in urban systems remain poorly understood, it is clear that N retention declines with increasing urbanization. We hypothesize that because impervious surfaces strongly influence the hydrology and biology of urban catchments, the proportion of impervious area drives N retention. We demonstrate this hypothesis using information from our spatially extensive catchments (0–30% impervious) sampled during WY01 (the dry year). We estimated TDN export concentrations in these catchments using measured DIN (Figure 4) and assuming DON concentrations are a positive function of wetland abundance ($r^2 = 0.57$; Pellerin 2004). The resulting TDN concentrations increase with impervious surfaces (Figure 6a), although the slope is somewhat shallower than for DIN because areas with low impervious surface area also correspond with more wetlands and higher DON concentrations (Pellerin 2004).

We estimated annual runoff in each catchment based on reported changes in runoff coefficient as a function of impervious surfaces (Table 2, Figure 5). We assumed differences in annual runoff are controlled primarily by impervious surface cover (for example, (Arnold and Gibbons 1996; Paul and Meyer 2001), and that the relationship is linear (Corbett and others 1997). Other factors (septic population density supplied by public water supplies, surficial geology) also affect runoff, but are likely not as important as impervious surfaces (Zarriello and Ries 2000). The resulting TDN export, as would be expected, is strongly related to impervious surface area (Figure 6b).

At the same time, N loading is maximized at moderate levels of impervious surfaces (peaking at $\sim 10\%$ impervious in our catchments) because impervious surface abundance is correlated with residential development, septic waste management, and the amount of lawn (Figure 6c). This

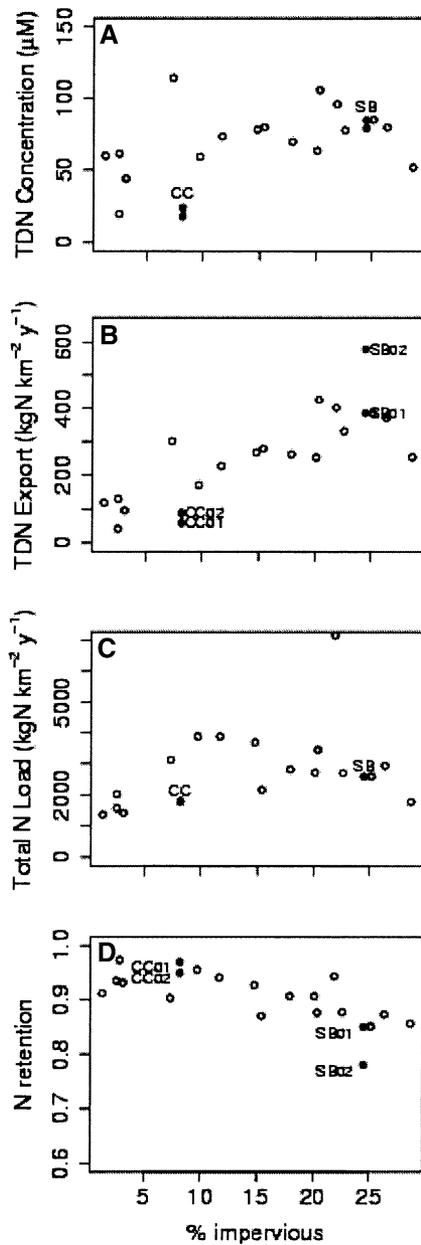


Figure 6. Relationship between impervious surface area and **a** TDN concentration (μM , calculated using measured DIN and estimated DON), **b** Estimated TDN flux ($\text{kg N km}^{-2} \text{y}^{-1}$; calculated assuming annual runoff vs. impervious relationship), **c** Estimated N loading ($\text{kg N km}^{-2} \text{y}^{-1}$), and **d** N retention, from the headwater catchments during WY01. Estimates from the two intensively monitored headwater sites for each water year (CC01,CC02, SB01,SB02) are shown for comparison. When only one value is shown for the intensively monitored sites, there is little difference between water years.

relationship was also confirmed using a larger number of headwater catchments (data not shown). The bell-shaped relationship in N loading

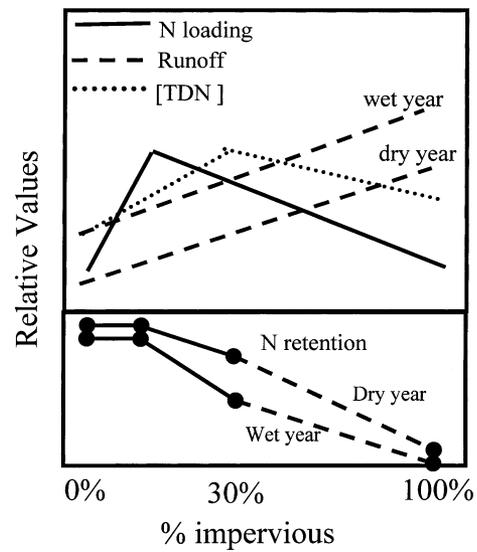


Figure 7. Conceptual model of how water runoff, N concentrations, and N loading vary in response to impervious surface area. Our findings suggest that these factors are linked in predictable ways to the level of imperviousness in urbanizing catchments. In our study, peak N loading occurs at 10% impervious, with N concentrations continuing to increase, but becoming more variable, at least until 30% impervious. Changes above 30% are hypothesized. Runoff is assumed to continue to increase through the entire range of imperviousness. As a result N retention declines. During wet years, runoff increases considerably, but N concentrations change relatively little. As a result, N retention declines more rapidly in catchments with moderate amounts of impervious area.

vs. impervious cover makes intuitive sense: if a catchment is 100% impervious, N loading would occur only via atmospheric deposition.

As a result of these changes, we calculate that during WY01, N retention remains high across our headwater catchments but trends downward with greater amounts of impervious surfaces. Using the high N load scenario, N retention declines to about 85% at 30% impervious cover (Figure 6d). Thus, N retention during the dry year declines by roughly 5% for every 10% increase in impervious area (up to 30%). During wetter years, N retention declines more rapidly (based on SB in WY02). Theoretically, a 100% impervious catchment should approach 0% retention because of increased water runoff and reduction in biologically active surfaces. The trajectory between 30 and 100% during both wet and dry years is unknown. Key questions then are: at what threshold do TDN exports peak and at what amounts? Are there thresholds of imperviousness at which N

retention drops rapidly? Testing this will require synthesis of similar information from sites that span the entire range of impervious surface levels. The relationships between important factors that we think are primary controls on N retention are summarized in Figure 7. We present these relationships as a hypothesis to be tested in other urbanizing areas.

CONCLUSION

Urbanization results in increased water runoff, N loading, and N exports. N exports increase relatively faster than N loading, corresponding with declines in N retention. Based on our results, we hypothesize that the proportion of impervious surfaces in the catchment controls the decline in N retention. This effect is consistent with earlier suggestions that impervious surface area is a unifying indicator responsible for a suite of environmental changes (Schueler 1994). Moisture conditions interact with impervious surfaces to further reduce N retention in wetter years. Although N retention declines with urbanization, retention remains relatively high. The mechanisms by which N retention remain high in urban systems are poorly known and warrant further study. Studies of N dynamics in small urban catchments face major challenges due to uncertainty in water flow paths, N loading estimates, and difficult-to-measure N transfers. As suburban sprawl with increased impervious surface continues, impacts on downstream aquatic systems are likely to increase. Management of impervious surfaces in these areas will be an important strategy for preventing increased export of N to coastal systems.

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