

Interaction between Urbanization and Climate Variability Amplifies Watershed Nitrate Export in Maryland

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We investigated regional effects of urbanization and land use change on nitrate concentrations in approximately 1,000 small streams in Maryland during record drought and wet years in 2001–2003. We also investigated changes in nitrate-N export during the same time period in 8 intensively monitored small watersheds across an urbanization gradient in Baltimore, Maryland. Nitrate-N concentrations in Maryland were greatest in agricultural streams, urban streams, and forest streams respectively. During the period of record drought and wet years, nitrate-N exports in Baltimore showed substantial variation in 6 suburban/urban streams (2.9–15.3 kg/ha/y), 1 agricultural stream (3.4–38.9 kg/ha/y), and 1 forest stream (0.03–0.2 kg/ha/y). Interannual variability was similar for small Baltimore streams and nearby well-monitored tributaries and coincided with

record hypoxia in Chesapeake Bay. Discharge-weighted mean annual nitrate concentrations showed a variable tendency to decrease/increase with changes in annual runoff, although total N export generally increased with annual runoff. N retention in small Baltimore watersheds during the 2002 drought was 85%, 99%, and 94% for suburban, forest, and agricultural watersheds, respectively, and declined to 35%, 91%, and 41% during the wet year of 2003. Our results suggest that urban land use change can increase the vulnerability of ecosystem nitrogen retention functions to climatic variability. Further work is necessary to characterize patterns of nitrate-N export and retention in small urbanizing watersheds under varying climatic conditions to improve future forecasting and watershed scale restoration efforts aimed at improving nitrate-N retention.

Introduction

Approximately 50% of the world's human population currently lives within 100 km of a coastline, and this percentage is projected to increase in the future (1). Human land use in coastal watersheds has been linked to increasing nitrogen loads and coastal eutrophication (2–4). The watershed of the Chesapeake Bay, the largest estuary in the United States, has experienced large inputs of nitrogen from agriculture and increasing urbanization (3). Coincident with land use change, this region and nearby watersheds have also recently experienced increased frequency of extreme droughts and wet years (e.g., 5–8). Here we investigate how urbanization influences regional patterns in nitrate concentrations in small streams in Maryland, and analyze how interactions between urbanization and climate variability can decrease retention and amplify nitrate export from small suburban and urban watersheds.

In 2002, the Chesapeake Bay watershed, along with 48% of the contiguous United States, experienced severe drought conditions (9) with some of the lowest rainfall amounts recorded over a 100-year period (10, 11). Severe drought was followed by near record high flows to Chesapeake Bay in 2003 (5–7). Extreme changes in precipitation during 2002 and 2003 coincided with some of the most severe water quality problems reported in Chesapeake Bay including hypoxia, changes in species composition, formation of harmful algal blooms, mortality in fish, oysters, aquatic grasses, and health risks to humans (5–7).

A growing body of research suggests that ecological risks associated with climate variability are expected to increase in the future (12, 13). During "dry" years, nitrogen is stored, and during "wet" years, N is flushed from watersheds contributing to eutrophication and hypoxia (e.g., 4, 14–16). Recent work in exurban, suburban, and urban watersheds (e.g., 15, 17–19) has raised concerns that hydrologic alterations associated with urbanization can amplify climate-driven export of nitrate-N from small watersheds. These alterations include "burial" of headwaters (20) and increases in impervious surfaces that alter hydrologic "connectivity" between urban streams and riparian areas, which is important in nitrate-N retention and removal (21). There has been a 60% increase in urbanization in the Chesapeake Bay watershed between 1990 and 2000 due to conversion of both agricultural and forest lands into residential areas (22). Understanding the effects of this increase on nitrogen export is critical for forecasting changes in water quality in response to climate and for guiding restoration and stormwater management practices in small watersheds (21, 23).

We investigated the relationship between land use change and nitrate concentrations in approximately 1,000 randomly

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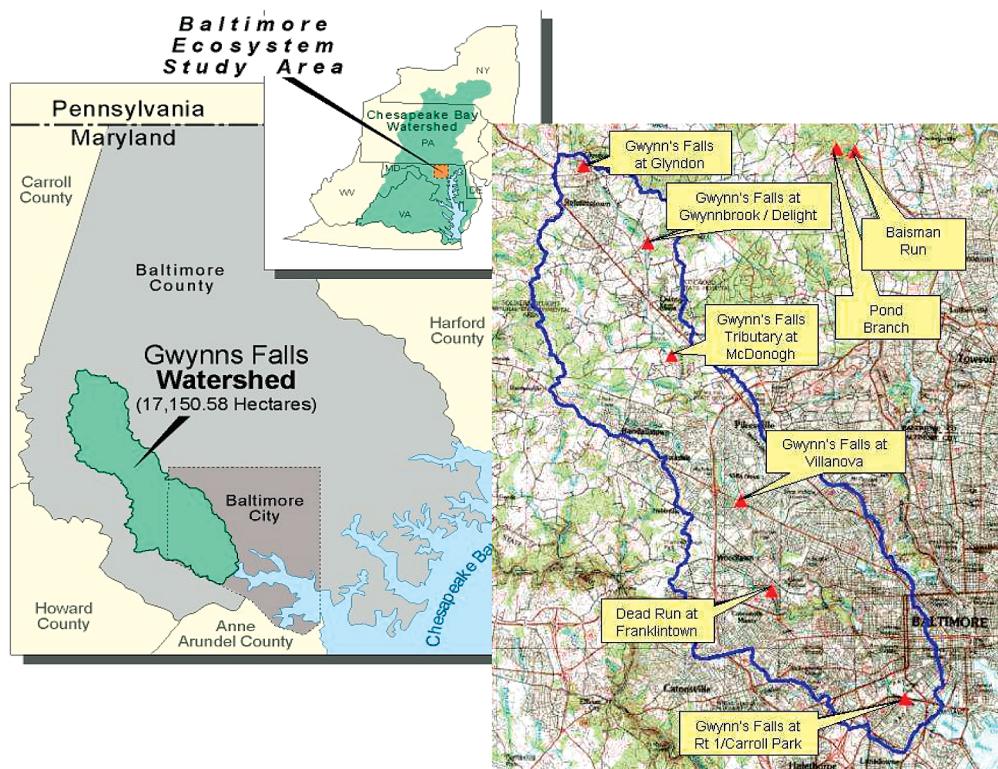
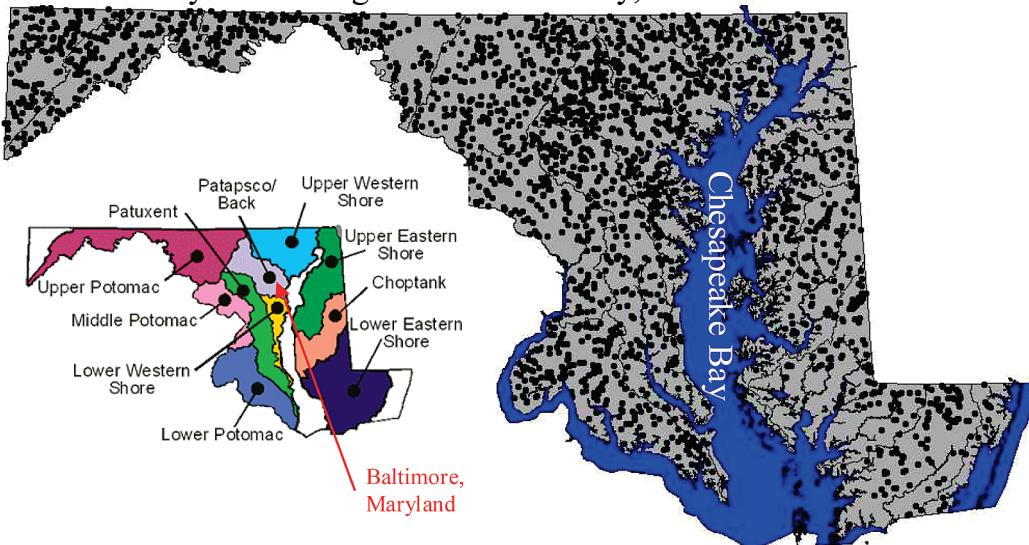


FIGURE 1. Map showing locations of Maryland Biological Stream Survey (MBSS) and Baltimore LTER study sites, including small watersheds (Glyndon (suburban), McDonogh (agricultural), Pond Branch (forested), Baisman Run (suburban), and Dead Run (urban), and the longitudinal sites along the Gwynns Falls (Glyndon, Delight/Gwynnbrook, Villa Nova, and Carroll Park).

selected small headwater streams in Maryland during 2001–2003 to evaluate regional effects of urbanization on stream nitrate-N concentrations. We also compared effects of record drought and wet years during the same time period on patterns of nitrate concentrations and export in 8 long-term monitoring sites in Baltimore, Maryland representing a rural to urban gradient. Our objectives were to: (1) identify regional effects of urban land use change on nitrate-N concentrations in small streams during 2001–2003, and (2) document temporal changes and variability in nitrogen retention and nitrate-N export in small watersheds during historic record drought and wet years.

Site Description and Methods

Precipitation Variability and Hydroclimatic Conditions. During 2002, approximately 48% of the contiguous United States was placed in the moderate and severe drought categories (National Climate Data Center Annual Review, <http://www.ncdc.noaa.gov/oa/climate/research/2002/ann/paleo-drought.html>) with the mid-Atlantic U.S. experiencing historic record drought levels (Figure 1 in the Supporting Information). In the year from October 2001 through September 2002, Baltimore-Washington International Airport recorded 60.6 cm of precipitation, less than 57% of the 100-year record average, and a deficit of more than 46 cm (10, 11).

TABLE 1. Annual Exports of Nitrate-N and Total N and Runoff from the Baltimore LTER Watersheds during 2000–2004

site	nitrate-N export (kg/h/y)					total N export (kg/ha/y)					annual runoff (mm/y)				
	2000	2001	2002	2003	2004	2000	2001	2002	2003	2004	2000	2001	2002	2003	2004
POBR (Forest)	0.1	0.1	0.03	0.1	0.2	0.9	0.4	0.1	0.8	2.0	333	233	100	396	542
BARN(Forest/Suburb)	6.3	4.0	1.4	7.5	8.9	6.5	3.9	1.8	7.8	8.3	433	242	106	503	569
MCDN (Ag)	20.1	12.8	3.4	27.7	38.9	17.8	12.6	4.1	41.0	38.9	485	319	93	734	732
GFGB(Suburb)	6.6	6.6	2.9	11.3	15.3	6.8	7.1	3.8	15.9	14.8	371	337	185	635	620
GFVN(Suburb)	5.7	4.6	2.0	8.2	10.6	6.5	5.3	2.2	11.6	11.3	452	360	214	731	619
GFGL(Suburb)	5.7	4.7	2.3	12.5	8.4	6.3	5.5	3.2	15.3	9.1	325	275	145	843	465
DRKR(Urban)	3.1	3.3	1.8	8.0	7.7	5.6	5.1	3.4	16.7	9.3	472	413	305	912	710
GFCP(Urban)	4.7	3.0	2.4	9.7	13.5	6.7	6.5	5.6	14.5	17.1	447	342	259	760	652

During this time, the City of Baltimore experienced its driest February since record-keeping began in 1871 and its fourth-driest winter (10, 11). In July, August, and September 2002, freshwater flow into Chesapeake Bay averaged 45%, 64%, and 61% below respective long-term (1937–2001) averages for these months (5). In 2002, total annual freshwater flow input from tributaries was estimated at 24% below the long-term average from 1937–2001 (U.S. Geological Survey Water Resources Division MD-DE-DC, 2002, http://md.water.usgs.gov/publications/press_release/current/#archive).

Greater precipitation than normal in October, November, and December of 2002 contributed to the end of the state drought emergency in Maryland (10, 11). In 2003, almost all monthly rainfall amounts were greater than the 100-year average (10, 11). Freshwater flow into the Chesapeake Bay was 83% above the long-term average (1937–2001) in July and 125% above the long-term average in August 2003 (9). In September 2003, Hurricane Isabel provided large amounts of rainfall to the Chesapeake Bay region (5–7), and freshwater flow into Chesapeake Bay was 400% above the long-term monthly average ((5), U.S. Geological Survey Water Resources Division MD-DE-DC, 2002, http://md.water.usgs.gov/publications/press_release/current/#archive). The combination of the historic record drought conditions followed by the very wet year coincided with one of the most severe zones of eutrophication and hypoxia reported in Chesapeake Bay in 2003 (5–7).

Urban Land Use and Nitrate Dynamics in Small Streams.

The relationship between urban land use change and nitrate-N concentrations in small Maryland streams was investigated by analysis of patterns in “raw” nitrate-N concentrations (not flow-adjusted) in approximately 1,000 streams sampled through the Maryland Biological Stream Survey (MBSS) and approximately 50 streams outside Washington, DC (www.palmerlab.umd.edu) (10, 11) (Figure 1). The MBSS sampled small streams (fourth order or less in size) across the state once during spring using standard U.S. EPA protocols, and detailed information on the sites and maps of sampling locations can be found online (<http://www.dnr.state.md.us/streams/mbss/index.html>) and in the Supporting Information. Nitrate-N concentrations (not discharge-weighted) were also measured in 4 watersheds (29–68 km²) on the northern outskirts (Montgomery County) of the Washington, DC metropolitan area in the Piedmont region of Maryland as part of a long-term study of the effect of urban land use change on streams. Multiple seasonal water samples, encompassing a range in discharge, were collected from each of 29 headwater streams and 24 second or third order streams during the drought of 2002.

The interactive effects of urban land use change and climatic variability on nitrate-N export in suburban/urban streams was explored in 8 long-term monitoring sites in and around the City of Baltimore, MD during drought and very wet years in 2000–2004. Sites were located across an urban to rural gradient primarily in the Gwynns Falls watershed in the Piedmont physiographic province and included forest,

agricultural, suburban, and urban watersheds that are sampled weekly (no bias toward storm versus baseflow) at sites with continuous streamflow monitoring as part of the Baltimore Long-term Ecological Research (LTER) project. Sites, methods, and sampling have been described previously (18) (Figure 1, Supporting Information Table 1, www.beslter.org).

Nitrate-N and total N exports for the Baltimore LTER watersheds were estimated using both a flow bin-averaging approach that accounts for relationships between nitrate and total N concentrations and discharge (18, 24, 25) and the Fluxmaster program developed by the USGS (26). Discharge-weighted mean concentrations were also calculated. The routine weekly sampling at these sites could have missed storm events, and we acknowledge that some bias may result if the discharge-concentration relations show a discontinuity above certain flow thresholds. Annual export estimates calculated using the bin averaging approach were highly consistent with estimates calculated using the USGS Fluxmaster program and produced nearly identical results with no censored observations (25). A regression of bin-averaged vs Fluxmaster mean annual load estimates showed slopes very close to 1 and *r*² values of 0.97 (25). Annual exports and standard errors computed using Fluxmaster can be found in the Supporting Information. Nitrate-N exports from the Baltimore LTER streams were also compared to recently published data from other small watersheds (27) and from monitoring stations on larger tributaries of the Chesapeake Bay in Maryland (28) during the same time period.

Input-output N budgets were computed for three of the Baltimore LTER watersheds (Glyndon (GFGL) the 81-ha suburban headwater subwatershed of the Gwynns Falls watershed; McDonogh (MCDN), the 8-ha agricultural small watershed; and Pond Branch (POBR), the 32-ha forested reference watershed) for the years 2002–2004 and compared to previously published values from 1999–2001 (18). Inputs of N from atmospheric deposition were taken from the U.S. Environmental Protection Agency’s Clean Air Status and Trends Network (CASTNET) site at Beltsville, MD, approximately 50 km south of the Gwynns Falls watershed. Both wet and dry N deposition are measured at this site and showed very little variation from 2002 to 2004, ranging from 7.0 to 9.0 kg N ha/y (18). Fertilizer input to lawns in the Glyndon watershed (14.4 kg N/ha/y 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 conducted in 2002 (29). Fertilizer inputs to the agricultural watershed were from Maryland Cooperative Extension Service recommended application rates for maize production (120 kg N/ha/y) and estimates of N fixation by soybeans (30 kg N ha/y) for a mean annual input of 60 kg N ha/y (18).

Results

Urban streams in Maryland generally had lower raw nitrate-N concentrations than streams draining agricultural water-

Maryland Biological Stream Survey, U.S.A.

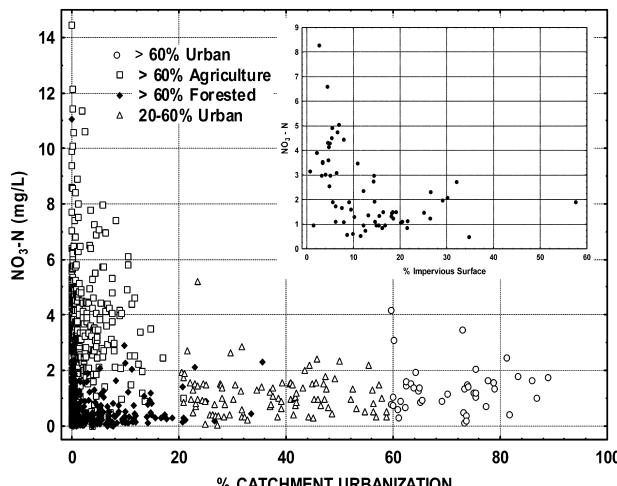


FIGURE 2. Nitrate-N concentrations at Maryland Biological Stream Survey sites and across a land use gradient in Montgomery County, Maryland near Washington, DC during 2001–2003 (inset). Concentrations represent raw concentrations for individual sampling events and are not discharge-weighted mean annual averages.

sheds, but higher raw nitrate-N concentrations than streams draining forest watersheds (Figure 2.) Urban lands comprised approximately 20% and agricultural lands comprised approximately 36% of the land area draining into small streams within Maryland's Chesapeake Bay tributary basins during the study period (Supporting Information Table 2). The Patapsco/Back River watershed, which contains the Gwynns Falls watershed and Baltimore LTER sites, contained one of the highest percentages of urban land use in Maryland, but showed intermediate raw nitrate-N concentrations relative to other streams in Maryland (Supporting Information Table 2).

In Baltimore LTER watersheds, there was considerable interannual variability in discharge during the drought and wet years, with prolonged low flows during the drought followed by peaks in discharge during 2003, including Hurricane Isabel in September (Supporting Information Figure 2). We observed a clockwise hysteresis in discharge-weighted mean annual nitrate-N concentrations (Figure 3, Supporting Information Table 3). Discharge-weighted mean annual nitrate-N concentrations declined during the severe drought in 2002, increased during the wet year of 2003, and continued to increase in 2004 as runoff declined in some watersheds; discharge-weighted mean annual nitrate-N concentrations therefore showed a variable tendency to decrease/increase with changes in annual runoff (Figure 3).

Annual nitrate-N export from the Baltimore LTER watersheds showed significant interannual variability between 2000–2004, with declines during severe drought (2002) and increases during extreme wet years (2003, 2004) (Figure 4, Table 1). Nitrate-N exports were considerably higher in suburban, urban, and agricultural watersheds (1.4–38.9 kg N/ha/y) than in the forested reference watershed (0.03–0.2 kg N/ha/y).

Watershed retention of N also varied substantially from 2002 to 2004, with much higher retention during drought years than wet years (Table 2). Retention ranged from 99% to 76% in the forested watershed, 94% to 41% in the agricultural watershed, and 85% to 35% 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. Sources of uncertainty in these estimates have been described

Small Watersheds

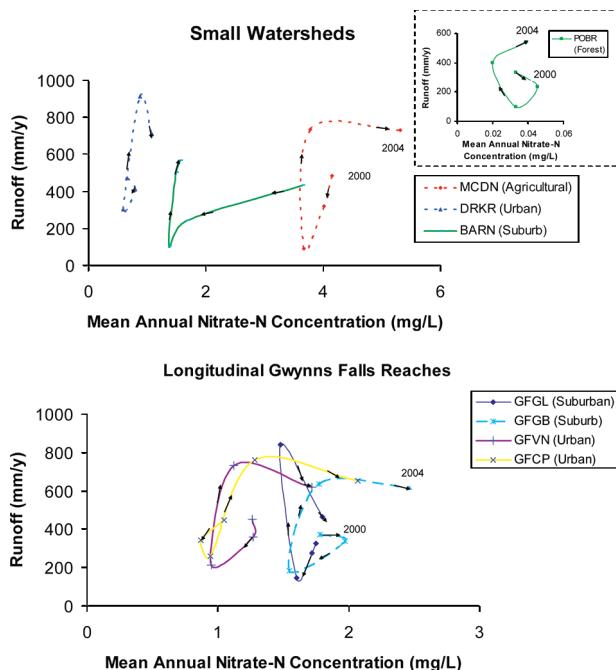


FIGURE 3. Discharge-weighted annual mean nitrate-N concentrations during periods of increasing and decreasing runoff in small Baltimore LTER watersheds (McDonogh (MCDN, agricultural), Pond Branch (POBR, forested), Baisman Run (BARN, suburban) and Dead Run (DRKR, urban)) and longitudinal reaches of the Gwynns Falls (Glyndon (GFGL), Delight/Gwynnbrook (GFGB), Villa Nova (GFVN), and Carroll Park (GFCP)) during 1998–2004.

previously (18), are presented further below, and also in the Supporting Information.

Discussion

As expected, the Maryland statewide survey showed that raw nitrate-N concentrations in streams draining urban and agricultural watersheds were higher than those in streams draining predominantly forested watersheds, and that urban streams had consistently lower nitrate-N concentrations than agricultural streams (e.g., refs 15, 17, 18).

Also as expected, raw concentrations of nitrate-N from the Maryland Biological Stream Survey were also considerably above estimated historical background concentrations of total nitrogen for this region (30), lower than concentrations in some other regional studies (28, 31), but higher than historical measurements from 100 years ago in the Susquehanna River (3). Dramatic increases in modern stream nitrogen concentrations compared to preindustrial conditions are globally observed and have been extensively documented in the literature (32).

We observed a clockwise hysteresis in discharge-weighted mean annual concentrations of nitrate-N in the Baltimore LTER watersheds. This pattern may have been driven by flushing of nitrate-N stored in soils and groundwater during dry years (33), decreased retention, or increases in nitrification due to “drying and re-wetting” events in soils, sediments, riparian zones, and stream banks (34). These results suggest a need for further study of nitrate-N sources and retention within suburban and urban watersheds, riparian zones, and streams in response to “drying and re-wetting” and climatic variability (34). Although discharge-weighted mean annual concentrations of nitrate-N varied interannually from 2000 to 2004, it is important to note that annual export of total N from watersheds strongly increased with annual runoff. Nitrate-N represents a mobile and biologically reactive fraction of the total N pool that may originate from different

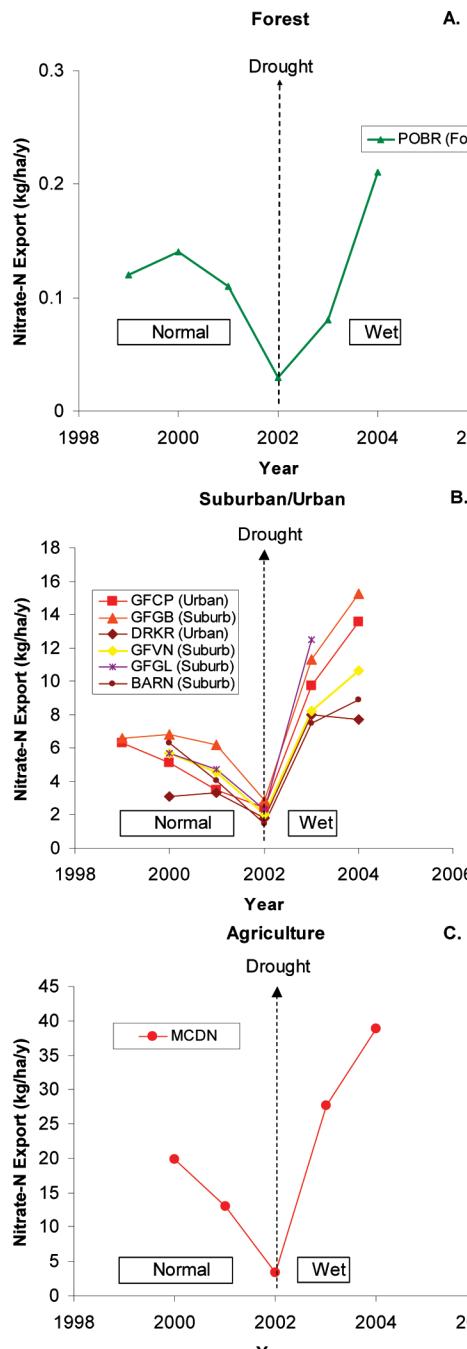


FIGURE 4. Annual nitrate-N exports from 8 Baltimore LTER watersheds during 2001–2004. Site abbreviations same as in Figure 3.

sources and undergo differential biotic and transport dynamics than dissolved and particulate organic N. The relative abundance of organic N may influence differences in the transport dynamics between the total nitrogen pool and nitrate in some small suburban/urban watersheds (18).

Nitrate-N exports from all Baltimore LTER watersheds responded strongly to climatic variability. As expected, nitrate-N exports and runoff were greater in the agricultural, suburban, and urban watersheds than in the forested reference watershed. Highest exports across years were in the agricultural watershed. There may have been differences in export in some urban watersheds because of differences in watershed size and differences in the contribution of nonpoint sources. Exports from the forested catchment were similar to those from other forested catchments in the eastern

U.S. (35, 36), and lower than those from other forested watersheds in the Piedmont of Maryland (4.0 kg N/ha/y) (37). Nitrate-N exports from Baltimore LTER agricultural, suburban, and urban watersheds during the wet years were similar to those reported for agricultural watersheds in the Piedmont of Maryland (7.0–30.0 kg N/ha/y) (37) and higher than values from an urban watershed in Massachusetts (3.3–5.0 kg N/ha/y) during the same time period (19). The percentage increase in nitrate-N export from dry to wet conditions appeared to be no greater in the suburban/urban and agricultural watersheds than in the forested watersheds. The lack of change in percentage nitrate-N export was surprising given the extensive hydrologic modification of suburban and urban watersheds, but may be due to the large effect of climatic conditions during the study period.

Interannual variability in nitrate-N export from the Baltimore LTER watersheds in response to climatic variability was high compared to reported observations of variability in small watersheds. Interannual variability in our study was greater than that reported following ice storm damage (38) and within the same range as experimental clear cutting at the Hubbard Brook Experimental Forest in New Hampshire (35), insect defoliation in small watersheds in the Appalachian Mountains (39), and greater than timber harvest in the Appalachian Mountains during the same period of climatic variability from 2000 to 2004 (27). The variation that we observed was greater than that observed in agricultural watersheds in Illinois that experienced similar drought conditions over the same time period as our study (8).

Some additional context for considering the interaction of climatic variability and nitrate-N export from the small Baltimore watersheds during the 2000–2004 period is provided by data from the larger nearby watersheds of the Potomac and Patuxent Rivers that are part of the Chesapeake Bay Input Monitoring Program (e.g., ref (28)). Similar to our study sites, these large watersheds showed marked increases in nitrate export (300% in the Patuxent, 600% in the Potomac) following the 2002 drought (Supporting Information Figure 3). High exports in response to high flow years were also observed in 1984 and 1996 in these rivers and during 1987–1990 in the Patuxent River. Long-term monitoring of the larger tributaries of the Chesapeake Bay has shown an increase in streamflow variability since the 1930s, with the highest flow variability occurring within recent decades (28). In particular, the high exports observed in 2003 and 2004 were coincident with severe eutrophication and water quality problems in Chesapeake Bay (5–7).

We observed considerable interannual variability in nitrogen retention during the severe drought and extreme wet years. High retention is commonly observed during dry years as the residence time of reactive nitrogen in the watershed is longer, facilitating retention by plant, soil, and microbial processes (4). In-stream processing of nitrogen is also facilitated by low flows and longer residence times (40). While retention is expected to decline in all watersheds during wet years, we observed marked declines in retention in the suburban watershed (from 85% to 35% from 2002 to 2003) and the agricultural watershed (from 94% to 41%). Several studies have shown that N retention in suburban and urban watersheds can be considerable, i.e. > 65% (18, 19, 41, 42). Our results here, however, suggest that suburban watersheds may also be prone to high nitrogen export during high flow conditions. This vulnerability can result from extensive hydrologic manipulation of suburban watersheds (20) that facilitates rapid export of nitrogen that accumulates during dry periods when high flow conditions return. There may also be a limited ability for interaction with biological “hot spots” of denitrification in urban streams during pulses of runoff from impervious surfaces during storms (18, 20, 21). This may be particularly important in the suburban/urban

TABLE 2. Inputs, Outputs, and Retention of Total Nitrogen for Suburban (GFGL), Forested (POBR), and Agricultural (MCDN) Baltimore LTER Watersheds

	suburban (kg N/ha/y)				forest (kg N/ha/y)				agriculture (kg/N/ha/y)			
	1999–2001 ^a	2002	2003	2004	1999–2001 ^a	2002	2003	2004	1999–2001 ^a	2002	2003	2004
inputs												
atmosphere	11.2	7.0	9.0	8.2	11.2	7.0	9.0	8.2	11.2	7.0	9.0	8.2
fertilizer	14.4	14.4	14.4	14.4	0.0	0.0	0.0	0.0	60.0	60.0	60.0	60.0
total	25.6	21.4	23.4	22.6	11.2	7.0	9.0	8.2	71.2	67.0	69.0	68.2
outputs												
streamflow	6.5	3.2	15.3	9.1	0.52	0.1	0.8	2.0	16.4	4.1	41.0	38.9
retention												
mass	19.1	18.2	8.1	13.5	10.7	6.9	8.2	6.2	54.8	62.9	28.0	29.3
percent	75	85	35	60	95	99	91	76	77	94	41	43

^a Values for 1999–2001 are from ref (18).

Baltimore LTER watersheds, where most of the nitrate-N export occurs during high flow (25).

Sources of error in the mass balance approach have been discussed previously (18) and are further discussed in the Supporting Information. Our focus here was on variation in the output of N in streamflow due to extremes in climatic conditions and its effects on estimates of N retention. Our assessment of these effects may be conservative as we may have underestimated hydrologic outputs of nitrate-N associated with storm events. Differences in watershed size between the forested and agricultural watersheds (small) and the suburban watershed (larger) may also have reduced the size of the land use effects that we observed, as storm events are most marked in smaller watersheds. On the input side, we assumed that our estimates of fertilizer inputs to lawns and crop fields from previous studies (18, 29) have not changed, and we did not assess the effects of climate variability on sewage leaks and septic discharges (which are idiosyncratic, but important sources of N in the Baltimore LTER watersheds) (18). There was also relatively high variability in the residential lawn inputs (29). Although there is uncertainty, the mass balance approach is useful for assessing how climatic variability and land use can influence N retention in small watersheds during extremes in hydrologic conditions, which is of critical interest in the Chesapeake Bay region.

Our results suggest that urban land use change may increase the vulnerability of ecosystem nitrogen retention functions to climatic variability through high export during high flow conditions. Interactions between climate and future land use change should be incorporated into efforts to forecast future nitrogen delivery from small urbanizing catchments. Efforts to reduce nitrogen delivery to Chesapeake Bay through source reductions, reducing effective impervious surface coverage, and “low” impact development design strategies to reduce runoff and increase hydrologic residence time within small watersheds should also simultaneously consider mechanisms that foster nitrogen retention and removal. Some of these strategies can involve introducing N sinks in the landscape by innovative stormwater management practices (23) and by increasing hydrologic “reconnections” between streams, floodplain wetlands, and retention ponds that facilitate denitrification (21, 43). Incorporating an improved understanding of the relationship between structure and basic ecosystem functions of small urbanizing watersheds into these strategies will be critical for achieving ecosystem restoration goals under changing environmental conditions.

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Note Added after ASAP Publication

One author was removed from the paper by request in the version published ASAP July 9, 2008; the corrected version published ASAP July 12, 2008.

Supporting Information Available

Maps of drought, stream hydrographs during drought and wet years, and long-term patterns in nitrate-N loads in major tributaries of the Chesapeake Bay; tables of site descriptions, arithmetic raw mean concentrations (not discharge-weighted) of 1,000 Maryland Biological Stream Survey sites draining into tributaries of the Chesapeake Bay, and discharge-weighted mean annual concentrations and annual runoff for Baltimore LTER streams; text describing sampling methods, mass balance estimates and uncertainties, and error estimates in N export. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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