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# Tracking Nonpoint Source Nitrogen Pollution in Human-Impacted Watersheds

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#### S Supporting Information

**ABSTRACT:** Nonpoint source nitrogen (N) pollution is a leading contributor to U.S. water quality impairments. We combined watershed N mass balances and stable isotopes to investigate fate and transport of nonpoint N in forest, agricultural, and urbanized watersheds at the Baltimore Long-Term Ecological Research site. Annual N retention was 55%, 68%, and 82% for agricultural, suburban, and forest watersheds, respectively. Analysis of  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup>, and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> indicated wastewater was an important nitrate source in urbanized streams during baseflow. Negative correlations between  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> in urban watersheds indicated mixing between atmospheric deposition and wastewater, and N source contributions changed with storm magnitude (atmospheric sources contributed ~50% at peak storm N loads). Positive correlations between  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> in watersheds suggested denitrification was removing septic system and agriculturally derived N, but N from belowground leaking



sewers was less susceptible to denitrification. N transformations were also observed in a storm drain (no natural drainage network) potentially due to organic carbon inputs. Overall, nonpoint sources such as atmospheric deposition, wastewater, and fertilizer showed different susceptibility to watershed N export. There were large changes in nitrate sources as a function of runoff, and anticipating source changes in response to climate and storms will be critical for managing nonpoint N pollution.

## INTRODUCTION

Human land use has dramatically increased watershed nitrogen (N) exports contributing to eutrophication and hypoxia in coastal waters.<sup>1,2</sup> Nonpoint N sources are a leading cause of water quality impairments in the United States and are difficult to manage due to a diversity of N sources in watersheds with mixed land use.<sup>3</sup> Because a large amount of N can be retained in watersheds,<sup>1</sup> it is critical to determine which sources are actually transported to streams and most susceptible to N export.<sup>3</sup> Agriculture and urban land-use change have contributed to increasing regional N loads in streams and rivers of the Chesapeake Bay, the largest estuary in the U.S.<sup>4</sup> Evaluating vulnerability of different nonpoint N sources to export in streams across land use and hydrologic variability will be critical in prioritizing effective nitrogen reduction strategies and guiding effective watershed restoration efforts. Nonpoint N sources originate from a variety of inputs on land surfaces such as fertilizers on lawns and agricultural crops<sup>5,6</sup> and atmospheric deposition.<sup>7</sup> N loading may also originate from belowground septic systems in suburban watersheds and sanitary sewer leaks in cities.<sup>8–10</sup> Although N loading from atmospheric deposition, agricultural fertilizer, and delivery via headwater alteration is considerable (e.g., agricultural tile drains, impervious surfaces, storm drains),<sup>11</sup> groundwater is still an important vector of N transport to streams.<sup>12</sup> Nitrogen can also be transformed en route to streams and rivers by subsurface soil and groundwater processes such as nitrification and denitrification.<sup>13</sup> Thus, strategies for N source reductions and watershed and stream restoration

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plans must consider the proximity of nonpoint N sources to streams and presence of nitrate sources below the rooting zone near groundwater, which may have the potential to disproportionately influence transport and transformation of N export along stream networks.<sup>8</sup>

In many cases, the origins of nonpoint sources of watershed N enrichment are not clear due to mixing of different nitrogen sources and spatial variability in inputs and transformations across variable hydrologic conditions. Dual nitrate stable isotopes (N and O) have been successfully used to track the contributions of nitrate from wastewater, fertilizer, and atmospheric deposition to aquatic systems.<sup>13</sup> Additionally, mass balance approaches have been used to predict watershed N exports based on watershed N inputs.<sup>1</sup> Thus a combination of nitrate isotopes, mass balance estimates, and routine water quality monitoring may be useful for elucidating the susceptibility of different nonpoint sources to contribute to stream N loads in human-impacted watersheds.

In this paper, we use watershed N mass balances and exports, coupled with stable isotope source-tracking techniques to identify sources and transformations of N in forested reference, agricultural, and a range of urban and suburban watersheds in the Baltimore metropolitan area. This study builds on long-term monitoring and hydrologic studies carried out as part of the Baltimore urban long-term ecological research (LTER) project, the Baltimore Ecosystem Study (BES),10,14,15 and addresses three key issues: (1) the dominant source of streamwater N in watersheds with multiple input types (sanitary sewer leaks, septic systems, fertilizer, atmospheric deposition); (2) the effects of hydrologic variability on sources of N in streams; and (3) the potential for watershed removal of different N sources under varying hydrologic conditions. We addressed these questions in subwatersheds characterized by various land uses by estimating N exports and retention and measuring  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup>, and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> across hydrologic conditions in and around the Gwynns Falls, the main BES long-term study watershed.

#### METHODS

Site Description. Study sites, sampling, and analytical methods for streamwater chemistry have been described elsewhere (e.g., refs 10 and 14, www.beslter.org, and Supporting Information). Briefly, the Baltimore LTER site includes almost 100% forested and agricultural watersheds, developing watersheds ranging from very low-density (<5% impervious surface), suburban watersheds serviced by septic systems to more dense (>40% impervious surface), and urban watersheds with no wastewater treatment plant inputs (Table S1, Figure S1). During 2005, annual runoff at the BES LTER site was intermediate compared to previous years (Figure 1). Baseflow in streams occurs in August-September and there are peaks in streamflow during the spring and fall in response to storms (Figure S2). In the agricultural watershed, chemical fertilizer is applied as close the planting season as possible (April-May), although manure can also be spread periodically throughout the year.

Watershed N Exports and Mass Balance Calculations. Detailed methods for estimating watershed N exports and mass balance calculations can be found in Supporting Information and elsewhere, <sup>10,14,15</sup> and this paper provides new estimates for 2005 (during the period of isotopic sampling). In 2005, nitrate-N and total N loads and standard errors characterizing uncertainty in annual loads for the study watersheds were estimated using the Fluxmaster program developed by the USGS.<sup>16</sup> Input–output N



Figure 1. (A) Relationship between annual runoff and watershed N retention in 3 small watersheds of the Baltimore Ecosystem Study LTER site during 1999–2005. N retention estimates are from Groffman et al.<sup>10</sup> and Kaushal et al.,<sup>14</sup> and are compared with estimates of N retention during 2005 annual runoff conditions (dashed circles). (B) Annual watershed exports of total N and nitrate during 2005. Error bars indicate standard errors and uncertainty in exports estimated from the USGS Fluxmaster program. (C) Relationship between nitrate-N concentrations and  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> across watersheds.

budgets were also computed for three of the Baltimore LTER watersheds, a forest reference watershed, a suburban watershed, and an agricultural watershed (Supporting Information).<sup>10,14</sup> Sources of uncertainty for inputs in the mass balance calculations are discussed in Supporting Information.

**Stable Isotopic Sampling and Analyses.** Stable isotopic analyses were carried out on stream samples collected biweekly from June 2005 through December 2005 as part of the routine Baltimore LTER sampling. Sites included POBR (forest), MCDN (agricultural), BARN (low-residential), GFGL (suburban), DRKR (urban), GFCP (urban), and RGHT (storm drain). Samples were also taken from a small tributary to the Gwynns Falls (GFGR), approximately 300 m above GFCP, that was highly contaminated with sewage. A major sewer leak to this stream (GFGR) was identified and repaired in April 2004. Stable isotopic analyses of soil water underneath fertilized lawns and atmospheric deposition were measured in long-term lawn study plots on the campus of the University of Maryland Baltimore

County<sup>17</sup> and from a National Atmospheric Deposition Program site in Carroll County, Maryland.<sup>7</sup>

Storm samples were also collected from 6 locations (DR1, DR3.1, DR3.2, DR4, DR5, DRKR gauge) within the Dead Run watershed over July 2005. At one site (DR3), two sets of samples were collected, one just above (DR3.1) and just below (DR3.2) an overflowing sewer. All stormflow samples were collected on the receding limb of the storm hydrograph, as the flashy nature of these urban streams makes sampling the rising limb difficult in terms of both timing and personal safety.

Frozen samples were analyzed for  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> using the denitrifier method at the USGS Stable Isotope Laboratory in Menlo Park. Briefly, denitrifying bacteria (*Pseudomonas auroeofaciens*) convert nitrate to gaseous nitrous oxide (N<sub>2</sub>O) for isotopic analysis.<sup>18,19</sup> A minimum of 60 nmol of nitrate was required to analyze samples on a continuous flow Micromass IsoPrime isotope ratio mass spectrometer (CF-IRMS). Samples were corrected using international reference standards IAEA-N3, USGS34, and USGS35 and values are reported in parts per thousand (‰) relative to atmospheric N<sub>2</sub> and Vienna Standard Mean Ocean Water, for  $\delta^{15}$ N and  $\delta^{18}$ O, respectively using the equation:

$$\delta(\%) = rac{(R)_{ ext{sample}} - (R)_{ ext{standard}}}{(R)_{ ext{standard}}} imes 1000$$

where *R* denotes the ratio of heavy to light isotope (e.g.,  ${}^{15}$ N/ ${}^{14}$ N or  ${}^{18}$ O/ ${}^{16}$ O). Sample duplicates had an average standard deviation of 0.2‰ for  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and 0.7‰ for  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup>. Analysis of stable isotopes of particulate organic matter involved filtration of a known volume of water onto a tared glass filter. Particulate organic matter was analyzed for  $\delta^{15}$ N-POM and  $\delta^{13}$ C-POM by CF-IRMS and an elemental analyzer that converted organic N into N<sub>2</sub> gas and organic C into CO<sub>2</sub> gas at the Stable Isotope Facility at UC Davis; precision was 0.3‰ for  $\delta^{15}$ N and 0.2‰ for  $\delta^{13}$ C for replicate analyses of reference standards.

# RESULTS

During 1999–2005, watershed retention of nonpoint source N in agricultural, suburban, and forest watersheds showed a significant negative correlation with annual runoff (p < 0.05)(Figure 1A). Annual runoff at the suburban GFGL site may have been underestimated because there may be loss of water due to potential infiltration into sanitary lines that affect runoff estimates. During 2005, watershed N retention was 55%, 68%, and 82% for agricultural, suburban, and forest watersheds, respectively. During 2005, export of total N (NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, organic N) was highest in the agricultural watershed followed by the urbanized watersheds, whereas export of total N was lowest in the forest watershed; nitrate comprised a substantial proportion of the total N export in forest, agricultural, and urbanized watersheds (Figure 1B). The  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and nitrate-N concentrations were lowest at the forest site (POBR), but  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and nitrate-N concentration increased at suburban and urban sites (Figure 1C). The agricultural site (MCDN) showed the highest nitrate-N concentrations, but its  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> values were lower than those of suburban and urban sites (Figure 1C).

Nitrate isotope data from rural watersheds indicated substantial transformations of nitrate in soils, riparian zones, and streams (Figure 2A). Soil water from lysimeters below fertilized lawns showed  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> in the range previously reported for soil N and fertilizer/rain<sup>20</sup> (Figure 2A). Atmospheric deposition



**Figure 2.** (A) Dual  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> source plots for rural watersheds. (B) Dual  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> source plots for suburban and urban watersheds. All data are from single sites at different times and discharges. Boxes represent ranges in isotopic signatures of N and O for different nitrate sources (e.g., Kendall et al.<sup>20</sup>). The soil N box represents is completely encompassed by the waste nitrate box.<sup>20</sup> These two sources plus the fertilizer and rain ammonium overlap, and this section is shaded in gray).<sup>20</sup>

from the nearby NADP site showed  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> in the range previously reported for atmospheric deposition from stationary and nonstationary sources.<sup>7,20</sup> The forested watershed (POBR) also generally showed low  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> in the range previously reported for soil N and fertilizer/rain (Figure 2A), however high  $\delta^{18}$ O values indicate significant atmospheric nitrate contributions to select samples. This was consistent with peaks in  $\delta^{18}$ O values at low nitrate concentrations in the stream (Figure S3). Low density residential (BARN) and agricultural (MCDN) watersheds showed intermediate values of  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> within ranges previously reported for soil/fertilizer and wastewater sources (Figure 2A). There were significant positive linear relationships (p < 0.05) between  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> in both the exurban (BARN) and agricultural (MCDN) watersheds (Figure 2A).

Nitrate isotope data from urbanized watersheds showed substantial wastewater N contributions and mixing with atmospheric sources in urban watersheds (Figure 2B). The suburban watershed (GFGL) had the highest  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> values (which were not correlated with  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup>), and they were within ranges previously reported for waste-derived nitrate from raw wastewater<sup>13,20</sup> (Figure 2B). Urban (DRKR, GFGR) and urban mixed land use (GFCP) catchments showed  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> that were intermediate between values previously



Figure 3. (A) Hydrograph of the urban watershed outlet of Dead Run, where a USGS gauging station is located (DRKR), during summer storms of 2005. A total of 6 sites were sampled for stable isotope analysis including DRKR and subwatersheds DR1, DR 3.1, DR 4, and DR 5. (B)  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> sampled along 6 locations of the Dead Run (DRKR) watershed during summer storms. Dashed line represents division between baseflow and stormflow, and isotopic range for atmospheric and wastewater N are indicated.  $\delta^{15}$ N values may increase at the highest flows due to sanitary sewer surcharges. (C) Relationship between nitrate-N concentration and runoff across 6 locations of the Dead Run watershed. (D) Relationship between  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> across 6 locations of Dead Run watershed. Symbols #, @, and  $\wedge$  are placed near data points and indicate stormflow, high stormflow, and low to moderate flow, respectively. \*Data in 4B, C, and D correspond to samples collected around the peaks in 4A; all the data in 4B, C, and D correspond directly to one another.

reported for soil/fertilizer and wastewater and atmospheric deposition endmembers (Figure 2B). There were significant inverse linear relationships between  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> for the 3 urban streams.

The storm drain (RGHT), which drained considerable watershed impervious surface coverage (54%), showed a significant positive relationship between  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> (p < 0.05) (Figure 2B); the  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> peaked when nitrate concentrations were lowest for this site (Figure 1C). The relatively high  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> for most values suggested inputs from atmospheric N deposition and/or modification via denitrification or biotic uptake/assimilation (Figure 2B). There were elevated levels of dissolved organic carbon (DOC) in the storm drain relative to other streams at the BES LTER site (Figure S4). In addition, the  $\delta^{13}$ C-POM in the storm drain was elevated compared to other watersheds potentially suggesting less degraded sources,<sup>21</sup> and  $\delta^{13}$ C-POM increased with increasing percentage impervious surface coverage (Figure S5).

Isotope values of nitrate showed varying relationships with daily runoff across all watersheds (Figure S6). For example, the agricultural watershed (MCDN) showed significant declines in  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> with increasing runoff; suburban

and urban watersheds showed varying patterns with increasing runoff (Figure S6). Highest  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> values occurred at the lowest nitrate concentrations across all sites, and forest, urban, and storm drain sites showed highest  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> values during high flow conditions. Isotopic values for  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O- $NO_3^-$  changed markedly in the urban watershed (DRKR) during 3 storm events sampled in summer 2005 from 6 locations spanning a range of runoff conditions (Figure 3A and B). Across 6 locations, low to moderate flows ( $\sim 1 \text{ mm/day}$ ) showed  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}\text{O-NO}_3^-$  values within the range for wastewater sources (Figures 3B). Stormflow ( $\sim 2 \text{ mm/day}$ ) showed  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> values typically reported for atmospheric N deposition across all locations (Figure 3B). High stormflow (> 8 mm runoff per day) produced  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> values within the range previously reported for soil and waste-derived nitrate and mixing with atmospheric sources (Figure 3B). Nitrate concentrations decreased with increasing runoff (except DR3.2 where there was a sewer leak) (Figure 3C). Samples were typically collected on the falling limb of the hydrograph, and the inverse concentration/discharge relationship may be expected as an initial nitrate-N flush would presumably take place on the rising limb. There was a strong significant

Table 1. Inputs, Outputs, and Retention of Total Nitrogenfor Suburban (GFGL), Forested (POBR), and Agricultural(MCDN) Baltimore LTER Watersheds during 2005

	suburban	forest	agriculture	
	(kg/N/ha/y)	(kg/N/ha/y)	(kg/N/ha/y)	
inputs				
atmosphere	6.8	6.8	6.8	
fertilizer <sup>a</sup>	14.4	0	60	
total	21.2	6.8	66.8	
outputs				
streamflow	6.7	1.2	29.8	
retention				
mass	14.5	5.6	37	
percent	68.4	82.4	55.4	
<sup>a</sup> Values are from ref 18.				

inverse linear relationship between  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> across 6 locations during storms in the urban watershed (DRKR) (Figure 3D). Potential changes in wastewater vs atmospheric N source contributions during storms in the urban watershed (DRKR) are discussed further below in the Discussion section using a two-endmember mixing model scenario.

#### DISCUSSION

Nonpoint source N is a leading contributor to water quality impairment in the U.S.,<sup>3</sup> and it can substantially contribute to coastal eutrophication and hypoxia.<sup>4</sup> Nonpoint N sources can exceed wastewater discharges of N in major watersheds.<sup>1</sup> Identifying nonpoint sources of N in streams draining mixed use watersheds has been a long-term challenge. In this study, combining isotope source identification techniques with more traditional routine monitoring and chemical analysis was effective for illustrating the importance of specific nonpoint N sources across land use and runoff and for showing the potential importance of watershed transformations on stream N export.

**Reference Forest Conditions.** Stable isotopic results from the forested reference stream (POBR) suggested that nitrate derived from microbial uptake, mineralization, and nitrification processes in watershed soils was a major source to the stream<sup>13,22</sup> (Figure 2). These results are consistent with previous studies in the POBR watershed that suggest that soil and watershed processes are capable of absorbing and transforming atmospheric N inputs during baseflow.<sup>17,23</sup> There was also evidence of atmospheric inputs in this forested stream characterized by  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> values >+30 that occurred during periods of increased runoff and peaks in  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> at lowest nitrate concentrations (Figure S3).

**Denitrification in Agricultural and Low-Residential Catchments.** As expected, the agricultural stream (MCDN) had much higher NO<sub>3</sub><sup>-</sup> concentrations than the forested stream (Figure 1C). More interesting was a ~2:1 positive linear relationship between  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> of samples from this watershed, which suggests isotopic fractionation processes associated with denitrification;<sup>24</sup> slopes for relationships between  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> were 2.81 and 1.98 for MCDN and BARN, respectively. The linear trend may have also been explained by mixing of a highly denitrified source (with a very long residence time) with a less denitrified source. Alternative mechanisms such as biotic uptake/assimilation may also influence N and O isotopic values, but these small streams are well shaded. Our results are most consistent with several previous studies using stable isotopes that have suggested denitrification in watersheds with agriculture and septic systems (e.g., refs 13 and 25).

Changes in isotope values with discharge suggested a marked decline in the importance of denitrification with increased runoff in this agricultural catchment (Figure S6); denitrification predominantly occurred during summer baseflow conditions similar to those in ref 13. There was a marginally significant linear relationship between  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and nitrate concentrations (p = 0.06) suggesting that although denitrification was occurring, it may not have been sufficient to reduce a substantial proportion of the elevated nitrate concentrations in the stream (Figure S7). This denitrification could have taken place in subsoils, the riparian or hyporheic zone, and/or within the stream channel itself.<sup>12,13</sup> These results suggest the importance of N transformations in MCDN, and a source that may have originated as mineral fertilizer or manure. These results also suggest that hydrologic residence times and elevated N concentrations in streams should be considered when attempting to reduce N exports from agricultural areas using N sinks (in conjunction with fertilizer reduction strategies). Given that  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> both showed significant negative correlations with daily runoff, it also suggests that higher flushing rates can contribute to shorter residence times in soils and a decreased time for removal via denitrification.

We also observed a 2:1 linear increase in  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> in the low-residential watershed served by septic systems (BARN) suggesting that denitrification also occurred in this watershed or in the stream. We hypothesize that denitrification occurred somewhere along the hydrologic flowpath from septic systems to streams as prior studies indicate a low potential for in-stream retention in this particular stream based on long-itudinal variations in stream nitrate uptake.<sup>26</sup> This is consistent with other work using multiple isotopic and geochemical tracers that indicates denitrification is an important mechanism for nitrate attenuation in septic plumes and contributes to increases in  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup>.<sup>25</sup> There may be transformation of NO<sub>3</sub><sup>-</sup> as septic system plumes travel across the landscape, and some potential for further enhancing denitrification sinks with improved septic designs.<sup>25</sup>

Importance of Wastewater vs Lawn Fertilizer in Catchments. A major question in low-residential watersheds is the importance of septic systems versus home lawn fertilizer (a major input) as the source of N to streams (Supporting Information Discussion). The isotopic values of  $NO_3^-$  in the BARN (low-residential) stream differ markedly from that collected beneath fertilized lawns, suggesting that lawns were not contributing N to the stream but rather wastewater from septic systems was a major source of  $NO_3^-$  to this stream (Figure 2A). Because fertilizer nitrate is isotopically similar to that of soil-derived nitrate, it can be difficult to distinguish the contribution of fertilizer as a nitrate source to aquatic systems.<sup>20</sup> Likely, septic systems contribute  $NO_3^-$  to BARN, and they should be addressed in efforts to reduce N loads from low-residential watersheds.

As in the BARN watershed, mass balance estimates indicate fertilizer and wastewater are the dominant N inputs to the GFGL suburban watershed (Table 1), with the important difference that the GFGL watershed is served by sanitary sewers and not septic systems. In this suburban watershed, a major question is also whether stream  $NO_3^-$  is leaching from fertilized lawns or leaking

from the sanitary sewer lines that run parallel to the stream. Of all the samples we collected, those from the GFGL stream have an isotopic composition most similar to wastewater, suggesting that leaky sewer lines are a more important source of N to this stream than lawn fertilizer (all isotopic measurements were distant from reported values for ammonium in fertilizer and rain). The potential importance of wastewater is consistent with information from other chemical tracers of sewage inputs at this site including fluoride, which increases along the Gwynns Falls as it traverses from suburban areas to progressively urban areas (Figure S8). We also saw no evidence for denitrification in the GFGL isotope data suggesting that leaky sewer lines may be a particularly problematic source of N; one that is released very close to the stream and groundwater, with little potential for denitrification. We hypothesize that lawn fertilizer is retained by residential lawns, and is not as vulnerable to watershed export as other sources delivered belowground that bypass zones of transformation via groundwater flow paths.<sup>27</sup> Although lawn fertilizer can be an important watershed input, delivery of wastewater N along subsurface flowpaths below the rooting zone may play a disproportional role in contributing to nonpoint source N loads.

N Transformations in an Urban Watershed Storm Drain (No Natural Drainage Network). Impervious surfaces and storm drains have the potential to enhance delivery of atmospheric deposition to urban streams.<sup>7,28</sup> However, we observed a weak but significant linear increase in  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> in the storm drain. This suggests that atmospheric inputs are minimal during baseflow and/or residual nitrate may be influenced by denitrification and/or microbial uptake/assimilation and can obscure the influence of atmospheric sources. The potential for N transformations in the storm drain was surprising but may have been stimulated by organic carbon availability during baseflow between storms. There were elevated DOC concentrations in the storm drain that were delivered from the watershed (Figure S4). Results from stable isotopic analysis indicate that  $\delta^{13}$ C-POM also increased in the storm drain and in streams with increasing percentage impervious surface coverage of watersheds (Figure S5). The increase in  $\delta^{13}$ C-POM values in the storm drain and with increasing urbanization may reflect terrestrial carbon sources that are less biologically degraded and/ or originate from microbial uptake and assimilation processes<sup>21,29</sup> (Supporting Discussion Information). Labile organic carbon, decreased light in the subsurface drain, seepage water to maintain wet conditions, and sufficient residence time between storms may influence N transformations during baseflow. Our results are consistent with other isotopic work suggesting denitrification in agricultural tile drains during baseflow<sup>30</sup> and N transformations via uptake/assimilation in concrete-lined drains.<sup>29</sup> We have no process level information on denitrification rates, but the potential for N transformations during baseflow in storm drains as part of the urban drainage network may warrant further investigation.<sup>3</sup>

Importance of Wastewater vs Atmospheric N Sources in Urban Catchments. In our most urban watersheds, potential sources of stream NO<sub>3</sub><sup>-</sup> include leaking sewers and atmospheric deposition (assuming there is less fertilized surface in increasingly urban areas). For example, the  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> of GFGR (site where major sewage leak was fixed in April 2004) still showed elevated  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> values in the range of sewage despite being fixed. We observed consistent, strong, negative correlations (p < 0.05) between  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> at all of the urban BES LTER sites indicating mixing between two sources (atmospheric deposition and wastewater). In urbanized

streams,  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> was typically within the range of wastewater and appeared to show no strong pattern with nitrate concentration. There were prominent peaks in  $\delta^{18}$ O values at low nitrate concentrations in Dead Run (DRKR) suggesting the importance of atmospheric sources during storms (Figure S32) (discussed further below). Recent studies have identified wastewater as a key source of N in streams and rivers;<sup>13,32</sup> however, limitations of using  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> to quantify the relative importance of atmospheric N inputs warrant caution when quantifying inputs (e.g., ref 33). For example, biotic and abiotic reactions can alter  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> values through isotopic fractionation and thus complicate interpretations of contributions from multiple sources.<sup>33</sup>

**Changes in N Sources during Storms.** The relative contribution of atmospheric N deposition and wastewater to stormflow appeared to span a continuum of watershed runoff. We were able to evaluate isotopic changes in NO<sub>3</sub><sup>-</sup> during three distinct storm events across 6 locations in one urban watershed (DRKR). Wastewater appeared to be a major source of NO<sub>3</sub><sup>-</sup> during baseflow conditions, but its relative importance decreased with increased runoff. The highest  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> values included some > +25‰, which indicated a large contribution from atmospheric nitrogen. These high  $\delta^{18}$ O values were observed during stormflow (~ 2 mm/day runoff) and high stormflow (> 8 mm/day runoff) and reflect a mixture of atmospheric and wastewater N. These results demonstrate how isotope values during stormflow are influenced by the residence times of different pools of N in watersheds, and by antecedent conditions.

Climate and storms can greatly impact N exports in suburban and urban watersheds.<sup>14,15</sup> It has been previously shown that approximately 75% of the cumulative watershed N export in Dead Run (DRKR) occurs at high flow (16.44 mm/day) and <25% of watershed N export occurs at moderate to low flows of <1 mm/day.<sup>15</sup> Stormflow may flush atmospheric N deposition that accumulates on impervious surfaces during dry periods, but stormflow may also contribute to sanitary sewer surcharges/ overflows and access deeper groundwater flow paths. Our isotopic results from  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> suggest that wastewater and atmospheric N deposition both are transported to urban streams, and the relative contribution varies with storm magnitude.

Estimating Atmospheric vs Wastewater Source Contributions. Overall, our isotopic data indicate the dominance of two major sources of nitrate to the Dead Run study watershed during storms. In particular, the strong inverse relationship between  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> suggested mixing between atmospheric and wastewater nitrate. The strong inverse relationship between nitrate-N concentration and runoff also suggested mixing between wastewater with high nitrate-N concentrations and atmospheric deposition with low nitrate-N concentrations. To estimate the potential contributions from each of these sources, we used a two-endmember mixing model to assess how sources of atmospheric vs wastewater N changed during three storms.  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> values were used to infer the proportion of wastewater vs atmospheric N during storms and were estimated by

$$\delta X_{\text{stream}} = P_{\text{wastewater}}(\delta X_{\text{wastewater}}) + (1 - P_{\text{wastewater}})(\delta X_{\text{atmospheric}})$$

where  $\delta X$  is the isotopic ratio of N in nitrate (in streams, wastewater, or atmospheric sources);  $P_{\text{wastewater}}$  is the proportion

Table 2. Mixing Model Estimates Showing Variability inPercentages of Wastewater N and Atmospheric N in StreamsDraining Subwatersheds of Dead Run during Storms<sup>a</sup>

site	% wastewater N	% atmospheric N		
DR1	7-50	8-92		
DR 3.1	13-53	6-87		
DR 3.2	24-90	10-76		
DR 4	11-76	24-89		
DR 5	18-95	5-82		
DRKR	13-79	21-94		
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<sup>*a*</sup> The mixing model uncertainties and caveats are discussed in the text, but it may provide insights into the variability in source contributions in an urban watershed across runoff.

of wastewater N. The  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> of wastewater can vary between +10 and +20.<sup>20</sup> We used an estimate of +13.5 as an intermediate value from a recent review.<sup>34</sup> This recent review also showed that  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> for atmospheric deposition typically ranged from -13 to +13,<sup>34</sup> and we used an intermediate  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> value of -0.2 for atmospheric deposition as an approximation.<sup>35</sup>

There can be multiple sources of uncertainty associated with the mixing model that should be acknowledged. One uncertainty is improper accounting of all sources that actually provide N contributions to the streams. Second, choice of isotopic endmembers in the mixing model may also contribute uncertainty in the mixing model estimates. Third, transformations of N along flowpaths, such as denitrification, may bias isotopic values toward wastewater values, and neglecting lawn fertilizer as an additional source may overestimate contributions from atmospheric N deposition. Overall results from the mixing model should be interpreted with caution, but provide insight into variability in urban nitrate source contributions across a range of hydrologic conditions.

Results from the mixing model indicate large variability in atmospheric contributions (between 5 and 94%) across runoff conditions during storms (Table 2, Figure S9). As expected, greatest atmospheric contributions occurred during stormflow and decreased during highest stormflow when sanitary sewer surcharges might have occurred. From the perspective of mass transport, atmospheric deposition accounted for ~50% of the highest nitrate-N loads during storms (Figure S10). Both atmospheric deposition and wastewater are important nitrate-N sources in urban streams that vary with streamflow conditions. As a consequence, watershed restoration strategies need to consider the potential for large changes in sources based on regional climate and magnitude of storms.

Previous work has suggested that atmospheric deposition may not always be evident during high flow in streams draining suburban watersheds.<sup>13</sup> Our highly urban watersheds in Baltimore City have substantial impervious surface coverage that may efficiently convey runoff to streams. There may be flushing of inputs from atmospheric deposition on impervious surfaces during light storms, and contributions from leaky sewers and deeper groundwater flow paths during higher stormflow. There is significant variability in sanitary infrastructure and impervious surface cover across residential areas of different age and density within the Baltimore metropolitan area. The contribution of wastewater vs atmospheric deposition sources during storms may vary across infrastructure age and density, and stable isotopes may provide additional information to managers in targeting sanitary infrastructure upgrades and needs for improved stormwater management strategies to remove N.

Management Implications. Our study indicates that sources of N from atmospheric deposition, wastewater, and fertilizer showed different vulnerability to watershed N export. There were also large changes in nitrate sources as a function of runoff, and prioritizing management strategies based on contribution of sources across climate and hydrologic variability will be critical for controlling nonpoint source N pollution (e.g., stormwater management). Wastewater was a major source of N in urban and suburban streams during baseflow conditions, but that there was a continuum of wastewater versus atmospheric sources that changed with runoff. Denitrification was removing septic system and agriculturally derived N, but N from belowground leaking sewers was less susceptible to denitrification. Efforts to reduce N export from agricultural, suburban, and urban watersheds should include maintenance and restoration of diverse watershed denitrification sinks that intercept key hydrologic flow paths and repair of aging sewer lines should be a priority. Managing and minimizing N inputs along hydrologic flowpaths near streams and groundwater (e.g., leaky sewers and septic systems) may play a disproportionate role in regulating watershed N exports and sustainable land-use management.

### ASSOCIATED CONTENT

**Supporting Information.** Maps of study sites and region; Land use/land cover information for study sites; Hydrographs for streams at the BES LTER Site during 2005; Relationship between  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> and nitrate-N concentration across sites; Dissolved organic carbon (DOC) concentrations in the RGHT storm drain compared to other sites; Patterns in  $\delta^{13}$ C-POM and  $\delta^{15}$ N-POM in the storm drain and streams across a gradient in watershed impervious surface coverage; Relationships between  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> of nitrate in streams across varying runoff; Relationships between  $\delta^{15}$ N-NO<sub>3</sub><sup>-</sup> and  $\delta^{18}$ O-NO<sub>3</sub><sup>-</sup> and nitrate concentrations in MCDN; Other chemical tracers of wastewater inputs (fluoride) in watersheds; Estimated proportions of wastewater vs atmospheric source contributions during storms at Dead Run across runoff, nitrate-N concentrations, and daily nitrate-N loads. This material is available free of charge via the Internet at http://pubs.acs.org.

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