# Nitrogen Fluxes and Retention in Urban Watershed Ecosystems

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# Abstract

Although the watershed approach has long been used to study whole-ecosystem function, it has seldom been applied to study human-dominated systems, especially those dominated by urban and suburban land uses. Here we present 3 years of data on nitrogen (N) losses from one completely forested, one agricultural, and six urban/suburban watersheds, and input-output N budgets for suburban, forested, and agricultural watersheds. The work is a product of the Baltimore Ecosystem Study, a longterm study of urban and suburban ecosystems, and a component of the US National Science Foundation's long-term ecological research (LTER) network. As expected, urban and suburban watersheds had much higher N losses than did the completely forested watershed, with N yields ranging from 2.9 to 7.9 kg N ha<sup>-1</sup> y<sup>-1</sup> in the urban and suburban

# INTRODUCTION

The watershed approach has long been fundamental in ecosystem ecology (Likens 1992; Golley 1993). This approach allows for evaluation of whole-ecosystem nutrient-cycling function through quantification of inputs and outputs, is ideal for comparison of different ecosystems, and has been extensively used for assessment of the effects of disturbance on ecosystem function (Likens and Bormann 1995). The watershed approach is useful for bridging the gap between basic and applied science, providing data at a scale relevant to watersheds compared with less than 1 kg N ha<sup>-1</sup> y<sup>-1</sup> in the completely forested watershed. Yields from urban and suburban watersheds were lower than those from an agricultural watershed (13–19.8 kg N ha<sup>-1</sup> y<sup>-1</sup>). Retention of N in the suburban watershed was surprisingly high, 75% of inputs, which were dominated by home lawn fertilizer (14.4 kg N ha<sup>-1</sup> y<sup>-1</sup>) and atmospheric deposition (11.2 kg N ha<sup>-1</sup> y<sup>-1</sup>). Detailed analysis of mechanisms of N retention, which must occur in the significant amounts of pervious surface present in urban and suburban watersheds, and which include storage in soils and vegetation and gaseous loss, is clearly warranted.

**Key words:** nitrogen; nitrate; watershed; urban; mass balance; long-term ecological research.

management of land for protection of receiving waters (Howarth and others 1996; Smith 1998).

Interest in the ecology of human-dominated ecosystems has increased in recent years. In the 1970s, ecologists began to study agricultural ecosystems (Loucks 1977; Robertson and Paul 1998) and, in the 1980s they began to focus on human settlements or *urban* ecosystems (McDonnell and Pickett 1990). Interest in urban ecosystems was driven by recognition that (a) they occupy large areas of the Earth's surface and are increasing in size (Frey 1984; World Resources Institute 1996); (b) they have dynamic fluxes of water, energy, and nutrients, with important implications for water and air quality (Bowen and Valiela 2001; Paul and Meyer 2001; Rose and Peters 2001; Howarth and others 2002); and (c) human–environment interactions, a relatively un-

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explored but important topic, are dynamic in cities and central to the environmental performance of these areas (Pickett and others 2001). Two urban ecosystem research sites (Baltimore and Central Arizona–Phoenix) were added to the US National Science Foundation's long-term ecological research (LTER) network in 1997 (Jensen 1998; Grimm and others 2000).

Despite the increased interest in urban systems, there are relatively few data on the basic functional properties of these ecosystems. The heterogeneity of urban ecosystems, with a mix of roads, buildings, grass, water infrastructure, agriculture, and natural and seminatural ecosystems, has made it difficult to evaluate basic ecosystem functions relevant to production, consumption, decomposition, and nutrient flux (Sukopp 1990; Pickett and others 1997, 2001). The interaction of physical, ecological, and social drivers of urban ecosystem structure and function has been a particular challenge to analysis of these ecosystems (Grove and Burch 1997).

Water quality in urban ecosystems has been relatively well studied, with a strong focus on the effect of storm runoff on receiving water quality (Heaney and others 1980; Makepeace and others 1995). However, the vast majority of these studies have been driven by the need for information for regulatory agencies, and much of the work has focused on short-term monitoring and storm events (Field and others 1998). Very few attempts have been made to evaluate long-term nutrient fluxes and budgets in urban watersheds with an approach similar to that taken in LTER [for example, see Likens and Bormann (1995) and Heaney (2001)]. Long-term flux and budget studies are necessary if we hope to be able to compare urban ecosystems with the less intensively managed ecosystems that dominate the LTER network. Such studies also provide a useful and unique addition to the database on pollutant delivery to receiving waters in urban watersheds. Most importantly, long-term studies provide opportunities to understand the dominant factors and processes that affect ecosystem behavior. The ability to differentiate and identify the dominant drivers of ecosystem change (for example, physical, ecological, and social) would advance our understanding of urban ecosystems.

In mixed land-use watersheds, there is great interest in characterizing the water-quality *signal* from different land-use classes, for example, forest, agriculture, urban/residential (US EPA 1994; Nikolaidis and others 1998; Valiela and others 2000; Jones and others 2001; Wickham and others 2002; Wayland and others 2003). Signals from agricultural and forest land uses tend to be better characterized than from urban uses (Jordan and Weller 1996; Miller and others 1997). There is a great need to quantify pollutant delivery better from urban ecosystems to receiving waters and to understand the factors (for example, altered hydraulics, population density, physical setting, and social factors) that influence this delivery.

In the Baltimore urban LTER (http://beslter.org, verified 20 March 2004), we are using the watershed approach to evaluate integrated ecosystem function. The LTER research is centered on the Gwynns Falls, a 17,150-ha watershed that traverses a land-use gradient from the urban core of Baltimore City, through older (1900–50) urban residential areas, through older (1950-80) suburban zones in the middle reaches, and finally through rapidly suburbanizing areas and a rural/suburban fringe in the headwaters in Baltimore County (Doheny 1999). Our long-term sampling network includes four main channel-sampling sites along the Gwynns Falls stream as well as several smaller (5–1000 ha) watersheds located within or near the Gwynns Falls. The longitudinal, main channel sites provide data on water and nutrient fluxes in the different land-use zones of the watershed (suburban, rapidly suburbanizing, old residential, and urban core) and the smaller, more homogeneous, watersheds provide more focused data on specific land-use types (forest, agriculture, suburban, and urban).

In this article, we present data from the first 3 years of watershed sampling for the Baltimore LTER and nitrogen (N) budgets for small forested, agricultural, and suburban watersheds in our study area. Our objectives were (a) to quantify variation in N yields among the urban and suburban watersheds in the Baltimore area, (b) to evaluate inputs, outputs, and retention of N in suburban, forested, and agricultural watersheds, and (c) to compare these urban and suburban watersheds with the less intensively human-modified ecosystems studied at other LTER sites. More detailed analysis of the hydrology of our watersheds and relationships between land use and N dynamics are presented elsewhere (Law and others 2004b).

# **M**ETHODS

## Site Description

The Gwynns Falls watershed (76°30', 39°15') lies predominantly within the Piedmont physiographic province, and drains 17,150 ha within the Patapsco River drainage basin (Figure 1). It flows through Baltimore County and Baltimore City, Maryland, to the Northwest Branch of the Patapsco River, which



Figure 1. Baltimore urban LTER (Baltimore Ecosystem Study) study area in the mid-Atlantic region of the United States. From Groffman and others (in press).

flows into the Chesapeake Bay. The main channel of the Gwynns Falls extends from the older, more densely populated portions of Baltimore City to the northwest, into progressively less densely populated suburban and rural portions of Baltimore County (Figure 2). Watershed population in the year 2000 was approximately 356,000 people, with subwatershed densities [estimated from 2000 census data (Law and others 2004b) ranging from 2.2 to 19.4 persons/ha. There was a large loss in population over the past two decades in the lower (Baltimore City) portion of the watershed, with a commensurate increase in the middle to upper areas in Baltimore County. The rapid conversion of agricultural, forest, and open land to suburban residential and commercial land use in the middle and upper portions of the watershed increased impervious surface areas, which resulted in substitution of natural hydrologic pathways and processes with engineered drainage and transport systems (Brun and Band 2001).

A small downstream portion of the Gwynns Falls watershed lies within the Atlantic Coastal Plain physiographic province, but our analysis and sampling are restricted to the Piedmont areas to avoid tidal influences. The topography of the watershed



**Figure 2.** Location of Baltimore Ecosystem Study long term sampling sites in and near the Gwynns Falls watershed, which begins in the rural/suburban fringe and ends in the urban core of Baltimore.

varies from "gently sloping" to "hilly" with locally steep slopes and bedrock outcroppings within drainage corridors (Froelich and others 1980). The Piedmont areas are underlain by igneous and metamorphic rocks and are dominated by Legore (fineloamy, mixed, active, mesic Ultic Hapludalfs), Joppa (loamy-skeletal, siliceous, semiactive, mesic Typic Hapludults), and Sassafrass (fine-loamy, siliceous, semiactive, mesic Typic Hapludults) soils.

The natural forest vegetation of the area (currently approximately 20% of the watershed) consists mostly of tulip poplar (*Liriodendron tulipifera*) and oaks, primarily chestnut (*Quercus prinus*), scarlet (*Q. coccinea*) and white (*Q. alba*) in the uplands and red maple (*Acer rubrum*), ash (*Fraxinus pennsyl*vanica), elm (*Ulmus americana*), birch (*Betula nigra*), and sycamore (*Platanus occidentalis*) in the lowlands (Brush and others 1977).

Average annual precipitation is approximately 1060 mm  $y^{-1}$ , and stream discharge is approximately 380 mm  $y^{-1}$  (Froelich and others 1980). The greatest rainfall intensities occur in the summer and early fall during convective events and occa-



**Figure 3.** Monthly runoff at the Gwynns Falls at Villa Nova (mid-point of the watershed) monitoring station from October 1998-December 2002.

sional tropical depressions. Precipitation during this period is about 10% higher than during the remaining three seasons of the year.

Precipitation is exceeded by runoff and evapotranspiration losses from April through September, with a water deficit generally depleting soil and groundwater levels during this time (O'Bryan and McAvoy 1966). Maximum evapotranspiration occurs in July, and groundwater reservoirs are recharged primarily between mid-September and March (Froelich and others 1980). In the Gwynns Falls watershed, the gauge at Villa Nova (midwatershed) has a long-term discharge of 412 mm (Doheny 1999), about 38% of the total precipitation, with the difference largely attributable to evapotranspiration (James 1986). Total monthly runoff (mm  $d^{-1}$ ) at the Villa Nova gauge for the past 3 years (1 October 1998 to 31 December 2002) illustrates the flashy runoff pattern typical of urban watersheds (Figure 3), with peak daily average storm flows of 43, 88, and 137  $\text{m}^3 \text{s}^{-1}$  at recurrence intervals of 2, 5, and 10 years, respectively (Dillow 1996). Seasonal dynamics in annual runoff patterns are still apparent, however, with lower runoff conditions during the summer and winter months and higher runoff during the spring and winter months.

Our long-term sampling network includes four longitudinal sampling sites along the main channel of the Gwynns Falls, two medium-sized (1414, 381 ha) mixed land-use watersheds, and two small (7–32 ha) watersheds with relatively homogeneous land uses (Table 1 and Figure 2). All are located within the Gwynns Falls watershed, except Pond Branch, the completely forested small watershed, and Baisman Run (a suburban watershed), which are both in the adjacent Gunpowder River watershed (less than 20 km from the Gwynns Falls). The longitudinal, main channel sites provide data on water and nutrient fluxes in the different land-use zones along the Gwynns Falls (suburban, rapidly suburbanizing, old residential, and urban core), and the smaller, more homogeneous, watersheds provide more focused data on specific land-use types (forest, agriculture, suburban, and urban).

Land-use information for study watersheds was based on year 2000 land-use/land-cover data provided by Maryland Property View from the Maryland Office of Planning. Land-use classification was based on aerial photography, satellite imagery, and ancillary parcel data. Geographic Information System (GIS) software (ARCView, ESRI, Redlands, CA, USA) and GRASS 5.0 was used to derive watershed boundaries from 5- to 30-m digital elevation models and estimate the percent of the main channel stations, segmented, or reach drainage areas were derived by subtracting the upstream contributing drainage area (and water volume and loads). These reach drainages therefore represent local watershed areas, since the drainage area, flows, and yields of the next upstream sampling station have been removed.

## **Discharge Records**

Stream gauging stations were built and maintained by the US Geological Survey (http://water.usgs. gov/osw/pubs/twri.html verified 20, May 2003) using methods described in the Techniques of Water-Resources Investigations of the US Geological Survey (http://water.usgs.gov/osw/pubs/twri.html, verified 20 May 2003). All small watersheds were outfitted with a weir and stilling well to facilitate accurate stage and discharge measurements. Waterlevel stages were recorded at a 3 mm (or better) resolution, at 5- to 15-min intervals, by using either a float gauge or pressure transducer. Flows were derived using stage-discharge rating curves developed for each site. Low flow ratings were maintained with base-flow discharge measurements conducted at 6-week intervals. High flow discharge measurements were obtained from nearby bridges until an acceptable high flow rating was established or when it was suspected that high flow runoff events might have altered an existing rating.

## Sampling for Stream Chemistry

Sampling locations were usually at or within a few meters of the gauging stations, ensuring that no additional tributary flow or seepage was contributing to the sample. The sampling location at Carroll Park was an exception in that the sampling point had to be located about 50 m away from the gauge, due to safety concerns related to access. The sam-

sted Residential Ag	riculture Impervious
47 0	22
68 6	17
50 8	19
52 5	27
0 0	0
0 100	) 0
34 1	1
43 41	41
	43 41

**Table 1.** Characteristics of Gwynns Falls Main Channel Watershed Reaches and Completely Forested,Agricultural, Suburban and Urban Small and Medium Size Watersheds

pling location in each gauge reach was chosen to ensure adequate mixing of stream flow and an adequate sampling depth. Where taking the sample might cause suspension of benthic sediments, sampling was done at a weir notch. This was necessary at the small watershed sites, where water residence times behind the weirs was short.

During low flow conditions, sampling was done by wading into the stream or by using an extension pole from the shore to obtain a sample just below the surface, in the center of the cross section. During elevated stages, sampling was done just short of the center or, rarely, when access presented serious safety problems, from a nearby bridge with a container at the end of a rope.

Weekly water-chemistry samples were collected and stored in 150-mL Nalgene low-density polyethylene bottles. The day of the week varied, but the date of sampling was decided the previous week or earlier, and no attempt was made to avoid wet weather, so as to retain a random component to the sampling scheme. Both filtered [nitrate  $(NO_3^{-})$ ] and unfiltered (total N) samples were analyzed. Filtering was done in the field by using a syringe and 47-µm Whatman (Whatman, Maidstone, Kent, UK) GF/A glass fiber and 47-µm nylon filters. Blanks and spikes were processed along with samples in our laboratory at the University of Maryland at Baltimore County each week before they were shipped to the Institute of Ecosystem Studies for chemical analysis.

# **Chemical Analyses**

Concentrations of  $NO_3^-$  were measured using a Dionex LC20 series (Dionex, Sunnyvale, CA, USA) ion chromatograph (Tabatabai and Dick 1983). Total N was analyzed by persulfate digestion followed by analysis of  $NO_3^-$  (Ameel and others 1993). Nitrate in these digests was analyzed on a Perstorp Flow Solutions 3000 flow-injection analyzer.

# Yield Calculations

Daily loads of N and NO<sub>3</sub><sup>-</sup> exported from watersheds were estimated based on runoff (mm  $d^{-1}$ ) versus concentration relationships derived from the weekly chemistry data by using the flow-interval method as described in Law and others (2004b). These relationships were generated from weekly NO<sub>3</sub><sup>-</sup>-concentration data and daily runoff values for water years 1999-2001. Daily mass loading (g d<sup>-1</sup>) was then estimated from average concentration values for a given interval of runoff data. Residual analyses of the daily load for estimated and measured weekly values confirmed that a nonbiased estimate of annual loads was achieved. Further, the frequency distribution of runoff conditions for the weekly sample collection was similar to the annual distribution of runoff conditions. Data from water years (October-September) 1999, 2000, and 2001 are presented in this article.

#### N Budgets

Input-output budgets and estimates of N retention for forested reference, agricultural, and suburban watersheds were produced by comparing stream outputs with inputs from atmospheric deposition and fertilizer. Inputs of N associated with lawn fertilizer in the suburban watershed were computed from results from a residential lawn care survey completed in the fall of 2001 (Law and others 2004a). Fertilizer and N fixation inputs for the agricultural watershed were estimated from Maryland Cooperative Extension Service recommended application rates for corn (maize) production (water year 2000) and estimates of N fixation by soybeans (water years 1999 and 2001) (Maryland Department of Agriculture Nutrient Recommendations by Crop, http://www.mda.state.md.us/nutrient/ nmcrprec.htm, 20 verified May 2003). Inputs of N from atmospheric deposition were taken from the US Environmental Protection Agency's Clean Air Status and Trends Network (CASTNET) site at Beltsville, Maryland, approximately 50 km south of the Gwynns Falls watershed. Both wet and dry N deposition are measured at this site. At all CAST-NET sites, atmospheric concentration data to calculate dry deposition are collected with open-faced, three-stage filter packs with a Teflon filter for collection of particulate species, a nylon filter for nitric acid, and a base-impregnated cellulose filter for sulfur dioxide (Baumgardner and others 2002). Fluxes associated with food consumption were not included in these budgets because there are no intentional discharges of sewage from municipal treatment plants or septic systems into monitored streams (except for Baisman Run, which has septic systems). However, unintentional leakage from sewers is an important source of N in certain streams (see the Discussion).

# RESULTS

Total precipitation was 753 mm (71% of average) in water year 1999 (October 1998–September 1999), 1274 mm (120% of average) in water year 2000, and 960 mm (90% of average) in water year 2001. Fall precipitation was most variable (34%, 143%, and 66% of normal in 1999, 2000, and 2001, respectively) and winter precipitation was least variable (87%, 87%, and 75% of normal in 1999, 2000, and 2001, respectively).

As expected,  $NO_3^-$  concentrations (Figure 4) and yields (Table 2) from the completely forested small watershed were very low relative to the urban and suburban watersheds. The mean N yield of all the



Figure 4. Nitrate concentrations in streams draining completely forested (Pond Branch), suburban (Glyndon) and agricultural (McDonogh) watersheds in Baltimore County, MD from October 1998-October 2001.

urban and suburban watersheds (6.7 kg N  $ha^{-1}$ ) was more than 10 times that of the completely forested watershed (0.52 kg N ha<sup>-1</sup>). Fluxes from the forested and agricultural watersheds were very similar to fluxes from similar watersheds reported in the literature (Table 2). The majority of N exported from the urban and suburban watersheds was as NO<sub>3</sub><sup>-</sup> The percentage of N exported as NO<sub>3</sub><sup>-</sup> was lowest in the most urban (Carroll Park) and completely forested watersheds. Ammonium concentrations were measured at one sample date and were less than 0.05 mg N  $L^{-1}$  at all sites except Carroll Park, where they were 0.28 mg N  $L^{-1}$ . Annual variation in yields was surprisingly low given marked variation in the amount and distribution of rainfall during the study.

We computed mean input–output N budgets for the Glyndon watershed, the 81-ha suburban headwater subwatershed of the Gwynns Falls watershed; McDonogh, the 8-ha agricultural small watershed; and Pond Branch, the 32-ha forested referenced watershed for the years 1999–2001 (Table 3). Atmospheric deposition (wet plus dry) ranged from 10.4 to 12.0 kg N ha<sup>-1</sup> y<sup>-1</sup> from 1998 to 2000, with a mean of 11.2 kg N ha<sup>-1</sup> y<sup>-1</sup>. This mean value was applied to all three watersheds. Fertilizer input to lawns in the Glyndon watershed (14.4 kg N ha<sup>-1</sup> y<sup>-1</sup> over the whole watershed area) was calculated from measurements of lawn area and a detailed survey of residential lawn-care practices in the Glyndon watershed (Law and others 2004a). Fertilizer inputs to the agricultural wa-

	Land Use/Context	Nitrate (kg N ha <sup><math>-1</math></sup> y <sup><math>-1</math></sup> )			$\frac{\text{Total N (kg N ha^{-1} y^{-1})}}{2}$		
Station		1999	2000	2001	1999	2000	2001
Longitudinal segments							
Glyndon	Suburban	4.8	5.7	6.1	5.5	6.8	7.3
Gwynnbrook	Suburban	6.6	6.8	6.2	7.9	7.4	6.8
Villa Nova	Suburban/Urban	5.6	5.6	4.4	6.7	6.3	4.9
Carroll Park	Urban	6.3	5.1	3.5	11.4	8.2	6.3
Smaller watersheds							
Pond Branch	Forested	0.12	0.14	0.11	.51	.58	.48
McDonogh	Agriculture	NA	19.8	13.0	NA	NA	NA
Baisman	Suburban	5.2	7.0	4.4	NA	7.2	4.5
Dead Run	Urban	3.1	3.0	2.9	5.9	5.5	5.0
Other watersheds							
Hubbard Brook <sup>1</sup>	Forested	3.6					
Coweeta <sup>2</sup>	Forested	< 0.25					
Maryland <sup>3</sup>	Forested	4.8					
Agriculture <sup>4</sup>	Agriculture	7–30					

**Table 2.** Yields of NO<sub>3</sub><sup>-</sup> and Total N for Gwynns Falls Watershed Segments and Completely Forested, Agriculture, Suburban and Urban Watersheds for Water Years 1999, 2000, and 2001. Literature Values for Similar Forest and Agricultural Watersheds are also Included

<sup>1</sup>Mean export from forested reference watershed from 1963–1974 as reported in Likens and Bormann (1995).

<sup>2</sup>Mean export from forested reference watersheds from 1972–1994 as reported in Swank and Vose (1997).

<sup>3</sup>Export from a greater than 97% forested watershed in the Piedmont of Maryland, 1991 as reported in Jordan and others (1997a).

<sup>4</sup>Export from eight watersheds with percent cropland ranging from 22–60% in the Piedmont of Maryland, 1991 as reported in Jordan and others (1997a).

NA - data not available.

Literature values for similar forest and agricultural watersheds are also included.

**Table 3.** Inputs, Outputs and Retention of N forSuburban (Glyndon), Forested (Pond Branch) andAgricultural (McDonogh) watersheds

	Suburban	Forested	Agriculture			
	$(kg N ha^{-1} y^{-1})$					
Inputs						
Atmosphere <sup>1</sup>	11.2	11.2	11.2			
Fertilizer <sup>2</sup>	14.4	0	60			
Total	25.6	11.2	71.2			
Outputs						
Streamflow <sup>3</sup>	6.5	0.52	16.4			
Retention						
Mass	19.1	10.7	54.8			
Percent	75	95	77			

<sup>1</sup>Mean deposition (wet plus dry) for 1998 and 1999, the latest data available for the CASTNET site at Beltsville.

 $^{2}$ For the suburban watershed, values are based on a home lawn survey (Law and others 2004a). For the agricultural watershed, values are estimated from Maryland Department of Agricultural recommended fertilizer rates for corn (120 kg N  $ha^{-1}y^{-1}$  in water year 2000) and estimated N fixation rates for soybeans (30 kg N  $ha^{-1}y^{-1}$  in water years 1999 and 2001). <sup>3</sup>Mean total N loads from 1999, 2000, and 2001 from Table 2.

tershed were computed from Maryland Cooperative Extension Service recommended application rates for maize production (120 kg N ha<sup>-1</sup> y<sup>-1</sup> in water year 2000) and estimates of N fixation by soybeans (30 kg N ha<sup>-1</sup> y<sup>-1</sup> in water years 1999 and 2001), for a mean annual input of 60 kg N ha<sup>-1</sup>  $y^{-1}$ . Watershed retention of N was estimated as 95% in the forested watershed, 77% in the agricultural watershed, and 75% in the suburban watershed. The retention estimate encompasses N stored in soils and vegetation, gaseous losses, and harvest and export of crops and residential grass clippings and leaves.

# DISCUSSION

As expected, the urban and suburban watersheds had high N fluxes relative to the completely forested watershed and to other forested sites. Yields of N in stream water in the completely forested watershed were similar to yields from forested watersheds at other LTER sites—for example, Hubbard Brook, New Hampshire (Likens and Bormann 1995); Coweeta, North Carolina (Swank and Vose 1997); and H. J. Andrews, Oregon (Henderson and others 1978). Our completely forested watershed  $NO_3^-$  yields were lower than those observed in another forested watershed in the Piedmont of Maryland (4.0 kg N  $ha^{-1} y^{-1}$ ) reported by Jordan and colleagues (1997b).

The  $NO_3^-$  concentrations that we observed in our urban, suburban, and agricultural watersheds were similar to those observed in other urban watersheds (Miller and others 1997; Rhodes and others 2001). Miller and colleagues (1997) compared concentrations in agriculture, forest, cropland, pasture, and urban watersheds in the Potomac River basin (approximately 100 km to the southwest). Our urban and suburban concentrations and yields are lower than those commonly observed in agricultural watersheds in our region (Jordan and others 1997a, 1997b; Miller and others 1997).

Detailed hydrologic analysis of these watersheds showed that runoff patterns were strongly influenced by the presence of impervious surface, as expected. Storm-flow runoff ratios ranged from 0.17 to 0.34 in most of the urban and suburban catchments compared with less than 0.05 in the forested reference catchment (Law and others 2004b). However, the majority of N export occurred during high-frequency, low-flow events rather than during less frequent but large magnitude flows; for example, greater than 50% of total N export from the Baisman Run and Gwynnbrook catchments occurred at flows less than 1 mm d<sup>-1</sup> (Law and others 2004b). The low annual variability and the importance of low flow yields suggest that the urban and suburban watersheds are not totally dominated by storm-water flows conveyed by human infrastructure, but rather that natural hydrologic pathways and processes are important regulators of water and N yield in these ecosystems. Storm flows are particularly important for particulate transport, which does not appear to be important for N export in our watersheds. Exports were dominated (greater than 90%) by  $NO_3^-$  at all of our sites except the completely forested (Pond Branch) and most urban sites (Carroll Park and Dead Run). Ongoing research will determine why this is so, but we suspect that Pond Branch is behaving like many forested watersheds, where inorganic N outputs are often low relative to organic outputs (Perakis and Hedin 2002; Kaushal and Lewis 2003; Vanderbilt and others 2003) and that sewage contamination is the source of organic N at the urban sites.

Our estimate of N retention for the suburban Glyndon watershed (75%) was surprisingly high, approaching values found in forested watersheds (Johnson 1992; Foster and others 1997; Fenn and others 1998). Valigura and coworkers (1996) and Whitall and Paerl (2001) estimated that N retention in urban watersheds ranges from 25% to 95%, with a "best estimate" of 40%. Baker and colleagues

(2001) also suggested that N retention in urban ecosystems could be high. Our retention estimates for our forested and agricultural watersheds are similar to those reported in other studies in our region and elsewhere (Likens and Bormann 1995; Jordan and others 1997b; Fox and others 2001).

Although there is uncertainty and variability associated with our estimates of N retention, the main parameters of the input-output balance are well constrained. Estimates of fertilizer input in our suburban watershed were based on field surveys in the watershed, and our estimates of deposition are likely conservative because our values do not account for "hotspots" of deposition that are common in urban areas (Weathers and others 2001; Lovett and others 2002) and because CASTNET values do not include organic N deposition and dry deposition of ammonia (Whitall and Paerl 2001; Neff and others 2002). CASTNET values are based on weekly sampling, which also leads to underestimation of deposition (Veseley 1990). The dominant output of N (stream flow) varied by less than 25% over 3 years. Even if we have underestimated hydrologic outputs by 50% (for example, by ignoring deep seepage or underestimating storm flow), retention would still be approximately 50%. This does not seem likely, however, because N yields from the Glyndon watershed were similar to those from our other suburban watersheds, suggesting that the budget for this watershed is typical/representative of suburban watersheds in our study area.

The N budget for the suburban watershed does not include inputs in food and outputs in sewage because there are no intentional sewage discharges by municipal treatment plants or septic systems in this watershed. Food input and sewage export of N should roughly balance because nearly all food is imported and sewage is pumped outside the watershed for disposal. Using an assumed human N consumption (and excretion) rate of 12 g of N per capita per day (Bleken and Bakken 1998) and population estimates for our watershed, we estimate the food-in-sewage-out flux to be approximately 35 kg N ha<sup>-1</sup> y<sup>-1</sup>. Small leaks (for example, less than 10%) from the sanitary infrastructure, which are common in urban ecosystems, could easily affect the N yields we have measured. Sewage leaks increase the apparent yield and decrease the apparent retention of N from the watershed. At the same time, infiltration of stream flow into sanitary sewers is a well-documented problem in urban areas and may remove a significant amount of both stream flow and N from our output computations. Although there is likely little variation in the density or age of sewage systems within the Glyndon watershed, there is likely great variation in sewage infrastructure among residential areas of different age and density within the metropolitan area.

Our N budget for the suburban watershed also does not include N input from pet waste, which Baker and coworkers (2001) suggest could be significant. Per capita pet waste production numbers from Baker and colleagues (2001) suggest that approximately 17 kg N ha<sup>-1</sup> y<sup>-1</sup> could be added to the Glyndon watershed in pet waste. Including this flux would increase our estimate of watershed N retention.

It is important to note that watersheds with dominantly residential land use may have significant amounts of pervious surface in the form of lawns, woodlots, and riparian areas, with soils and vegetation capable of processing and storing N. Further, urban storm-water practices that promote infiltration and biological uptake of water are increasingly being used for new developments in municipalities across North America (Brown and Schueler 1997). If we consider the presence of these areas of "natural" soils and vegetation, the N retention rates (mass per area per year) that we measured are not any higher than those measured in forest fertilization experiments (Magill and others 2000). Moreover, surprisingly high retention is frequently observed in highly altered watersheds. For example, Jordan and colleagues (1997b) found greater than 50% retention in ten agricultural watersheds in the Piedmont of Maryland. Baker and colleagues (2001) observed high N retention in the Central Arizona-Phoenix urban ecosystem.

Given that there is great interest in reducing N and P (especially N) loading to Chesapeake Bay, further study of the mechanisms behind the high N retention in these watersheds is clearly needed. Jordan and coworkers (1997a) suggested that Piedmont watersheds in Maryland have an inherently lower capacity for N retention than Coastal Plain watersheds in Maryland, due to the greater capacity for riparian zones to function as "sinks" for N in the coastal plain. Other Baltimore LTER research is addressing the effects of urbanization on riparian zones (Groffman and others 2002), as well as the possible importance of uniquely urban sinks (for example, storm-water retention basins). There are also active efforts to determine whether the N retention that we measured is gaseous loss (some of which can be recycled back to the watershed) versus storage in soils and vegetation. The complexity of urban watersheds is underscored by the fact that there were not straightforward relationships between percent residential land use and/or impervious surface and N yields among our watersheds (Table 2) (Law and others 2004b). Variation in the nature, intensity, and juxtaposition of specific land uses within the residential class must be important regulators of N in these watersheds.

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#### REFERENCES

- Ameel JJ, Axler RP, Owen CJ. 1993. Persulfate digestion for determination of total nitrogen and phosphorus in low nutrient waters. Am Environ Lab 10:1–11.
- Baker LA, Hope D, Xu Y, Edmonds J, Lauver L. 2001. Nitrogen balance for the central Arizona–Phoenix (CAP) ecosystem. Ecosystems 4:582–602.
- Baumgardner RE, Lavery RF, Rogers CM, Isil SS. 2002. Estimates of the atmospheric deposition of sulfur and nitrogen species: clean air status and trends network, 1990–2000. Environ Sci Technol 36:2614–29.
- Bleken MA, Bakken LR. 1998. The nitrogen cost of food production: Norwegian society. Ambio 26:134–42.
- Bowen JL, Valiela I. 2001. The ecological effects of urbanization of coastal watersheds: historical increases in nitrogen loads and eutrophication of Waquoit Bay estuaries. Can J Fish Aquat Sci 58:1489–500.
- Brown W, Schueler T. 1997, National pollutant removal performance database for stormwater BMPs. Silver Spring (MD): Center for Watershed Protection, pp 220.
- Brun SE, Band LE. 2001. Simulating runoff behavior in an urbanizing watershed. Comput Environ Urban Syst 24:5–22.
- Brush G.S., Link C., Smith J. 1977. The natural forests of Maryland: an explanation of the vegetation map of Maryland. Prepared by Department of Geography and Environmental Engineering, Johns Hopkins University, for the Maryland

Power Plant Siting Program, Maryland Department of Natural Resources. Annapolis (MD).

- Dillow J.J.A. 1996. Technique for estimating magnitude and frequency of peak flows in Maryland. Water-resources investigations report 95-4154. Baltimore (MD): US Geological Survey.
- Doheny E. 1999. Index of hydrologic characteristics and data resources for the Gwynns Falls watershed, Baltimore County and Baltimore City, Maryland. Open-file report 99-213. Baltimore (MD): US Geological Survey.
- Fenn ME, Poth MA, Aber JD, Baron JS, Bormann BT, Johnson DW, Lemly AD, McNulty SG, Ryan DE, Stottlemyer R. 1998. Nitrogen excess in North American ecosystems: predisposing factors, ecosystem responses, and management strategies. Ecol Appl 8:706–33.
- Field R, Borst M, O'Connor TP, Stinson MK, Fan C-Y, Perdek JM, Sullivan D. 1998. Urban wet-weather flow management: research directions. J Water Resour Plann Manage 124:168–80.
- Foster DR, Aber JD, Melillo JM, Bowden RD, Bazzaz FA. 1997. Forest response to disturbance and anthropogenic stress. Bioscience 47:437–45.
- Fox RH, Zhu Y, Toth JD, Jemison JM Jr, Jabro JD. 2001. Nitrogen fertilizer rate and crop management effects on nitrate leaching from an agricultural field in central Pennsylvania. Sci World 1:181–6.
- Frey, HT (1984) Expansion of urban areas in the United States: 1960–1980. US Department of Agriculture Economic Research Service staff report AGES83615.
- Froelich, AJ, Hac, JT, Otton, EG (1980) Geologic and hydrologic map reports for land-use planning in the Baltimore–Washington urban area. US Geological Survey circular 806. Reston (VA): US Geological Survey
- Golley FB. 1993, A history of the ecosystem concept in ecology: more than the sum of its parts. New Haven: Yale University Press, pp 254 p.
- Grimm NB, Grove JM, Pickett STA, Redman CL. 2000. Integrated approaches to long-term studies of urban ecological systems. Bioscience 50:571–84.
- Groffman PM, Bain DJ, Band LE, Belt KT, Brush GS, Grove JM, Pouyat RV, Yesilonis IC, Zipperer WC. 2003. Down by the riverside: urban riparian ecology. Front Ecol Environ. 6: 315– 321
- Groffman PM, Boulware NJ, Zipperer WC, Pouyat RV, Band LE, Colosimo MF. 2002. Soil nitrogen cycling processes in urban riparian zones. Environ Sci Technol 36:4547–52.
- Grove JM, Burch WR Jr. 1997. A social ecology approach and applications or urban ecosystem and landscape analyses: a case study of Baltimore, Maryland. Urban Ecosyst 1:259–75.
- Heaney JP. 2001. Long-term experimental watersheds and urban stormwater management. Water Resour IMPACT 3:20–3.
- Heaney, JP, Huber, WC, Lehman, ME (1980) Nationwide assessment of receiving water impacts from urban stormwater pollution: volume 1. Report EPA-6-/2-81-025 (NTIS PB 81-161 812). Cincinnati (Ohio): US Environmental Protection Agency.
- Henderson GS, Swank WT, Waide JB, Grier CC. 1978. Nutrient budgets of Appalachian and Cascade region watersheds: a comparison. For Sci 24:385–97.
- Howarth RW, Billen G, Swaney D, Townsend A, Jaworski N, Lajtha K, Downing JA, Elmgren R, Caraco N, Jordan T, and others. 1996. Regional nitrogen budgets and riverine N&P

fluxes for the drainages to the North Atlantic Ocean: natural and human influences. Biogeochemistry 35:75–139.

- Howarth RW, Sharpley A, Walker D. 2002. Sources of nutrient pollution to coastal waters in the United States: implications for achieving coastal water quality goals. Estuaries 25:656–76.
- James, RW Jr (1986) Maryland and the District of Columbia surface-water resources. In: U.S. Geological Survey, National water summary 1985–Hydrologic events and surface-water resources: US Geological Survey water-supply paper 2300. p 265–70.
- Jensen M. 1998. Ecologists go to town. Sci News 153:219-21.
- Johnson DW. 1992. Nitrogen retention in forest soils. J Environ Qual 21:1–12.
- Jones KB, Neale AC, Nash MS, Van Remortel RD, Wickham JD, Riitters KH, O'Neill RV. 2001. Predicting nutrient and sediment loadings to streams from landscape metrics: a multiple watershed study from the United States Mid-Atlantic region. Landscape Ecol 16:301–12.
- Jordan TE, Correll DL, Weller DE. 1997a. Nonpoint source discharges of nutrients from Piedmont watersheds of Chesapeake Bay. J Am Water Resour Assoc 33:631–45.
- Jordan TE, Correll DL, Weller DE. 1997b. Relating nutrient discharges from watersheds to land use and streamflow variability. Water Resour Res 33:2579–90.
- Jordan TE, Weller DE. 1996. Human contributions to terrestrial nitrogen flux. Bioscience 46:655–64.
- Kaushal SS, Lewis WM Jr. 2003. Patterns in the chemical fractionation of organic nitrogen in Rocky Mountain streams. Ecosystems. 6: 483–492
- Law NL, Band LE, Grove JM. 2004a. Nutrient inputs to urban watersheds from fertilizer usage. J Environ Planning and Management (Forthcoming).
- Law NL, Band LE, Groffman PM, Belt KT. 2004b. Water quality trends and determnants in urban–suburban catchments: Hydrological Processes (Forthcoming).
- Likens GE. 1992, The ecosystem approach: its use and abuse. Oldendorf/Luhe (Germany): Ecology Institute, pp 166, (Excellence in ecology, book 3.).
- Likens GE, Bormann FH. 1995, Biogeochemistry of a forested ecosystem. 2nd ed. New York: Springer-Verlag, pp 159.
- Loucks OL. 1977. Emergence of research on agro-ecosystems. Annu Rev Ecol Syst 8:173–92.
- Lovett GM, Traynor MM, Pouyat RV, Carreiro MM, Zhu WX, Baxter JW. 2002. Atmospheric deposition to oak forests along an urban–rural gradient. Environ Sci Technol 34:4294–300.
- Magill AH, Aber JD, Berntson GM, McDowell WH, Nadelhoffer KJ, Melillo JM, Steudler P. 2000. Long-term nitrogen additions and nitrogen saturation in two temperate forests. Ecosystems 3:238–53.
- Makepeace DK, Smith DW, Stanley SJ. 1995. Urban stormwater quality: summary of contaminant data. Crit Rev Environ Sci Technol 25:95–139.
- McDonnell MJ, Pickett STA. 1990. The study of ecosystem structure and function along urban–rural gradients: an unexploited opportunity for ecology. Ecology 71:1231–7.
- Miller CV, Denis JM, Ator SW, Brakebill JW. 1997. Nutrients in streams during baseflow in selected environmental settings of the Potomac River basin. J Am Water Resour Assoc 33:1155–71.
- Neff JC, Holland EA, Dentener FJ, McDowell WH, Russell KM.

2002. Atmospheric organic nitrogen; implications for the global N cycle. Biogeochemistry 57/ 58:99–136.

- Nikolaidis NP, Heng H, Semagin R, Clausen JC. 1998. Non-linear response of a mixed land use watershed to nitrogen loading. Agric Ecosyst Environ 67:251–65.
- O'Bryan, D, McAvoy, RL 1966. Gunpowder Falls Maryland, uses of a water resource, today and tomorrow. Geological Survey water-supply paper 1815. Washington (DC): US Government Printing Office
- Paul MJ, Meyer JL. 2001. Streams in the urban landscape. Annu Rev Ecol Syst 32:333–65.
- Perakis SS, Hedin LO. 2002. Nitrogen losses from unpolluted South American forests mainly via dissolved organic compounds. Nature 415:416–9.
- Pickett STA, Burch WR Jr, Dalton SE, Foresman TW, Grove JM, Rowntree R. 1997. A conceptual framework for the study of human ecosystems in urban areas. Urban Ecosyst 1:185–99.
- Pickett STA, Cadenasso ML, Grove JM, Nilon CH, Pouyat RV, Zipperer WC, Costanza R. 2001. Urban ecological systems: linking terrestrial ecological, physical, and socioeconomic components of metropolitan areas. Annu Rev Ecol Syst 32: 127–57.
- Rhodes AL, Newton RM, Pufall A. 2001. Influences of land use on water quality of a diverse New England watershed. Environ Sci Technol 35:3640–5.
- Robertson GP, Paul EA. 1998. Ecological research in agricultural ecosystems: contributions to ecosystem science and to the management of agronomic resources. In: Pace ML, Groffman PM, Eds. Successes, limitations and frontiers in ecosystem science. New York: Springer-Verlag. p 165–94.
- Rose S, Peters NE. 2001. Effects of urbanization on streamflow in the Atlanta area (Georgia, USA): a comparative hydrological approach. Hydrol Process 15:1441–57.
- Smith VH. 1998. Cultural eutrophication of inland, estuarine and coastal waters. In: Pace ML, Groffman PM, Eds. Successes, limitations and frontiers in ecosystem science. New York: Springer-Verlag. p 7–50.
- Sukopp H. 1990. Urban ecology and its application in Europe. In: Sukopp H, Hejny S, Kowarik I, Eds. Urban ecology: plants and plant communities in urban environments. The Hague (The Netherlands): SPB Academic. p 1–22.

Swank WT, Vose JM. 1997. Long-term nitrogen dynamics of

Coweeta forested watersheds in the southeastern United States of America. Global Biogeochem Cycles 11:657–71.

- Tabatabai MA, Dick WA. 1983. Simultaneous determination of nitrate, chloride, sulfate and phosphate in natural waters by ion chromatography. J Environ Qual 12:209–13.
- [US EPA] US Environmental Protection Agency. 1994. National water quality inventory: 1992 report to Congress. Report EPA 841-F-94-002 (NTIS PB 94-181377). Washington (DC): US EPA.
- Valiela I, Tomasky G, Hauxwell J, Cole ML, Cebriàn J, Kroeger KD. 2000. Operationalizing sustainability: management and risk assessment of land-derived nitrogen loads to estuaries. Ecol Appl 10:1006–23.
- Valigura RA, Luke WT, Artz RS, Hicks BB. 1996, Atmospheric nutrient input to coastal areas: reducing the uncertainties. Silver Spring (MD): NOAA Coastal Ocean Program. (Decision analysis series 9.).
- Vanderbilt KL, Lajtha K, Swanson F. 2003. Biogeochemistry of unpolluted forested watersheds in the Oregon Cascades: temporal patterns of precipitation and stream nitrogen fluxes. Biogeochemistry 87:67–117.
- Veseley J. 1990. Stability of pH and the contents of ammonium and nitrate in precipitation samples. Atmos Environ 24A: 3085–9.
- Wayland KG, Long DT, Hyndman DW, Pijanowski BC, Woodhams SM, Haack SK. 2003. Identifying relationships between baseflow geochemistry and land use with synoptic sampling and R-mode factor analysis. J Environ Qual 32:180– 90.
- Weathers KC, Cadenasso ML, Pickett STA. 2001. Forest edges as nutrient and pollutant concentrators: potential synergisms between fragmentation, forest canopies, and the atmosphere. Conserv Biol 15:1506–14.
- Whitall DR, Paerl HW. 2001. Spatiotemporal variability of wet atmospheric nitrogen deposition to the Neuse River Estuary, North Carolina. J Environ Qual 30:1508–15.
- Wickham JD, O'Neill RV, Riitters KH, Smith ER, Wade TG, Jones KB. 2002. Geographic targeting of increases in nutrient export due to future urbanization. Ecol Appl 12:93–106.
- World Resources Institute. 1996, World resources: a guide to the global environment—the urban environment. New York: Oxford University Press, pp 400.