Streamflow distribution of non–point source nitrogen export from urban-rural catchments in the Chesapeake Bay watershed

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1. Introduction

Nitrogen (N) export from urban and urbanizing watersheds is a major contributor to water quality degradation and eutrophication of receiving water bodies. Methods to reduce N exports using best management practices (BMP) have targeted both source reduction and hydrologic flow path retention. Stream restoration is a BMP targeted to multiple purposes but includes increasing flow path retention to improve water quality. As restorations are typically most effective at lower discharge rates with longer residence times, distribution of N load by stream discharge is a significant influence on catchment nitrogen retention. We explore impacts of urbanization on magnitude and export flow distribution of nitrogen along an urban-rural gradient in a set of catchments studied by the Baltimore Ecosystem Study (BES). We test the hypotheses that N export magnitude increases and cumulative N export shifts to higher, less frequent discharge with catchment urbanization. We find that increasing development in watersheds is associated with shifts in nitrogen export toward higher discharge, while total magnitude of export does not show as strong a trend. Forested reference, low-density suburban, and agricultural catchments export most of the total nitrogen (TN) and nitrate (NO3−) loads at relatively low flows. More urbanized sites export TN and NO3− at higher and less frequent flows. The greatest annual loads of nitrogen are from less developed agricultural and low-density residential (suburban/exurban) areas; the latter is the most rapidly growing land use in expanding metropolitan areas. A simple statistical model relating export distribution metrics to impervious surface area is then used to extrapolate parameters of the N export distribution across the Gwynns Falls watershed in Baltimore County. This spatial extrapolation has potential applications as a tool for predictive mapping of variations in export distribution and targeting stream channel restoration efforts at the watershed scale.


1. Introduction

Anthropogenic activity has significantly increased the availability and cycling of nitrogen (N) throughout the world [Vitousek et al., 1997, Galloway et al., 2004]. A number of studies have linked urban and agricultural land cover to increased N export [e.g., Jordan et al., 1997, 2003; Jordan et al., 2003, 2005; Jordan et al., 2006]. Despite the interest in improving water quality by stream restoration, mechanisms controlling nitrogen export from suburban and urban catchments, including the effects of in-stream retention, remain poorly understood. Stream restoration generally aims to increase nitrogen uptake and retention by slowing the movement of water, increasing residence time through the channel and riparian zone, and increasing hyporheic exchange between the water column and hyporheic exchange.

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sediment [Kasahara and Hill, 2006]. Recently, Bernard and Palmer [2007] discussed the difficulty of achieving water quality improvement through restoration of urban streams because of the lack of space to develop greater channel complexity and the altered flow distributions dominated by stormflow with reduced surface water–groundwater interaction. Retention efficiency of dissolved and suspended material is generally inversely proportional to stream discharge, as water circulation through the bed and banks and in backwaters is less effective under high-flow conditions. Therefore, in addition to the total quantity of nitrogen exported, the distribution of nitrogen export by stream discharge should be considered when evaluating the potential of stream restoration projects.

[s] The export flow distribution of nitrogen as a function of land cover has not been extensively studied. The distribution of solute loads by streamflow is dependent on both the flow duration curve and the concentration-discharge relationship. Some recent studies have either found no significant difference between base and stormflow N concentrations in urban watersheds [e.g., Taylor et al., 2005], or that urban NO3 concentrations display a weak relationship to stream discharge when compared with a forested watershed [Wollem et al., 2005]. These findings suggest that dilution of N or NO3 concentration at high flows is not significant in urban catchments, promoting dominant N loads at high-flow conditions. In less developed catchments, greater base flow concentrations might reduce the weighting of N export to high-flow conditions. Jordan et al. [1997] found that annual nitrate export from a range of catchments in the Chesapeake Bay watershed increases with the proportion of base flow contribution to annual runoff, while total organic nitrogen exports decline. However, Royer et al. [2006] recently analyzed the flow distribution of nitrogen load in Midwest agricultural watersheds to evaluate the potential of low-flow nitrogen reduction in reducing nitrate export in tributaries of the Mississippi. They found that most N is exported at high flow during spring runoff, and that little potential existed in restoration efforts that would target low-flow regimes.

[s] Burns et al. [2005], Sherlock and McDonnell [2003], and Heisig [2000], working in the New York City (NYC) water supply area, and Poor and McDonnell [2007] working in Oregon analyzed runoff production from catchments in a mix of land uses. While peak flows increase with development, there is also some evidence of base flow and nitrate export augmentation by septic fields in the New York catchments. This contribution by septic systems would increase the cumulative export of nitrate at low flow. Poor and McDonnell [2007] found stormflow from a suburban catchment (without septic systems) shows consistently increased nitrate export relative to a forest catchment, suggesting a lawn fertilizer source, while high-N concentrations and export from an agricultural catchment was restricted to a period following fall fertilizer application. In comparison to the NYC watershed catchments served by septic systems, the lawn sources in the Oregon suburban site show increased stormflow nitrogen exports, with low-flow export reduced by small wetlands, but higher flows effectively transporting nitrogen load through the wetland with little retention.

[s] These and other studies, as well as Royer et al. [2006] highlight the significance of types, location and timing of non-point sources of nutrients (agricultural and suburban lawn fertilizer, septic systems, impervious surface wash-off, sanitary/combined sewer leakage and surcharging) on the discharge distribution of export, as well as the potential for retention at low flow. In most cases, nitrogen shows the characteristics of flushing, in which mobile nitrogen accumulates in specific parts of the landscape in dry periods at low flow, and is transported (flushed) as groundwater, soil water and surface water flow paths activate during storm events or seasonal wet periods [e.g., Creed et al., 1996; Creed and Band, 1998a, 1998b; Burns, 2005]. The wetness, or flow, thresholds for each flush may result in a range of responses from frequent recharge from localized sources as in the case of distributed septic systems [Burns et al., 2005; Heisig, 2000], storm water mobilization of lawn fertilizer from suburban lawns and nutrients accumulated on impervious surfaces, or fertilizer from larger portions of the landscape during wet-up in the agricultural catchments [Poor and McDonnell, 2007; Royer et al., 2006]. The timing of fertilization events or biogeochemical evolution of mobile nutrients, combined with the frequency and areal extents of flushes and the connectivity of sources to drainage lines contribute to the discharge distribution of nitrogen export in these and other landscapes.

[s] In this paper we investigate how nitrogen export flow distribution and magnitude vary over the range of land cover, N sources and infrastructure in a gradient of rural to urban catchments in the Baltimore metropolitan area. This gradient includes the range of flushing conditions discussed by Burns [2005] in urban to forested catchments. We test the following hypotheses:

[s] 1. The export flow distribution of N is positively associated with increased levels of development. Development is indicated by land cover classification and impervious surface area.

[s] 2. The magnitude of N export is also positively associated with increased development.

[s] 10. We use our findings to develop simple statistical and GIS methods to predict indices of flow distribution of nitrogen export on the basis of readily observed watershed characteristics. The information can provide significant improvement in our ability to prioritize streams for restoration on the basis of quantity and timing of nitrogen export.

[s] 11. Nitrogen loads were estimated from concentration and discharge measurements sampled in 1998–2004 (covering a period of major drought and recovery). This information was used to develop the nutrient duration curve, which is an estimate of the cumulative annual nitrogen export by streamflow runoff for each catchment. Note that while we can develop similar curves for other nutrients, we focus here on nitrogen as a major concern for the Chesapeake Bay restoration effort. Rather than focusing on the dynamics of individual storm events, we analyze long-term weekly sampling of stream chemistry in eight catchments to develop annual and interannual statistics characterizing the range of hydrologic water and nutrient export behavior within the mix of land uses in the metropolitan region.

2. Data and Methods
2.1. Study Site
12. The Baltimore Ecosystem Study (BES) (http://www.besler.org) was established in 1998 to monitor and
explore long-term ecological form and process in urban areas. The BES is part of the United States Long-term Ecological Research (LTER) network. The BES is focused primarily on the Gwynns Falls watershed (76°30′, 39°15′, Figure 1) extending from the rapidly developing areas at the rural/suburban fringe of Baltimore County, southeast through the urban center of the city of Baltimore, and draining into the Chesapeake Bay.

Figure 1. Gwynns Falls watershed and study sites in Baltimore city and county.

[13] Watershed population in the year 2000 was approximately 356,000 people, with subwatershed densities ranging from 2.2 to 19.4 persons ha⁻¹. Average annual precipitation is 1060 mm a⁻¹ and stream discharge is 380 mm a⁻¹ [Froelich et al., 1980; Doheny, 1999]. Topography varies from “gently sloping” to “hilly” with locally steep slopes and bedrock outcroppings within drainage corridors [Froelich et al., 1980]. The majority of the Gwynns Falls watershed lies within the Piedmont Physiographic Province and is underlain primarily by crystalline bedrock [Doheny, 1999]. Saprolite can be locally deep on interfluvies with shallower soils and bedrock outcrops downslope. Valley bottoms have alluvial soils that can be locally thick from accumulated agricultural sediment.

[14] Water quality samples are collected at sites within the Gwynns Falls and at two nearby sites in the Gunpowder Falls watershed [Groffman et al., 2004]. Watershed areas range over four orders of magnitude from several hectares to 164 km², and encompass a variety of land use types (Table 1). Four of the sites (Glyndon, Gwynnbrook, Villa Nova and Carroll Park) are located along the main stem of the Gwynns Falls and traverse a rural/suburban to urban gradient. McDonogh is a tributary to the Gwynns Falls draining a watershed dominated by row crop agriculture (corn, soybeans) between the Glyndon and Gwynnbrook stations. Dead Run is a more highly urbanized tributary to the Gwynns Falls between the Villa Nova and Carroll Park stations. Baisman Run and Pond Branch are located in the nearby Gunpowder Falls watershed. Baisman Run is a mix of forest and very low density exurban development, while Pond Branch serves as a forested reference site. The majority of the Gwynns Falls is served by city or county sanitary sewer lines, with a number of septic systems having been replaced with sanitary sewer infrastructure during the 1970s and 1980s [Law, 2003]. However, some small areas on septic still exist in the Gwynnbrook catchment, and the Baisman Run catchment has no sanitary sewer infrastructure with all development on septic systems. There are no wastewater treatment plants upstream of any sites considered in this paper.

[15] Land use change associated with urbanization over the last few decades has been shown to increase storm water runoff in these catchments [Brun and Band, 2000] and reduce ecosystem nutrient retention by decreased infiltration and residence time in soil, groundwater and hyporheic zones [e.g., Groffman et al., 2004]. Coupled water, carbon and nitrogen cycling in the forest reference site were discussed by Band et al. [2001] who recognized riparian areas as a primary source of growing season nitrate export with the highest stream water nitrate concentrations sampled at the lowest flows. Law [2003] extended this analysis to septic dominated catchments in low-density suburban catchments. Unlike the forest reference site, these catchments show order of magnitude increases in loads, and a decrease of stream water nitrate concentration at the lowest flows.

[16] Baltimore city and county have each entered into a consent decree with the U.S. Environmental Protection

Table 1. Impervious Surface and Land Cover Composition of Catchments

<table>
<thead>
<tr>
<th>Catchment</th>
<th>Area (ha)</th>
<th>Impervious Surface</th>
<th>Cultivated Crop</th>
<th>Forest</th>
<th>Open</th>
<th>Low</th>
<th>Medium</th>
<th>High</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pond Branch</td>
<td>38</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Baisman Run</td>
<td>382</td>
<td>&gt;0.26</td>
<td>2</td>
<td>71</td>
<td>1.4</td>
<td>0.19</td>
<td>0</td>
<td>0</td>
<td>25</td>
</tr>
<tr>
<td>Glyndon</td>
<td>81</td>
<td>19</td>
<td>5</td>
<td>19</td>
<td>26</td>
<td>19</td>
<td>12</td>
<td>4</td>
<td>15</td>
</tr>
<tr>
<td>Gwynnbrook</td>
<td>1065 (984)</td>
<td>15 (15)</td>
<td>8 (8)</td>
<td>17 (16)</td>
<td>21 (20)</td>
<td>25 (25)</td>
<td>6 (5)</td>
<td>5 (1)</td>
<td>18 (25)</td>
</tr>
<tr>
<td>Villanova</td>
<td>8349 (7284)</td>
<td>17 (17)</td>
<td>10 (10)</td>
<td>24 (24)</td>
<td>17 (16)</td>
<td>21 (21)</td>
<td>9 (10)</td>
<td>2 (3)</td>
<td>17 (16)</td>
</tr>
<tr>
<td>Dead Run</td>
<td>1414</td>
<td>31</td>
<td>2</td>
<td>5</td>
<td>27</td>
<td>41</td>
<td>16</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>Carroll Park</td>
<td>16378 (6617)</td>
<td>24 (32)</td>
<td>6 (1)</td>
<td>18 (14)</td>
<td>20 (22)</td>
<td>26 (29)</td>
<td>15 (21)</td>
<td>5 (9)</td>
<td>10 (4)</td>
</tr>
<tr>
<td>McDonogh</td>
<td>7.8</td>
<td>0</td>
<td>70</td>
<td>26</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4</td>
</tr>
</tbody>
</table>

aSegment area values are given in parentheses.
Agency (EPA), agreeing to spend approximately $800 million each to reduce the quantity of N they discharge into the Chesapeake Bay [United States of America and State of Maryland versus Mayor and City Council of Baltimore, Maryland, 2002; U.S. Environmental Protection Agency (USEPA), 2005]. This reduction will primarily be effected through improvement of sanitary infrastructure, but a commitment has also been made to restoring degraded streams [USEPA, 2005]. Given the need and interest in reducing N loading, analyses that could lead to prioritization of streams for restoration are of particular interest in the Baltimore area and the Chesapeake Bay watershed.

2.2. Data
[17] Stream discharge is continuously monitored by the U.S. Geological Survey at all stations. Stream chemistry is sampled on a weekly basis at each of the stream gauging stations. Although the exact day of the week sampling occurs on is not fixed, the sampling schedule is determined during the preceding week, and is not scheduled to coincide with or to avoid wet weather conditions; sampling thus retains an element of randomness and the samples are representative of the range of flow conditions that occur in each stream. Over the long-term record, flow frequency distributions of the water quality samples do not differ significantly from the flow frequency distribution of the entire record. Following collection, samples are sent to the Institute of Ecosystem Studies (IES), Millbrook, New York, for chemical analysis. Concentrations of nitrate (NO₃⁻) are measured on filtered samples using a Dionex LC20 series ion chromatograph [Tabatabai and Dick, 1983]. Total N is analyzed on unfiltered samples by persulfate digestion followed by analysis of NO₃⁻ [Ameel et al., 1993]. Nitrate in these digests was analyzed on a Perstorp Flow Solutions 3000 flow injection analyzer.
[18] Both stream discharge and chemistry data cover the period October 1998 to September 2004, with the exception of the Baisman Run and McDonogh watersheds, where water chemistry sampling did not begin until October 1999. This period covers a range of rainfall conditions, including severe drought in 2002 with annual precipitation at 67% of the annual mean, a period of extreme precipitation in water year 2003 with precipitation at 132% of the annual mean, and several extreme, concentrated precipitation events, including Hurricanes Floyd (September 1999) and Isabel (September 2003). Discharge time series over the study period are shown for several catchments in Figures 2a–2c.
[19] Catchment land cover and impervious surface data are from the National Land Cover Database (NLCD). This database includes land cover, impervious surface, and canopy cover data derived from a set of Landsat Thematic Mapper images collected over the period 1999–2001 (http://www.mrlc.gov/mrls2k.asp). Spatial resolution of all layers used in our analysis is 30 m. Construction of the layers available in the NLCD is discussed in detail by Homer et al. [2003]. While we note that the NLCD shows classification confusion between spectrally similar classes, we use it here as a uniformly, and nationally (United States) available data set.

2.3. Total Nitrogen and NO₃⁻ Load Estimates and Cumulative Frequency Distributions
[20] Plots of concentration and discharge (given as runoff depth to normalize for catchment drainage area) show different forms in each catchment depending on land use. Figures 3a–3d show concentration/discharge (c-q) plots for the Pond Branch, Baisman Run, Dead Run and McDonogh...
catchments which cover a range of land use from forest, low-density suburban, urban and agriculture. We estimated total nitrogen (TN) and NO$_3$ concentrations for non-sampled days using a bin-averaging approach, similar to that described by Groffman et al. [2004] (working on these same watersheds) and Quilbé et al. [2006]. In this method, concentrations of NO$_3$ and TN samples are sorted and grouped by discharge to generate bins with a minimum of three samples. The method was not sensitive to substituting different minimum sample size per bin. The volume-weighted mean bin concentration of samples is for all discharges falling within the range of the bin. These estimated concentrations are multiplied by daily discharge to construct daily loads. Because of considerable interannual variability in runoff range and nutrient concentrations during periods of extreme drought and extreme precipitation (Figures 4a–4c); we treated samples from each water year in the study period separately when developing daily load estimates. Figures 5a and 5b show estimated and observed daily stream export of NO$_3$ for the Baisman Run and Dead Run catchments. Mean annual TN and NO$_3$ export estimates calculated using the bin averaging approach also compared well to annual estimates calculated using the Fluxmaster program developed by USGS [Schwarz et al., 2006]. For a set of the catchments, a regression with zero intercept of bin-averaged versus Fluxmaster annual load estimates showed slopes close to 1 and $r^2$ values of 0.90 (TN) and 0.97 (NO$_3$) ($p < 0.05$).

Concentration-discharge relationships show some seasonal variation in the BES catchments, with higher winter concentrations and lower summer/fall concentrations at similar discharges in most cases (e.g., Figures 3a–3c). However, seasonal variation in concentrations at fixed discharge are an order of magnitude lower than intersite variability, and significantly lower than variation across the range of runoff levels. We tested the impacts of observed seasonality in the c-q relationships by recomputing a subset of loads by season (winter, December–February; spring, March–May; summer, June–August; and autumn, September–November), aggregating to annual loads and nutrient duration curves and comparing to annually based calculation (e.g., Figures 6a–6c). Although some seasonal variations are present in BES catchments, they do not have a significant impact on annual loads.

Nutrient duration curves of TN and NO$_3$ export were computed from estimated daily loads for each catchment. These curves show the cumulative distribution of annual N export by flow rate. Flow duration curves were also con-
structured using daily discharge data. In the case of the three downstream sites along the main Gwynns Falls channel (Gwynnbrook, Villanova, and Carroll Park), we also compute the segment loads associated with the drainage areas below upstream gauges by subtracting upstream daily loads (in the case of the Carroll Park station, loads from both Villanova and Dead Run were subtracted). The nutrient duration curves for the segment drainage areas are then computed using the same methods. We also develop an estimate of nitrogen export from unforested portions of the BES by assuming N loads per unit area for Pond Branch are representative of all forest in the study area, and subtracting estimated forested contribution and area from each catchment. This assumption is necessarily approximate, although the developed and agricultural catchments have order of magnitude larger loads per unit area than the forest catchment. This adjustment allows for further exploration of what types of development have the greatest impact on the quantity of nitrogen export.

2.4. Extraction of Land Cover Data/Weighted Flow Accumulations

[23] We test the hypothesis that land cover significantly influences the flow distribution of N export. We used regression analysis between land cover variables and a parametric description of the N duration curves. We considered impervious surface and five additional land cover classes: open, low-intensity, medium-intensity, and high-intensity development, and cultivated cropland (Table 2).

Figure 4. Time series of NO$_3^-$ for (a) Pond Branch (forest), (b) Baisman Run (exurban), and (c) Dead Run (urban) catchments.

Figure 5. Modeled versus observed daily NO$_3^-$ loads for (a) Baisman Run (exurban) and (b) Dead Run (urban) catchments. Observed daily loads (x axis) are calculated from the mean daily discharge and NO$_3^-$ concentration measured in water chemistry samples, while modeled daily loads (y axis) are loads estimated on the same dates using the bin averaging approach described in section 2.3.
These land cover classes consider a range of rural, suburban, and urban development. NLCD data was clipped to fit each catchment boundary and the fraction of total catchment area occupied by each land class and total percent impervious were calculated. We used the NLCD data with a digital elevation model (DEM) of the catchments to develop a weighted flow accumulation grid showing area in a given land class upslope of any point within the catchment using TauDEM [Tarboton, 1997] (see http://hydrology.neng.usu.edu/taudem/). Dividing the land cover specific flow accumulation by the total flow accumulation results in surfaces showing percent upslope area in each land cover class, and percent impervious cover across the Gwynns Falls watershed.

2.5. Export Flow Distribution as a Function of Impervious Surface and Land Cover

[24] To quantify the relationship between nitrogen export flow distribution and land cover, we consider TN and NO₃⁻ export as a function of upstream impervious surface and land cover. Using the nutrient duration curves constructed in 2.3, we determined flow percentiles for 25, 50, and 75% of cumulative export runoff levels (referred to throughout as F_{25}, F_{50}, and F_{75} given in units of mm d⁻¹) in each catchment and use these numbers as a metric indicative of overall catchment export flow distribution. Correlations were generated between the upstream land cover metrics and F_{25}, F_{50}, and F_{75} of both TN and NO₃⁻ export for each catchment.

[25] We then extrapolated relationships between these export flow distribution metrics and land cover across the Gwynns Falls watershed. Using the weighted flow accumulation grids generated in 2.4, we applied equations relating land cover to export flow distribution to create a continuous grid of estimated F_{75} values across the Gwynns Falls stream network.

3. Results and Discussion

3.1. Load Magnitude and Volume-Weighted Concentrations

[26] Both the volume weighted concentrations and mean annual export of N show a considerable variation between catchments. The forested reference catchment has significantly lower volume-weighted mean concentrations of TN and NO₃⁻ while the agricultural McDonogh catchment has the highest, with the urbanized catchments intermediate (Figures 7 and 8). Nitrogen export per unit area is lowest from the forested reference catchment with higher levels of export from the developed catchments. However, the variation was not entirely consistent or monotonic along the urban-rural gradient, with the most heavily developed catchment, Dead Run, displaying low mean annual NO₃⁻ export and concentration relative to other developed catchments. Least squares regression analysis revealed no significant correlation between either TN or NO₃⁻ mean annual export and impervious surface or any of the land cover classes considered (p > 0.4 in all cases). The weakness of the load–land cover relationship is largely attributable to the high nitrogen loading from the agricultural catchment, McDonogh. However, exclusion of this catchment from the analysis still did not result in a significant correlation between impervious surface and the quantity of nitrogen export. There was also no significant relation between land cover or impervious surface and either TN or NO₃⁻ concentrations, with the agricultural catchment included in (p > 0.3 in all cases) or excluded from (p > 0.15 in all cases) the data set.

Figure 6. Quantile-quantile plots of annually (y axis) and seasonally (x axis) based values of nutrient duration curve quantiles for TN at (a) Pond Branch (forest) in water year 2002, (b) Baisman Run (exurban) in water year 2000, and (c) Dead Run (urban) in water year 2004. Quantile values for a discharge are plotted against each other.
Watershed size might also be a potentially important factor in explaining export variations and characteristics, with a larger watershed (with longer stream lengths) being able to process much more N in stream. We therefore include export estimates from several segments in the study which allowed for some control of scaling effects. In the case of the three sites where segment loads were also calculated, NO\textsubscript{3} and TN load contributed from the segment was within 5% of the load contributed from the entire upstream area for the two suburban mainstream sites of Gwynnbrook and Villanova. The third mainstream site, Carroll Park, showed markedly higher mean annual NO\textsubscript{3} and TN loads contributed from the segment downstream of Villanova and Dead Run compared to loads exported from the entire upstream area (from 6.95 to 8.49 kg ha\textsuperscript{-1} a\textsuperscript{-1} NO\textsubscript{3} and 9.67 to 13.43 kg ha\textsuperscript{-1} a\textsuperscript{-1} TN, respectively). Compared to the Gwynnbrook and Villanova segments, the Carroll Park segment shows a marked increase in impervious area in the segment relative to the total upstream area (the Carroll Park segment impervious area rises to 32% compared to 24% for entire Carroll Park watershed, while both the Villanova and Gwynnbrook segments show a <1% difference between segment and overall catchment percent impervious area). This difference may explain, in part, the increase in N export, but factors such as density and age of sewer infrastructure also contribute. For example, while Carroll Park and Dead Run segments have similar impervious surface area, differences in development age and infrastructure may differentiate the total N loads and flow distribution. Development in the Carroll Park segment dates back to the late nineteenth and early twentieth century, while the Dead Run area was built out largely in the mid twentieth century. The Carroll Park segment area is also topographically lower and belowground pipes are more likely to be closer to the water table, facilitating infiltration into the sewer system.

On average, TN and NO\textsubscript{3} concentrations from the Carroll Park segment alone are approximately one third higher than those from the entire upstream area, suggesting sources of nutrients such as sanitary leaks, pet wastes, and lawn fertilization. Mean annual discharge (normalized for area as runoff depth), shows a 10% increase, reflecting the increased impervious surface cover in this segment. However, the impervious area cover nearly doubles between Villanova and the Carroll Park segment, from 17% in the Villanova segment to 32% in the Carroll Park segment. The drainage areas of Villanova and the Carroll Park segment are comparable (81 km\textsuperscript{2} and 66 km\textsuperscript{2}, respectively, Table 1). While Dead Run also contributes to Carroll Park and has a high impervious surface cover (31%), it has a considerably smaller drainage area (14 km\textsuperscript{2}). The small increase in discharge, relative to the impervious surface increase, suggests that there may be substantial loss of water to sanitary sewer lines (currently recognized and being addressed in the consent decree activities). During high-flow events, older infrastructure would also result in a flush of nutrients resulting from surcharging and overflow of sanitary sewer lines, common in older urban areas. The state of the sanitary

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**Table 2. Descriptions of NLCD Land Classes Used in the Analysis**

<table>
<thead>
<tr>
<th>Land Class</th>
<th>Description</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Developed, open space</td>
<td>Mostly vegetation in form of lawn grasses; &lt;20% impervious surface</td>
<td>Large-lot single family housing units, parks, golf courses</td>
</tr>
<tr>
<td>Developed, low intensity</td>
<td>Mix of constructed materials and vegetation; 20–49% impervious surface</td>
<td>Single-family housing units</td>
</tr>
<tr>
<td>Developed, medium intensity</td>
<td>Mix of constructed materials and vegetation; 50–79% impervious surface</td>
<td>Single-family housing units</td>
</tr>
<tr>
<td>Developed, high intensity</td>
<td>Highly developed areas, people reside or work in high numbers; 80–100% impervious surface</td>
<td>Apartment complexes, row houses, commercial/industrial</td>
</tr>
<tr>
<td>Cultivated crop</td>
<td>used for the production of annual crops and perennial woody crops; &gt;20% crop vegetation</td>
<td>corn, soybeans, veget ables, tobacco, cotton, orchards, vineyards</td>
</tr>
</tbody>
</table>

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**Figure 7.** Mean annual TN and NO\textsubscript{3} exports from BES catchments. Bars are arranged in order from least to most impervious surface area.

**Figure 8.** Volume-weighted mean annual TN and NO\textsubscript{3} concentrations of BES catchments. Bars are arranged in order from least to most impervious surface.
sewer systems in Baltimore has been recognized as a source of nutrients, leading to the current consent decree to upgrade sanitary infrastructure [United States of America and State of Maryland versus Mayor and City Council of Baltimore, Maryland, 2002].

[29] Our final analysis of load magnitude, estimating nitrogen contributed from unforested areas (obtained by assuming the Pond Branch catchment is representative of forest N export rates across the BES), suggested that very low density development may be an even greater contributor to N load magnitude than aging, leaky, infrastructure and high levels of impervious surface. Unforested portions of the catchment with the lowest level of development, Baisman Run, are exporting TN at a rate of 19.4 kg N ha$^{-1}$ a$^{-1}$ and NO$\textsubscript{3}^-$ at a rate of 19.1 kg N ha$^{-1}$ a$^{-1}$, significantly more than the unforested areas in almost all of the more developed catchments (the agricultural catchment, McDonogh, continues to show the greatest export of N ha$^{-1}$). When “unforested” export estimates from all catchments are compared, the lightly developed suburban area of Baisman Run export is contributing double the nitrogen of some of the more developed catchments, and over four times the nitrate load of the most urban catchment, Dead Run (Figure 9). The high levels of N export from Baisman Run may be due in part to the presence of septic systems (there is no sanitary sewer infrastructure in the Baisman Run catchment) providing a nitrogen-rich water source under all but the very lowest-streamflow conditions. This hypothesis is supported by the time series of NO$\textsubscript{3}^-$ concentrations (Figure 4b).

During extreme drought conditions in 2002, NO$\textsubscript{3}^-$ concentrations in Baisman Run plummeted, suggesting a decoupling and increased retention of upslope N from sources such as septic systems. This sharp drop in NO$\textsubscript{3}^-$ concentrations during the drought was not seen in catchments with sanitary sewer infrastructure, such as Dead Run (Figure 4c). This apparent connectivity in areas where septic systems are used to treat and dispose of wastewater indicates that breaking the septic-stream connectivity may significantly reduce N export. Since the extreme conditions that brought about the break seen in this data set are both undesirable and infrequent, other steps, such as upgrading septic systems, increasing setbacks from streams, and improving riparian buffers to reduce source and drainage connectivity by increased uptake, should be considered as a priority.

[30] Our findings suggest that, in addition to agricultural areas, very low density suburbs served by septic systems are major contributors to downstream nitrogen loading, despite their relatively low populations. The hydrology of these catchments, however, may still retain features similar to undeveloped catchments. An examination of flow frequency curves from Pond Branch, Baisman Run, McDonogh and Dead Run (Figure 10) supports this hypothesis that the exurban and agricultural catchments (Baisman Run and McDonogh) retain many of the hydrologic characteristics of the reference site (Pond Branch); flow frequency distributions are nearly identical for the two sites. In contrast, the flow frequency curve at Dead Run is markedly different, with a greater proportion of high-flow events or very low flow events, and fewer moderate-flow events. This combination of high-N export and relatively “natural” hydrology has important implications for restoration and mitigation efforts as restorations generally aim to increase nutrient retention under the low- to moderate-flow conditions which occur frequently in the low-density catchment, while the current high-N export suggests that there is potential for a meaningful reduction.

3.2. Cumulative Frequency Distributions of Nitrogen Export and Effect of Land Use

[31] The nutrient duration curves and F$\textsubscript{75}$ values for both TN and NO$\textsubscript{3}^-$ display marked variation along the urban-rural gradient (Figures 11a and 11b and Table 3). In the forested reference site, Pond Branch, a large proportion of nutrient export occurred under low- to moderate-flow conditions (<1 mm d$^{-1}$). The lightly developed suburban and agricultural catchments, Baisman Run and McDonogh, and to a lesser extent Gwynnbrook, exhibited similar characteristics in their export flow distribution of nitrogen. More heavily developed catchments displayed considerably different characteristics, with much less of the overall load exported under low- to moderate-flow conditions. In the most heavily developed catchment, Dead Run, <25%
of either TN or NO₃ export occurred at flows <1 mm d⁻¹ (note that we use 1 mm d⁻¹ as an arbitrary representation of moderate to low flow, without indicating whether this is base flow). Of the three nested sites where the duration characteristics was also calculated for a segment between gauges, segment export distribution characteristics were similar to total upstream export distribution in the case of the suburban Villanova and Gwynnbrook catchments. However, the third mainstream catchment, Carroll Park, showed a sharp increase in F₇₅, with a much greater proportion of TN and NO₃ exported under high-flow conditions. As mentioned above, Carroll Park has a much higher impervious surface area and sanitary sewer density and age compared to upstream areas. This increase in F₇₅ also indicates that the chronic augmentation of N levels at low to moderate flows from sanitary sewer leakage is being outweighed by flushing of N under high-flow conditions from sources such as sanitary sewer surcharging and surface N mobilization.

We found a significant correlation between catchment impervious surface area and discharge at which 75% of TN and NO₃ is exported (Figures 12a and 12b). As the fraction of impervious surface in a catchment increases, a correspondingly higher proportion of the nitrate load is exported during high-flow events. Strong but slightly less significant correlations were also found between F₇₅ of nitrogen export and the developed land cover classes considered in this study (Table 4). No significant correlation existed between F₇₅ and the fifth class, cultivated crops, but agriculture is a very small component of the catchments with the exception of McDonogh. Land cover was also not a significant predictor of either F₅₀ or F₂₅.

This correlation between F₇₅ and upslope impervious surface shows that impervious area is closely associated with

![Figure 11](image1)

**Figure 11.** Cumulative (a) TN and (b) NO₃ export as a function of discharge at Pond Branch (forested), Baisman Run (exurban), Glyndon (suburban), Dead Run (urban), and McDonogh (agricultural) catchments. Discharge representative of 75% of cumulative TN and NO₃ export is summarized for all sites in Table 3.

<table>
<thead>
<tr>
<th>Site</th>
<th>TN F₇₅ (mm d⁻¹)</th>
<th>NO₃ F₇₅ (mm d⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pond</td>
<td>0.76</td>
<td>1.56</td>
</tr>
<tr>
<td>Baisman Run</td>
<td>1.92</td>
<td>1.98</td>
</tr>
<tr>
<td>Villanova</td>
<td>5.71 (6.11)</td>
<td>4.31 (4.34)</td>
</tr>
<tr>
<td>Carroll Park</td>
<td>7.69 (34.00)</td>
<td>6.21 (29.25)</td>
</tr>
<tr>
<td>Gwynnbrook</td>
<td>5.74 (5.52)</td>
<td>5.28 (5.05)</td>
</tr>
<tr>
<td>Glyndon</td>
<td>6.04</td>
<td>8.75</td>
</tr>
<tr>
<td>Dead Run</td>
<td>21.29</td>
<td>16.44</td>
</tr>
<tr>
<td>McDonogh</td>
<td>2.70 (2.95)</td>
<td>2.79 (2.45)</td>
</tr>
</tbody>
</table>

aSegment values are given in parentheses.
the streamflow distribution of nitrogen export in human-dominated ecosystems, with more heavily impervious areas tending to have a greater N export occurring under high-flow conditions. One possible explanation for this relationship is that the increase in directly connected impervious surface in the form of roads draining into storm sewers may more effectively route N fertilizers and other surface sources of N that are mobilized by overland flow and thus only flushed from adjacent developed areas during storm events. Five of the catchments in this study (DR, CP, GB, GL, and VN) contain at least 15% impervious surface, sufficient to exhibit this hydrologic change. In contrast, in areas with very little impervious surface, more “natural” hydrologic characteristics are retained, and the majority of N export takes place under low- to moderate-flow conditions (even when overall N export is quite high).

[34] In addition to the direct hydrologic connection, impervious surface can also be an indicator for types of development or practices within a catchment [Arnold and Gibbons, 1996] that impact the availability and spatial distribution of nitrogen within a catchment. Developed catchments have direct inputs of nitrogen in the form of lawn and garden fertilizer applications, as well as septic or sanitary sewer leakage. Increased impervious surface area can be an indicator for the ratio of septic to sanitary infrastructure. In areas with sanitary sewers, either combined or separate, storm events can cause sanitary sewer overflow and surcharging, greatly increasing the proportion of N exported under high-flow conditions, as evidenced by the high F75 values seen in the Carroll Park segment where sanitary infrastructure is dense and aging. While the majority of the Baltimore city and county sewers are separate, remnant areas of combined sewers still exist. In contrast, low levels of impervious surface area are generally associated with on-site septic waste treatment, which is associated with increased base flow [e.g., Burns et al., 2005], and higher N concentrations [Heisig, 2000; Kaushal et al., 2006].

[35] Impervious surface may also be an indicator of factors affecting surface N availability. For example, a survey of residential lawn care practices conducted in the Glyndon and Baisman Run catchments found a higher rate of fertilizer application per unit lawn area in Glyndon (more impervious) than in Baisman Run [Law, 2003]. If this trend is widespread, it would result in a greater availability of surface N to be mobilized during storm events. Another factor to consider is that N deposition may be high immediately adjacent to high traffic volume roads and highways, which would further increase accumulation of surface N in between storm events. Thus, impervious surface area appears to be a strong predictor of the N export characteristics in developed catchments for a variety of potential reasons.

### Table 4. Regression Equations and $r^2$ and $p$ Values Describing Relationship Between Land Cover and Cumulative Export Flow Values

<table>
<thead>
<tr>
<th>Land Cover</th>
<th>TN Equation</th>
<th>$r^2$</th>
<th>$p$</th>
<th>NO3 Equation</th>
<th>$r^2$</th>
<th>$p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impervious</td>
<td>$y = 1.57e^{0.08x}$</td>
<td>0.86</td>
<td>&lt;0.005</td>
<td>$y = 2.01e^{0.06x}$</td>
<td>0.89</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>Open</td>
<td>$y = 1.51e^{0.08x}$</td>
<td>0.77</td>
<td>&lt;0.005</td>
<td>$y = 1.89e^{0.06x}$</td>
<td>0.87</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>Cultivated crops</td>
<td>$y = 4.65e^{0.01x}$</td>
<td>0.02</td>
<td>0.75</td>
<td>$y = 4.95e^{-0.01x}$</td>
<td>0.04</td>
<td>0.62</td>
</tr>
<tr>
<td>High intensity</td>
<td>$y = 2.32e^{0.29x}$</td>
<td>0.79</td>
<td>&lt;0.005</td>
<td>$y = 2.32e^{0.29x}$</td>
<td>0.79</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>Medium intensity</td>
<td>$y = 2.12e^{0.11x}$</td>
<td>0.82</td>
<td>&lt;0.005</td>
<td>$y = 2.11e^{0.11x}$</td>
<td>0.82</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>High intensity</td>
<td>$y = 2.32e^{0.29x}$</td>
<td>0.79</td>
<td>&lt;0.005</td>
<td>$y = 2.32e^{0.29x}$</td>
<td>0.79</td>
<td>&lt;0.005</td>
</tr>
</tbody>
</table>

3.3. Extrapolation of Export Timing Across the Stream Network

[36] The regression equations correlating land cover and F75 nitrogen export were then used to estimate TN and NO3 F75 values as a function of percent upstream impervious area across the portion of the Gwynns Falls in Baltimore County. Given that our sample sites had a maximum impervious area of 31%, we chose to limit our extrapolation to areas with an impervious surface area similar to those of our sample sites—estimates of F75 are presented only for areas with less than one third impervious surface upstream. Further sampling is needed to identify behavior of the F75—land cover relationship beyond our current data range. This constraint still leaves a substantial portion of the BES stream network to which our regression model can be realistically applied. The resulting map of F75 values for NO3 is shown in Figure 13.

![Figure 13. Predicted NO3 F75 across Baltimore County portion of Gwynns Falls network. F75 values were not estimated for areas where impervious surface >33%. Portions of network with >33% upslope impervious surface are shown in red.](image-url)
F75 values similar to those found in the exurban catchment, Baisman Run, are seen primarily in low-developement first-order and headwater streams above the Gwynnbrook gauge, although there are also segments with low F75 values further downstream. These sites, with the majority of export occurring under low- to moderate-flow conditions, are likely better suited to restoration than more developed areas with high F75 values. Additionally, the low density of development in these catchments also suggests that more space may be potentially available for a restoration, placement of buffers, or other actions that promote increased N retention. Although other factors also need to be taken into consideration (e.g., access, restoration cost, community acceptance and total export magnitude), estimated F75 values are based on readily available data and provide a valuable and objective tool for evaluating likely impact of a restoration on water quality.

4. Conclusions
4.1. Export Flow Distribution Correlated With Development

[37] Our findings support the hypothesis that export flow distribution is well correlated with simple indicators of development. Nutrient duration curves vary significantly along an urban-rural gradient, less densely developed areas export the majority of nitrogen under low- to moderate-flow conditions and more developed, urbanized areas export less nitrogen during low-flow periods and larger proportions of their nitrogen load under high-flow conditions. This variation is significantly correlated to the presence of impervious surface; F75 increases exponentially with increases in impervious surface. This correlation is attributed to several factors. Increased runoff from impervious surfaces and other disturbed cover is coupled with increased N inputs such as atmospheric deposition, leaf litter and pet waste, which accumulate and mobilize largely under high-flow conditions. Second, impervious surface and associated street curbs and storm sewers have a direct influence through increased basin connectivity, resulting in more effective routing of surface N during high-flow events. Finally, impervious surface is also an indirect explanatory variable as it can also serve as a likely indicator of other development factors [Arnold and Gibbons, 1996] that can influence export flow distribution such as lawn and garden fertilization, more heavily compacted soils, and sanitary drainage infrastructure in a catchment.

4.2. No Direct Relationship Between Development Magnitude and N Export

[38] Despite the strong correlation between export flow distribution and impervious surface, our second hypothesis, that magnitude of annual N loads is positively associated with simple indicators of development, was not strongly supported. In Baisman Run, a headwater catchment with very low-density development, a high rate of export is attributed to the high connectivity of septic system plumes to groundwater flow and streamflow, a connection which only appears to decrease under extreme drought conditions. The two most developed areas in the analysis, Dead Run and the Carroll Park segment, further highlighted the lack of clear association between development and magnitude of N export, with the Carroll Park segment exporting approximately twice as much N as the Dead Run segment despite similar fractions of impervious surface area. In this case, the high export levels from the Carroll Park segment are attributed in large part to a higher density of older sanitary sewers and storm inflow and surcharging of combined and separate sanitary–storm sewer systems during high-flow events.

4.3. Prioritizing Stream Channel Restoration for Water Quality Improvement at the Watershed Scale

[39] These results have important implications for the planning and targeting of river restoration techniques designed to reduce N delivery to receiving waters. If in-channel restoration techniques are most effective at low flow, then they should be targeted at areas with high annual loads and lower F75, or coupled with storm water remediation efforts that reduce F75 through alteration of flow duration characteristics.

[40] These findings also have potential applications to land use decisions in rapidly developing exurban areas. Areas of low-density development served by septic systems are potentially large sources of nitrogen, especially on a per capita basis. These areas also appear to have the most potential for mitigating environmental impact through restoration and zoning policies as they have the combination of high load magnitude and export flow distribution (low F75 values) that is most likely to respond to a stream restoration. In more developed catchments, restoration may not always be a practical approach. As discussed by Bernhardt and Palmer [2007], urban stream restorations can be particularly challenging because of the lack of space available to reconfigure the stream channel. Our findings suggest that these areas may also show the least response to restorations, as they appear to export a large proportion of N under high flow. In these catchments, more appropriate actions might include repair and maintenance of sanitary sewers to minimize leakage and surcharging. Reducing increased nitrogen inputs that are primarily mobilized at high flow and the high connectivity of engineered pathways (e.g., impervious surface, curbs) that currently facilitate rapid delivery of surface N to receiving waters during storm events also needs to be a priority. We note that this is currently being addressed by both city and county of Baltimore.

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