EXPORT FLOW DISTRIBUTION AND RESTORATION POTENTIAL OF STREAMS ALONG AN URBAN-RURAL GRADIENT

Catherine A. Shields

A thesis submitted to the faculty of the University of North Carolina at Chapel Hill in partial fulfillment of the requirements for the degree of Master of Arts in the Department of Geography

Chapel Hill

2007

Approved By:

Lawrence E. Band

Martin W. Doyle

Conghe Song

ABSTRACT

Catherine A. Shields: Export Flow Distribution and Restoration Potential of Streams Along an Urban-Rural Gradient (under the direction of Lawrence E. Band)

An investigation of nitrogen export and the potential of restoration as a tool for water quality management in catchments along an urban-rural gradient. Quantity of N exported and flow conditions dominating N export are investigated. These variables are of interest as stream restorations typically aim to increase retention under low-moderate flow. We present a metric characterizing export flow distribution, F_{75}, and develop regressions relating F_{75} to development. We extrapolate F_{75} across a stream network to identify areas where export flow distribution is most favorable for restoration. We then examine potential to increase N retention via restoration. We develop post-restoration N export estimates for a range of uptake velocities (v_f). Results show drainage area is a dominant explanatory variable for reduction; F_{75} may be an important factor within drainage area. Reductions at v_f comparable to other restorations were low, suggesting limited potential for water quality improvement.

ACKNOWLEDGEMENTS

This thesis owes its completion to a great many people and organizations beyond the author. My advisor, Dr. Lawrence Band, deserves particular acknowledgment for his support and encouragement over the past two years of my graduate study, and also for the contagious sense of curiosity and enthusiasm for scientific inquiry in general and ecohydrology in particular which first piqued my interest in this topic as an undergraduate. My committee members, Dr. Martin Doyle and Dr. Conghe Song also provided valuable input that greatly improved the quality of the final thesis. Thanks are also due to Dr. Peter Groffman at the Institute of Ecosystem Studies and Dr. Sujay Kaushal at the University of Maryland Appalachian Research Laboratory for their review of and contributions to drafts of the first chapter. Fellow graduate students Monica Smith, Katerina Savvas, and Carolyn Klocker all provided assistance with field work, analysis, or contribution of supporting data. Finally, I would like to thank my parents, Ian Shields and Patricia McQuaid, for their lifetime of love and support, and their unwavering belief in me.

Funding was provided through a Merit Assistantship from the Graduate School at the University of North Carolina at Chapel Hill, and by the Baltimore Ecosystem Study project, National Science Foundation Long-Term Ecological Research program, grant number DEB 9714835, and by the EPA-NSF joint program in Water and Watersheds, project number GAD R825792. We thank the USDA Forest Service Northeastern Research Station for site management, and in kind services to the BES. In addition we thank the University of Maryland, Baltimore County for their contribution to office and laboratory space at the Research Technology Center on their campus. The City of Baltimore Department of Parks and Recreation and Department of Public Works, the Baltimore County Department of Parks, the Maryland Department of Natural Resources, and the McDonogh School all kindly provide access or management of land used by the Baltimore Ecosystem Study for ecological, hydrological, and meteorological field studies. Additional support and assistances has been provided by agencies, communities and individuals who are specifically acknowledged in the datasets and publications summarizing work the facilitated.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

STREAMFLOW DISTRIBUTION OF NON-POINT SOURCE NITROGEN EXPORT FROM URBAN-RURAL CATCHMENTS IN THE CHESAPEAKE BAY WATERSHED

Abstract

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 flowpath retention. Stream restoration is a BMP targeted to multiple purposes, but includes increasing flowpath 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 increasing development in watersheds is associated with shifts in nitrogen export towards 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 (NO_3^-) loads at relatively low flows. More urbanized sites exports TN and NO_3^- 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 identifying variations in export distribution and targeting stream channel restoration efforts at the watershed scale.

1.1 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, Pontius et al 2000, Weller et al 2003, Boyer et al 2002, Strayer et al 2003, Wollheim et al 2005, Walsh et al 2005, and others). In the Chesapeake Bay, as in other estuaries worldwide, non-point source N export from urban and urbanizing coastal watersheds is considered a major contributor to eutrophication (Howarth et al 2002, Glibert et al 2005, Boyer et al 2002) and degradation of water quality, fisheries and other ecosystem services.

A recognized need to mitigate and reverse impacts of human-dominated ecosystems on water quality has made stream restoration a multi-billion dollar industry, with a majority of stream restoration projects listing improvements in water quality as a goal (Bernhardt et al 2005). 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 sediment (Kasahara and Hill 2005). Recently, Bernhardt and Palmer (2007) discussed the difficulty of achieving water quality improvement through restoration of urban streams due to 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 are 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.

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 NO_3 concentrations display a weak relationship to stream discharge when compared with a forested watershed (Wollheim et al 2005). These findings suggest that dilution of N or

NO_3^- concentration at high flows is not significant in urban catchments, promoting dominant N loads at high flow conditions. In less developed catchments, greater baseflow 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 baseflow 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.

Burns et al (2005b), Sherlock et al (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 septics, the lawn sources in the Oregon suburban site show increased stormflow nitrogen exports, with low flow export reduced by small wetlands acting as a nitrogen sink,but that higher flows effectively transport nitrogen load through the wetland with little retention.

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 flowpaths activate during storm events or seasonal wet periods (e.g. Creed et al 1996, Creed and Band 1998a,b, 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), stormwater mobilization of lawn fertilizer from surburban lawns and nutrients accumulated on impervious surfaces, and fertilizer from larger portions of the landscape during wet-up in the agricultural catchments in Oregon (Poor and McDonnell 2007) and the Midwest of the United States (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.

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:

- 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
- The magnitude of N export is also positively associated with increased development

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

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.

1.2. Data and Methods

1.2.1 Study site

The Baltimore Ecosystem Study (BES, http://www.beslter.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 1.1) 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.

Watershed population in the year 2000 was approximately 356,000 people, with sub-watershed densities ranging from 2.2 to 19.4 persons/ha. Average annual precipitation is 1060 mm y^{-1} and stream discharge is 380 mm y^{-1} (Froelich et al. 1980,

Figure 1:1 Gwynns Falls watershed and study sites in Baltimore City and County.

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 interfluves with shallower soils and bedrock outcrops downslope. Valley bottoms have alluvial soils that can be locally thick from accumulated agricultural sediment.

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 km^2, and encompass a variety of land use types (Table 1.1). 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 waste water treatment plants upstream of any sites considered in this paper.

Table 1.1: Impervious surface and land cover composition of catchments (segment area values in parentheses)

Catchment	Percent of catchment in land class								
					Developed classes				
	area (ha)	Impervious surface	Cultivated Crop	Forest	Open	Low	Medium	High	Other
Pond Branch	38	0	0	100	0	0	0	0	0
Baisman Run	382	>0.26	2	71	1.4	0.19	0	0	25
Glyndon	81	19	5	19	26	19	12	4	15
Gwynnbrook	1065 (984)	15 (15)	8 (8)	17 (16)	21 (20)	25 (25)	6 (5)	5 (1)	18 (25)
Villanova	8349 (7284)	17 (17)	10 (10)	24 (24)	17 (16)	21 (21)	9 (10)	2 (3)	17 (16)
Dead Run	1414	31	2	5	27	41	16	6	3
Carroll Park	16378 (8029)	24 (32)	6 (1)	18 (14)	20 (22)	26 (29)	15 (21)	5 (9)	10 (4)
McDonogh	7.8	0	70	26	0	0	0	0	4

Land use change associated with urbanization over the last few decades has been shown to increase stormwater 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 streamwater 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 streamwater nitrate concentration at low flow

Baltimore City and County have each entered into a consent decree with the US Environmental Protection Agency (EPA), agreeing to spend approximately $800 million each to reduce the quantity of N they discharge into the Chesapeake Bay (EPA 2002, 2005). This reduction will primarily be effected through improvement of sanitary infrastructure , but a commitment has also been made to restoring degraded streams (EPA 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.

1. 2.2 Data

Stream discharge is continuously monitored by the US 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 (NO_3^-) 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 NO_3^- (Ameel et al. 1993). Nitrate in these digests was analyzed on a Perstorp Flow Solutions 3000 flow injection analyzer.

Both stream discharge and chemistry data cover the period October 1998-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), extreme precipitation (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 Figure 1.2a-c.

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

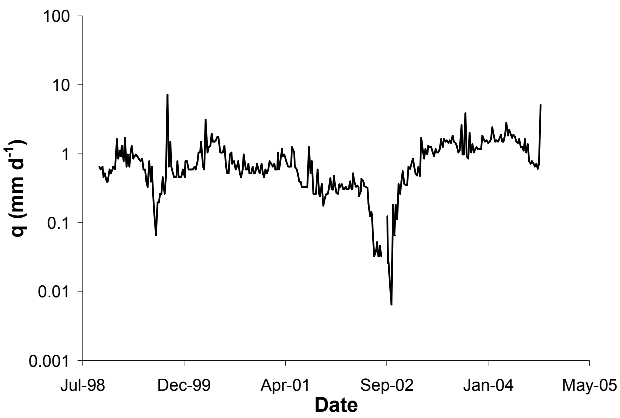

Figure 1.2a

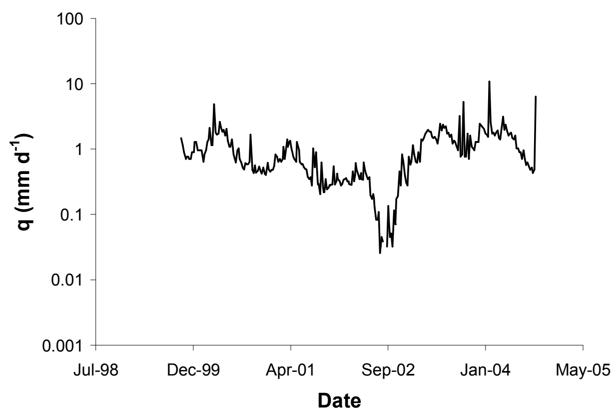

Figure 1.2b

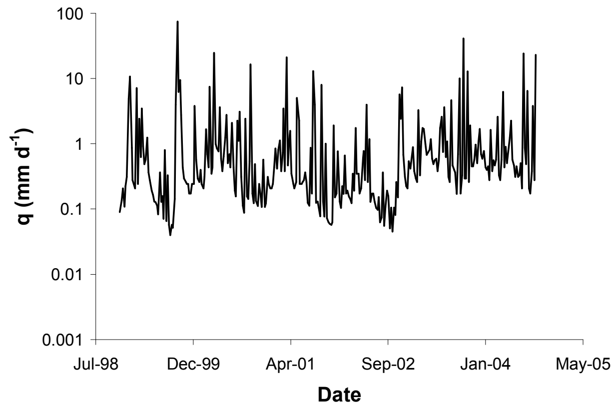

Figure 1.2c

Figures 1.2a-c: Time series of stream discharge for Pond Branch (forest, a), Baisman Run (exurban, b), and Dead Run (urban, c) catchments. Discharge has been normalized for area and is shown as a depth, mm/d.

used in our analysis is 30 meters. Construction of the layers available in the NLCD is discussed in detail in 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.

1.2.3 TN and NO_3^- load estimates and cumulative frequency distributions

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 1.3a-c show concentration/discharge (c-q) plots for the Pond Branch, Baisman Run and Dead Run catchments which cover the range of land use from forest, low density suburban and urban. We estimated 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 estimates of export. Due to considerable interannual variability in runoff range and nutrient concentrations during periods of extreme drought and extreme precipitation (Figures 1.4 a-c), we treated samples from each water year in the study period separately when developing daily load estimates.

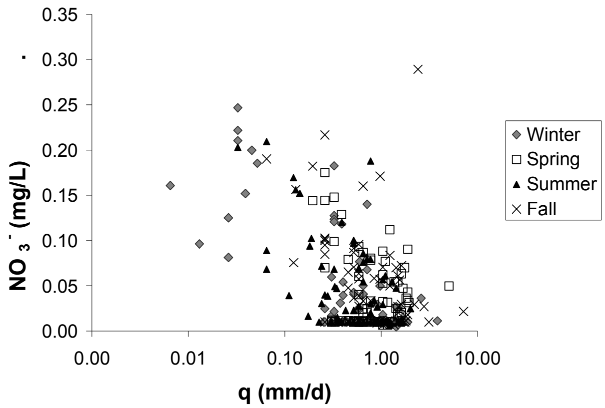

Figure 1.3a

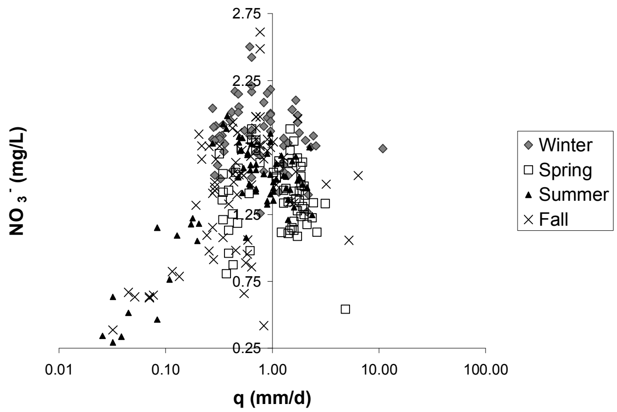

Figure 1.3b

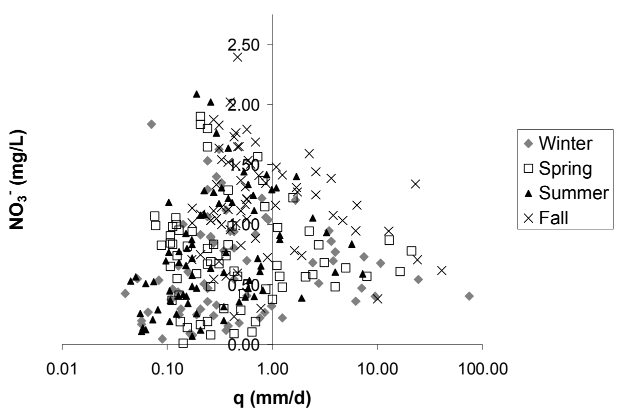

Figure 1.3c

Figures 1.3a-c: NO_3^- as a function of discharge at the Pond Branch (forest, a), Baisman Run(exurban, b), and Dead Run (urban, c) catchments. Concentration-discharge relationships are nonmonotonic and display some seasonal variation, with highest NO_3^- concentrations generally occuring in the winter months (December-February).

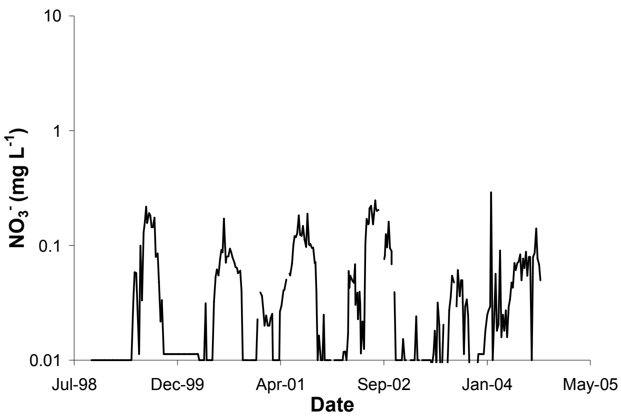

Figure 1.4a

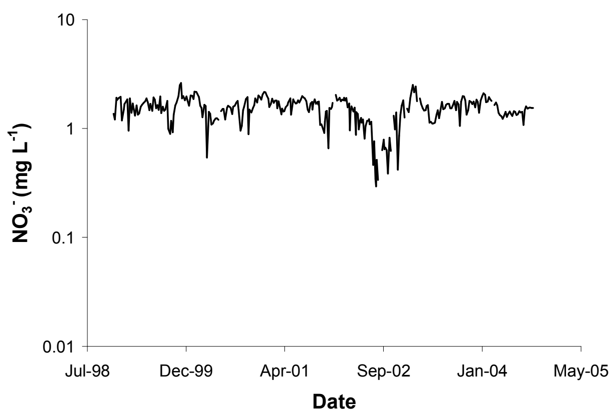

Figure 1.4b

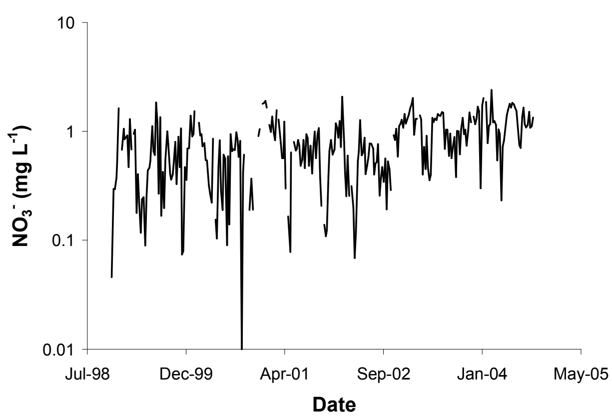

Figure 1.4c

Figures 1.4a-c: Time series of [NO_3^-] for the Pond Branch (forest, a), Baisman Run (exurban, b), and Dead Run (urban, c) catchments.

Figures 1.5a and b 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 mean annual estimates calculated using the Fluxmaster program developed by USGS (Schwarz 2006). For a set of the catchments, a regression with zero intercept of bin-averaged vs. 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 (c-q) 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. Figure 1.3a-c). However, seasonal variation in concentrations at fixed discharge are an order of magnitude lower than inter-site 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, Autumn: September-November), aggregating to annual loads and nutrient duration curves and comparing to annually based calculation (e.g. Figures 1.6a-c). 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; flow duration curves were also constructed 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

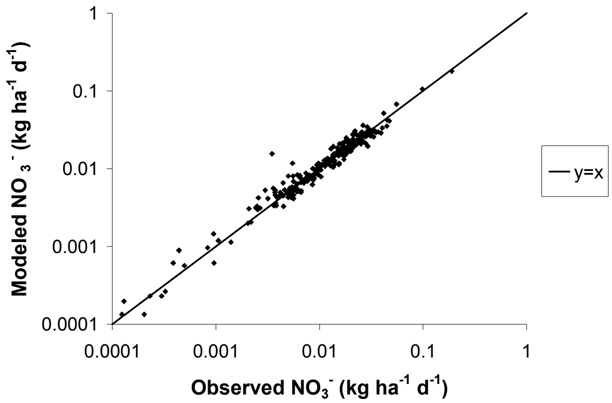

Figure 1.5a

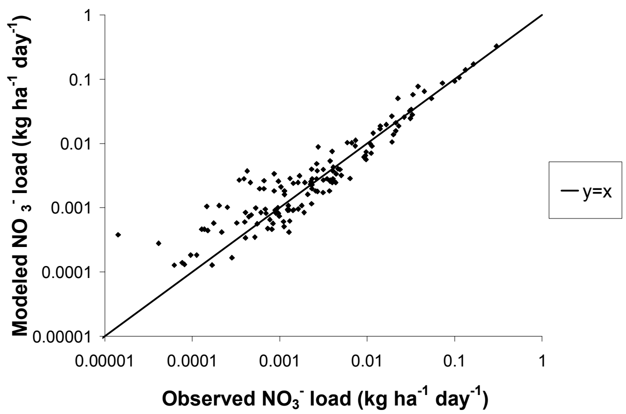

Figure 1.5b

Figures 1.5a-b: Modeled vs. Observed daily NO_3^- loads for the Baisman Run (exurban, a) and Dead Run (urban, b) catchment. 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.

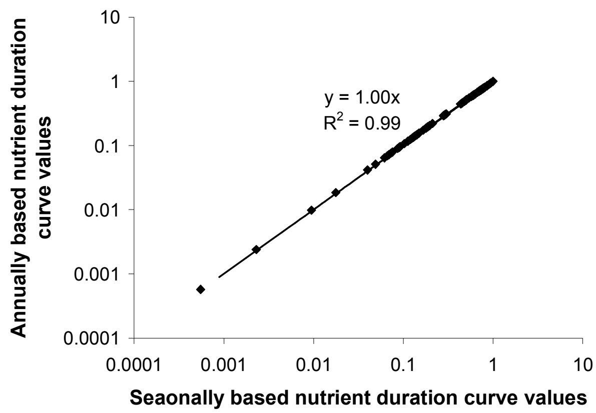

Figure 1.6a

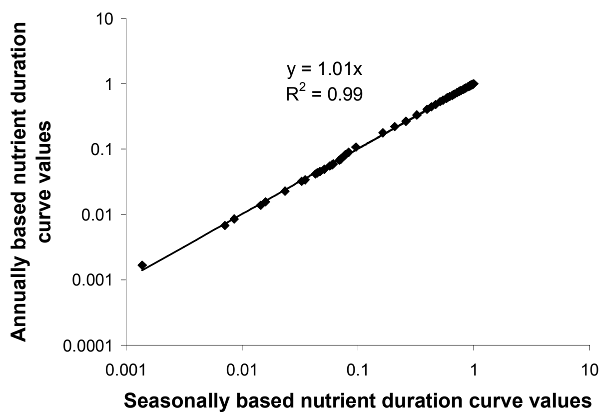

Figure 1.6b

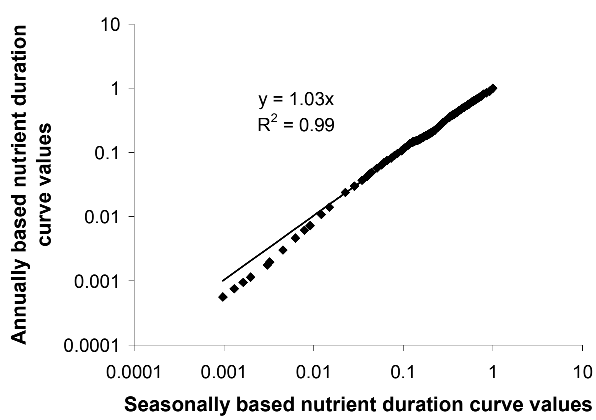

Figure 1.6c

Figure 1.6 a-c: Quantile-Quantile plots of annually (y-axis) and seasonally (x-axis) based values of nutrient duration curve quantiles for TN at Pond Branch (forest, a) in water year 2002, Baisman Run (exurban, b) in water year 2000, and Dead Run (urban, c) in water year 2004. Quantile values for a discharge are plotted against each other.

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.

1.2.4 Extraction of land cover data/weighted flow accumulations

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 1.2). 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 in 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, http://hydrology.neng.usu.edu/taudem/).

Table 1.2: Descriptions of NLCD land classes used in analysis

Land class	Description	Examples
Developed, Open space	Mostly vegetation in form of lawn grasses <20% impervious surface	Large-lot single family housing units Parks Golf courses
Developed, Low intensity	Mix of constructed materials and vegetation 20-49% impervious surface	Single family housing units
Developed, Medium intensity	Mix of constructed materials and vegetation 50-79% impervious surface	Single family housing units
Developed, High intensity	Highly developed areas, people reside or work in high numbers 80-100% impervious surface	Apartment complexes Row houses Commercial/industrial
Cultivated Crop	used for the production of annual crops and perennial woody crops >20% crop vegetation	corn, soybeans, vegetables, tobacco, cotton orchards, vineyards

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.

1.2.5 Export flow distribution as a function of impervious surface and landcover

To quantify the relationship between nitrogen export timing and land cover, we consider TN and NO_3^- 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 (referred to throughout as F_{25}, F_{50}, and F_{75}) 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 NO_3^- export for each catchment. 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.

1.3. Results and Discussion

1.3.1 Load magnitude and volume weighted concentrations

Both the volume weighted concentrations and mean annual export of N show a considerable variation between catchments. The forested reference catchment has significantly lower mean concentrations of TN and NO_3^- while the agricultural

McDonogh catchment has the highest, with the urbanized catchments intermediate. (Figures 1.7 and 1.8). 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 linear along the urban-rural gradient, with the most heavily developed catchment, Dead Run, displaying low mean annual NO_3^- export and concentration relative to other developed catchments. No significant correlation was found between either TN or NO_3^- 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 NO_3^- concentrations, with the agricultural catchment included in ($p>0.3$ in all cases) or excluded from ($p>0.15$ in all cases) the dataset.

Watershed scale 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_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_3^- and TN loads contributed from the segment downstream of Villanova and Dead Run compared to

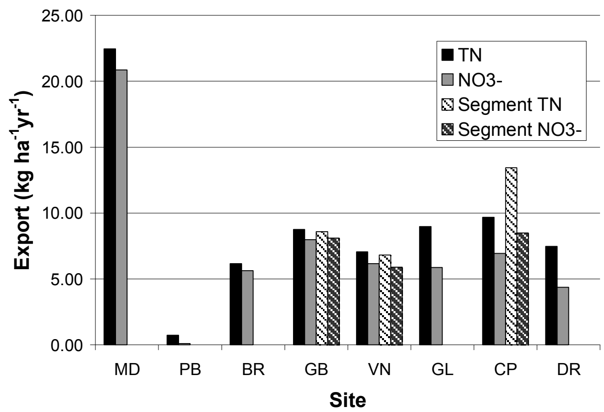

Figure 1.7

Figure 1.7: Mean annual TN, NO_3^- export from BES catchments. Bars are arranged in order from least to most impervious surface area

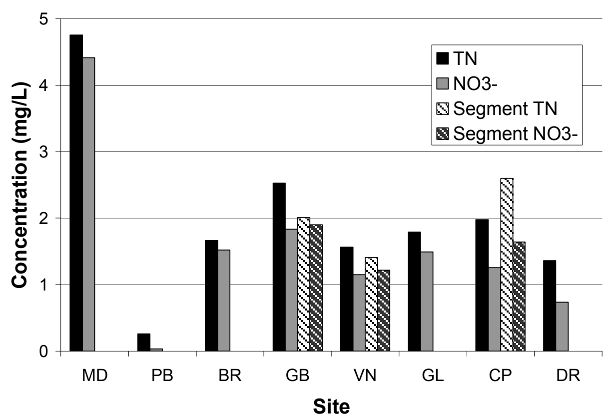

Figure 1.8

Figure 1.8: Volume weighted mean annual TN, NO_3^- concentrations of BES catchments. Bars are arranged in order from least to most impervious surface

loads exported from the entire upstream area (from 6.95 to 8.49 kg/ha NO_3^- and 9.67 to 13.43 kg/ha 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 (8% more area in the Carroll Park segment compared to <1% changes in both the Villanova and Gwynnbrook segments). 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. The Carroll Park segment area is also topographically lower and belowground pipes are more likely to be closer to the water table, facilitating interaction between stream and sewer. On average, TN and NO_3^- concentrations from the Carroll Park segment alone are approximately one-third higher than those from the entire upstream area. Discharge (normalized for area as runoff depth), shows only a 10% increase, suggesting sources of nutrient rich water from sources such as sanitary leaks, pet wastes, and lawn fertilization. The relatively small increase in discharge suggests that there may be substantial inflow and infiltration (I/I) to sanitary sewer lines (currently being addressed in the consent decree activities), further magnifying the effect of urban sources on stream N concentrations. 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 sewer systems in Baltimore has been recognized as a source of nutrients, leading to the current consent decree to upgrade sanitary infrastructure (EPA 2002).

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} yr^{-1} and NO_3^- at a rate of 19.1 kg N ha^{-1} yr^{-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). When "unforested" export estimates from all catchments are compared, the lightly developed Baisman Run catchment 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 1.9). 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 even under all but the very lowest streamflow conditions. This hypothesis is supported by the time series of NO_3^- concentrations (Fig 1.4b). During extreme drought conditions in 2002, NO_3^- concentrations in Baisman Run plummeted, suggesting a decoupling and increased retention of upslope N sources such as septic systems. This sharp drop in NO_3^- concentrations during the drought was not seen in catchments with sanitary sewer infrastructure, such as Dead Run (Fig 1.4c). This apparent connectivity with septic systems also indicates that in areas where septic systems are used to treat and dispose of wastewater, breaking the septic-stream connectivity may be key to reducing N export, and potentially more effective than actions

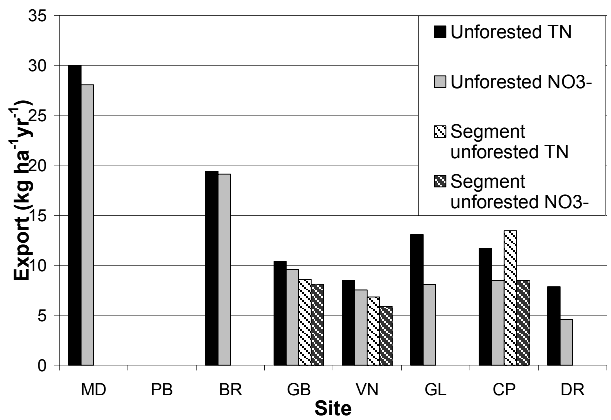

Figure 1.9

Figure 1.9: Mean annual TN, NO_3^- export from unforested areas of BES catchments. Unforested export estimates are calculated assuming forested areas across the BES export N at the same rate as the forested reference site. Forested export is then removed from total export and the remaining N export is divided by unforested catchment area.

such as stream channel restorations. Since the extreme conditions that brought about the break seen in this dataset are both undesirable and infrequent, other steps, such as distancing septic systems from the riparian area and placing buffers to disrupt drainage connectivity by increased uptake, should be considered.

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 1.10) 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.

1.3.2 Cumulative frequency distributions of nitrogen export and effect of land use

The nutrient duration curves and F_{75} values for both TN and NO_3^- display marked variation along the urban-rural gradient (Figures 1.11a-b, Table 1.3). In the forested

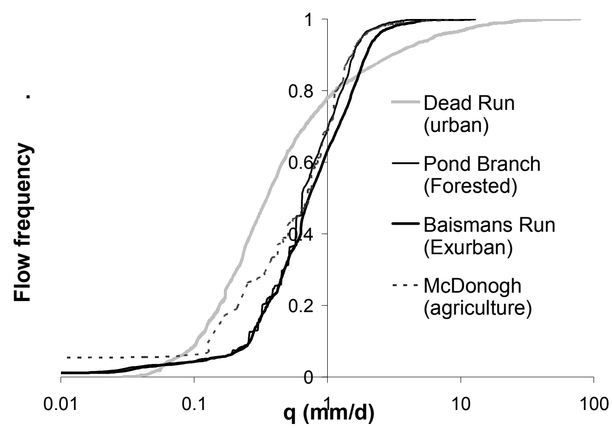

Figure 1.10

Figure 1.10: Catchment flow distribution from Pond Branch (forest), Baisman Run (exurban), Dead Run (urban), and McDonogh (agriculture). Discharge is normalized for area and shown as mm d^{-1}.

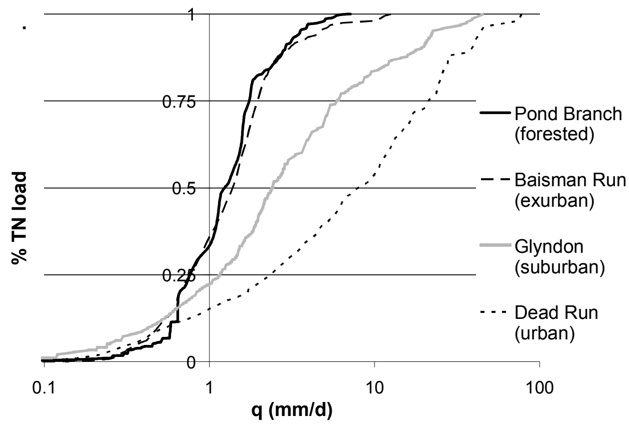

Figure 1.11a

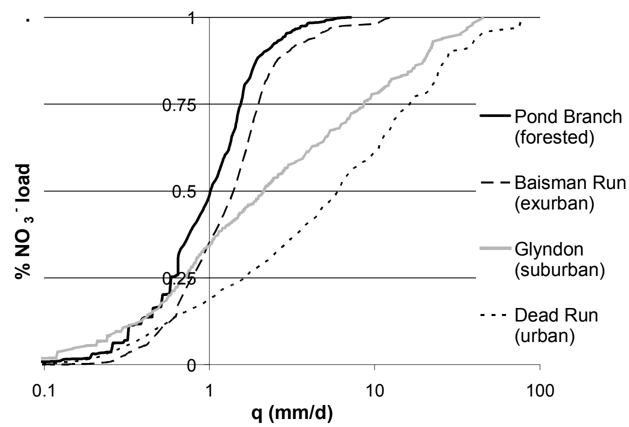

Figure 1.11b

Figure 1.11a-b: Cumulative TN (a) and NO_3^- (b) export as a function of discharge at Pond Branch (forested), Baisman Run (exurban), Glyndon (suburban), and Dead Run (urban) catchments. Discharge representative of 75% of cumulative TN and NO_3^- export is summarized for all sites in Table 1.3

Table 1.3: F_{75} values for each catchment, with segment values in parentheses.

Site	TN F_{75} (mm/d)	NO_3^- F_{75} (mm/d)
Pond	0.76	1.56
Baisman Run	1.92	1.98
Villanova	5.71 (6.11)	4.31 (4.34)
Carroll Park	7.69 (34.00)	6.21 (29.25)
Gwynnbrook	5.74 (5.52)	5.28 (5.05)
Glyndon	6.04	8.75
Dead Run	21.29	16.44
McDonogh	2.70	2.79

reference site, Pond Branch, a large proportion of nutrient export occurred under low to moderate flow conditions (<1 mm/d). 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 NO_3^- export occurred at flows <1mm/d (note that we use 1mm/day as an arbitrary representation of moderate to low flow, without indicating whether this is baseflow). Of the three nested sites where the duration curve was also calculated for a segment between gauges, the segment exhibited export distribution characteristics 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 F_{75}, with a much greater proportion of TN and NO_3^- 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 F_{75} also indicates that the chronic augmentation of N levels at low to moderate flows from sanitary inflow 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 NO_3 is exported (Figures 1.12a-b). 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

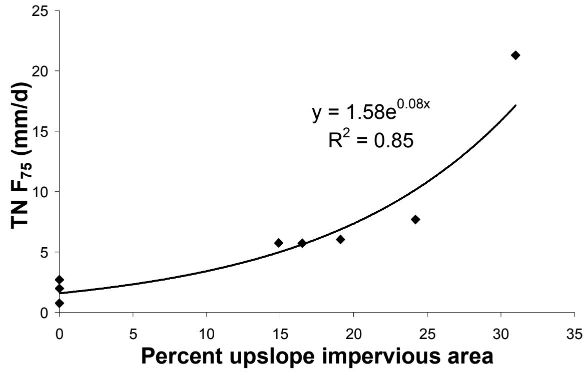

Figure 1.12a

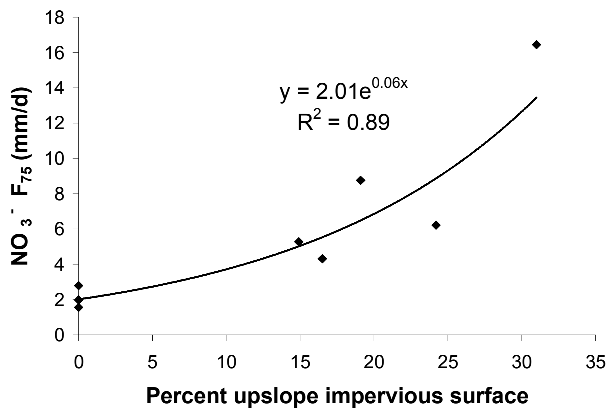

Figure 1.12b

Figure 1.12a-b: TN and NO_3^- F_{75} vs. upslope impervious surface area significant correlations were also found between F_{75} of nitrogen export and the developed land cover classes considered in this study (Table 1.4). No significant correlation existed between F_{75} 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 F_{50} or F_{25}.

This correlation between F_{75} and upslope impervious surface shows that impervious area is closely associated with 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).

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

Table 1.4: Regression equations, r^2 and p values describing relationship between landcover, cumulative export flow values and mean annual export.

Land Cover	TN equation	r^2	p	NO_3^- equation	r^2	p
Impervious	$y=1.57e^{(0.08x)}$	0.86	<0.005	$y=2.01e^{(0.06x)}$	0.89	<0.005
Open	$y=1.51e^{(0.08x)}$	0.77	<0.005	$y=1.89e^{(0.06x)}$	0.87	<0.005
Cultivated Crops	$y=4.65e^{(0.01x)}$	0.02	0.75	$y=4.95e^{(-0.01x)}$	0.04	0.62
High Intensity	$y=2.32e^{(0.29x)}$	0.79	<0.005	$y=2.32e^{(0.29x)}$	0.79	<0.005
Medium Intensity	$y=2.12e^{(0.11x)}$	0.82	<0.005	$y=2.11e^{(0.11x)}$	0.82	<0.005
High Intensity	$y=2.32e^{(0.29x)}$	0.79	<0.005	$y=2.32e^{(0.29x)}$	0.79	<0.005

with sanitary sewers, either combined or seperate, 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 F_{75} 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).

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.

1.3.3 Extrapolation of export timing across the stream network

The regression equations correlating land cover and F_{75} nitrogen export were then used to estimate TN and NO_3^- F_{75} 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 F_{75} are presented only for areas with less than one-third impervious surface upstream. Further sampling is needed to identify behavior of the F_{75}-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 F_{75} values for NO_3^- is shown in Figure 1.13. F_{75} values similar to those found in the exurban catchment, Baisman Run, are seen primarily in low development first order and headwater streams above the Gwynnbrook gauge, although there are also segments with low F_{75} 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 F_{75} 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 F_{75} values are based on readily available data and provide a valuable and objective tool for evaluating likely impact of a restoration on water quality.

1.4. Conclusions

1.4.1. Export flow distribution correlated with development

Our findings support the hypothesis that export flow distribution is well-correlated with simple indicators of development. Nutrient duration curves vary

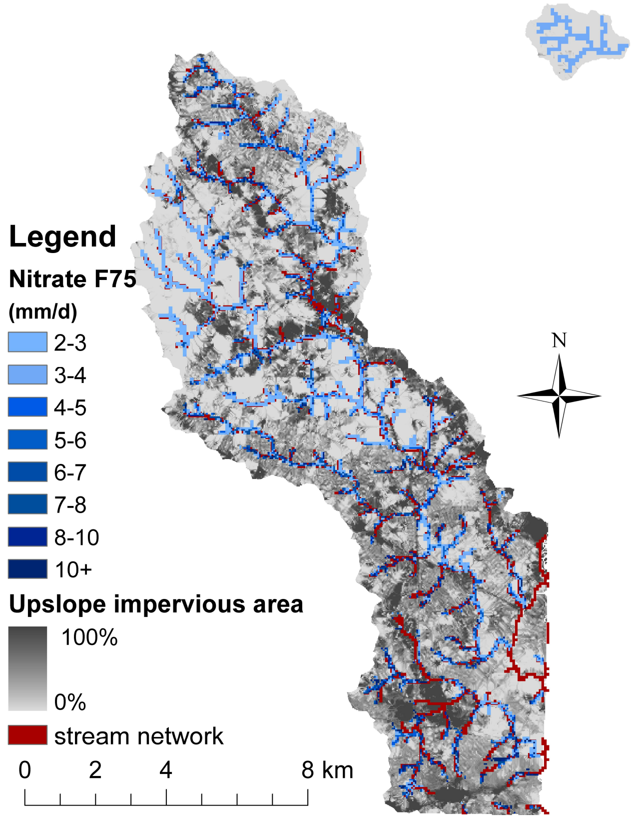

Figure 1.13

Figure 1.13: Predicted NO_3^- F_{75} across Baltimore County portion of Gwynns Falls network. F_{75} values were not estimated for areas where impervious surface >33%. Portions of network with >33% upslope impervious surface are shown in red.

significantly along an urban-rural gradient, less densely developed areas exporting the majority of nitrogen under low to moderate flow conditions and more developed, urbanized areas exporting 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, F_{75} increases exponentially with increases in impervious surface. This correlation is attributed to several factors. Increased N inputs from sources such as atmospheric deposition, leaf litter and pet waste accumulate on impervious surfaces and mobilize largely under high flow conditions. Secondly, 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.

1.4.2 Magnitude of N export does not show direct relationship with development

Despite the strong correlation between export flow distribution and impervious surface, our second hypothesis, that magnitude of 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, ahigh 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.

1.4.3. Prioritizing stream channel restoration for water quality improvement at the watershed scale

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 F_{75}, or coupled with stormwater remediation efforts that reduce F_{75} through alteration of flow duration characteristics.

These findings also have potential applications to land use decisions in rapidly developing exurban areas. 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 F_{75} 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 due to 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.

1.4.4 Future Research

Future analyses could utilize a more refined land cover classification—NLCD is appealing because it is widely used and available. However, alternative classifications might better account for human influences and infrastructure contributing to nitrogen loading, such as septic systems (Cadenasso et al. 2007). Additionally, an expansion of our study sites to include areas outside the BES with different land cover compositions would allow for further refinement of the model. Further work is also needed to determine how applicable this model is to other developed areas. Finally, although we found impervious surface area to be a significant explanatory variable of export flow distribution, our analysis did not include data from areas with more than a third of contributing area classed as impervious, as no such data currently exists within the BES. Increased sampling of such areas would allow us to identify the point at which the exponential relationship between F_{75} and land cover begins to asymptote, and adjust our model accordingly.

SUMMARY AND TRANSITION

The first chapter of this thesis investigated export flow distribution of nitrogen along an urban-rural gradient in Baltimore, MD and presented a metric for characterizing this distribution, the F_{75}. We then established a significant link between catchment F_{75} and development, as indicated by percent upslope impervious surface. We suggest that export flow distribution is an important factor to consider in prioritizing streams for restoration, as restoration typically aims to improve nitrogen retention under low to moderate flow conditions. A stream with low F_{75} and high NO_3^- export would therefore presumably be most likely to respond well to a restoration.

The second chapter builds on these findings by investigating the restoration potential of each of the developed study sites. We assume a typical restoration length and apply first order uptake models using a range of uptake velocity values comparable to those found in relevant literature. We simulate nitrate export in each catchment over the 1998-2004 period assuming a series of elevated uptake velocities. We then compare these estimates to the quantity of nitrate estimated to have actually been exported over the same period. Three possible explanatory variables for changes in export are considered: F_{75}, catchment drainage area, and current NO_3^- export. Based on our modeled estimates and post-restoration uptake velocities reported at sites in the Baltimore area, we conclude that increases in NO_3^- retention resulting from restoration are likely to be modest. Further post-restoration monitoring of effectiveness and stability is needed at a range of sites to more firmly establish this finding.

CHAPTER II.

EVALUATING THE POTENTIAL OF STREAM RESTORATION AS A TOOL FOR INCREASED NUTRIENT RETENTION

Abstract

Stream and river restoration is frequently presented as a useful tool for improving water quality in degraded areas. However, the potential of a restoration to achieve water quality goals may vary depending on local site and contributing watershed conditions. The ability of a stream restoration to achieve significant increases in retention (or reduction in loads) is based on a number of factors, including pre-restoration loads, export flow distribution of nutrients, and channel size or other geomorphic characteristics. However, little monitoring of post-restoration water quality currently occurs in most regions and the level of reduction in nutrient export that can reasonably be achieved is not well-defined or understood. Here, we present estimates of nitrate (NO_3^-) export expected to result from restorations assuming specific increased uptake velocity (v_f) levels in a set of catchments along an urban-rural gradient in Baltimore, Maryland. Drainage area (through variation in discharge, depth and velocity) is the dominant determinant of percent reductions in NO_3^- load, which are greatest in small headwater

catchments with moderate to high rates of annual NO_3^- export. However, greatest absolute reductions in magnitude may potentially occur in larger streams, assuming elevated v_f values can be maintained. Although not statistically significant within our sample set, catchment land use and export flow distribution of NO_3^- appears to also have a potential role, with sites less developed sites where the majority of NO_3^- export occurs under low to moderate flow conditions showing a greater reduction in NO_3^- than more developed sites where a greater proportion of NO_3^- is exported under high flow conditions.

2.1 Introduction

In recent decades, concern over the degradation of stream and river ecosystems stemming from human activity and development has been widespread. One frequently proposed method of combating this degradation is a restoration of the degraded area, with the goal of returning the degraded waterway to something more closely resembling its "natural" condition. The restoration approach has been applied at multiple sites globally (Bernhardt et al 2005, Holmes 1998, Henry et al 2002). Within the US, restoration is now a multibillion dollar industry (Palmer et al 2005). The Chesapeake Bay Watershed (CBW), where the catchments presented in our analysis are located, is a particular restoration hotspot, with an estimated $426 million spent on restoration projects since 1990 (Hassett et al 2005).

The goals of stream restorations range from restoring degraded habitat for aquatic species to simply improving the aesthetics of the riparian area. Within the Chesapeake Bay watershed, improved water quality is the second most frequently listed goal of restorations, and the primary goal of most urban restorations (Hassett et al 2005). However, the effectiveness of restorations in realizing these goals is currently not well understood. Very little post-restoration monitoring of water quality is currently required or undertaken in most regions, including the Chesapeake. As a result, information concerning the advisability of restoring for water quality, what restoration techniques are most effective in improving water quality, or what kinds of streams and catchments might respond most favorably to a restoration is limited. Royer et al (2006) found that in a set of tile drained agricultural catchments in the Midwestern U.S. actions such as restoration, aimed at increasing nutrient retention at low to moderate flows, were unlikely to result in a significant reduction in either N or P export. This finding was attributed to the high percentage of overall export occurring under high flow conditions, export which is less likely to be reduced as a result of restoration.

Given the high level of interest in using restoration as a tool for water quality improvement, and the likelihood that not every site will respond equally well, criteria for selecting sites that are likely to show significant improvements in water quality following a restoration are needed. Within the stream channel, a restoration typically aims to slow the movement of water through the channel and increase hyporheic exchange, resulting in increased N retention (Kasahara and Hill, 2005). Typically, streams exporting large quantities of nutrient under low to moderate flow conditions are considered likely candidates; as these flow conditions are most conducive to the increased residence time and hyporheic exchange that facilitate nutrient retention. In a previous paper, we investigated the export flow distribution of nitrogen from a set of catchments along and urban-rural gradient in Baltimore, MD. We found that less developed sites tended to export more N under low to moderate flow conditions, while more developed sites exported N largely under high flow conditions. We then presented a metric indicative of export flow distribution characteristics, the $F_{75,}$, the discharge representative of 75% of cumulative nutrient (in this case, N) export, and suggested that sites with low F_{75} values (greater nutrient export under low to moderate flow conditions) and relatively high nutrient export would show the most response to restoration. In addition to F_{75}, another factor to be considered is the current nitrogen export. At sites with relatively low export, there is less potential for reduction regardless of the retention improvements achieved. In contrast, at sites with high rates of export, even a relatively small increase in the rate of retention can potentially lead to a large reduction in the quantity of nitrogen exported. A third variable that needs to be considered is the size of the stream. Studies carried out as part of the Lotic Intersite Nitrogen Experiment (LINX) (e.g. Peterson et al 2001, Wolheim et al 2001) have found that small, headwater streams show a high potential for nitrogen uptake and retention, suggesting that when these streams are degraded, restoring them to their natural state might result in significant increases in retention capacity.

Here, we present estimates of reductions in nitrogen export that would result from increased uptake velocities (v_f) in a set of catchments in the Baltimore Ecosystem Study (BES). Baltimore City and County have each entered into a consent decree with the US Environmental Protection Agency (EPA), agreeing to spend approximately $800 million each to reduce the quantity of N they discharge into the Chesapeake Bay (EPA 2002, 2005); an analysis of potential reduction in N export through stream restoration is thus particularly appropriate to this area. Furthermore, restoration in urban and suburban areas such as those contained by the BES is particularly challenging (Bernhardt and Palmer 2007) as existing infrastructure, and the high peak flows common in urban streams limit the extent and stability of restorations. High property values around urban streams and floodplains drive up the cost of land acquisition, making restoration in urban areas an expensive proposition. Appropriate placement of urban and suburban restorations is thus all the more critical if the results are to justify the difficulty and expense required. Based on findings reported in the literature and our prior analyses of this data set, we hypothesize that reductions in mean annual NO_3^- export will be a function of the following variables:

- Current export flow distribution: Sites exporting NO_3^- largely at low to moderate flow are expected to show greatest reduction in NO_3^- export, while sites where the majority of NO_3^- export occurs under high flow conditions are expected to show more modest reductions.

- Current mean annual NO_3^- export rates: Higher current rates of export are expected to result in larger export reductions

- Drainage area: Small, headwater streams are expected to show greater reductions in export than larger downstream catchments

Note that although this paper focuses on nitrogen, it could be similarly applied to other nutrients or pollutants of interest (e.g. phosphorus, sediment).

2.2 Data and Methods

2.2.1 Study Area

The Baltimore Ecosystem Study (BES, http://www.beslter.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 and is focused primarily on the Gwynns Falls watershed (76°30', 39°15', Figure 2.1). The Gwynns Falls extends 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. Two additional catchments in the neighboring Gunpowder Falls watershed, Pond Branch (a forested reference site), and Baisman Run (a low density suburban site) are also monitored by the BES.

Watershed population in the year 2000 was approximately 356,000 people, with sub-watershed densities ranging from 2.2 to 19.4 persons/ha. Mean annual precipitation is 1060 mm y^{-1} and stream discharge is 380 mm y^{-1} (Froelich et al. 1980, Doheny 1999).

Figure 2.1: Gwynns Falls watershed and study sites in Baltimore City and County.

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 interfluves with shallower soils and bedrock outcrops downslope. Valley bottoms have alluvial soils that can be locally thick from accumulated agricultural sediment.

Our analysis is focused on seven of the main BES catchments, and calculations are based on data collected over the 1998-2004 periods. Catchment land cover and N export characteristics are summarized in Tables 2.1 and 2.2. These catchments all show some level of development, ranging from small scale agriculture and low-density suburbs to densely developed urban areas (a forested reference site, Pond Branch, was not used in this analysis as restoration is not necessary). Previously, we used this data set to develop estimates of export flow distribution of nitrogen at each site. Nutrient duration curves were found to vary widely across the urban-rural gradient (Figure 2.2), with more developed sites exporting a greater proportion of nitrogen under high flow conditions. Here, we use the discharge representative of 75% of cumulative NO_3^- export (F_{75}) as a single metric representative of catchment export flow distribution characteristics.

Table 2.1: Drainage area and land cover composition of study sites

Catchment	Percent of catchment in land class								
					Developed classes				
	area (ha)	Impervious surface	Cultivated Crop	Forest	Open	Low	Medium	High	Other
Pond Branch	38	0	0	100	0	0	0	0	0
Baisman Run	382	>0.26	2	71	1.4	0.19	0	0	25
Glyndon	81	19	5	19	26	19	12	4	15
Gwynnbrook	1065	15	8	17	21	25	6	5	18
Villanova	8349	17	10	24	17	21	9	2	17
Dead Run	1414	31	2	5	27	41	16	6	3
Carroll Park	16378	24	6	18	20	26	15	5	10
McDonogh	7.8	0	70	26	0	0	0	0	4

Table 2.2: Mean annual NO_3^- export and F_{75} values of study sites

Site	NO_3^- export (kg ha^{-1} yr^{-1})	NO_3^- F_{75} (mm/d)
Baisman Run	5.63	1.98
Villanova	6.16	4.31
Carroll Park	6.95	6.21
Gwynnbrook	7.99	5.28
Glyndon	5.87	8.75
Dead Run	4.37	16.44
McDonogh	20.86	2.79

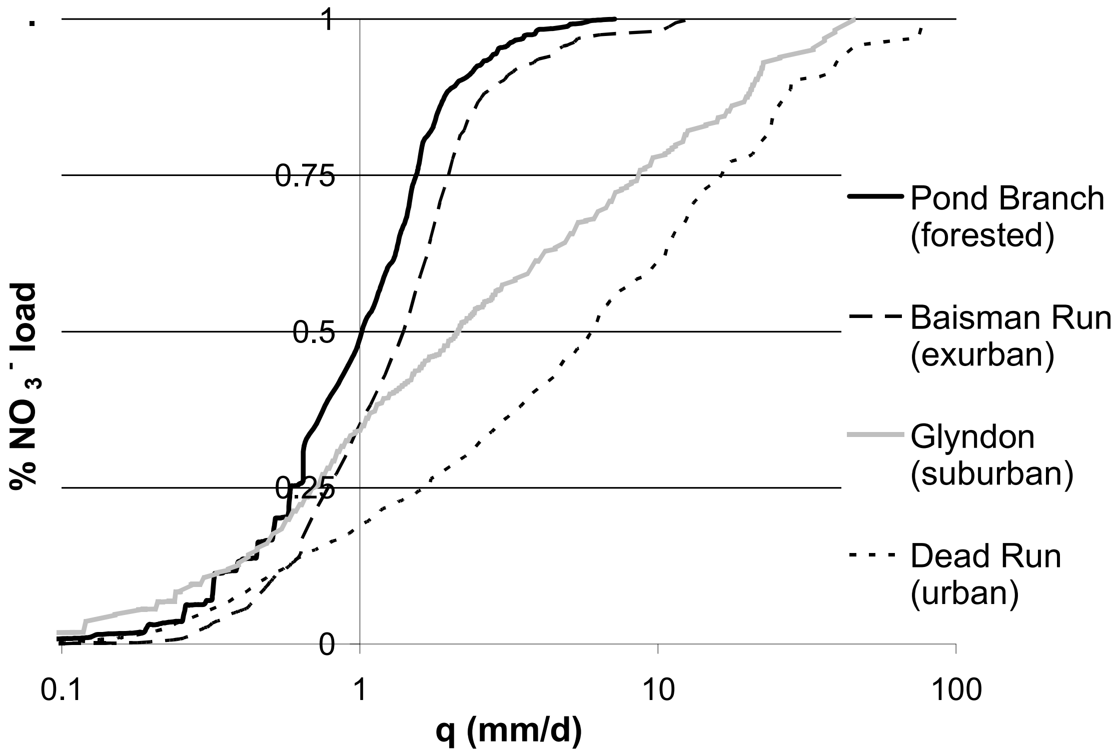

Figure 2.2: Cumulative NO_3^- export as a function of discharge at Pond Branch (forested), Baisman Run (exurban), Glyndon (suburban), and Dead Run (urban) catchments. Discharge representative of 75% of cumulative NO_3^- export is summarized for all sites in Table 2.2

2.2.2 Modeling export reduction

We base our calculations on a series of nutrient uptake formulas given by the Stream Solute Workshop (Stream Solute Workshop, 1990). Modeled variations in mean annual export values are reliant primarily on changes in uptake velocity (or transfer coefficient), v_f, and channel discharge and load conditions. Our model assumes a first order exchange rate and reasonably uniform channel conditions. We further simplify matters by assuming no additional external inputs or new release of nutrients from within the stream along the length of the modeled reach. Attenuation of downstream nutrient concentrations are assumed to follow an exponential decline downstream:

$$C_x = C_0 e^{(-K_c x)} \qquad (1)$$

Where C_0 is the initial concentration, C_x is the concentration at x distance downstream, and K_c is the first-order uptake rate coefficient (m^{-1}). K_c can be written as a function of channel reach flow velocity (u), water column depth (d), and uptake velocity (v_f):

$$K_c = \frac{v_f}{ud} \qquad (2)$$

Taking discharge (Q) to equal the product of u and cross sectional area:

$$u = \frac{Q}{wd} \qquad (3)$$

where w is stream width. Substituting (2) and (3) back into (1) results in:

$$C_x = C_0 e^{(-v_f x w Q^{-1})} \qquad (4)$$

Discharge (Q) is monitored continuously at each of the BES gauge sites and reported as a mean daily value by the USGS. Stream width (w) is also estimated from channel geometry-discharge relationships developed by USGS. Water quality samples are collected on an approximately weekly basis and NO_3^- concentration is measured by the Institute of Ecosystem Studies (IES), Millbrook, New York. Estimates of daily NO_3^- concentrations (C_0) are developed using a bin-averaging approach.

Current uptake velocities in the study streams are assumed to be negligible; velocities measured at the Baisman Run, Glyndon, and Dead Run sites support this assumption (L. Claessens, pers. communication, C. Klocker, pers. communication). V_f values used in (4) range from 0.01-5.5 mm/min. This range is based on the literature review compiled by Ensign and Doyle (2006), which collected reported v_f values from ~50 studies.

The median length of a restoration in the CBW is 450m (Hassett et al 2005), while urban restoration lengths average 600m within the U.S. (Bernhardt and Palmer 2007).

Therefore, we set x equal to 500m, assuming a 500m restoration that achieved the increased v_f value along its entire length.

2.3 Results and Discussion

2.3.1 Percent reductions in NO_3^- export

Greatest percent reductions were seen in the agricultural catchment, McDonogh, also the catchment with the highest mean annual NO_3^- load and the smallest drainage area (Figure 2.3). In the McDonogh catchment, reductions approach 100% if maximum v_f values are reached. Three other catchments: Baisman Run, Glyndon, and Gwynnbrook also show high rates of reduction occurring at some point within the range of applied v_f values, although the v_f required for these catchments to achieve high rates of reduction was somewhat higher than for McDonogh. The three remaining, more developed sites (Dead Run, Carroll Park, and Villanova) showed much more modest reductions. Although the potential percent reduction varied widely between sites, all sites did show appreciable percent reductions in NO_3^- export under some portion of the range of v_f values applied, with all but one site showing at least a 10% reduction with a v_f of 1.0 mm min^{-1} or less. Overall, the potential for reduction in NO_3^- export appeared to be highest in small, less developed catchments, and progressively decline as development and drainage area increased.

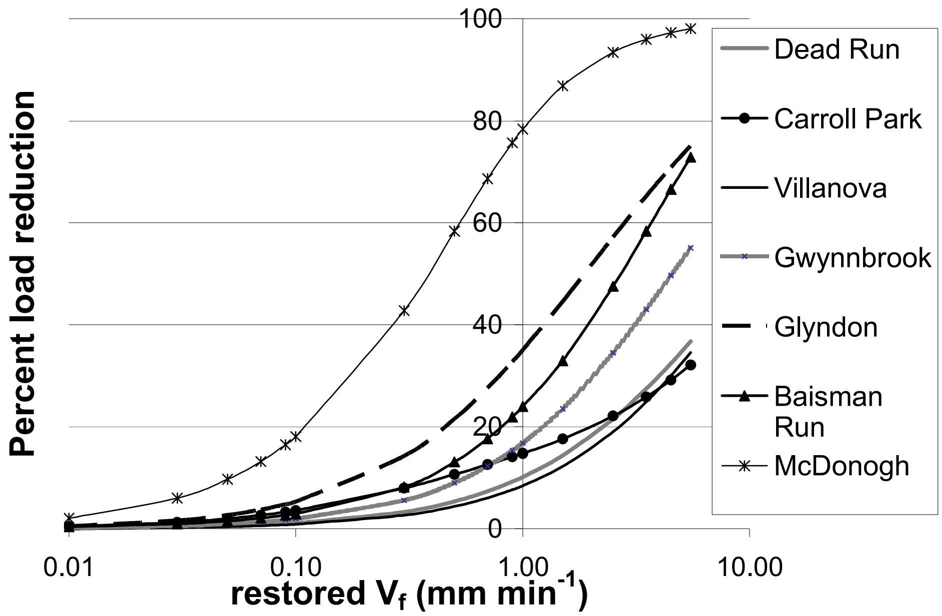

Figure 2.3: Percent reduction in NO_3^- as a function of v_f values ranging from 0.01 to 5.5 mm min^{-1}. Sites are listed from most to least developed in legend.

While these modeled results seem to indicate significant potential for reducing nitrate export, high levels of export reduction are dependent on achieving high v_f values that can be sustained through repeated floods. The feasibility of achieving v_f values required for an appreciable reduction in NO_3^- export is currently uncertain at best. Post-restoration v_f values obtained from two restorations in the Baltimore area showed a maximum v_f value of 0.05 mm min^{-1}. At this uptake velocity, only McDonogh shows a reduction in export exceeding 5%. A site in Kentucky (Bukaveckas 2007) reported somewhat higher v_f values post-restoration, 0.13 mm min^{-1}. At this rate, the potential for NO_3^- reduction is more promising, but still modest, with less than a 10% reduction in export at most sites. If the v_f values achieved by these restorations are typical, the potential for increased NO_3^- retention through restoration may be limited to catchments such as McDonogh; very small and with a high per hectare yield of NO_3^-, with the majority of export occurring largely under low to moderate flow conditions. Cultivated cropland, the dominant land use in McDonogh and source of the vast majority of the NO_3^- exported from the catchment, accounts for only six percent of the area in the Gwynns Falls, so the potential for restoring these sorts of sites is limited in developed, urbanizing areas such as Baltimore.

A statistical analysis of percent reduction in export as a function of current NO_3^- considered percent reduction in export as a function of current NO_3^- export, F_{75}, drainage area, or a combination of the three produced mixed results. Percent reductions achieved under four increased v_f scenarios (v_f= 0.01, 0.1, 1.0, 5.5 mm min^{-1}) were analyzed as a function of our three dependent variables. We found a strong correlation between percent reduction in NO_3^- export and the natural logarithm of the drainage area ($p<0.04$ in all cases), with increasing drainage area accounting for a decreasing percent export reduction. This finding was consistent with prior studies suggesting that small, headwater streams have a greater potential for nutrient retention than larger ones (Peterson et al. 2001, Wolheim 2001).

Current mean annual NO_3^- export (in kg ha^{-1} yr^{-1}) was also a strong explanatory variable, with a higher mean annual export resulting in a higher percent reduction. This regression was driven largely by the McDonogh catchment's very high annual export (more than twice that of any other catchment) and correspondingly high percent reduction in export. If McDonogh is removed from the analysis, export load is no longer a significant explanatory variable. The correlation with area also showed some dependence on McDonogh. If this site is removed from the analysis, area is no longer a significant explanatory variable for reductions achieved using the lower two v_f values, but still exhibits a significant relationship with percent reduction at v_f=1.0 and 5.5 mm min^{-1}. Our final explanatory variable, F_{75} did not show a significant correlation with percent reduction in export, either alone or in combination with the other two variables. Although a strong quantitative relationship could not be found, it is possible that F_{75} may be a significant predictor within basins of similar size. For example, the Dead Run and Gwynnbrook catchments, the two sites closest in drainage area (1413 and 1064 ha, respectively), show very different percent reductions in export and very different F_{75}

values. Gywnnbrook, with a lower F_{75} (5.28 mm d^{-1}) shows a much greater percent reduction in NO_3^- export than Dead Run, a site with a considerably higher F_{75} value (16.44 mm d^{-1}). This difference may also be partially attributable to load: Gwynnbrook currently has a mean annual NO_3^- export rate several kg ha^{-1} higher than Dead Run. Our relatively small sample size (seven sites and a range of sizes) prevented a more in depth analysis of whether increasing F_{75} is associated with lower NO_3^- reductions in similarly sized catchments.

2.3.2 Quantity of NO_3^- reduction achieved

The mean annual quantity of NO_3^- export reduction (in kg N yr^{-1}) was greatest in the two largest catchments, Carroll Park and Villanova (Figure 2.4), with smaller levels of export reduction being achieved in the remaining catchments. This finding suggests that scale is a key factor to consider in restoration. For example, the smallest v_f value modeled, 0.01 mm min^{-1} results in an approximately 450 kg yr^{-1} reduction in NO_3^- export. The only other catchment to show a 450 kg yr^{-1} reduction in export is Baisman Run, and this catchment requires a v_f of 1.0 mm min^{-1}, to show such a reduction. In general, this difference in NO_3^- retention is explained largely by the difference in magnitude of current NO_3^- export. A site such as McDonogh, for example, although currently exporting NO_3^- at a rate of approximately 20 kg ha^{-1} yr^{-1} contributes slightly less than 2% of the total Gwynns Falls NO_3^- export. In contrast, Villanova, with a drainage area several orders of

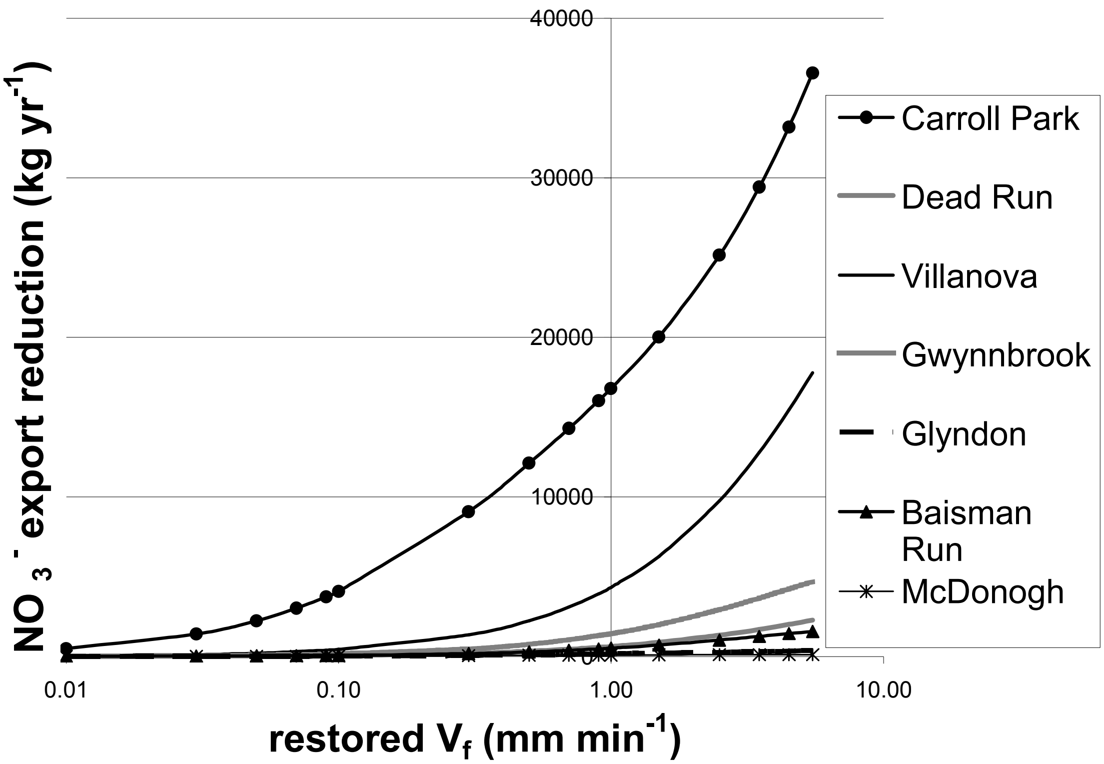

Figure 2.4: Mean annual reduction in NO_3^- export (in kg yr^{-1}) as a function of v_f values ranging from 0.01 to 5.5 mm min^{-1}. Sites are listed from most to least developed in legend.

magnitude greater than McDonogh, accounts for 45% of total mean annual NO_3^- export from the Gwynns Falls, although the per hectare rate of export is considerably smaller. On a per hectare basis, the greatest potential reduction is seen at McDonogh (Figure 2.5), a potential largely attributable to the high current rate of export. In general, the per hectare reduction potential again follows the urban-rural gradient, with more developed catchments showing a smaller per hectare retention in NO_3^- export. Statistical relationships were similar to those seen with percent retention as the dependent variable. Area was again a significant variable ($p<0.05$ in all cases) in explaining the per hectare decrease in export, as was current NO_3^- export rate, and F_{75} was not. However, in this case both area and export were dependent on the McDonogh catchment for their significance; exclusion of this site resulted in no significant relationships between per hectare export reduction and either current export or area.

Overall, this finding suggests that restoration of larger streams may be more effective than generally thought if the goal is reducing NO_3^- exports to a receiving water body such as the Chesapeake, up to a point. In prioritizing larger versus smaller streams for restoration, water quality requirements at a variety of scales needs to be considered. For example, restoring a 500 m segment at the base of the Carroll Park watershed may do the most for reducing NO_3^- export to the Chesapeake, but would not result in and improvements in water quality within Baltimore, while a headwater restoration would presumably result in some improvement in water quality further downstream.

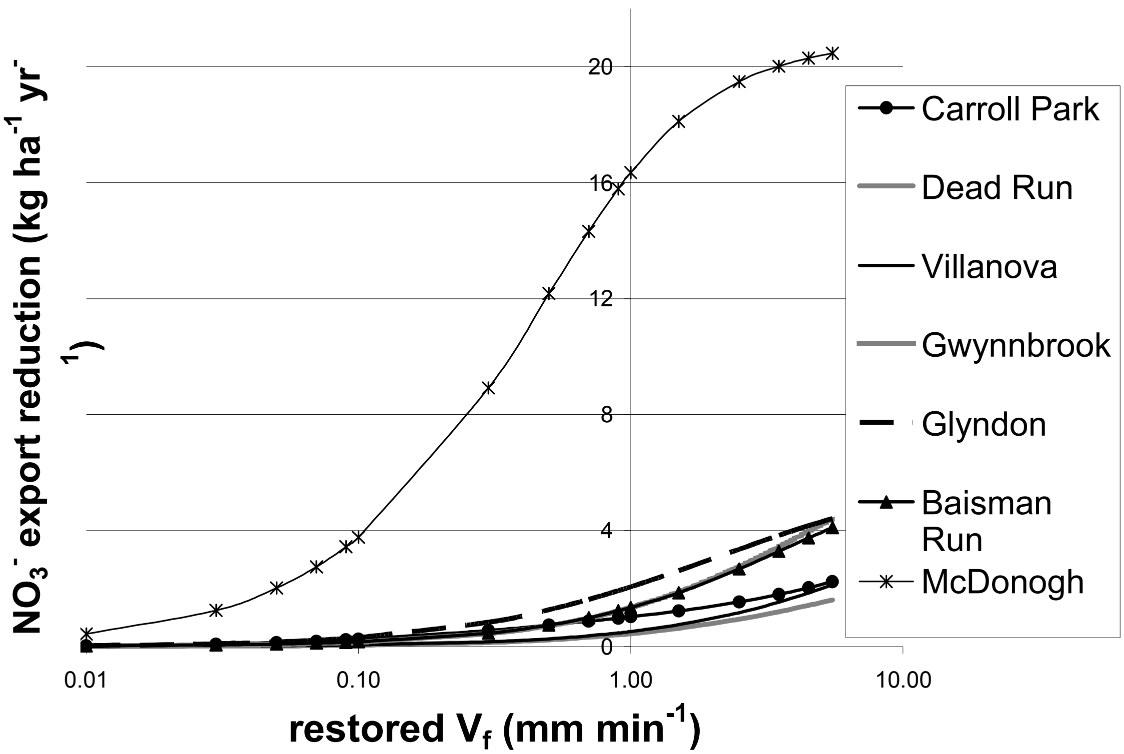

Figure 5: Mean annual reduction in NO_3^- export (in kg ha^{-1} yr^{-1}) as a function of v_f values ranging from 0.01 to 5.5 mm min^{-1}. Sites are listed from most to least developed in legend.

The practicality of restoring a large channel as opposed to several small channels should also be considered, as large channel restorations may be much more expensive and difficult to achieve. A large channel restoration may require more intensive and less sustainable engineering, and a greater quantity of land in a single area must be acquired. In the Baltimore area and other metropolitan areas, the land around larger streams is also more developed and urbanized, another factor that may result in increased costs. In the CBW, median cost of restorations in an urban area is nearly twice that of restorations in rural areas (Hassett et al 2005), despite the fact that urban restorations typically deal with a shorter stream reach. These obstacles may make restoring multiple small streams a much more attractive and feasible option. Smaller restorations may also be preferable as a hedge against failure—if restoration is spread amongst many headwater reaches, one failure does not result in a complete loss of water quality benefits.

2.4 Conclusions

2.4.1 Drainage area dominates export reduction potential

We found that drainage area was the key explanatory variable of reduction in NO_3^- export, with smaller catchments exhibiting a much greater potential for a high percent reduction in NO_3^- export. However, amongst our study sites, larger catchments, while showing only modest percent reductions in NO_3^- export, exhibited the greatest potential in terms of the total quantity of NO_3^- removed from mean annual export, and large reductions in NO_3^- export (relative to other sites) were seen even at very low v_f values. This finding indicates that if reducing NO_3^- export to a water body with a large drainage area (such as the Chesapeake), is the goal of a water quality management program, larger, non-headwater streams may also merit consideration, up to a point. The goal of reducing NO_3^- export to receiving water bodies should, be weighed against the need to improve local water quality conditions at points within a large watershed, as more localized need would not be aided by a restoration miles downstream.

Although large stream restoration may show the greatest potential for reducing export to a receiving water body, small catchments should not be ignored. A larger v_f value may be achievable in smaller streams—if a smaller stream has the potential for a restored v_f value several orders of magnitude greater than a large stream, the small stream is likely the better candidate for restoration. Smaller stream restoration may also be less expensive and more sustainable, and spreading restorations among several small streams rather than one large one lessens the consequences of a restoration failing. Further investigation of the costs of restoration implementation, maintenance, and rates of failure in headwater and larger stream channels is needed to more fully weigh the costs and benefits associated with restoration of a range of channel sizes.

2.4.2 Usefulness of stream restoration as a water quality management tool

Although all of our sites showed appreciable reductions in NO_3^- export at some point, v_f values exceeding 1.0 mm min^{-1} were required in most cases for the rate of reduction to exceed 10%. Three sites, two in Baltimore (C. Klocker, pers. communication) and one in Kentucky (Bukaveckas 2007), all reported post-restoration v_f values an order of magnitude or more less than 1.0 mm min^{-1}. Currently, a lack of routine post-restoration monitoring means that it is unclear whether these values are typical or if these projects were particularly poorly situated or executed. These sites do, however, highlight the possibility that the difference between the theoretically possible and the realistically achievable may be substantial. Further post-restoration monitoring is needed at a variety of sites to determine what level of increase in v_f may be reasonably expected following a restoration. Based on our current findings and the relatively low v_f values seen at several sites post-restoration, we conclude that stream restoration may be of limited value as a water quality management tool and should not be viewed as a panacea for all degraded streams. In small, headwater streams with high rates of NO_3^- export occurring under low to moderate flow conditions, such as the McDonogh catchment, our results suggest that restoration has potential to greatly improve water quality. However, a limited number of these sites may exist in urban areas as remnant agriculture is replaced with urban development and the export flow distribution of nitrogen shifts to favor more extreme flow events.

In areas where the potential for NO_3^- restoration is lower, we conclude that reducing the quantity of NO_3^- reaching the stream may be a more realistic approach to reducing NO_3^- export and should take priority over increasing the retention capacity of the stream itself. This reduction could be achieved through improvement and maintenance of sanitary sewer infrastructure, or in the case of areas not serviced by sanitary sewers, improved septic system design and location to reduce hydrologic connectivity with nearby streams. Finally, reducing the overall hydrologic connectivity of a catchment will slow the movement of water to the stream and allow for the possibility of increased retention throughout the catchment, rather than placing the entire burden of retention on the stream and riparian area. We acknowledge also that although it is a common impetus for restoration, improved water quality may not always be the only goal, and other goals may require a restoration to be successfully realized. Restoring habitat for aquatic species, for example, or satisfying the desires of nearby residents for a more "natural" channel appearance. We do not suggest that restoration should be abandoned completely as a management tool, rather that the potential for reducing nutrient export may be limited and should not be expected from or used to justify the expense of all projects.

CONCLUSIONS

Two major findings may be drawn from this thesis. First, that export flow distribution of N is strongly tied to catchment development. This finding allowed for extrapolation of a metric indicative of export flow distribution, the F_{75}, across a stream network. An extrapolation such as this one can then potentially be utilized as a tool to prioritize areas of a network for restoration based on the flow conditions at which the majority of N export occurs. Further research across a variety of sites is needed to determine if the relationship we observed in Baltimore can be generalized across a wider geographic extent. This research could also be further improved by incorporating a wider variety of development indicators into the analysis, such as sanitary sewer density and fertilization practices.

The second major finding of this thesis is that stream restoration appears to have limited potential to improve water quality through increasing the uptake velocity, v_f. Although significant reductions in N export can be achieved at high v_f values, currently available post-restoration data indicate that these v_f values are not attainable. Further post-restoration monitoring is needed to determine the maximum level of v_f that can be reasonably achieved. Post-restoration monitoring is also needed to determine what factors are causing elevated v_f values. That is, whether the restoration itself is achieving these values, or whether byproducts of the restoration, such as increased light availability resulting from removing vegetation, are responsible.

REFERENCES

Ameel, J.J., R.P. Axler, and C.J. Owen. (1993), Persulfate digestion for determination of total nitrogen and phosporus in low nutrient waters. *Am Environ Lab 10:* 1-11.

Arnold, C. and J. Gibbons. (1996). Impervious surface coverage: The emergence of a key environmental indicator. *Journal of the American Planning Association* 62(2): 243-258.

Bernhardt, E.S., and M.A. Palmer (2007), Restoring streams in an urbanising world. *Freshwater Biology 52(4)*: 738-751.

Bernhardt, E.S., M.A. Palmer, J.D. Allan, G. Alexander, K. Barnas, S. Brooks, J. Carr, S. Clayton, C. Dahm, J. Follstad-Shah, D. Galat, S. Gloss, P. Goodwin, D. Hart, B. Hassett, R. Jenkinson, S. Katz, G.M. Kondolf, P.S. Lake, R. Lave, J.L. Meyer, T.K. O'Donnell, L. Pagano, B. Powell, E. Sudduth (2005), Ecology—Synthesizing US river restoration efforts. *Science 308 (5722):* 636-637.

Boyer, E.W., and R.W. Howarth (2002), Special issue—the nitrogen cycle at regional to global scales—foreward. *Biogeochemistry 57(1):* vii-ix.

Boyer, E.W., C.L. Goodale, N.A. Jaworsk, and R.W. Howarth (2002), Anthropogenic nitrogen sources and relationships to riverine nitrogen export in the northeastern USA. *Biogeochemistry 57(1):* 137-169.

Bukaveckas, P.A. (2007). Effects of channel restoration on water velocity, transient storage, and nutrient uptake in a channelized stream. *Environ. Sci. Technol. 41:*1570-1576.

Burns, D. (2005a) What do hydrologists mean when they use the term flushing? *Hydrological Processes, 19(6):* 1325-1327.

Burns, D., T. Vitvar, J. McDonnell, J. Hassett, J. Duncan, and C. Kendall (2005b), Effects of suburban development on runoff generation in the Croton River basin, New York, USA. *J. of Hydrology 311 (1-4):* 266-281.

Cadenasso, M.L., S.T.A. Pickett and K. Schwarz (2007), Spatial heterogeneity in urban ecosystems: reconceptualizing land cover classifications. *Frontiers in Ecology and Environment. 5(2):* 80-88.

Creed, I.F., LE. Band, N.W. Foster, I.K. Morrison, J.A. Nicolson, R.S. Semkin, and D.S. Jeffries (1996). Regulation of nitrate-N release from temperate forests: A test of the N flushing hypothesis. *Water Resour. Res. 32(11)*: 3337-3354.

Creed, I.F. and Band, L.E. (1998a). Exploring functional similarity in the export of nitrate-N from forested catchments: A mechanistic modeling approach. *Water Resour. Res. 34(11)*: 3079-3093.

Creed, I.F. and Band, L.E. (1998b). Export of nitrogen from catchments within a temperate forest: Evidence for a unifying mechanism regulated by variable source area dynamics. *Water Resour. Res. 34(11)*: 3105-3120.

Doheny, E. J. and G.T. Fisher (2007). Hydraulic Geometry Characteristics of Continuous-Record Streamflow-Gaging Stations on Four Urban Watersheds Along the Main Stem of Gwynns Falls, Baltimore County and Baltimore City, Maryland. U.S. Geological Survey Scientific Investigations Report 2006-5190.

Doheny, E. (1999), Index of Hydrologic Characteristics and Data Resources for the Gywnns Falls Watershed, Baltimore County and Baltimore City, Maryland. Open-file report 99-213, Baltimore (MD): US Geological Survey

Ensign, S. H. and M.W. Doyle (2006) Nutrient spiraling in streams and river networks. *J. Geophys. Res.-Biogeosciences, 111* G04009 doi: 10.1029/2005JG000114.

Froelich AJ, Hack JT, Otton EG. (1980), Geologic and hydrologic map reports for land-use planning in the Baltimore-Washington urban area. US Geological Survey circular 806. US Geological Survey, Reston, VA.

Galloway J.N., F.J. Dentener, D.G. Capone, E.W. Boyer, R.W. Howarth, S.P. Seitzinger, G.P. Asner, C.C. Cleveland, P.A. Green, E.A. Holland, D.M. Karl, A.F. Michaels, J.H. Porter, A.R. Townsend, and C.J. Vorosmarty (2004), Nitrogen cycles: past, present, and future. *Biogeochemistry 70(2):* 153-226

Glibert, P.M., T.M. Trice, B. Michael, L. Lane (2005), Urea in the tributaries of the Chesapeake and coastal bays of Maryland. *Water, Air, and Soil Pollution 160 (1-4):* 229-243.

Groffman, P.M., N.L. Law, K.T. Belt, L.E. Band, and G.T. Fisher (2004), Nitrogen fluxes and retention in urban watershed ecosystems. *Ecosystems 7(4)*, 393-403.

Hassett, B., M. Palmer, E. Bernhardt, S. Smith, J. Carr, D. Hart (2005), Restoring watersheds project by project: trends in Chesapeake Bay tributary restoration. *Frontiers in Ecology and Environment 3(5),* 259-267.

Heisig, P. (2000) Effects of residential and agricultural land uses on the chemical quality of small streams in the Croton Watershed, southeastern New York. US Geological Survey Water Resources Investigation Report 99-4173.

Henry, C.P., C. Amoros, N. Roset (2002) Restoration ecology of riverine wetlands: a 5 year post-operation survey on the Rhone River, France. *Ecological Engineering 18*: 543-554.

Holmes, N.T.H. (1998) *A Review of River Rehabilitation in the U.K., 1990-1996.* Technical Report W175. Environment Agency, Bristol, UK.

Homer, C., C. Huang, L. Yang, B. Wylie and M. Coan (2003), Development of a 2001 national land cover database for the United States. *Photogrammetric Engineering and Remote Sensing 70 (7),* 829-840.

Howarth, R.W., A. Sharpley, D. Walker (2002), Sources of nutrient pollution to coastal waters in the United States: Implications for achieving coastal water quality goals. *Estuaries 25 (4B):* 656-676.

Jordan, T. E., D. L. Correll, and D. E. Weller (1997), Relating nutrient discharges from watersheds to land use and streamflow variability, *Water Resour. Res.*, 33(11), 2579–2590.

Jordan, T.E., D.E. Weller and D.L. Correll (2003), Sources of nutrient inputs to the Patuxent River estuary. *Estuaries*, 2A, 226-243.

Kasahara, T. and A.R. Hill (2006), Effects of riffle-step restoration of hyporheic zone chemistry in N-rich lowland streams. *Can. J. of Fisheries and Aquatic Sciences 63(1)*: 120-133.

Kaushal, S.S.. W.M. Lewis, J.H. McCutchan (2006). Land use change and nitrogen enrichment of a Rocky Mountain watershed. *Ecological Applications 16(1):* 299-312.

Law, N.L. (2003), Analysis of water quality trends in urban-suburban watersheds. Dissertation, University of North Carolina at Chapel Hill.

Palmer, M.A., E.S. Bernhardt, J.D. Allan, P.S. Lake, G. Alexander, S. Brooks, J. Carr, S. Clayton, C.N. Dahm, J.F. Shah, D.L. Galat, S.G. Loss, P. Goodwin, D.D. Hart, B. Hassett, R. Jenkinson, G.M. Kondolf, R. Lave, J.L. Meyer, T.K. O'Donnell, L. Pagano, E. Sudduth (2005). Standards for ecologically successful river restoration. *Journal of Applied Ecology 42(2):* 208-217.

Peterson, B.J., W. Wollheim, P.J. Mulholland, J.R. Webster, J.L. Meyer, J.L. Tank, Marti, E., W.B. Bowden, H.M. Valett, A.E. Hershey, W.H. McDowell, W.K. Dodds, S.K. Hamilton, S.V. Gregory, and D.D. Morrall (2001). Control of nitrogen export from watersheds by headwater streams. *Science 292*:86-90.

Pontius, R.G., L. Claessens, C. Hopkinson, Jr., A. Marzouk, E.B. Rastetter, L.C. Schneider and J. Vallino (2000), Scenarios of land use chage and nitrogen release in the Ipswich watershed, Massachusetts, USA. 4th International Conference on Integrating GIS and Environmental Modeling (GIS/EM4), Banff, Alberta, Canada, Sept.2-8.

Poor, C.J., and J.J. McDonnell (2007) The effects of land use on stream nitrate dynamics. *J. of Hydrology 332(1-2)*: 54-68

Quilbé, R., A.N. Rousseau, M. Duchemin, A. Poulin, G. Gangbazo, J.P. Villeneuve (2006), Selecting a calculation method to estimate sediment and nutrient loads in streams: Application to the Beaurivage River (Quebec, Canada). *J. of Hydrology 326 (1-4):* 295-310.

Royer, T.V., M.B. David, and L.E. Gentry (2006). Timing of riverine export of nitrate and phosphorus from agricultural watersheds in Illinois: Implications for reducing nutrient loading to the Mississippi River. *Environmental Science and Technology 40(13)*: 4126-4131.

Schueler, R., and R. Claytor (1997), Impervious cover as an urban stream indicator and a watershed management tool, in *Effects of watershed development and management in aquatic ecosystems: proceedings of an engineering workshop*, edited by L.A. Roesner, pp 513-529, pp 513-529, New York, ASCE.

Schwarz, G.E., A.B. Hoos, R.B. Alexander, and R.A. Smith (2006), The SPARROW surface water-quality model: Theory, application, and user documentation, U.S. Geological Survey Techniques and Methods Report, Book 6, Chapter B3

Sherlock, M.D., and J.J. McDonnell (2003), A new tool for hillslope hydrologists: spatially distributed groundwater level and soilwater content measured using electromagnetic induction. *Hydrological Processes 17(10)*: 1965-1977.

Strayer, D.L, R.E. Beighley, L.C. Thompson, S. Brooks, C. Nilsson, G. Pinay, and R.J. Naiman. 2003. Effects of Land Cover on Stream Ecosystems: Roles of Empirical Models and Scaling issues. *Ecosystems* 6: 407-423.

Stream Solute Workshop (1990). Concepts and methods for assessing solute dynamics in stream ecosystems, *J. N. Am. Benthol. Soc., 9:* 95-119.

Tabatabai, M.A. and W.A. Dick (1983), Simultaneous determination of nitrate, chloride, sulfate, and phosphate in natural waters by ion chromatography. *J. of Environ. Qual. 12:* 209-213

Tarboton, D. G. (1997), A New Method for the Determination of Flow Directions and Contributing Areas in Grid Digital Elevation Models, *Water Resour. Res., 33(2)*: 309-319.

Taylor,G.D, T.D. Fletcher, T.H.F. Wong, P.F. Breen, and H.P. Duncan. 2005. Nitrogen composition in urban runoff—implications for stormwater management. *Water Research* 39:1982-1989.

Vitousek, P.M., J.D. Aber, R.W. Howarth, G.E. Likens, P.A. Matson, D.W. Schindler, W.H. Schlesinger, and D.G. Tilman (1997), Human alteration of the global nitrogen cycle: Sources and consequences. *Ecological Applications 7(3):* 737-750.

U.S. Environmental Protection Agency, 2002. Consent Decree: City of Baltimore Civil Judicial Settlement. http://www.epa.gov/Compliance/resources/decrees/civil/cwa/baltimore-cd.pdf

U.S. Environmental Protection Agency 2005. $1 Billion Clean-up Settlements Reached with Baltimore Co. and Washington Suburban Sanitary Commission. EPA Region 3 Press Release.

Walsh, C.J., A.H. Roy, J.W. Feminella, P.D. Cottingham, P.M. Groffman, and R.P. Morgan (2005), The urban stream syndrome: current knowledge and the search for a cure. *Journal of the North American Benthological Society 24(3):* 706-723.

Weller, D.E., T.E. Jordan, D.L. Correll and Z.J. Liu (2003). Effects of land use change on nutrient discharges from the Patuxent River watershed. *Estuaries*, 2A, 244-266.

Wollheim, W.M., B.J. Peterson, L.A. Deegan, J.E. Hobbie, B. Hooker, W.B. Bowden, K.J. Edwardson, D.B. Arscott, A.E. Hershey, and J. Finlay (2001). Influence of stream size on ammonium and suspended particulate nitrogen processing. *Limnology and Oceanography 46*:1-13.

Wollheim W.M., B.A. Pellerin, C.J. Vörösmarty, and C.S. Hopkinson (2005). N Retention in Urbanizing Headwater Catchments. *Ecosystems* 8:871-844.