AN INVESTIGATION INTO THE EFFECTS OF FOREST FRAGMENT STRUCTURE AND SPATIAL CONTEXT ON RAINFALL REDISTRIBUTION AND SOLUTE FLUX WITHIN A CITY AND ALONG AN URBAN TO RURAL GRADIENT

by

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A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Geography

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ABSTRACT

Urban green space has increasingly been utilized as a natural means by which to mitigate the negative environmental impacts of expansive and often unchecked urbanization. Much effort has been placed on increasing urban forest cover, as trees have been found to provide an array of cultural, supporting, provisioning, and regulating ecosystem services that collectively help to sustain, and in some respects, improve both human life and environmental function. There remains, however, a knowledge gap with respect to our understanding of subcanopy hydrologic and solute fluxes that occur within remnant metropolitan forest patches. Filling this gap is crucial for better identifying the threats and aids to the sustainable management of urban wooded ecosystems, in addition to aiding in the development of more strategic initiatives for the management and expansion of urban forest cover.

This dissertation utilizes *in situ* measurements from remnant forest fragments in the Wilmington, Delaware, USA metropolitan region to quantify and characterize the hydrologic and solute fluxes that take place within them. It is the first study to utilize the flux-based enrichment ratio for stemflow in relation to throughfall to determine the degree to which net precipitation chemistry is altered due to its interaction with the canopy, with specific emphasis on the relative contributions of stemflow and throughfall to subcanopy nutrient cycling. Flux-based enrichment ratios for stemflow were consistently found to be higher for *Quercus rubra* than *Quercus alba* (due to variability in bark morphology between the two species), and in urban

rather than non-urban remnant forests. Additional quantification of throughfall fluxes determined that within highly developed portions of a metropolitan region, throughfall solute flux is governed largely by intensity of urban land use and related emissions, rather than solely by location along an urban to rural gradient (i.e., within city limits vs. within a suburban community). Knowledge of the biotic and abiotic factors that govern both water and solute fluxes within these metropolitan forest ecosystems was used to develop a prescriptive guide upon which urban land managers may base tree selection and management strategies to optimize the yield of select hydrologic and hydrochemical ecosystem services.

Chapter 1

INTRODUCTION

1.1 Background

Over the past half-century, metropolitan areas around the world have been consistently growing in both population and extent (United Nations 2012). This global-scale trend towards expansive urbanization had not occurred without environmental consequence; rather, there has been wide-spread, long lasting degradation of environmental quality both in and around cities as a result. This has included, but not been limited to decreased floral and faunal biodiversity, compromised air quality, heightened urban air temperatures, and increased frequency of excessive stormwater runoff and subsequent localized and regional flash flooding (Leopold 1968, Oke 1982, Smith et al. 2005, Grimm et al. 2008, Ravindra et al. 2008, Ramamurthy and Bou-Zeid 2017, Squizzato et al. 2017). These negative impacts on environmental quality within metropolitan regions have had concurrent negative impacts on the quality of life for the residents who inhabit these areas.

In recent decades, there has been both an increase in both the awareness of the degree to which urbanization has unfavorably changed environmental function and the proactiveness of land managers at various spatial scales to enact policies and initiatives aimed at reversing these ill-effects of rapid expansive development (e.g., City of Philadelphia 2010). Considerable efforts have been made in many metropolises to

increase urban forest canopy cover, as urban trees have been found to provide a vast array of ecosystem services that improve both environmental conditions and the quality of life for both fauna and people within these urban areas. These services include expansion of faunal habitat and food sources, mitigation of urban heat island effects, amplification of residential mental health conditions, increased property values, regulation of air quality, and stormwater runoff reduction (Avila-Flores and Brock Fenton 2005, Nowak et al. 2006, Nowak et al. 2013, Taylor et al. 2015, Escobedo et al. 2015, Livesley et al. 2016, Synk et al. 2017). As such, many cities have implemented initiatives aimed at increasing total canopy cover, with large emphasis on the addition of isolated urban street trees when and where space becomes available to do so.

While this use of urban canopy cover serves as important means by which to increase green space in cities, contribute to urban sustainability goals, and regulate urban environmental quality, it is imperative that future canopy expansion initiatives be based not solely on these aims, but rather be based on a stronger understanding of how the ability to achieve these aims can be affected by the structural characteristics of the urban forest. There is now a growing need for an improved understanding of the nuanced processes – both biotic and abiotic – that impact the health and functioning capacity of the urban canopy. This nuanced understanding would encompass several aspect s of urban forest function, including the role of species heterogeneity and forest stand structure, in regulating urban canopy health and provision of ecosystem services.

1.2 Study Area and Regional Context

Following the recent unprecedented growth of the global urban population to 3.6 billion people (United Nations 2012), there has been a heightened awareness of the

negative environmental impacts of urban expansion. This growth occurs at the expense of the natural environment, as the existing extent of green space is reduced and further fragmented for the purpose of accommodating the residential, commercial, and transportation needs of urban populations. The resulting environmental impacts are evident in regional water resources, where there is increased potential for flooding and decreased water quality in urbanizing areas (Leopold 1968, Hollis 1975, Smith et al. 2005, Seilheimer et al. 2007). This higher flood frequency occurrence has been associated with infrastructure failure (Ashley et al. 2005), and the decreased water quality has been associated with human health issues, including contaminant-related illnesses (Wang et al. 2011, Vrhovnik et al. 2013). In severe cases, there have even been probable links to cancer (Graney and Eriksen 2004).

Urban expansion has been occurring in the greater Wilmington, DE area for several decades (Figure 1.1). Wilmington is located within the continuously expanding Philadelphia-Camden-Wilmington metropolitan statistical area, which is the nation's fifth largest metropolitan region (United States Census Bureau 2013). Development in the greater Wilmington area has resulted in the occurrence of many adverse environmental impacts, including severe flooding in many parts of the region and threatened quality of both surface and ground-water resources (Delaware Department of Natural Resources and Environmental Control 2006). Some of the nation's highest cancer rates have been observed within this region of northern Delaware (Delaware Division of Public Health 2012) and have been partly accredited to poor decisions made regarding land use and water resources. These issues make it imperative to develop best management practices that will provide well-managed, high quality natural resources for residents of the

Wilmington, DE metropolitan region. Lessons learned from this study may be applicable to other areas in the megalopolis. Strategic urban forestry initiatives may serve as a viable option to mitigate the area's water quantity and quality issues.

1.3 Increased Forest Fragmentation: Filling an Existing Data Gap

When expansion occurs in urban areas, existing green space is often fragmented to accommodate this growth. This results in forested areas that were once of a relatively large size being reduced to fragments, only a fraction of their original extent (Alig et al. 2004). Many of these fragments exist in the greater Wilmington, DE area (Figure 1.1). This study will focus on the variation in the water resource-related ecosystem functions of various urban forest fragments with respect to their size, shape, and location both within the city of Wilmington *and* along an urban-rural gradient in the region. For the purpose of this study, the fragment characteristics of interest will include fragment size, shape, and structure (*e.g.*, stand density, basal area, species composition). There will be maximum variation in fragment characteristics amongst the three proposed inner-city study sites, and maximum variation of surrounding land use amongst sites along the urban-rural gradient. By incorporating sites with significant variability amongst these parameters, this work will allow for the identification of how each of these values contributes to changes in the physical and chemical hydrology of urban forest fragments in an attempt to answer the following question: *to what effect do these parameters impact the chemical and hydrological ecosystem services of urban forests?* Thus, this study looks within an urban area *and* along an urban-rural gradient to discern what effect the size and shape of fragments will have on the hydrology and chemistry of urban forests. To account for variability in hydrology and hydrochemistry, full plot inventories will be

conducted to characterize each fragment. Inventories will consist of identification of dominant soils and tree species, in addition to measurements of leaf area index (LAI), stand basal area, and stand density.

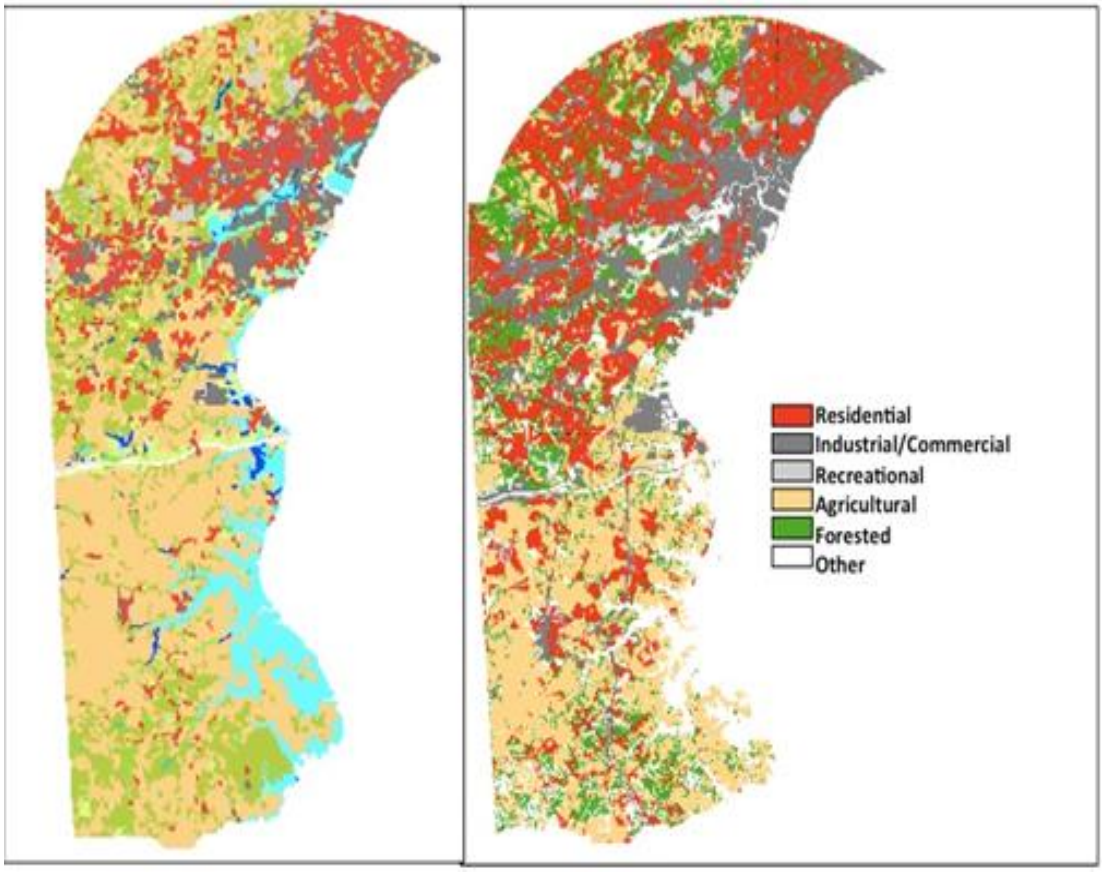

Figure **1.1**. Land use/land cover change in New Castle County, DE from 1984 (left) to 2002 (right). The 1984 map depicts water and wetlands (blue), and displays forested areas in light green. The 1984 map was adapted from Mackenzie (1997). The 2002 map was compiled using 2002 Delaware land use/land cover data. (Source: http://www.state.de.us/planning/info/lulcdata/2002_lulc.htm)

1.4 Ecosystem Services of Urban Forests

1.4.1 Physical Hydrology

Urban forests provide a wide array of ecosystem services, defined by Dobbs et al. (2011) as "the conditions and processes through which natural ecosystems, and the species that inhabit them, sustain and fulfill human life." With respect to water resources, the ecosystem services supplied by urban forests aid in the reduction of stormwater volume and flow rates, and in the improvement of its quality. This occurs in several ways. The canopy cover of urban forests allows for increased interception and evaporation of precipitation (Boggs and Sun 2011). Additionally, the partitioning of precipitation into throughfall and stemflow that occurs within forested urban areas allows for a higher percentage of incident precipitation to be infiltrated through the soils and thus serve as groundwater recharge (Bartens et al. 2009). This essentially provides the benefit of securing a higher water supply for future usage. In addition, the partitioning of precipitation by urban forests into throughfall, stemflow, and that which is intercepted and evaporated from the canopy, reduces the amount of incident precipitation that becomes stormwater runoff. This subsequently results in reductions in peak flow, flood frequency, and sediment transport in urban and suburban streams (Matteo et al. 2006).

Much of our current understanding of urban forest hydrology can be attributed to modeling and field-based studies which attempt to quantify the degree to which urban forests attenuate stormwater runoff. Using the i-Tree hydro model, Kirnbauer et al. (2013) determined that four deciduous tree species often planted in urban areas intercept and evaporate approximately 6.5-27% of total incident rainfall during the leaf-on period. Armson et al. (2013) determined that urban plots containing trees generated significantly

less runoff than those solely containing impervious cover. In plots containing asphalt, runoff accounted for 62% (winter) and 53% (summer) of total rainfall, whereas runoff accounted for only 26% (winter) and 20% (summer) of total rainfall in plots containing trees.

Several studies have been conducted which focus on the partitioning of precipitation by urban trees. Xiao and McPherson (2011), Asadian and Weiler (2009), and Guevara-Escobar et al. (2007) investigated how the canopy structure of varying tree species affected throughfall and stemflow volume in urban areas in the United States, Canada, and Mexico, respectively. The studies were all conducted, however, using a small number of street trees from which data was collected (n = 3, 6, and 1, respectively). It is possible that these limited sample sizes fail to capture the full function of urban forest fragments with respect to the partitioning of precipitation.

While observations of individual trees are important for understanding the processes by which urban trees aid in precipitation partitioning and runoff reduction, it must be acknowledged that urban trees also exist in fragmented forest patches, and, as such, display hydrological patterns observed at the stand scale.

1.4.2 Chemical Hydrology

Excluding studies that identify trends in throughfall solute composition, relatively little work has been done which examines the ecosystem services provided by urban forests with respect to hydrochemistry. Church (1997) described that the biogeochemical processes that occur in forested catchments determine the quality of water that is eventually extracted from these landscapes for human usage. The leaching of solutes (such as H^+ ions deposited through polluted precipitation) from forested soils to

groundwater and surface water sources can significantly alter the pH of water (in addition to other water quality parameters), making it unsafe for plant and animal life, and subsequently, for human consumption. Beyond water usage for human consumption, this alteration of the chemical composition of precipitation interacting with the canopy can have both positive and negative impacts on the health and function of the urban canopy, thus offering what may be considered hydrochemical services and disservices. Whether hydrochemical services or disservices are performed by the urban canopy can be determined by a myriad of anthropogenic and natural factors. These include, but are not limited to atmospheric deposition rates of varying elements, proximity of a given urban forest fragment to distinct forms of urban land use, and the heterogeneity of woody and herbaceous vegetation within these metropolitan wooded lots. It should be noted that the provision of these hydrochemical services and disservices by the urban canopy are facilitated in large part by the transport of solutes via throughfall and stemflow, yet there remains a paucity of research within the current literature as to solute fluxes occurring via these two flux mechanisms within urban forest fragments.

1.5 Research Objectives

In recent years, there has been significant efforts made to increase total urban canopy cover so as to maximize their yield of ecosystem services that may aid in improving environmental quality, in addition to the quality of life enjoyed by inhabitants of established and expanding metropolitan areas. Additionally, through the advent of urban forest modeling software, such as i-Tree multi-tiered model, there has been noteworthy advances made in both forecasting and quantifying ecosystem service yield by the urban canopy, which has been of great use to urban forest planners and managers

both domestically and abroad. However, in both research and practice, there remains the need for a more precise understanding of how the constituent trees within the urban canopy aid in providing ecosystem services, specifically at the scale of urban wooded lots. As the ability of trees to provide these services varies significantly based on their respective health conditions, age, size, and species, it is imperative to develop an improved understanding of how ecosystem yield by the urban canopy varies according to tree species, atmospheric deposition load, and the spatial configuration of the remnant forest fragments of interest.

It is thus the intended goal of this research to utilize data collected via in situ sampling in remnant forest fragments within a densely populated metropolitan region to expand our current understanding of the provision of hydrologic and hydrochemical ecosystem services by the urban canopy. This goal is obtained through three projects described in the manuscripts which summarize this work. The first of these manuscripts applies a thorough review of the urban forest, hydrology, and biogeochemistry literature to the development of a prescriptive guideline for tree selection in the urban canopy, specifically when the intended goals of urban afforestation efforts included the provision of hydrologic and hydrochemical ecosystem services. The second manuscrips utilizes flux-based enrichment ratios for stemflow to explore the complex relationship between species heterogeneity, spatial configuration (i.e., location within a city or along an urban-to-rural gradient), and the chemical enrichment of precipitation as it interacts with and passes through the urban canopy. The third and final paper challenges our current conceptual understanding of the "urban" through approaching the concept from a hydrochemical perspective. It applies a comparative analysis of hydrochemical fluxes

occurring via throughfall within urban fragments located within the boundaries of a relatively large city, and those occurring within a suburban forest fragment. Implications for monitoring urban forest health, and for urban forest planning. A summary of the main themes and findings of these papers is provided in Table 1.1.

Table 1.1 Overview of dissertation constituent manuscripts and additional chapters, including major themes and findings.

Paper/Dissertation Section	Chapter (page)	Main themes and findings
A PRESCRIPTIVE GUIDE FOR URBAN TREE SELECTION TO ENHANCE HYDROLOGIC AND HYDROCHEMICAL ECOSYSTEM SERVICES	2 (pg. 14)	- Ecosystem service yield by urban trees is largely dependent on species composition and canopy structure. - Distinct structural characteristics aid in the provision of hydrologic (i.e., rainfall interception and runoff reduction) and hydrochemical (e.g., acid neutralization) ecosystem services. - Production of hydrologic and hydrochemical ecosystem services by urban canopy can by maximized by strategic management strategies that incorporate knowledge of trees with the characteristics and biodiversity aims known to aid in provision of these ecosystem services - Focus of this paper is informing decision-making regarding urban afforestation at the forest-patch scale.
COMPARISONS OF FLUX-BASED STEMFLOW ENRICHMENT RATIOS FOR TWO QUERCUS SPP. WITHIN THE MEGALOPOLIS OF THE EASTERN USA	3 (pg. 51)	- Chemical alteration of precipitation occurs due to interaction with the canopy. - The degree to which precipitation is chemically altered varies according to that portion of the canopy with which interaction occurs (e.g., foliar vs. woody surfaces).

		- Flux-based enrichment ratios for stemflow in relation to (a) gross precipitation and (b) throughfall used to quantify chemical enrichment of precipitation interacting with both urban and non-urban canopies, and relative contribution of throughfall and stemflow to total sub-canopy nutrient flux. - Spatial patterns in nutrient delivery to forest soils are impacted by this alteration at the intra-fragment, intra-urban, and transregional scale. - Implications for use of flux-based enrichment ratio as a proxy for urban forest health are explored.
IMPACTS OF LAND USE VARIABILITY ON THROUGHFALL SOLUTE FLUX WITHIN REMNANT URBAN AND SUBURBAN FOREST FRAGMENTS	4 (pg. 91)	- Significant spatial variability in throughfall solute flux for remnant fragments in highly develop extents of metropolitan regions - Observed solute fluxes for some elements higher in suburban site, rather than in sites within city - Emissions affiliated with various forms of urban land use likely driver of elevated atmospheric deposition and subsequently elevated levels of solute flux - Implications for urban forest management
DISCUSSION	5 (pg. 116)	- Contextualization of novelty of dissertation research - Practical implications for findings of dissertation research
SUMMARY	6 (pg. 120)	- Summary of main findings of the dissertation

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Chapter 2

A PRESCRIPTIVE GUIDE FOR URBAN TREE SELECTION TO ENHANCE HYDROLOGIC AND HYDROCHEMICAL ECOSYSTEM SERVICES

2.1 Abstract

Expansive urbanization is nearly always accompanied by environmental degradation. Growing metropolises around the world exhibit amplified air temperatures, increased air pollution, altered floral and faunal biodiversity, impaired environmental health, and heightened production of stormwater runoff in an around cities. The reintroduction and expansion of urban forest cover has become an important means by which many cities are working to mitigate, and when possible, reverse these negative, urbanization-induced environmental impacts. This desire for increased tree cover is due, in large part, to urban trees providing a vast array of ecosystem services. Optimization of the production of these ecosystem services by the urban canopy depends heavily on the structural makeup of the trees. This paper provides a review of forest hydrology and biogeochemistry literature to identify the urban forest structural characteristics that aid in maximizing its provision of two highly valued ecosystem services: the interception and infiltration of stormwater, and acid neutralization. We utilize knowledge of forest structure and species composition to provide a prescriptive guide for tree selection to maximize the delivery of these ecosystem services within urban forests.

Key words: urban sustainability, stormwater mitigation, interception, acid neutralization, urban forest health, urban forest management plan

2.2 Introduction

Currently the number of people living in cities exceed those inhabiting rural areas (United Nations 2012). A growing urban population has led to expansive land conversion to urban land uses (e.g., residential, transportation, commercial) (Levia 1998; Alig 2004, Sun 2018). The environmental impacts of urbanization are substantial, and include increased air temperatures, declining air quality, altered floral and faunal biodiversity, and increased urban stormwater runoff and flooding (Leopold 1968, Oke 1982, Smith et al. 2005, Grimm et al. 2008, Ravindra et al. 2008, Ramamurthy and Bou-Zeid 2017, Squizzato et al. 2017).

In response to this environmental degradation, a growing number of cities have implemented urban greening initiatives to decelerate, and where possible, reverse the negative impacts of urbanization on environmental quality and function (Li et al. 2005, McPherson et al. 2011). The urban greening initiatives often include urban trees and forests. This inclusion is due, in large part, to the wide range of cultural (e.g., increased property values, improved mental health), supporting (e.g., faunal habitat), provisioning (e.g., food production), and regulating (e.g., carbon sequestration, air quality improvement, stormwater runoff reduction) ecosystem services provided by urban forests (Costanza et al. 1997, Avila-Flores and Brock Fenton 2005, Nowak et al. 2006, Nowak et al. 2013, Taylor et al. 2015, Escobedo et al. 2015, Synk et al. 2017). In many cities, street trees have been the focus of the initiatives (Donovan and Butry 2010), but some

metropolises, have expanded their efforts to include afforestation at the forest scale (Sullivan et al 2009).

Urban forests are comprised of individual trees as well as trees in small groups or larger forest stands. Urban forests provide ecological benefits (Dobbs et al. 2014) and in comparison to isolated urban trees, forest stands likely produce more ecosystem services per unit area due their relatively large areas with more concentrated leaf area. Ramalho et al. (2014) further suggest that larger urban forest stands have a higher conservation potential than do smaller stands. They are less susceptible to fragmentation effects (e.g., species extinction) due to reduced habitat extent and decreased seed dispersal) than are smaller fragments, thus increasing the likelihood of sustained succession within these stands, and the prolonged production of ecosystem services.

As space for trees is often limited within urban areas, it is important that new forest stands be strategically located and populated to optimize ecosystem services (Oldfield et al. 2015). Knowledge of canopy characteristics that maximize ecosystem services is essential in the successful establishment and maintenance of urban afforestation efforts (Doroski et al. 2018).

The purpose of this paper is to review urban forest hydrology and biogeochemistry literature to identify which urban forest structural characteristics impact hydrologic and hydrochemical ecosystem services. From this review, a prescriptive guideline is developed to aid urban land managers in tree selection to enhance stormwater mitigation (hydrologic ecosystem service) and acid neutralization (hydrochemical ecosystem service) within urban forests.

2.3 Assessing Hydrologic and Hydrochemical Ecosystem Service Yield via *In Situ* Sampling and Quantitative Analysis

2.3.1 Quantifying Hydrologic and Hydrochemical Fluxes in Urban Ecosystems

To assess the hydrologic and hydrochemical ecosystem services provided by urban forests, the water and solute fluxes affected by the urban canopy must be quantified. Hydrologic fluxes are calculated using a mass balance equation that accounts for the three potential fates of precipitation (*P*) that interacts with the canopy: (1) interception (*I)* is precipitation that is captured by foliar and woody surfaces, which it is subsequently stored or evaporated; (2) throughfall (*TF)* is precipitation which passes through the canopy *en route* to the soil, either falling through canopy gaps or interacting with foliar or woody surfaces along the way; and (3) stemflow (*SF)* is precipitation that is transported to forest soils via tree trunks. Thus, precipitation is distributed as

$$P = I + TF + SF \quad (1)$$

P, *TF*, and *SF* are most often directly measured in the field, with *I* often solved based on the missing variable in the equation. However, direct measurement can also be used to determine *I* (Huang et al. 2005, Friesen et al. 2015; Van Emmerik et al. 2017).

2.3.2 Volumetric Measurements of Throughfall and Stemflow

Various methods can be used to quantify the hydrologic fluxes occurring via throughfall and stemflow within the urban canopy. For both throughfall and stemflow, field-based volumetric measurements can be converted to depth equivalents using equations (1) and (2) in Table 2.1. The derived values can subsequently be used in equation 1 above to quantify the partitioning of incident precipitation into throughfall,

stemflow, and interception. Throughfall fluxes are generally determined with individually standing collectors (either stationary or roving) or troughs placed beneath the canopy. Both methods have been successfully employed in studies conducted to quantify the relationship between throughfall flux and interception by the urban canopy (e.g., Guevara-Escobar et al. 2007, Xiao and McPherson 2011).

To quantify the hydrologic fluxes that occur via stemflow, impermeable collars are affixed to the bark exterior and oriented in a helix-like fashion. These stemflow collars can be constructed using a variety of materials, including polyurethane, flexible tubing, tarpaulin, and aluminum or plastic foil (Likens and Eaton 1973, Levia and Germer 2015). The collars are secured to the tree bark with sealant that closes any gaps that may exist between the collars and the stem. The stemflow that is generated during precipitation events is channeled by the collars to a rain gauge or collection bin to determine total water flux during the sampling period. Livesley et al. (2014) utilized this method to determine how different eucalypt species contribute to stormwater mitigation in Melbourne, Australia. Carlyle-Moses and Schooling (2015) also employed similar techniques to identify the relationship between tree structure and stemflow yield in an urban park in British Columbia, Canada.

2.3.3 Quantifying Hydrochemical Fluxes in Throughfall and Stemflow

To assess hydrochemical services, a comparison must be made between solute fluxes occurring beneath the canopy and those occurring in nearby non-forested areas. Such comparisons demonstrate how the chemical composition of incident precipitation is altered as a result of interacting with tree canopies. The collection techniques used to sample throughfall and stemflow for hydrochemical analysis are generally the same as

those outlined above. Once gathered, samples may be left unfiltered for examination of particulate matter, or filtered for inspection of dissolved material. The preservation of samples, storage materials (e.g., plastic or glass), and sample storage times should follow standard guidelines and protocols (e.g., APHA, AWWA, and WEF 1998) to ensure sample integrity of the chemical constituents.

Once throughfall and stemflow chemistry have been determined and their respective hydrologic fluxes accounted for, flux-based enrichment ratios for the two parameters can be quantified (Levia and Herwitz 2000; Levia and Germer 2015). The enrichment ratio metric [Table 2.1, equation (4)] can be utilized to specify the degree to which precipitation chemistry is altered due to interaction with plant surfaces. Schooling et al. (2017) utilized this metric to quantify solute fluxes from isolated urban trees in British Columbia, Canada. Levia and Germer (2015) introduced a flux-based enrichment ratio for stemflow in relation to throughfall that makes it possible to identify the relative contributions to subcanopy solute flux made by both parameters.

Sampling for hydrochemical fluxes within the urban forest canopy may occur at the spatial and temporal scales best suited for each respective study. Event-based fluxes from isolated trees and larger forest stands may aid in determining how the water quality-related services and disservices vary due to an array of environmental conditions (e.g., antecedent dry period, storm type). Sampling characterized by a more coarse temporal resolution (i.e., weekly, monthly, seasonally) may provide insight into general patterns in hydrochemical fluxes that occur as a result of urban forests. Simkin et al. (2004) suggest the use of ion exchange resins for studies in which there are larger time gaps between sampling. While this technique requires a significant amount of laboratory based

preparation and analysis work, its application is recommended for certain ions as it provides accurate measures of Cl^-, NO_3^-, and SO_4^{2-} in precipitation samples when the sampling frequency is low.

Both stemflow yield and chemical composition will vary based on different bark characteristics, including microrelief (Section 2.4.1.1). Generalizable measurements of bark microrelief can be made via field-based observations that utilize laser technology (Sioma et al. 2018, Van Stan et al. 2010) and manually-derived measurements (Yarranton 1967, Schooling and Carlyle-Moses 2015). Schooling and Carlyle-Moses (2015) utilized a bark roughness index (BRI) to quantify bark microrelief. They calculated BRI as the ratio of the furrowed circumference of a tree bole to its unfurrowed circumference, with their observed values ranging from 1 (smooth bark) to 1.43 (rough bark). Use of this method may be of practical utility for the quantitative, standardized assessment of bark microrelief within the urban canopy.

2.4 Canopy Structural Characteristics which Maximize Ecosystem Service Provision

2.4.1 Hydrologic Ecosystem Service Provision: Rainfall Interception and Stormwater Runoff Reduction by the Urban Canopy

2.4.1.1 Relationships between Urban Forest Structure and Stormwater Mitigation

Urban trees mitigate stormwater runoff by intercepting precipitation and increasing precipitation infiltration into soils by slowing precipitation rates beneath the canopy and creating space in soils for infiltration via roots and transpiration of soil water. For both broadleaved and coniferous species, the proportion of total rainfall intercepted

by the urban canopy can be relatively large (Table 2.2). Xiao and McPherson (2011) determined three broadleaved species on a residential lot in Oakland, California, USA intercepted 14-27% of *P* on average. Guevara-Escobar (2007) found that during low magnitude precipitation events, a *Ficus benjamina* tree in Quateraro City, Mexico could intercept up to 100% of *P*. Asadian and Weiler (2013) further found that urban coniferous trees in British Columbia, Canada intercepted an average 71% of *P*. However, as storm intensities increase, the percent intercepted by trees decreases as trees have a finite capacity for intercepting precipitation (e.g., Carlyle-Moses and Schooling 2015). After storm events, the capacity of tree canopies to intercept rainfall is refreshed as water intercepted and storm in the canopy is evaporated back to the atmosphere.

The evaporation of water stored in the canopy via rainfall interception is affected by an array of abiotic and biotic factors (Figure 2.1). Environmental conditions such as the characteristics of a given storm event (e.g., duration, magnitude, intensity), antecedent dry period, wind speed and direction, air temperature, and relative humidity have been found to have significant impact on interception loss (Crockford and Richardson 2000, Xiao et al. 2000, Levia and Frost 2006). Guevara-Escobar et al. (2007) postulated that within metropolitan districts, the rate of interception might actually be greater than in natural forests due to the urban heat island effect that increases local air temperatures. Increased temperatures would increase evaporation rates thus potentially increasing the amount of water that could be intercepted within a year. Though environmental conditions serve as important controls on interception loss by the urban canopy, their high temporal variability make them more difficult to incorporate into plans for the strategic use of urban woodlands for water resource management. However, a

sound understanding of the biotic traits or physical characteristics of trees that determine their ability to intercept precipitation can be used to aid water resource management using urban forests.

Canopy water storage capacity, which is the maximum amount of precipitation that can be stored by the canopy's foliar and woody surfaces before saturation is reached, has been identified as a dominant physical trait impacting interception loss from urban trees (Xiao et al. 2000). Higher water storage capacities have been correlated with reduced throughfall and stemflow yield, as they allow for a greater proportion of precipitation to be retained by the canopy (Levia and Herwitz 2005). Herwitz (1986) found that the storage by woody material is substantially higher than that of foliar surfaces per unit area. Xiao et al. (2000) determined that the foliar surfaces of an isolated broadleaved cork oak tree had a maximum water storage capacity of 0.7mm per unit leaf area. Iida et al. (2017) determined that bark water storage capacity for Japan's most common tree, the Japanese cedar, varied from 3.7-5.7mm per unit bark volume, depending on environmental conditions (e.g., calm vs. high winds). Levia and Herwitz (2005) quantified the normative bark water storage capacity for sweet birch, red oak, and pignut hickory trees in northeastern United States woodland. Their findings indicated that the potential maximum bark water storage by these species ranged 40L (sweet birch) to 500L (red oak). Because canopy water storage capacity varies significantly among species (Xiao and McPherson 2016), the strategic selection of species displaying high water storage capacity will likely positively impact the reduction of runoff in urban areas.

Canopy water storage capacity can be affected by various bark and leaf characteristics. With respect to woody surfaces, attributes of a tree's bark morphology

are critical in determining if a significant proportion of precipitation will be intercepted and retained by the bark, thus potentially minimizing stormwater runoff. Bark morphology can be characterized by the presence, shape, and orientation of plates, scales, and furrows on bark surfaces (Sadjak 1967, Whitmore 1962). These features collectively affect both water storage capacity and the ability of wood surfaces to impede or generate stemflow production. For example, while relatively smooth bark and linearly aligned furrows promote stemflow production, bark characterized by relatively high microrelief and deep, intricately interstitched furrows have been found to have higher water storage capacities, and as such, generate smaller stemflow yields (Levia and Herwitz 2005, Livesely et al. 2014). Collectively these characteristics increase both the contact time of precipitation with the bark and the likelihood that this precipitation will be retained by the woody surfaces. Xiao and McPherson (2011) found that a rough-barked *Ginko biloba* L. (gingko) tree on a residential lot was notably less efficient at stemflow production than a neighboring smoother-barked sweetgum (stemflow accounted for 1.0% and 4.1% of *P*, respectively), thus making a notably smaller contribution to water reaching the soils via stem flow. To maximize potential runoff reduction in an urban forest, trees with rough, intricately fissured bark with interstiched furrows should be used to enhance rainfall interception.

Stemflow production can also be affected by canopy architecture, which, in part, determines the funneling capacity of the tree crown (as evidenced by funneling ratio values; Table 2.1, equation 3) (Schooling and Carlyle-Moses 2015). While trees with plagiophile branching structures (i.e., oriented toward 45°) effectively funnel precipitation to the bole, planophile branching structure (i.e., oriented toward the

horizontal) is not effective at funneling. More funneling will produce higher stemflow yields. Levia and Herwtiz (2002) and Levia et al. (2015 a) determined that branchflow and stemflow yields were greatest for branches inclined at angles between 38° and 39.2° above the horizontal. Levia et al. (2015 a) further suggest that for trees with more erectophile branching structures, projected stem area is low, thus reducing funneling capacity and stemflow yield, and increasing the potential for throughfall production.

Foliar surfaces characteristics such as length of foliation period and leaf geometry, area, and hydrophobicity play an important role in regulating water storage capacity and interception losses by the urban canopy. Similar to patterns observed with tree bark, the ability of leaf surfaces to intercept and retain precipitation is affected by their geometry and roughness (Crockford and Richardson 2000, Levia and Frost 2006). Leaves with relatively high surface rigidity and complex geometric shape, both the total leaf surface area and interception capacity tend to have greater interception rates. Keim et al. (2006) determined that interception by coniferous species consistently exceeded that by broadleaved species, attributing this observation to the comparatively more complex surface structure of coniferous needles than that displayed by broadleaves, and the associated higher total leaf area that results from this more complex surface area.

While the surface area of individual leaves has a significant impact on canopy water storage capacity, the influence that the total leaf area of a given tree – or of an urban forest – has a large effect on interception loss. There is a direct relationship between leaf area index (LAI: m^2 on sided leaf area per m^2 of ground area beneath canopy) and canopy water storage capacity, with higher LAI corresponding to greater canopy water storage and interception loss (Aston 1979, Fleischbein 2005). LAI can be

affected by several factors, including species, foliation period, age, and canopy maintenance practices (Helvey and Patric 1965, Link et al. 2004, Pypker et al. 2005). For broadleaved deciduous species, total interception and water storage capacity are higher during the leaf-on season, when LAI is at a maximum. Further, potential foliar water storage capacity for broadleaved evergreen species is higher than for their deciduous species due to year-round presence of foliage (Xiao and McPherson 2011). Incorporating evergreen deciduous species into urban forests can maximize the reduction in stormwater runoff, especially in cities characterized by a Mediterranean climate where most precipitation occurs during the winter months (Xiao and McPherson 2016).

Livesely et al. (2014) found that plant area index (PAI, a metric which quantifies both foliar and woody surface area per unit ground area) is also important in determining interception by the canopy. They found that interception values were highest (and thus throughfall and stemflow lowest) for canopies characterized by higher PAI values in Melbourne, Australia. As such, urban forests with high PAI could enhance stormwater mitigation.

Holder (2013) found that canopy storage capacity is also affected by leaf hydrophobicity, which describes the degree to which water interacting with a leaf is likely to be repelled from its surface. One factor that affects the likelihood of foliar surfaces to retain or repel water is trichome presence and density, with a generally direct relationship found between the presence trichomes and the retention of water by foliar surfaces (Holder 2012). Leaves that are more highly hydrophobic are more likely to repel rain droplets, have lower water storage capacities, and intercept less precipitation than those that are more hydrophilic. Foliar hydrophobicity can vary significantly amongst the

various tree and shrub species that are commonly found within urban canopies (Holder 2013, Holder and Gibbes 2017).

2.4.1.2 Prescriptive Tree Selection for Optimized Runoff Reduction by Urban Forests

Runoff reduction by the urban canopy is significantly aided by the presence of trees characterized by high canopy water storage capacities. Accordingly, tree selection for urban forests to mitigate stormwater should be based on foliar and woody surface attributes that increase canopy water storage capacity, reduce the likelihood of throughfall or stemflow production, and thus heighten interception losses. For woody surfaces, trees should have a complex bark morphology (e.g., overlapping plates, interstiched furrows) that allow for higher water storage capacities (Figure 2.1), in addition to trees in which the canopy architecture minimizes the funneling of net precipitation to the bole for the subsequent generating of stemflow (i.e., planophile branching structure). Recommended species that fit these criteria and would aid in optimizing interception by urban woodlots include: *Quercus macrocarpa* (bur oak), *Quercus alba* (white oak), *Pistacia chinensis* (Chinese pistache), *Liriodendrun tulipifera* (yellow-polar), and *Gleditsia triacanthos* (honeylocust) (Table 2.3).

Foliar surface characteristics can also help increase interception (e.g., leaf area, foliation period). Inclusion of species that display these characteristics can help reduce runoff. For potential year-round interception, broadleaved evergreen species with high canopy storage should be used, such as *Quercus ilex* (holly oak), *Mangolia grandifolia* (southern magnolia), and *Cinnamomum camphora* (camphor). Additionally, trees with complex foliar geometry and relatively high leaf area can aid in increasing canopy

interception and regulating runoff. As the leaf area of conifer needles is characteristically high, conifer species such as *Picea abies* (Norway spruce), *Cedrus atlantica* (atlas cedar), *and Psuedotsuga menziesii* (Douglasfir) often have high leaf area for maximizing these benefits (Figure 2.1). As hydrophilic leaves aid in retaining P, species with foliar surfaces that increase water retention (i.e., trichome presence and density) such as *Carya ovata* (shagbark hickory), *Ulmus pumila* (Siberian elm) and *Populus deltoides* (eastern cottonwood) could be used to maximize reduction in stormwater runoff (Holder 2013). Also, species with relatively high transpiration or water use rates (e.g., Costello and Jones 1994) would be helpful in drying out soils between rain events and thus allowing from greater soil infiltration during rain events.

Reductions in stormwater runoff by the urban forests tend to be maximized when tree canopies are over impervious surfaces because these surfaces tend to rapidly generate runoff due to limited infiltration capacity (Nowak et al. 2008). Thus, planting trees to cover impervious cover or soils with low infiltration capacity (e.g., compacted soils) could maximize the impact of afforestation efforts on reducing stormwater runoff.

2.4.2 Hydrochemical Ecosystem Service Provision: Neutralization of Acidic Atmospheric Deposition

2.4.2.1 Relationship between Urban Forest Structure and Acid Neutralization

Urban trees also perform hydrochemical services which aid in balancing the delivery to and availability of nutrients in urban forest soils, thereby helping to regulate forest health and functions. One of these hydrochemical ecosystem services is the neutralization of acidic material deposited from the atmosphere onto the canopy. This

acid neutralization is impacted by the structural characteristics of urban forests, including tree species composition. Acid neutralization potential will depend upon how much acidic material is in the atmosphere or precipitation (e.g., proximity to pollution sources).

Atmospheric deposition to forests serve as one conduit by which nutrients are sourced to the canopy (Weathers and Ponette-Gonzalez 2011). The deposition of these nutrients can occur in one of three processes: dry deposition, (i.e., the direct settling of gaseous or particulate matter from the atmosphere onto the canopy), wet deposition (i.e., the placement of gaseous and particulate matter onto the canopy via precipitation); and occult deposition (i.e., direct deposition from fog or clouds in contact with the canopy) (Lovett and Lindberg 1984, Weathers and Ponette-Gonzalez 2011) (Figure 2.2). There are myriad terrestrial and anthropogenic origins from which atmospheric deposition may be sourced. Amato et al. (2009a) determined that much of the terrestrially-sourced airborne particulate matter in cities, such as potassium and magnesium, enters the atmosphere via increased human movement. A sizeable proportion of the airborne particulate matter in cities, including iron, copper, and antimony, are byproducts of automobile brakes from urban roadways (Amato et al. 2009b). Polycyclic aromatic hydrocarbons (PAHs) from incomplete combustion of biofuels and biomass (i.e., emissions from vehicles, industrial and domestic land use) can also be problematic in urban areas (Ravindra et al. 2008). Urban canopies also receive relatively high levels of atmospherically deposited nitrogen oxides (NO_x) and sulfur oxides (SO_x) due to the elevated occurrence of fossil fuel combustion in and around cities (Weathers and Ponette-Gonzalez 2011). The NO_x and SO_x deposited on urban canopies can be acidic in nature (i.e., high concentration of hydrogen ions, H^+). The excessive deposition to and

subsequent transport of highly acidic precipitation by urban canopies via throughfall and stemflow can have deleterious effects on urban forest health and function if not managed for, including the occurrence of aluminum toxicity and podzolization within forest soils (Cronan and Grigal 1995, Likens et al. 1996, Levia et al. 2015 b).

Within forested ecosystems, canopy exchange processes take place which allow for a proportion of this acidic deposition to be neutralized (Lovett and Lindberg 1984, Neary and Gizyn 1994, Lindberg et al. 1986). Essentially, through proton buffering, H^+ deposited on the canopy is exchanged for base cations, including potassium (K^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}), during contact with foliar and woody surfaces. This process helps to provide an environmental buffer against the transport of acidic compounds through the canopy to forest soils via throughfall and stemflow. Following acid neutralization by the urban canopy, the precipitation that is transported to forest soils is chemically altered and its acidity is neutralized. These chemical transformations help provide for more balanced distribution of the essential nutrients and help sustain healthy and functional forests.

The extent to which urban forests are able to neutralize acidic precipitation is in part determined by the species composition, which partly governs the pH of the bark, contact time of intercepted precipitation with the tree surface, and proton buffering capacities. Numerous studies have shown that broadleaved trees consistently display a higher capacity for acid neutralization than do coniferous species (e.g., Pucket 1990, Neary and Gizyn 1994, De Schrijver et al. 2007). Acid neutralization occurs on the surfaces of both deciduous and coniferous trees. However, Neary and Gizyn (1994) and Jung et al. (2011) determined that the relatively high scavenging capacity of densely

packed conifer needles leads to relatively high deposition of acidic material, thereby increasing the likelihood of conifers being net acidifiers. These characteristics lead to a higher risk for the transport of acidic throughfall and stemflow to forest soils below conifers (Neary and Gizyn 1994, Jung et al. 2011).

In addition to foliar surface characteristics, bark attributes also contribute to the ability of a tree to neutralize acids. Generally, proton buffering increases when the residence time of stemflow increases (Levia et al. 2011). Levia et al. (2011) found that the concentrations of base cations in stemflow were significantly higher for yellow poplar than for *Fagus grandifolia* (American beech) in a Maryland USA-situated forest. They attributed this observation to the bark of yellow poplar being more morphologically complex, which impedes the transport of stemflow and increases its residence time on woody surfaces, and subsequently, increases canopy cation exchange activity.

2.4.2.2 Prescriptive Tree Selection for Optimized Acid Neutralization by the Urban Canopy

To maximize the acid neutralization forests should be populated with a greater proportion of broadleaved rather than coniferous species. Additionally, acid neutralization can potentially be maximized by incorporating species with high stemflow residence times. Stemflow residence times are increased in species with more morphologically complex bark and branches that are marginally oriented above the horizontal to allow for greater leaching of base cations via relatively high residence times, (e.g., approximately 20°, Levia and Herwitz 2002). Species with such characteristics include yellow poplar, *Quercus montana* (chestnut oak), *Carya glabra* (pignut hickory), *Acer negundo* (boxelder), *Acer nigron* (black maple), *Fraxinus*

pennsylvanica lancelota (green ash), *Tilia americana* (American linden), and *Liquidambar styraciflua* (sweetgum) (Figure 2.2).

2.5 Implications for Urban Forest Planning and Management

Optimization of the hydrologic and hydrochemical ecosystem services detailed above does not rely solely on the identification of canopy characteristics and tree species that aid in their provision, but also on the implementation of urban forest management plans (UFMPs) designed to ensure their sustainable production. Because the urban forest is a dynamic landscape that is susceptible to various biotic (e.g., pest and disease attacks; Eastgate 2000, Ball et al. 2007, Lovett et al. 2016) and abiotic (e.g., the urban heat island effect, predicted climate variability) stressors which may threaten its health and productivity (Zwack et al. 1999, Laćan and McBride 2008, Ordóñez and Duinker 2014), these UFMPs must account for the need to establish and maintain a biologically diverse urban canopy that is resilient to both abrupt and long-term changes to the urban environment. The inclusion of biodiversity initiatives into UFMPs must therefore be strategic as the former serves a vital role in guaranteeing the longevity of urban forest health, function, and ecosystem service provision (Mace et al. 2012). A detailed review of the linkages between urban forest biodiversity and ecosystem service provision is beyond the scope of this study (the reader is directed to Oliver et al. 2015). However, we assert that tree selection intended to optimize hydrologic and hydrochemical ecosystem service yield should incorporate plans to establish a biologically diverse urban canopy characterized by optimal yield of these services and resilience to natural and anthropogenic stressors. Table 2.3 outlines common urban tree species and their respective structural characteristics that may aid in stormwater mitigation by the urban

canopy. It may serve as a useful guide for both tree selection and the strategic establishment of a biologically diverse urban canopy.

2.6 Conclusion

As metropolitan regions continue to expand, urban forest will be needed to help mitigate the negative environmental impacts of urban growth. Species selections will be critical to enhancing future urban forest ecosystem services, and can impact hydrologic and hydrochemical processes to improve urban water resource quantity and quality. In applying knowledge of the structural characteristics to the development and implementation of urban forest management plans, urban land managers will be well-equipped with the decision tools necessary to expand and manage extensive, resilient urban canopy cover from which hydrologic and hydrochemical ecosystem service yield can be optimized.

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TABLES

Table 2.1 Commonly used equations for quantifying hydrologic and hydrochemical fluxes via throughfall and stemflow

Metric	Formula	Variables Defined	Purpose	Reference (where applicable)
Throughfall volume depth equivalent (TF_D)	$TF_D = \frac{V_T}{A}$	V_T = throughfall volume A = collector orifice area	Convert TF volume to depth when measured with non-automated collectors	
Stemflow yield (depth) per unit crown area (SF_D)	$SF_D = \frac{V_S}{A_c}$	V_S = stemflow volume A_c = projected crown area	Convert measured stemflow volume to depth equivalent	
Funneling ratio (F)	$F = \frac{V_S}{(P_g * B)}$	P_g = gross precipitation depth B = tree basal area	Identify degree to which outlying portions of tree crown have contributed to stemflow yield	Herwitz 1986
Flux-based enrichment ratio for stemflow in relation to gross precipitation	$E_S = \frac{V_S * C_S}{P_g * B * C_p}$	C_S = ion concentration in stemflow C_p = ion concentration in gross precipitation, B = tree basal area	Quantify the enhancement of rainwater chemistry resulting from interaction with the forest canopy	Levia and Herwitz 2000

Flux-based enrichment ratio for stemflow in relation to thoughfall ($E_{T,,B}$)	$E_{T,B} = \frac{V_S * C_S}{TF_D * B * C_T}$	C_T = ion concentration in throughfall, B = tree basal area	Determine heterogeneities in nutrient fluxes to forest floor via differing modes of transport (e.g., stemflow vs. throughfall)	Levia and Germer 2015

Table 2.2 Mean percentage of total rainfall intercepted by select isolated urban trees as reported in previous studies. [a] B_E = *broadleaf evergreen;* B_D = *broadleaf deciduous; C =conifer.* ***** indicates the listing of values from 1 of 3 trees of species featured as reported in given reference.

Species	Common name	Classification[a]	Mean percentage of total rainfall intercepted	Reference
Ficus benjamina	Weeping fig	B_E	68.9%	Guevara-Escobar (2007)
Citrus limon	Lemon	B_E	27.0%	Xiao and McPherson (2011)
Liquidambar styraciflua	Sweetgum	B_D	14.3%	Xiao and McPherson (2011)
Ginko biloba	Ginkgo	B_D	25.2%	Xiao and McPherson (2011)
*Pseudotsuga menziesii**	Douglas fir	C	64.1%	Asadian and Weiler (2009)
*Thuja plicata**	Western red cedar	C	71.1%	Asadian and Weiler (2009)
Eucalpytus saligna	Sydney blue gum	B_E	27.3%	Livesely et al. (2014)

Eucalyptus nicholii	Willow-leaved peppermint	B_E	43.9%	Livesely et al. (2014)

Table 2.3. Recommended species for inclusion into urban forests designed to provide precipitation interception (INTERC) or acid neutralization (ACID). *BD* denotes broadleaf deciduous, *BE* broadleaf evergreen, and *C* coniferous species. Relative LAI is determined by foliation period and general estimates of leaf surface area. Degree of relative hydrophobicity is assigned based on known leaf characteristics (i.e., glossy surface vs. presence of trichomes). Arrow directions indicate the degree to which each species can be classified with each respective characteristic. Note: This is a general list of suggested species. Final selection should be based on the trees that will be best suited for the environmental and climatic conditions which characterize the intended afforestation site(s).

Species	Common name	Tree classification	Funneling capacity	Bark morphology	Relative LAI	Degree of foliar hydrophobicity	Ecosystem service	USDA hardiness zone
Acer negundo	boxelder	BD	↑	↑	↓	↓	INTERC, ACID	2-10
Acer nigrum	black maple	BD	↑	↑	↓	↓	INTERC, ACID	4-8
Carya ovata	shagbark hickory	BD	↓	↑	↓	↓	INTERC, ACID	4-9
Catalpa speciosa	northern catalpa	BD	↑	↑	↓	↓	ACID	4-8
Cedrus atlantica	atlas cedar	C	↓	↑	↑	↑	INTERC	6-9
Cinnamomum camphora	camphortree	BE	↑	↑	↑	↑	INTERC	8-10
Carya glabra	sweet pignut hickory	BD	↓	↑	↓	↑	INTERC, ACID	4-9
Eucalyptus nicholii	narrow-leaved black peppermint	BE	↑	↑	↑	↑	INTERC	8-10
Fraxinus pennsylvanica	green ash	BD	↓	↑	↓	↑	ACID	3-9
Gingko biloba	gingko	BD	↑	↑	↓	↑	INTERC	3-8
Gleditsia triacanthos	honeylocust	BD	↓	↑	↓	↑	INTERC, ACID	3-9
Liquidambar styraciflua	sweetgum	BD	↑	↑	↓	↑	INTERC	5-9
Liriodendron tulipifera	yellow-poplar	BD	↓	↑	↓	↑	INTERC, ACID	4-9
Magnolia grandiflora	southern magnolia	BE	↓	↓	↑	↑	INTERC	6-10
Picea abies	Norway spruce	C	↑	↑	↑	↑	INTERC	3-7

Pinus resinosa	red pine	C	↓	↑	↑	↑	INTERC	2-5
Pistacia chinensis	Chinese pistache	BD	↓	↑	↓	↑	INTERC	6-9
Populus deltoides	eastern cottonwood	BD	↑	↑	↓	↓	INTERC	2-9
Psuedotsuga menziesii	Douglasfir	C	↓	↑	↑	↑	INTERC	6-9
Quercus alba	white oak	BD	↓	↑	↓	↑	INTERC, ACID	3-9
Quercus ilex	holly oak	BE	↑	↑	↑	↑	INTERC	7-11
Quercus lobata	valley oak	BD	↓	↑	↓	↑	INTERC	7-11
Quercus macrocarpa	bur oak	BD	↓	↑	↓	↑	INTERC	3-8
Quercus montana	chestnut oak	BD	↑	↑	↓	↑	ACID	4-8
Quercus suber	cork oak	BE	↑	↑	↑	↑	INTERC, ACID	8-10
Thuja plicata	western redcedar	C	↓	↑	↑	↓	INTERC	5-7
Tilia americana	American basswood	BD	↓	↑	↓	↑	INTERC, ACID	3-7
Tsuga canadensis	eastern hemlock	C	↓	↑	↑	↑	INTERC	3-8
Ulmus pumila	Siberian elm	BD	↑	↑	↓	↑	INTERC	4-9

FIGURES

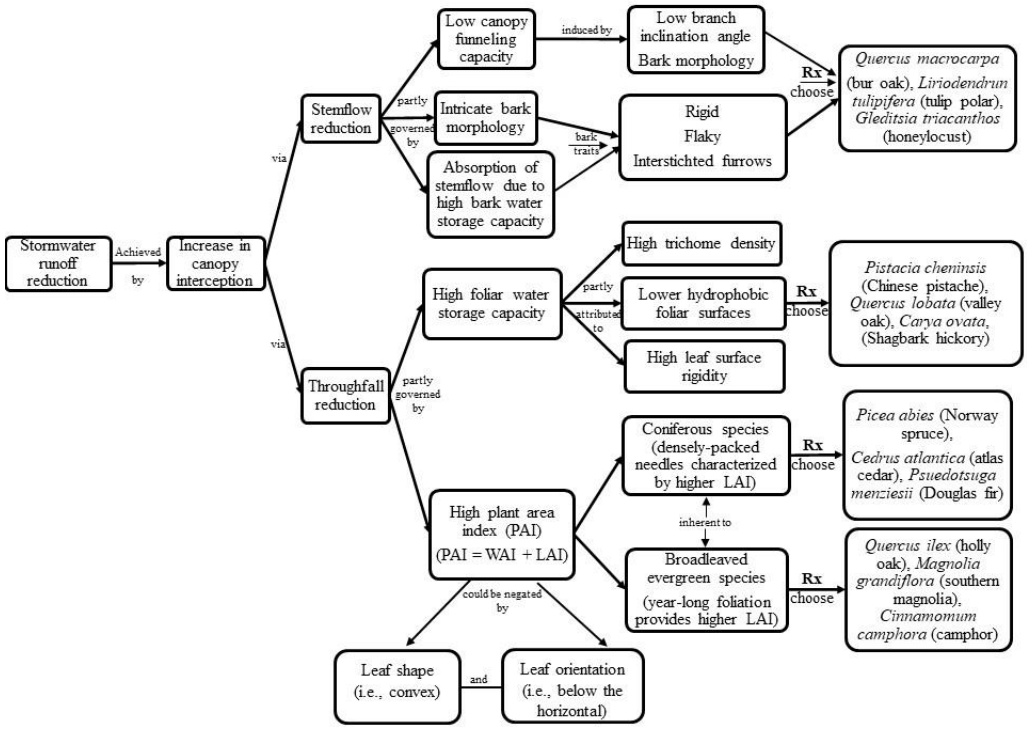

Figure 2.1 Conceptual map of the structural characteristics of urban trees that determine their capacity to intercept precipitation and reduce stormwater runoff. Suggestions of species likely to yield these services is included.

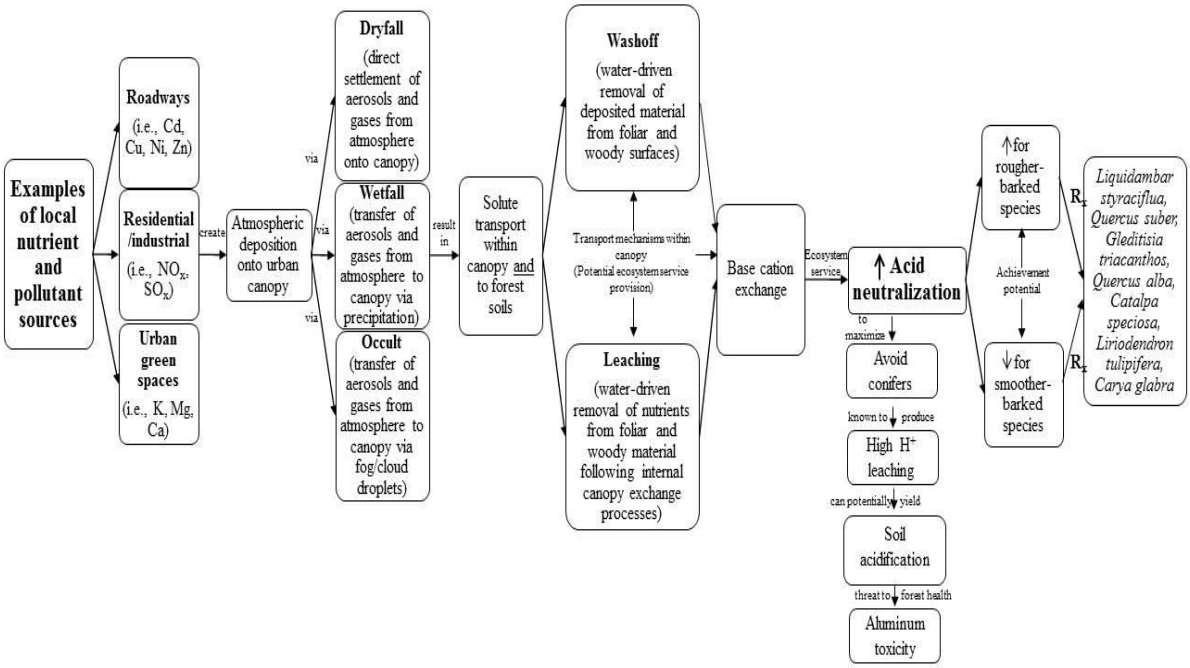

Figure 2.2 Conceptual map of the anthropogenic and environmental processes by which atmospheric deposition occurs within the urban canopy. The diagram also displays the structural characteristics and sub-canopy processes that govern the capacity of urban (and rural) trees to provide the hydrochemical service of acid neutralization.

Chapter 3

COMPARISONS OF FLUX-BASED STEMFLOW ENRICHMENT RATIOS FOR TWO QUERCUS SPP. WITHIN THE MEGALOPOLIS OF THE EASTERN USA

3.1 Abstract

Relative to rural forests, stemflow inputs in urban forest fragments are poorly understood despite their potential importance to a variety of ecosystem services. Stemflow inputs (water and solutes) were measured for over one year among three urban forest fragments in the megalopolis of the eastern USA and across an urban-to-rural gradient. Employing both the original and a new variant of the stemflow flux-based enrichment ratio, we quantified differences in stemflow inputs (e.g., water, K, Ca, Mg, Mn, S, NO_3) for two *Quercus* species. Two of the main findings of this study are: (1) flux based enrichment ratios for stemflow were consistently higher for red oaks than for white oaks, and in urban, rather than non-urban fragments; and (2) intra-urban variability in solute fluxes was present among urban fragments, especially for K and Ca, suggesting a potential link to intra-urban variability in anthropogenic activity. Use of the two enrichment ratios was helpful in identifying spatial and interspecific patterns in solute fluxes and nutrient uptake within remnant urban fragments, and, as such, may prove beneficial in developing urban forest health assessments and management strategies.

Key words: stemflow, throughfall, flux-based enrichment ratios, urban greening, oak

3.2 Introduction

Forested ecosystems are converted to urban land use at a higher rate than any other form of natural land cover (Alig et al. 2003). As societal pressures mount to accommodate unprecedented urban population growth, forested lands within expanding metropolitan regions are often reduced in extent and fragmented to allow for continued development (Kupfer 2006). The remnant forest fragments within cities and their surrounding suburbs are important components of the urban ecosystem and, in conjunction with their rural counterparts, play a vital role in regional hydrologic and biogeochemical cycling (Kermanvar and Vilhar 2018, Carreiro and Tripler 2005).

Hydrologic and biogeochemical cycling occurring within rural and urban woodlands is complex, as there are multiple factors that govern the transport of water and nutrients to and within these ecosystems. Processes including atmospheric deposition via wetfall, dryfall, and cloud deposition, in addition to the weathering of terrestrial surfaces, serve as important delivery mechanisms for nutrient and pollutant mechanisms to urban and rural forests (Weathers and Ponette-Gonzalez 2011). Throughfall and stemflow further serve as important means by which water and solutes are distributed within forests and transported to forest soils (Germer 2010, Levia and Frost 2006), with throughfall and stemflow respectively two distinct pathways for elemental cycling beneath the canopy.

Despite the importance of these processes in both rural and urban ecosystems, much of our current knowledge of the biotic and abiotic factors governing their respective functions has been limited to studies based predominantly in rural forests (e.g., Roseir et al. 2015, Neary and Gizyn 1994). A large proportion of the current urban forest hydrology literature has focused on rainfall partitioning by isolated urban trees (e.g., Livesley et al. 2014, Asadian and Weiler 2013, Guevara-Escobar et al. 2007, Xiao et al.

2000). Further, the literature on biogeochemical cycling within urban wooded ecosystems, itself limited in extent, has centered primarily on comparative analysis between urban forests and their non-urban counterparts, with little to no emphasis on the variability of solute fluxes within urban fragments, or between fragments located within a given city. For example, Chiwa et al. (2003) compared the concentrations of major inorganic ions in urban-adjacent forested ecosystems outside of Hiroshima City, Japan with those observed in a mountain-facing woodland, noting higher concentrations in the sites closer to the city. Similarly, Takagi et al. (1997) determined that stemflow from isolated *Ilex rotunda* trees in Fukuoka City, Japan had higher concentrations of Na^+, K^+, Mg^{2+}, Ca^{2+}, and NO_3^- than did isolated trees of the same species located in a nearby suburb.

While utilizing solute concentrations aids in identifying throughfall and stemflow enrichment, it is limited in that it is not flux-based. Levia and Herwtiz (2000) introduced the flux-based enrichment ratio for stemflow in relation to bulk precipitation, $E_{P,B}$, as one way to examine stemflow inputs. Using $E_{P,B}$, Levia and Herwtiz (2000) determined that stemflow enrichment of Mn^{2+} could exceed that of open rainfall by magnitudes of more than 4000 for pignut hickory trees in central Massachusetts, USA. André et al. (2008) utilized $E_{P,B}$ to investigate interspecific variability in stemflow enrichment within a mixed oak-beech stand in the Belgium, noting that enrichment ratios for Na^+, NH_4^+, Cl^-, NO_3^-, and SO_4^{2-} were higher for beech than for oak trees during the leafed period. Similarly, Zhang et al. (2013) used $E_{P,B}$ to identify interspecific heterogeneities in stemflow enrichment for xerophytic shrubs in a Chinese desert. They found a range in enrichment ratio values of 122.8 (NH_4^+-N) – 1667.0 (Cl^-) for *Caragana korshinskii* Kom. and 12.6

(NH_4^+-N) – 1306.0 (K^+) for *Artemesia ordosica* Krasch. Excluding a study in which Schooling et al. (2017) identified variability in $E_{P,B}$ among isolated urban trees in British Columbia, Canada, the overwhelming majority of work utilizing $E_{P,B}$ has been limited to rural forests. This has created a paucity of knowledge with respect to stemflow solute fluxes within urban forest fragments.

Levia and Germer (2015) developed another enrichment ratio, the flux-based enrichment ratio for stemflow in relation to throughfall, $E_{T,B}$, that could be utilized to quantify the relative contributions of throughfall and stemflow to solute transport using a single metric. Based on the respective solute flux data for stemflow and throughfall, rather than of open precipitation, this new enrichment ratio may serve as an important tool for broadening our understanding of the physical processes that drive nutrient cycling in both rural and urban forested ecosystems. Its use, however, has not yet been documented in the literature.

Accordingly, to fill an existing data gap in the literature, the aim of this paper is to expand our current understanding of nutrient cycling within urban forest fragments through use of both flux-based enrichment ratios for stemflow ($E_{P,B}$ and $E_{T,B}$). We seek specifically to utilize $E_{P,B}$, and $E_{T,B}$ to quantify spatial variability in solute fluxes via throughfall and stemflow. Utilizing *in situ* measurements from fragments in metropolitan Wilmington, Delaware, located within the northeast USA megalopolis, we investigate the following:

1. How do $E_{P,B}$ and $E_{T,B}$ vary as a function of location within a metropolitan region?
2. How do $E_{P,B}$ and $E_{T,B}$ vary among urban forest fragments within the same city?

3. How does species heterogeneity affect spatial variability in $E_{P,B}$ and $E_{T,B}$ within remnant forest fragments?

Answers to these questions are necessary to better gauge the effect of forest fragments on elemental cycling within cities and along land use gradients. In particular, comparisons between $E_{P,B}$ and $E_{T,B}$ are necessary to fill the void in our understanding on the relative differential enrichment of fluxes per unit basal area between stemflow and throughfall. To answer these questions, we have utilized hydrologic and hydrochemical sampling techniques to compare stemflow enrichment from trees of varying bark characteristics, specifically trees of the rough-barked white oak and the relatively smooth-barked (in comparison to the former) red oak groups. In an era in which urban forests are increasingly being relied upon for their ecosystem service provision, answers to these questions are vital for providing a more accurate quantification of spatial patterns in the delivery of solutes to forest soils. Use of such knowledge will likely aid in determining natural aids and threats to urban forest health and resilience, and, as such, in assessing the ability of these urban ecosystems to provide goods and services sustainably.

3.3 Materials and Methods

3.3.1 Study Area

This study was conducted within the Wilmington, Delaware, USA metropolitan region. Wilmington is located within the southern portion of the Boston-Washington, D.C. megalopolis, approximately 50km southwest of Philadelphia, Pennsylvania. It is the largest city in the state of Delaware; the surrounding metropolitan region is comprised of approximately 540,000 residents (approximately 60% of Delaware's population; US Census Bureau 2017).

The study area is within a transitional climate region situated between the humid subtropical and humid continental climate zones (Office of the Delaware State Climatologist 2018). Precipitation occurs regularly throughout the year, with convective systems providing most summertime precipitation, and frontal systems dominating precipitation delivery throughout other seasons. Thirty-year mean (1981-2010) annual precipitation totals range from approximately 1100mm-1250mm across the region (NCEI 2018). The regional mean annual temperature is approximately 12.7°C, with average summer (July) and winter (January) temperatures of 23.9°C and1.34°C, respectively (NCEI 2018).

Data were collected from October 2015 – August 2017 from five mixed deciduous forest fragments within metropolitan Wilmington, with hydrochemical sampling occurring during ten rainfall events between April 2016 and August 2017. For this study, a forest fragment is defined as a closed canopy woodlot with boundaries determined by either natural (e.g., grassland, water body) or anthropogenic (e.g., roadway; rail infrastructure; residential, industrial land use) borders. The five fragments included in this study are oriented along an urban-to-rural gradient beginning in Wilmington and extending to the region's western rural terminus. Site selection was determined by accessibility and the intended goal of the research to identify patterns in nutrient cycling at three spatial scales: (1) *intra-plot*, (2) *intra-urban*, and (3) *intra-regional*. As such, three sites were selected in Wilmington to determine variability within the city [e.g., Alapocas Run State Park (hereon Alapocas), Rockford Park (hereon Rockford), Delaware Art Museum (hereon Art Museum)], while one suburban site (e.g., Banning Park; hereon Banning), and one rural site (e.g., Fair Hill Natural Resources

Management Area; hereon Fair Hill) were included to quantify variability in solute fluxes across the entire study region (Figure 3.1).

Leaf area index (LAI, m^2m^{-2}, measured with a Li-Cor LAI-2000 Plant Canopy Analyzer under uniformly overcast skies) values for the three urban sites – Alapocas, Rockford, and the Art Museum – were 4.17 m^2m^{-2}, 3.66 m^2m^{-2}, and 4.04 m^2m^{-2}, respectively. The suburban site, Banning, had an LAI of 3.83 m^2m^{-2}, and the rural site, Fair Hill, had an LAI of 4.11 m^2m^{-2}.

The three urban sites are located within a 3.3 km^2 area of north Wilmington. Each of the sites is distanced from one another by approximately 0.6km "as the crow flies." Alapocas is the largest of the three urban sites, occupying an area of 90 ha. Dominant species there include *Quercus* spp.(oak), *Liriodendron tulipifera* L. (tulip poplar), *Fagus grandifolia* Ehrh. (American beech), *Acer* spp. (maple), *and Prunus serotina* Ehrh. (black cherry). It is bordered by the Brandywine Creek to the west, industrial land use to the north, a local roadway to the east, and residential development to the southeast. Rockford is the second largest of the urban sites, with an area of 12.4 ha. Like Alapocas, dominant species at Rockford include various oak and maple species, tulip poplar, American beech, and *Betula lenta* L. (sweet birch). Rockford is bordered by the Brandywine Creek to the north and by residential land use in all other directions. The Art Museum occupies 1.93ha and is the smallest of the urban sites. Dominant species there include oak and maple species, American beech, and black cherry. This site is bordered by commercial land use to the southeast, a local roadway to the northwest, and residential land use in all other directions. All of the urban fragments are underlain by well-drained silt-loam soils (Neshaminy-Montalto), except for a small portion along the southern-central border of

Alapocas, which is underlain by poorly drained soils of the Hatboro complex (US NRCS 2018). All urban sites are within the Coastal Plain physiographic province.

The suburban fragment, Banning, is located approximately 6km west of Wilmington along the eastern border of Newport, Delaware, USA and within the Coastal Plain physiographic province. Banning occupies 44.0ha and is predominantly comprised of oak and maple species, tulip poplar, American beech, black cherry, and *Liquidambar styraciflua* L. (sweetgum). It is bordered to the south by an active railroad line, to the north by a major regional thoroughfare, to the west by residential land use, and to the east by a combination of commercial and residential land use. Soils at Banning include poorly-drained Othello silt-loams in the site's western and central portions, well-drained Elsenboro silt-loams along the park's northern extent, and a small section of urban soils (Mattapex-urban land complex) along the portion bordered by rail infrastructure (US NRCS 2018).

Fair Hill (rural site) is located within the Piedmont physiographic province in northeast Maryland, USA, approximately 40km west of Wilmington. It is surrounded by agricultural land use and low-density exurban residential development. Fair Hill is underlain by well-drained loams (Glenleg; US NRCS 2018), with dominant tree species including tulip poplar, American beech, red maple, and various oak species (additional stand characteristics for Fair Hill and other sites provided in Table 3.1).

3.3.2 Experimental Design

In situ throughfall, stemflow, and bulk rainfall samples were manually collected on an event basis from a network of collectors distributed among each of the research sites. To ensure adequate stemflow yield for hydrochemical analysis, data collection was

limited to storms generating rainfall ≥7.0mm. Throughfall and bulk precipitation were collected in 3.7L HDPE containers with non-dyed HDPE funnels affixed to the top aperture. Funnels ranged in size from 203.2mm-230.0mm and were used to maximize throughfall capture efficiency. All throughfall and bulk precipitation collectors were anchored to the ground using garden stakes affixed to the HDPE bottles with weatherproof duct tape. Glass wool was placed within funnel stems to help prevent contamination by anthropogenic and natural debris sources. Glass wool replacement occurred periodically over the study period. All throughfall collectors were rinsed with deionized water 1-2 days before each sampling period to ensure that solute flux data represented each respective storm event.

Stemflow was collected using polyethylene tubing that was cut longitudinally and placed around the tree bole in a double-helix manner. The tubing was installed at approximately dbh level (1.37m) and attached to the trunk using staples. Gaps between the tubing and trunk were sealed using silicone sealant. All captured stemflow drained to sealed 121.1L containers lined with inert plastic liners to prevent the leaching of chemicals from the collector into the samples. The liners were removed from the stemflow bins following each data collection, and new liners were installed 1-2 days before an upcoming sampling period. Overflow bins were installed to capture excess stemflow yield for trees that routinely produced more than 121.1L of stemflow. The smaller overflow bins (volume = 75.7L) were connected to the larger collectors using uncut polyethylene tubing. Stemflow sampling for hydrochemical analysis was limited to the larger collectors. Stemflow collection was limited to trees from the genus *Quercus*, specifically white and red oak. Species selection was based on the widespread

distribution of these trees at all study sites, and allowed for analysis of interspecific variability in solute fluxes.

Each of the five study fragments was instrumented with 1 bulk precipitation, 25 throughfall, and 7 stemflow collectors (Figure 3.1b). Collectors were systematically placed to provide spatial coverage of each respective site. Throughfall and stemflow were placed along five transects beginning at the edge and extending into the fragment interior at five set distances (*e.g.*, 0, 10, 20, 30, 60m) (Figure 3.1b). Five throughfall collectors were placed along each transect, while 3 stemflow collectors were placed along the edge, and one at each remaining interior distance. For this study, fragment edge was defined as that border which is oriented perpendicular to the mean direction of storm propagation across the region, identified by Zishka and Smith (1980) as southwest to northeast.

For the Art Museum, Banning, and Fair Hill, bulk rainfall collectors were placed in non-wooded areas on the grounds of each respective study plot. Bulk precipitation for Rockford was initially collected in an open field on the grounds of a local school approximately 0.3km away from the study plot, but collection was suspended due to consistent vandalism. Bulk precipitation samples for the Art Museum were thus subsequently used for both the Art Museum and Rockford. For Alapocas, bulk precipitation samples were collected in an open courtyard of a neighborhood school, approximately 0.75 km away from the study site.

3.3.3 Quantifying Hydrologic and Biogeochemical Fluxes

Gross rainfall data were collected from three fully equipped automated weather stations operated by the Delaware Environmental Observing System: (a) Wilmington, Delaware-Talley (39.7753°N, -75.5278°W) for the urban sites; (b) Wilmington,

Delaware-Prices Corner (39.7492°N, -75.6108°W) for the suburban site; and(c) Fair Hill, Maryland-Natural Resources Management Area (39.7099°N, -75.8386°W) for the rural site. The Fair Hill weather station is equipped with a Geonor T-200B vibrating wire rain gauge (Oslo, Norway), while Texas Electronic TE525 tipping bucket rain gauges (Dallas, Texas, USA) are in use at the Wilmington-Talley and Wilmington-Prices Corner weather stations. Precipitation data at all three sites is recorded in five-minute intervals.

All hydrochemical samples were collected within 48 hours of each storm event. To quantify solute fluxes via stemflow and gross rainfall, 250mL samples were collected from each of the instrumented trees and bulk rainfall collectors, respectively. For throughfall, individual 250mL samples were collected from each gauge in the field. These samples were then transported to the laboratory, where volume-weighted 250mL samples were aggregated for each transect representing one of the five set distances from the fragment edge per site. That is, for each study plot and storm event, there was one representative 250mL sample made for throughfall collected 0, 10, 20, 30, and 60m from the edge, yielding 5 throughfall samples per site. To remove particulate matter, samples were filtered with 0.45µm filters and stored at 4°C until hydrochemical analysis was conducted. All samples were processed using inductively coupled plasma – optical emission spectroscopy (ICP-OES) analysis to determine solute concentrations. All hydrochemical testing was performed by the University of Delaware Soil Testing Program. ICP-OES analysis conducted prior to 15 July 2016 was performed using a Thermo Scientific iCAP™ 7600 ICP-OES Duo Analyzer, while a Thermo Scientific Iris Intrepid II XSP Duo View ICP-OES Analyzer (Waltham, Massachusetts, USA) was utilized after that date.

In this study, we focused on solute fluxes of the macronutrients potassium (K), calcium (Ca), magnesium (Mg), sulfur (S), and nitrate (NO_3), and the micronutrient manganese (Mn), all of which are vital for the health and maintenance of vegetation. Potassium, which is highly mobile, is an essential element in osmoregulation, and is thus vital in plant-water relations (Marschner 1995). Calcium aids in regulating plant cell metabolism and growth (Marschner 1995). Magnesium serves as a binding element in the processes by which plant RNA and proteins are created, and is required for the growth and function of chloroplasts (Marschner 1995). Nitrate and S are important components of plant proteins and nucleic acids, therefore contributing significantly to plant structural characteristics (Marschner 1995). Manganese activates the plant enzymes that create lignin, and aids in the proper conductance of photosynthesis (Marschner 1995). Interactions between these elements can be dynamically complex, with environmental excesses in some potentially disturbing the natural balance of others. Deficient or excessive availability of these elements for plant uptake can thus result in nutrient levels that may threaten the function of woody vegetation.

Elemental detection limits for ICP-OES analysis for K, Ca, Mg, S, NO_3, and Mn were 0.1, 0.1, 0.01, 0.03, 0.02, and 0.005mg l^{-1}, respectively. For K, Ca, Mg, and S, observations were always above the detection limits, but some readings for Mn and NO_3 fell below these limits. Such observations were excluded from analysis.

In situ stemflow depth observations were converted to volumetric measurements using a volume-depth equivalent allometric equation. Stemflow production by individual trees was quantified using the funneling ratio introduced by Herwtiz (1986) and defined as $F = V_S/ (P*B)$, where F denotes the funneling ratio (unitless), V_S stemflow volume, P

gross rainfall depth, and *B* trunk basal area. Funneling ratios larger than one indicate that outlying portions of the tree crown contribute to stemflow production.

Solute fluxes were quantified using the flux-based enrichment ratios introduced by Levia and Herwitz (2000) and Levia and Germer (2015). The chemical enhancement of precipitation interacting with woody surfaces in the canopy was calculated using the flux-based enrichment ratio for stemflow in relation to gross rainfall ($E_{P,B}$), calculated as

$$E_{P,B}=(V_S*C_S)/(P*C_P*B),$$

where C_S denotes stemflow solute concentration and C_P solute concentration in gross rainfall (Levia and Herwitz 2000). The flux-based enrichment ratio for stemflow in relation to throughfall ($E_{T,B}$) introduced by Levia and Germer (2015) was used to determine the relative contributions of stemflow to throughfall to total solute flux and was calculated as,

$$E_{T,B}=(V_S*C_S)/(T*C_T*B),$$

where T denotes the throughfall depth equivalent and C_T solute concentration in throughfall. All calculated enrichment ratios are unitless.

3.3.4 Statistical Analysis

Statistical analysis was performed using version 13.3 of the Statistica software package (Tibco Software 2017). Paired *t*-tests were used to determine statistical significance in $E_{P,B}$ and $E_{T,B}$ between red and white oak groups, and between observations made in urban and non-urban fragments. Because our data were not normally distributed, the non-parametric Kruskal-Wallis H test was utilized to assess the significance of intra-urban variability in solute fluxes observed between the three urban sites. *Post hoc*

planned comparison tests were conducted to identify the sources of variability in enrichment ratio values among the urban fragments.

3.4 Results

3.4.1 Stemflow Hydrologic Flux and Solute Concentrations

Hydrologic fluxes via stemflow were found to vary between the oak groups. Over the study period, red oaks consistently generated larger stemflow yields than did white oaks, with stemflow accounting for 0.01-12.5% of gross rainfall for red oaks, and <0.01-5.4% of gross rainfall for white oaks (when calculated per unit crown area). Median stemflow yield for red and white oaks was 26.4 L and 2.4 L, respectively, and $F_{red\ oak}$ (median = 7.55) $F_{white\ oak}$ (median = 0.49) by more than fifteen-fold.

With respect to solute concentrations, $C_S > C_T > C_P$ (Table 3.2). C_P displayed regional variability, with $C_{P(urban)}$ exceeding $C_{P(non\text{-}urban)}$ for all solutes except Ca (not shown). These trans-regional differences (e.g., urban vs. non-urban), however, were not found to be statistically significant. Additionally, C_S displayed interspecific variability, with white oaks consistently having higher C_S than red oaks (Table 3.3).

3.4.2 Flux-based Enrichment of Stemflow in Relation to Gross Precipitation ($E_{P,B}$)

3.4.2.1 Variability in $E_{P,B}$ between Urban and Non-urban Fragments

$E_{P,B}$ varied greatly between the solutes and across the study region (Table 3.4, Figure 3.2). $E_{P,B}$ values were generally highest for Mn and lowest for Mg. With respect to interspecific variability, $E_{P,B}$ was persistently larger for red oaks than for white oaks (Figure 3.2).

When comparing trans-regional variability in $E_{P,B}$ within oak groups, $E_{P,B}$ for urban red oaks exceeded that of non-urban red oaks for all solutes except Mn (Figure 3.2). Trans-regional differences were significant for S and K, with $E_{P,B(red\ oak,\ urban)} > E_{P,B(red\ oak,\ non\text{-}urban)}$ by factors of 1.7 and 2.5, respectively. For NO_3 and Ca $E_{P,B(red\ oak,\ urban)}$ was also higher than $E_{P,B(red\ oak,\ non\text{-}urban)}$, though these differences respectively displayed slight ($\alpha < 0.10$) or no significance. Mn behaved differently than all other solutes (Figure 3.3)], as $E_{P,B(red\ oak,\ non\text{-}urban)}$ exceeded $E_{P,B(red\ oak,\ urban)}$, but this difference was statistically insignificant.

White oaks also displayed a consistent pattern of $E_{P,B(white\ oak,\ urban)} > E_{P,B(white\ oak,\ non\text{-}urban)}$ for all solutes excluding Mn (Figure 3.2). S displayed significant trans-regional variability ($p < 0.01$) in $E_{P,B}$, with $E_{P,B(white\ oak,\ urban)}$ being 3.5 times larger than $E_{P,B(white\ oak,\ non\text{-}urban)}$. For K, Ca, Mg, and NO_3, $E_{P,B(white\ oak,\ urban)}$ was 2.7 to 7.2 times larger than $E_{P,B(white\ oak,\ non\text{-}urban)}$, but differences were not statistically significant. $E_{P,B}$ for Mn was slightly larger for non-urban, rather than urban white oaks, though the variability was statistically insignificant.

3.4.2.2 Intra-urban Variability in $E_{P,B}$

Intra-urban patterns in fragment-to-fragment variability in $E_{P,B}$ were present, but not always consistent or significant (Figure 3.3). $E_{P,B}$ for K, Ca, Mg, and S, was higher at Alapocas than Rockford and the Art Museum for both red and white oaks. Red oaks displayed notable intra-urban variability in $E_{P,B}$ for several solutes, including K, for which $E_{P,B}$ varied by more than seven fold across the city. This was the only solute for which intra-urban variability was significant among red oaks ($p < 0.001$). For white oaks, intra-urban variability in $E_{P,B}$ was significant for Ca, K, and Mg, with $E_{P,B}$ differing by

factors of 1.8, 32.9, and 3.3, respectively, among urban fragments. *Post hoc* tests determined that $E_{P,B}$ for red oaks at Alapocas varied significantly between those at the Art Museum and Rockford ($p < 0.05$), but not between those at Rockford and the Art Museum (Table 3.5). A similar pattern was observed for Mg for white oaks, while for Ca, significant variability was observed only between white oaks at Alapocas and the Art Museum.

3.4.3 Flux-Based Enrichment of Stemflow in Relation to Throughfall ($E_{T,B}$)

3.4.3.1 General Patterns and Interspecific Variability in $E_{T,B}$

Median $E_{T,B}$ for all solutes was approximately ≥ 1.0, indicating that solute inputs via stemflow exceeded those of throughfall within the study fragments (Table 3.4). In general, $E_{T,B}$ was usually less than $E_{P,B}$ for K, Mg, and NO_3; and was slightly larger than $E_{P,B}$ for Ca and S. For Mn, $E_{T,B}$ was notably larger than $E_{P,B}$ (Table 3.4)]. This unexpected pattern in $E_{T,B}$ excess was observed when considering both all samples and interspecific variability. Additional interspecific variability in $E_{T,B}$ was observed across the study region, with $E_{T,B(red\ oak)}$ consistently larger than $E_{T,B(white\ oak)}$.

3.4.3.2 Variability in $E_{T,B}$ between Urban and Non-urban Fragments

Trans-regional differences in $E_{T,B}$ were observed for all solutes, with $E_{T,B(urban)}$ consistently larger than $E_{T,B(non\text{-}urban)}$ for both oak groups. For red oaks, $E_{T,B\ B}$ was notably higher within urban fragments than in non-urban fragments (Figure 3.4). For example, for both S and Mn, $E_{T,B}$ for urban red oaks was two or more times larger than for non-urban red oaks, with this variability being significant for S ($p < 0.01$). Observed trans-regional

variability in $E_{T,B}$ for Ca, K, Mg, and Mn displayed slight statistical significance ($p <$ 0.10).

As with red oaks, $E_{T,B(urban)}$ exceeded $E_{T,B(non\text{-}urban)}$ for white oaks (Figure 3.4). For S and NO_3, $E_{T,B}$ for urban white oaks was more than three times larger than for their non-urban counterparts. Trans-regional variability for these solutes was significant at the $p < 0.05$ level. $E_{T,B}$ for urban white oaks was 1.7–3.2 times larger than for non-urban white oaks for K, Ca, Mg, Mn, though these differences were not statistically significant.

3.4.3.3 Intra-urban Variability in $E_{T,B}$

As with $E_{P,B}$, intra-urban variability in $E_{T,B}$ was present, but not in consistently significant patterns (Figure 3.5). For red oaks, the highest values for $E_{T,B}$ for Ca, K, Mg, and S were observed at the Art Museum. $E_{T,B}$ for K varied by a factor of more than 2.5 among urban red oaks, but the intra-urban variability was generally smaller for all other solutes for this oak group.

For white oaks, $E_{T,B}$ for Ca, K, Mg, and NO_3 was highest at Alapocas, and at Rockford Park for Mn and S (Figure 3.5). Intra-urban variability in $E_{T,B}$ ranged in magnitude for the different solutes, with fragment-fragment differences, with maximum values ranging from being 1.6 (Mn) to 4.0 (NO_3) times higher than the intra-urban minima. Mg was the only solute for which the observed intra-urban variability was statistically significant ($p < 0.05$), with significant variability ($p < 0.05$) observed between white oaks at Alapocas and those at the Art Museum and Rockford, but not between white oaks at the Art Museum and Rockford (Table 3.5).

3.5 Discussion

3.5.1 Interspecific Variability in Hydrologic Fluxes, Stemflow Chemistry, and $E_{P,B}$, and $E_{T,B}$

That red oaks produced more stemflow than white oaks in the study agree with findings from Brown and Barker (1970) and can be attributed to variability in bark characteristics between the two groups. Bark characteristics such as bark morphology, microrelief, and water storage capacity are known to have significant impact on stemflow production (Livesley et al. 2014, Levia et al. 2010, Crockford and Richardson 2000). The bark of white oaks is more morphologically complex than that of red oaks, with the former characterized by bark of greater rigidity and microrelief, which Levia and Herwitz (2005) and Van Stan et al. (2016) found to be directly related to both bark water storage capacity and impediments to vertical water flow, and inversely related to stemflow yield. Conversely, red oaks in the study had less morphologically complex bark and is characterized by linear furrows which helped to facilitate, rather than hinder, stemflow transport. These factors collectively contributed to the higher stemflow yields produced by red oaks.

Our finding of $C_{S\ (white\ oak)} > C_{S\ (red\ oak)}$ also results from variability in bark morphology. The stemflow transport impediments introduced by white oak bark increases stemflow residence time and the potential for nutrient exchange between water and bark, thus producing higher C_S. Germer et al. (2012), André et al (2008), and Levia and Herwitz (2005) had similar findings, all noting higher C_S for rough-barked trees which created higher stemflow residence times.

Though C_S was always higher for red oaks, $E_{P,B}$ *and* $E_{T,B}$ for this oak group always exceeded that of white oaks, regardless of a fragment's geographic context. This may be attributed to variability in stemflow yield, as red oaks consistently produce higher stemflow yields, and thus higher fluxes of solutes via stemflow. Similarly, Levia et al. (2011) found that when comparing $E_{P,B}$ for American beech (consistently high stemflow yield) and tulip poplar (comparatively low stemflow yield), $E_{P,B}$ produced by American beech would exceed that produced by tulip poplar by more than twelve fold.

For K and Mg, $E_{T,B}$ values were consistently exceeded by those of $E_{P,B,}$ in accordance with findings from Levia and Germer (2015). This was also true for urban red and white oaks for Ca and S; for non-urban red oaks for Mn, NO_3, and S; and for non-urban white oaks for Mn and NO_3. These patterns may be attributed to the fact that throughfall is generally more enriched than gross precipitation. As such, flux-based enrichment ratios for stemflow in relation to gross precipitation will generally be higher than those calculated in relation to throughfall.

For Mn, $E_{T,B}$ exceeded $E_{P,B}$ by more than two-fold in red oak in the urban fragments, a finding which may suggest foliar uptake of Mn by urban red oak trees (Parker 1983). This observation highlights the complex processes which determine the physical and chemical properties of throughfall. First, it is probable that the urban red oaks may be under a form of stress which places higher demand for Mn on this oak group, thus potentially accounting for foliar uptake and the higher $E_{T,B}$ observations. Further, Levia et al. (2017) discussed the fact that throughfall can be divided into three main categories – free, canopy drip, and splash throughfall – all of which have different chemical signatures depending on their contact (or lack thereof) with canopy or forest

soils. The division of throughfall into these groups may result in a chemical signature for Mn that is muted in relation to gross precipitation, and as such, may yield the higher $E_{T,B}$ we observed for urban red oaks. These observations, in conjunction with the work of Richardson (2016), further justify ongoing investigation into the potential drivers of this interspecific variability of Mn enrichment within urban (and other spatially oriented) fragments.

3.5.2 Trans-regional Variability in $E_{P,B}$ and $E_{T,B}$

$E_{P,B}$ values in our study were within the range of previous findings in mixed-deciduous stands (Siegert et al. 2017, Schooling et al. 2017, Levia et al. 2011, André et al. 2008, Levia and Herwitz 2000). The elevated $E_{P,B}$ values observed in the urban fragments can be attributed to the excess of anthropogenic activity that occurs in the more highly urbanized portions of the study region. Atmospheric deposition is a substantial source of NO_3 and S, and are both by-products of fossil fuel combustion (Weathers and Ponette-González 2011). Because this combustion occurs within closer proximity to the urban fragments, it was expected and confirmed that the larger $E_{P,B}$ observations would be made there. That the differences in $E_{P,B}$ for NO_3 between urban and non-urban fragments was not found to be significantly different for white oaks may result from the complex processes of NO_3 uptake by the canopy (Parker 1983), and that white oak's characteristically longer residence time may contribute to the complexity of those processes. This may warrant further study to better quantify the significance of trans-regional variability in stemflow NO_3 enrichment of white oaks and other trees characterized by intricate bark morphology.

For the elements sourced by terrestrial materials, including K, Ca, and Mg, the observations of larger $E_{P,B}$ and $E_{T,B}$ values in the urban, rather than non-urban fragments can likely be attributed to the creation and resuspension of urban dust, or that airborne particulate matter resulting from anthropogenic activity in developed areas (Amato et al. 2009a, Amato et al. 2009b, Hopke et al. 1980). In a Barcelona, Spain-based air quality study, Amato et al. (2009b) linked observed levels of particulate K and Mg to the heightened resuspension of urban soils due to both the routine daily movement of humans and animals, and natural land maintenance (i.e., gardening, landscaping) within the city. Amato et al. 2009 (a, b) further determined that the suspension of particulate matter from construction materials (e.g., concrete and other aggregates), often released through human movement on pavement and active construction sites, served as an important source of atmospheric Ca within urban environments. These variants of urban activity amplify the suspension and subsequent atmospheric deposition of K, Mg, and Ca in and around cities. This in turn likely results in the enhanced wash-off (in conjunction with leaching) of these solutes within the urban fragments, as suggested by the trans-regional variability in $E_{P,B}$ and $E_{T,B}$ observed in our study.

3.5.3 Intra-urban Variability in $E_{P,B}$ and $E_{T,B}$

Intra-urban variability in $E_{P,B}$ *and* $E_{T,B}$ was present but lacked statistical significance, which may be attributed to the relative close proximity of the urban fragments and likely near-uniform exposure to atmospheric deposition. Boogaard et al. (2011) found no significance in intra-urban variability atmospheric concentrations of Ca and S in a study comparing air quality among five Dutch cites. Observations like these

may propagate into insignificant variability in atmospheric deposition and stemflow enrichment within confined urban neighborhoods.

Further, $E_{P,B}$ was higher at the Alapocas site for four of the solutes we studied, but this pattern was not observed for $E_{T,B.}$ Instead, local $E_{T,B}$ maxima were observed at varying urban sites for both red and white oak trees. This urban-scale spatially variant distribution of solute fluxes via stemflow and throughfall as indicated by the flux-based enrichment ratios may indicate intra-urban variability in the foliar uptake of both macro- and micronutrients, possibly owing to varying levels of plant stress and nutrient needs among the sites. More work is needed to improve our understanding of intra-urban variability of solute fluxes within remnant fragments, as this may help to (a) identify fragment-based nutrient use, demands, and excesses; (b) aid in determining regional-scale spatial variability in fragment-based nutrient cycling; and (c) establish linkages between nutrient cycling and urban forest health. Future use of $E_{T,B}$ in quantifying solute fluxes via throughfall and stemflow may prove beneficial in these efforts.

Use of $E_{P,B}$ *and* $E_{T,B}$ offers an important means by which to characterize biogeochemical cycling within urban forest fragments. The utility of $E_{P,B}$ and $E_{T,B}$ extend beyond quantifying solute fluxes within these wooded ecosystems; both may be critical in identifying spatial patterns of nutrient delivery or demand (i.e., areas of localized or diffuse solute flux minima, maxima) within urban fragments, in addition to the type of species that may correlate with this spatial partitioning of nutrients. This may have important implications for urban forest management, as use of this knowledge may help to pinpoint current or potential biogeochemical hotspots within the urban canopy, and areas of initial or advanced plant stress, and as such, may help to inform decision-making

processes regarding healthy, sustainable urban forest maintenance and expansion (Harvey et al 1999).

3.6 Conclusion

Using flux-based enrichment ratios for stemflow calculated in relation to rainfall and throughfall, this study provides an important quantification of interspecific, trans-regional, and intra-urban variability in hydrologic and solute fluxes occurring within urban and non-urban remnant forest fragments. Our findings support previous work linking interspecific variability in solute fluxes via stemflow to differing bark characteristics. Additionally, for most solutes, spatial patterns in flux-based enrichment ratios were identified, with a trend toward higher stemflow enrichment occurring in urban, rather than non-urban fragments. This resulted in $E_{P,B}$ values being more than 2.5 times greater in urban fragments for some solutes, and in urban $E_{T,B}$ exceeding that observed in non-urban fragments by a factor of 3 or larger for others. We attribute the higher enrichment of stemflow in urban fragments to the relatively high anthropogenic activity, occurring in the forms of heightened fossil fuel combustion and the creation and resuspension of urban dust, which characterizes land use within proximity to fragments within cities.

Further, this study provides an important quantifiable assessment of the intra-urban variability in solute fluxes via stemflow and throughfall that occurs within urban fragments. We found that while not all observed variability in solute fluxes was statistically significant, there were noteworthy patterns with respect to sites for which solute fluxes were consistently highest, and how these local maxima changed when observing $E_{P,B}$ and $E_{T,B}$. We contend that the observed site-to-site variability, though not

always significant, provides insight into the spatially-variable demands for nutrients between remnant fragments within the same city. Such findings were made possible through the combined use of both flux-based enrichment ratios, and consequently, may prove beneficial in future attempts to assess and predict intra-urban variability in forest fragment health, function, and resilience. As such, we recommend future utilization of both $E_{P,B}$ and $E_{T,B}$ in future exploratory and applied research on biogeochemical cycling within the urban canopy.

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TABLES

Table 3.1. Summary of stand characteristics for study forest fragments. Metrics from Fair Hill are based upon data from Shiklomanov and Levia (2014) as data collection occurred from the same area within Fair Hill for both studies.

Site	Classification	Mean dbh (cm)	Mean tree height (m)	Stand density (trees ha^{-1})	Stand basal area (m^2 ha^{-1})
Alapocas State Park	Urban	37.0	20.1	566	100.3
Rockford Park	Urban	33.8	19.0	566	69.0
Delaware Art Museum	Urban	29.5	18.0	517	50.0
Banning Park	Non-urban	31.8	18.8	716	84.2
Fair Hill	Non-urban	40.8	27.8	225	36.8

Table 3.2. Solute concentrations in stemflow (C_S), throughfall (C_T), and gross precipitation (C_P) for all study trees and sites. Solute concentrations are in mg l^{-1}. Values below machine detection limit are denoted "N/D."

Concentration	**Solute**	**Median**	**μ**	**Min**	**Max**	**σ**	***n***
C_S	K	10.19	12.92	1.91	67.92	9.531	288
	Ca	3.83	7.31	0.23	52.34	8.75	289
	Mg	0.56	0.86	0.03	7.61	1.005	287
	Mn	0.07	0.15	N/D	2.80	0.24	290
	S	1.08	1.56	0.13	11.33	1.50	287
	NO_3	0.61	1.02	0.21	9.92	0.08	274
C_T	K	4.40	5.90	0.95	27.8	4.64	249
	Ca	1.54	2.23	0.05	16.2	2.00	249
	Mg	0.59	0.91	0.19	8.95	0.94	312
	Mn	0.04	0.02	N/D	0.38	0.05	201
	S	0.47	0.56	0.15	2.25	0.34	249
	NO_3	0.32	0.48	0.01	4.91	0.58	188
	K	0.40	1.31	0.02	9.24	2.03	29

C_P	Ca	0.83	1.43	0.16	12.3	2.19	30
	Mg	0.31	0.35	0.03	0.91	0.20	30
	Mn	0.004	0.01	N/D	0.11	0.02	24
	S	0.25	0.43	0.12	3.82	0.67	30
	NO_3	0.17	0.20	0.03	0.56	0.14	24

Table 3.3. Interspecific variability in stemflow solute concentrations for all study trees. Solute concentrations are in mg l^{-1}.

	Median C_S	
Solute	Red oak (n = 24)	White oak (n = 10)
K	10.06	10.93
Ca	2.17	11.36
Mg	0.34	0.96
Mn	0.05	0.12
NO_3	0.54	0.70
S	0.89	1.50

Table 3.4 Median values for flux-based enrichment ratios (unitless) for stemflow in relation to (a) gross precipitation ($E_{P,B}$) and (b) throughfall ($E_{T,B}$). Values are reflective of all trees in the study.

	Median Enrichment Ratio	
Solute	$E_{P,B}$	$E_{T,B}$
K	37.8	9.4
Ca	8.15	8.8
Mg	3.85	2.8
Mn	51.7	63.8
S	8.8	11.4
NO_3	8.5	8.3

Table 3.5 Results from planned comparison post hoc tests to determine source of significance in intra-urban variability in $E_{P,B}$ and $E_{T,B}$. *P*-values are shown for cases in which variability was significant among urban fragments. *P*-values are not shown for insignificant relationships.

Enrichment ratio	Site	Alapocas	Art Museum	Rockford
K $E_{P,B}$ (red oak)	**Alapocas**		<0.001	<0.001
	Art Museum	<0.001		
	Rockford	<0.001		
K $E_{P,B}$ (white oak)	**Alapocas**		0.008	0.004
	Art Museum	0.008		
	Rockford	0.004		
Ca $E_{P,B}$ (white oak)	**Alapocas**		0.008	
	Art Museum	0.008		
	Rockford			
Mg $E_{P,B}$ (white oak)	**Alapocas**		0.039	0.048
	Art Museum	0.039		
	Rockford		0.048	
Mg $E_{T,B}$ (white oak)	**Alapocas**			0.05
	Art Museum			
	Rockford	0.05		

FIGURES

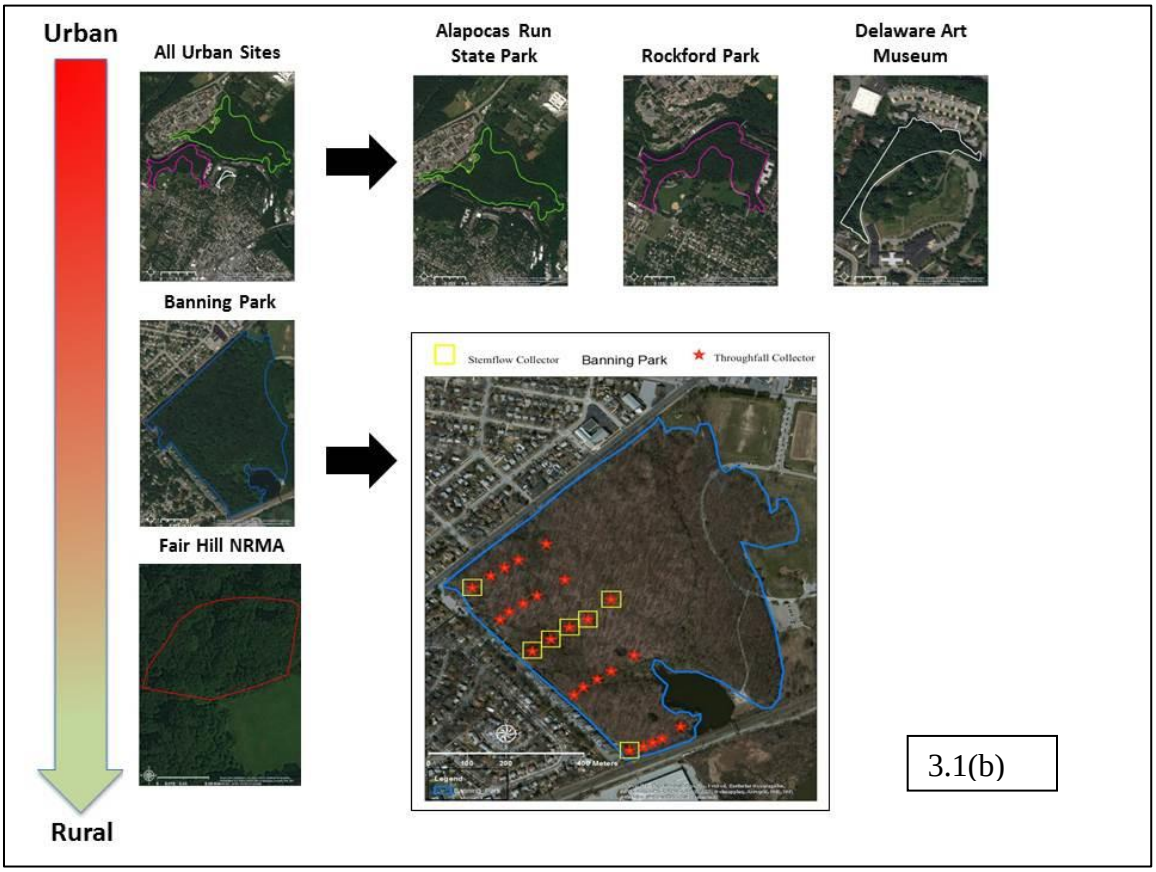


Figure 3.1 (a-b) The five study sites within the Wilmington, Delaware, USA metropolitan region (a). Sites displayed horizontally are within Wilmington (3 urban sites); those displayed vertically are along an urban-to-rural gradient (1 suburban, 1 rural site). The first horizontal map displays the relative proximity of the urban sites. (b) Example of configuration of throughfall and stemflow collector placement at Banning Park (suburban site). All five sites are equipped similarly, with 25 throughfall and 7 stemflow collectors placed along transects at 5 set distances (0, 10, 20, 30, and 60m) from forest edge.

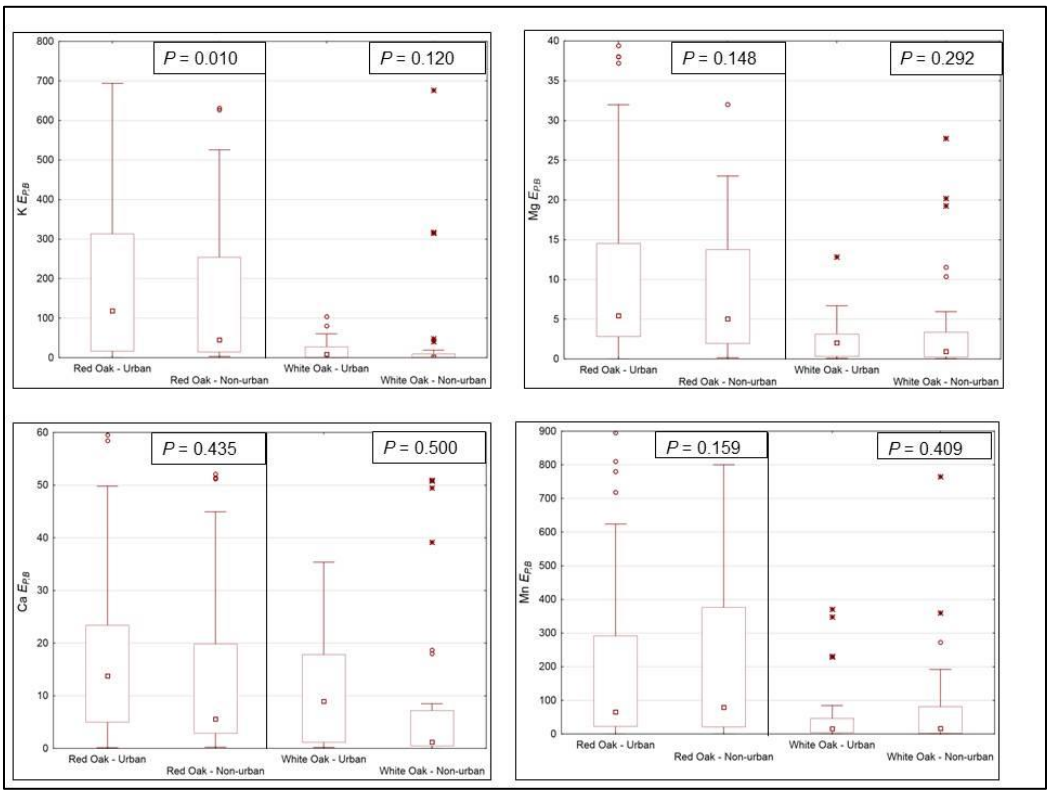
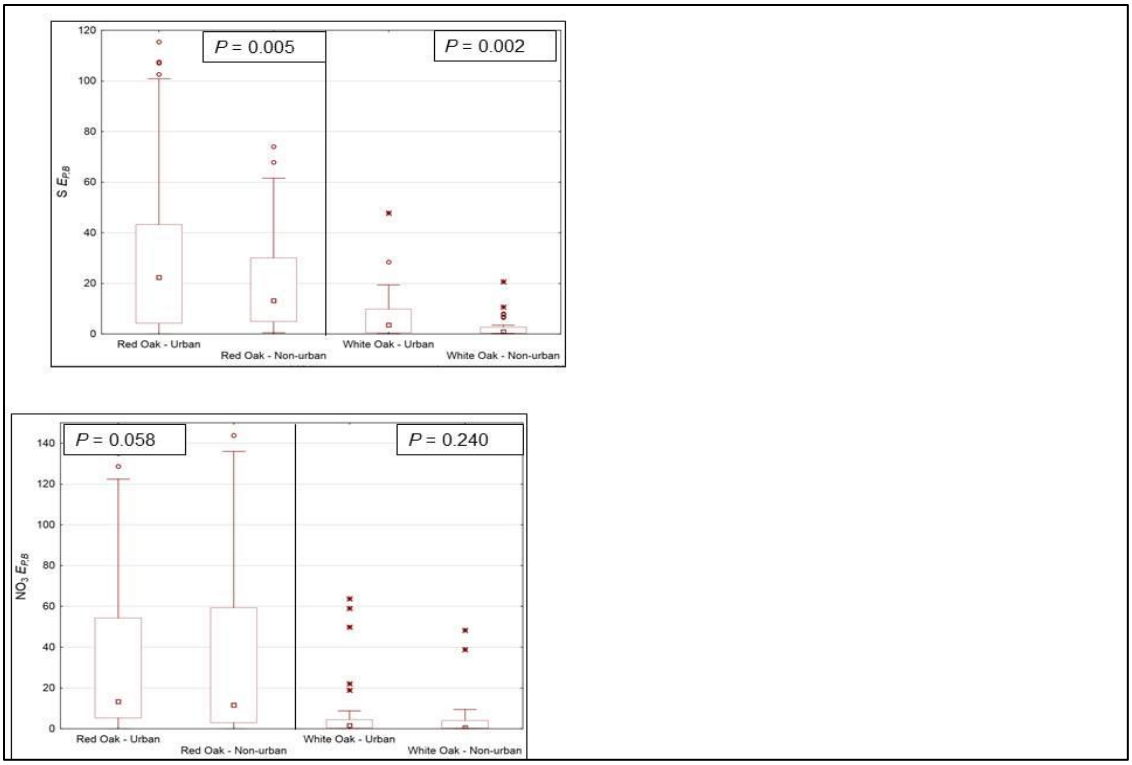


Figure 3.2 Trans-regional interspecific variability in flux-based enrichment ratios for stemflow in relation to gross rainfall ($E_{P,B}$) for all solutes.


P = 0.005
P = 0.002
S E_{PB}
120
100
80
60
40
20
0
Red Oak - Urban
Red Oak - Non-urban
White Oak - Urban
White Oak - Non-urban
P = 0.058
P = 0.240
NO_3 E_{PB}
140
120
100
80
60
40
20
0
Red Oak - Urban
Red Oak - Non-urban
White Oak - Urban
White Oak - Non-urban

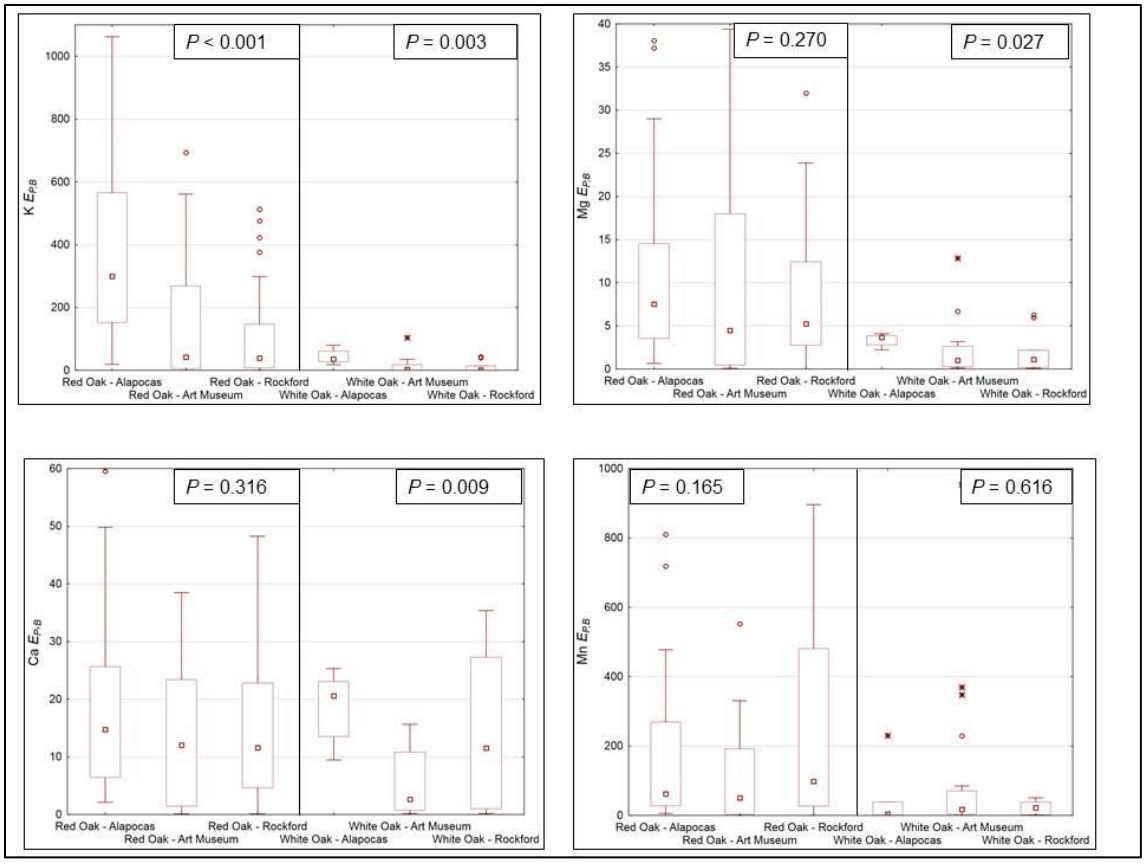
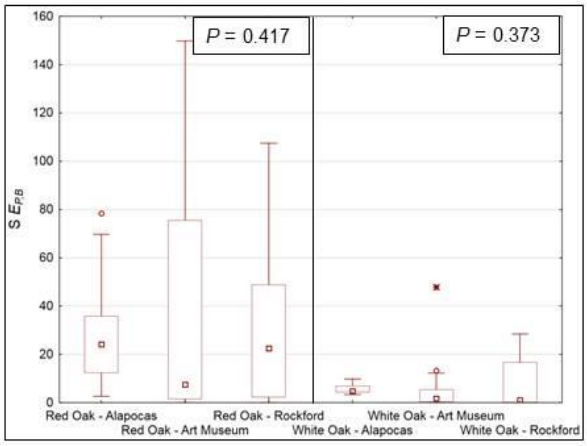
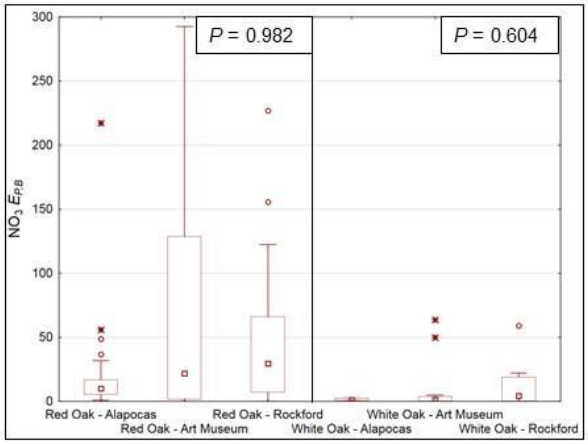


Figure 3.3 Intra-urban variability in flux-based enrichment ratios for stemflow in relation to gross rainfall ($E_{P,B}$) for all solutes


P = 0.417
P = 0.373
S $E_{P,B}$
160
140
120
100
80
60
40
20
0
Red Oak - Alapocas
Red Oak - Art Museum
Red Oak - Rockford
White Oak - Alapocas
White Oak - Art Museum
White Oak - Rockford


P = 0.982
P = 0.604
NO_3 $E_{P,B}$
300
250
200
150
100
50
0
Red Oak - Alapocas
Red Oak - Art Museum
Red Oak - Rockford
White Oak - Alapocas
White Oak - Art Museum
White Oak - Rockford

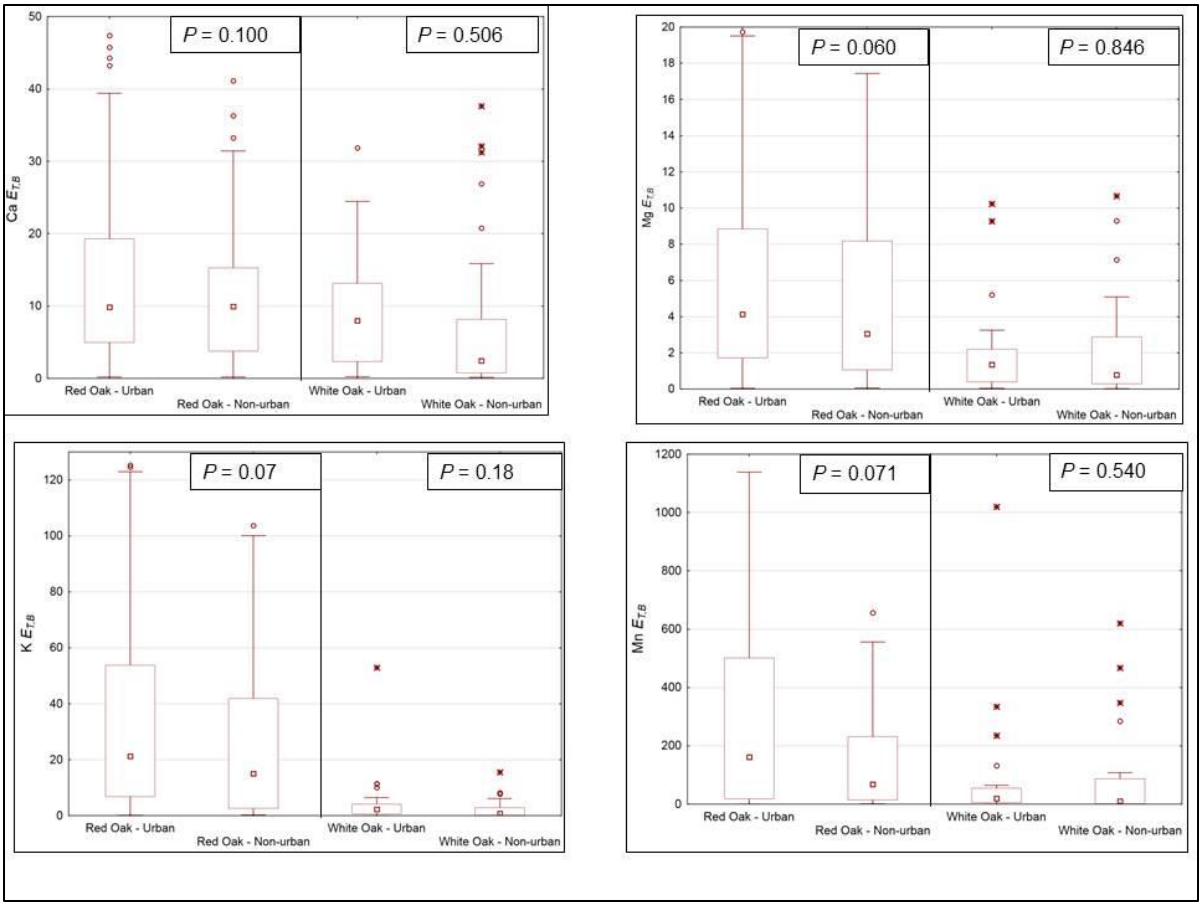
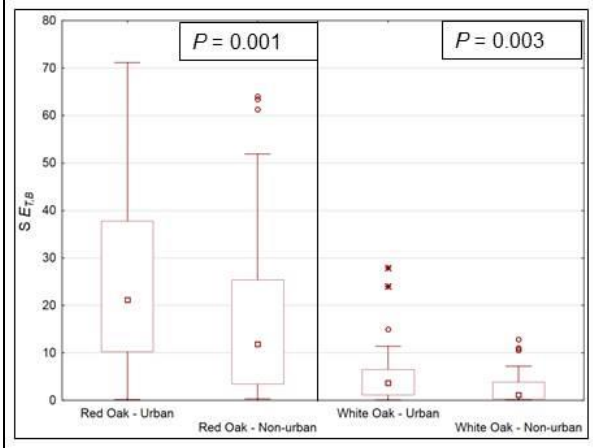
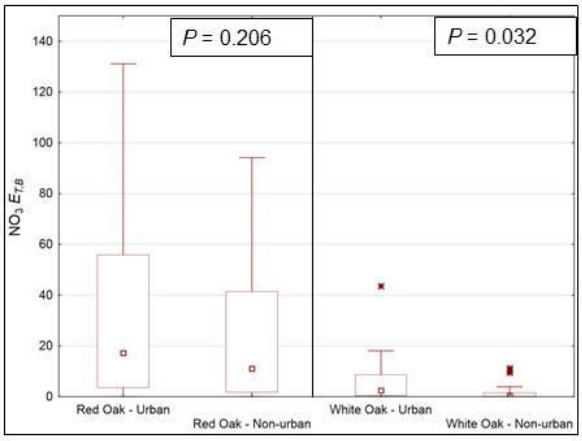


Figure 3.4 Trans-regional interspecific variability in flux-based enrichment ratios for stemflow in relation to throughfall flux ($E_{T,B}$) for all solutes.


P = 0.001
P = 0.003
S $E_{T,B}$
80
70
60
50
40
30
20
10
0
Red Oak - Urban
Red Oak - Non-urban
White Oak - Urban
White Oak - Non-urban


P = 0.206
P = 0.032
NO_3 $E_{T,B}$
140
120
100
80
60
40
20
0
Red Oak - Urban
Red Oak - Non-urban
White Oak - Urban
White Oak - Non-urban

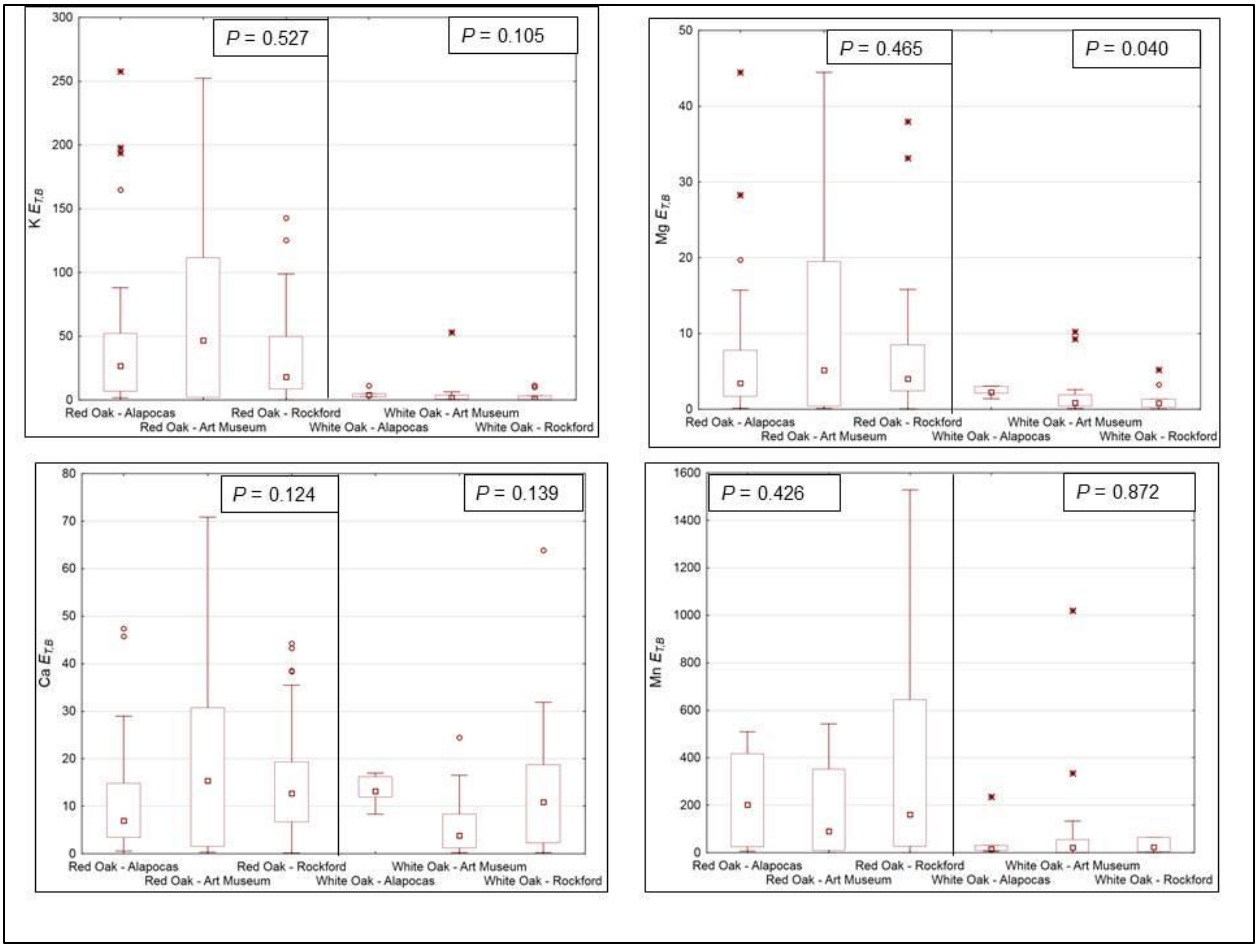
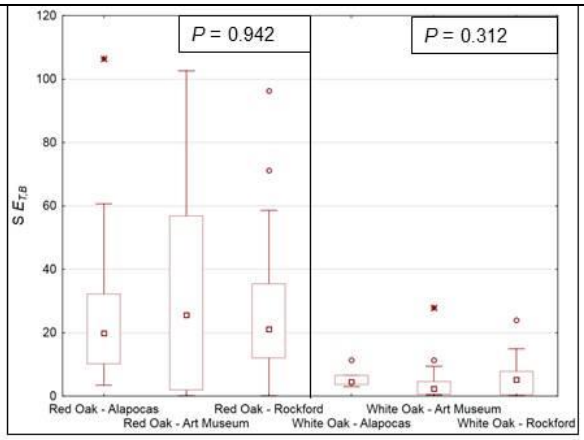
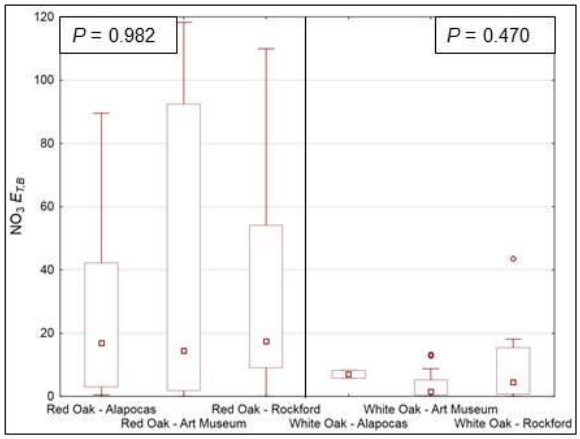


Figure 3.5 Intra-urban variability in flux-based enrichment ratios for stemflow in relation to throughfall ($E_{T,B}$) for all solutes.


P = 0.942
P = 0.312
S $E_{T:B}$
120
100
80
60
40
20
0
Red Oak - Alapocas
Red Oak - Art Museum
Red Oak - Rockford
White Oak - Alapocas
White Oak - Art Museum
White Oak - Rockford


P = 0.982
P = 0.470
NO_3 $E_{T:B}$
120
100
80
60
40
20
0
Red Oak - Alapocas
Red Oak - Art Museum
Red Oak - Rockford
White Oak - Alapocas
White Oak - Art Museum
White Oak - Rockford

Chapter 4

IMPACTS OF LAND USE VARIABILITY ON THROUGHFALL SOLUTE FLUX WITHIN REMNANT URBAN AND SUBURBAN FOREST FRAGMENTS

4.1 Abstract

While land use, emissions, and atmospheric deposition vary between urban and rural areas, there is also considerable variability in these parameters within highly developed portions of metropolitan regions. Within urban wooded ecosystems, this can be evidenced by variability in throughfall solute fluxes. In this study, we investigated the relationships between land use, atmospheric deposition sources, and Ca, K, Mg, Mn, NO_3-N, S, and Zn fluxes in throughfall among four remnant forest fragments in metropolitan Wilmington, Delaware, USA. Three of the sites were within Wilmington, and one was in a suburb approximately 6km west of the city. Variability in throughfall fluxes among the four sites were significant for Mn, NO_3-N, and Zn, but not for Ca, K, Mg, and S. Median flux values were highest at the suburban site for Mn, NO_3-N, and Zn, which may be attributed to the intensity of urban land use in the land within close proximity to this site (i.e., dense road networks, frequently utilized railroad infrastructure). Findings suggest that surrounding land use and the associated emissions and atmospheric deposition, rather than location along an urban to rural gradient, should be used as proxy for subcanopy nutrient cycling within urban wooded ecosystems. Implications for strategic tree selection in highly developed environments are discussed.

Key words: nutrient cycling, atmospheric deposition, urban forestry, urban land management, forest hydrology, urban-to-rural gradient

4.2 Introduction

Atmospheric deposition serves as an essential source of nutrients for forested ecosystems (Weathers and Likens 1997, Chadwick et al. 1999). Throughfall, (i.e., that precipitation which passes through canopy gaps or interacts with canopy surfaces en route to the forest floor) subsequently aids in the cycling of these nutrients beneath the canopy and subsequent transport to forest soils, where they are accessible for plant uptake and usage (Levia and Frost 2006, Zimmerman et al. 2007). The chemical composition of atmospheric deposition and throughfall can be significantly impacted by the elemental makeup of the gaseous and particulate matter emitted by both natural and anthropogenic sources (e.g., weathering, sea spray, combustion of biomass or fossil fuels) (Weathers and Ponette-González 2011, Izquieta-Rojano 2016).

Atmospheric deposition and subsequent solute fluxes via throughfall have been found to be notably higher for urbanized areas than in those characterized by lower degrees of development (Chiwa et al. 2003, Aikawa et al. 2006, Quan et al. 2008, Lin et al. 2011, Tsai et al. 2016). Quan et al. (2008) found that sulfur deposition was consistently higher within highly developed suburbs in southwestern China than in rural areas within the same region. Both Chiwa et al. (2003) and Aikawa et al. (2006) identified significant differences in throughfall solute fluxes between urban-adjacent and rural sites within Japan, with each study noting that urban solute fluxes notably exceeded those observed in the areas of comparatively lower development for several ions, including, but not limited to Ca^{2+}, NO_3^-, K^+, Mg^{2+}, and SO_4^{2-}.The regional variability in

aerosol composition, atmospheric deposition, and subsequent throughfall flux observed in these studies can be attributed to the relative differences in the quantity and density of emission sources between the urban and non-urbanized portions of the respective study areas. The higher throughfall solute fluxes that occur within the urban forested areas are indicative of higher delivery loads of nutrients to forest soils within these ecosystems (Gautam et al. 2017).

The literature has well established that regional variability in throughfall fluxes exist due to heterogeneity in type and intensity of land use between urban and non-urban areas. However, there remains a knowledge gap with respect to the impact of spatial variability in land use and intensity on solute fluxes within wooded ecosystems located in highly developed areas. Aikawa et al. (2013) identified a linkage between land use and localized differences in emissions in various Japanese neighborhoods; however, similar linkages between localized land use, emissions, and subcanopy solute fluxes has yet to be quantified in remnant metropolitan area forest fragments. The purpose of this paper is to identify land use and emissions-based drivers of spatial variability in throughfall solute fluxes occurring within metropolitan remnant wooded ecosystems. The development of a quantified record of these fluxes will expand our current understanding of nutrient transport and availability within these components of urban and community forests, which is essential for the adequate assessment of current and future threats to their function.

4.3 Methods

4.3.1 Study Area

This study was conducted in the Wilmington, Delaware, USA metropolitan area. Wilmington is a city within the larger Philadelphia, Pennsylvania – New Jersey – Delaware – Maryland US Census Bureau-designated urbanized area. Wilmington is the largest city in the state of Delaware, with approximately 60% (e.g., 560,000 residents) of the state's total population residing in the city and its accompanying metropolitan area (US Census Bureau 2017). There is spatial variability in the intensity of urbanization across the region, with the greatest development occurring along an east-west corridor bisected by the region's main thoroughfare, US Interstate 95. The extent of development generally decreases south of this urbanization corridor, although there are some isolated hotspots in which there have been rapid recent increases in development. All study sites for this project are located within this urbanization corridor.

The Wilmington metropolitan corridor is located within a climate transition zone, with humid subtropical climate conditions that characterize areas south of the region, and humid continental climate conditions that characterize areas to its north (Office of the Delaware State Climatologist 2018). Mean annual temperature within the study region is approximately 12.6°C, with the annual maximum temperature observed in July (24.9°C), and minimum temperature in January (0.22°C). Across the region, total annual precipitation ranges from approximately 1100mm to 1250mm (National Centers for Environmental Information 2018).

Data were collected from four remnant forest fragments located within the study region. Three of these fragments are in Wilmington, and one is in the suburban

community of Newport, Delaware, USA, approximately 6km west of the city (Figure 4.1). The three urban sites are comprised of closed-canopy wooded portions of Alapocas Run State Park, Rockford Park, and the Delaware Art Museum (hereon Alapocas, Rockford, and Art Museum, respectively), all of which are located within a 3.3km^2 area of north Wilmington. Alapocas is the largest of the urban sites (90ha) and is bordered by the Brandywine Creek to its west, industrial land use to its north, a local roadway to its east, and residential land use to its southeast. Rockford occupies approximately 12.4ha and is bordered by the Brandywine Creek to its north, and by residential development in all other cardinal directions. The Art Museum is the smallest of the urban sites (1.93ha) and is bordered by commercial land use and an access road to its southeast, a local roadway to its northwest, and residential land use in all other cardinal directions.

The suburban site is located within a closed-canopy wooded section of Banning Park (hereon Banning). Based on themes introduced by Teaford (2008) and Forsyth (2012), we define suburb as a locality within a designated metropolitan area that is beyond the geographic and political boundaries of the region's major city. Banning has an areal extent of 44.0ha, and is bordered by a heavily-traveled regional thoroughfare to its north; both a smaller local traffic artery and residential land use to its east; residential development to its west; and railroad infrastructure utilized by freight, commuter, and national rail lines to its south. More detailed descriptions of each of the research sites are provided in Dowtin and Levia (2018, under revision).

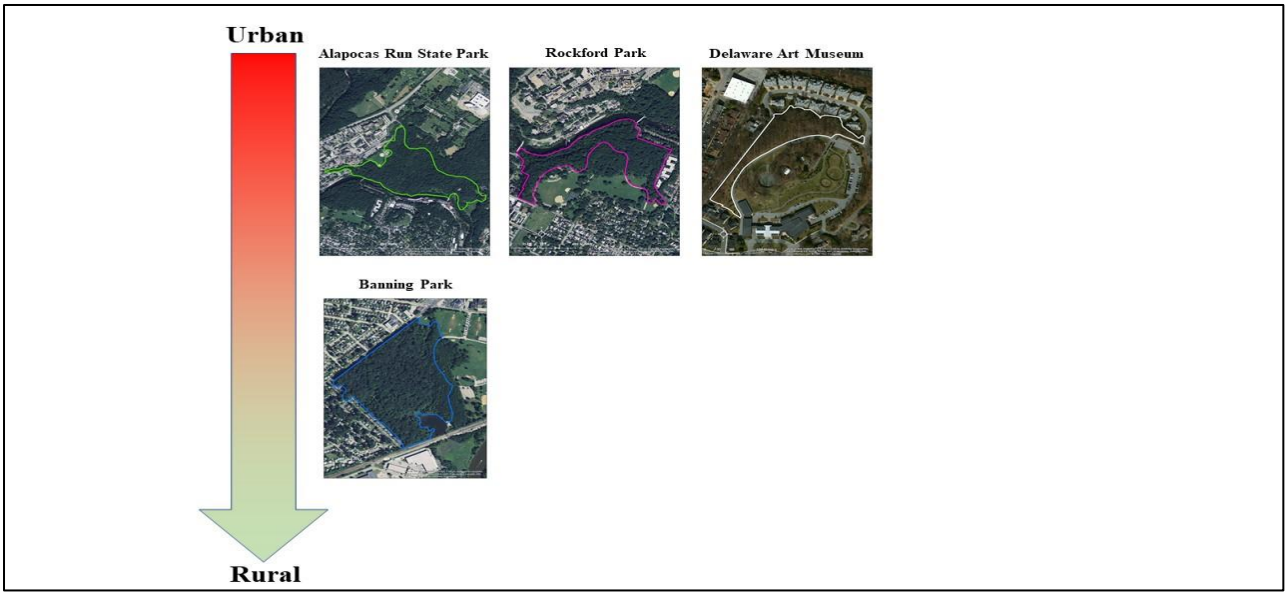


Figure 4.1. Map of respective study sites with relative location along an urban to rural gradient.

4.3.2 Sampling Design

All study sites were instrumented with twenty-five throughfall collectors and one bulk precipitation collector that was placed in a non-wooded area outside of the respective fragments. Both the throughfall and bulk precipitation collectors consisted of 3.7L HDPE containers that were anchored to the ground using plastic stakes affixed to the collectors with duct tape. All collectors were instrumented with clear HDPE funnels that ranged from 203.2mm to 230mm in diameter. These relatively large funnels were utilized to increase the capture efficiency of the collectors. Inert glass wool was placed within all funnel necks to prevent natural and anthropogenic debris from entering and contaminating the collected throughfall and bulk precipitation samples. The glass wool was replaced periodically throughout the study period to reduce the likelihood of sample

contamination from debris that had accumulated on the material. All collectors were rinsed with deionized water prior to each storm event to ensure that hydrochemical analyses were solely representative of the individual events for which sampling occurred.

At each site, throughfall collectors were placed in a gridded network consisting of 5 transects oriented at the following five set distances from the forest edge: 0m, 10m, 20m, 30m, and 60m. For this study, fragment edge was defined as that forest boundary that is perpendicular to the mean direction of storm propagation across the region, which Zishka and Smith (1980) determined was from southwest to northeast. Each of the 5 transects was instrumented with 5 stationary throughfall collectors that were distributed in a spatially representative manner; that is, collector placement allowed for adequate sampling to occur from the broad expanse of the designated sampling zones at each site (see Dowtin and Levia 2018, under revision, Figure 4.1, for a depiction of the sampling design).

Volumetric throughfall samples were collected on an event-basis from October 2015 to August 2017, with hydrochemical sampling occurring for a subset of ten storms from April 2016-August 2017. Sampling was limited to storms in which gross rainfall (P_g) ≥ 7.0mm to ensure that an adequate volume of throughfall would be generated to run hydrochemical analysis of the samples. *In situ* sampling was conducted within 48 hours of the end of each storm event. Volumetric measurements were made for each of the individual collectors, with 250mL of each sample additionally collected and stored to determine throughfall chemical composition. For each transect, the individual 250mL samples were aggregated into one volume-weighted 250mL sample that was representative of throughfall elemental flux along that transect. That is, for each storm

event at each site, five throughfall samples were prepared for hydrochemical analysis, one for each distance from the fragment edge (i.e., one 250mL sample for 0m, 10m, 20m, 30m, and 60m). All aggregated samples were filtered with 0.45µ filters and stored at 2.8℃ until processed.

4.3.3 Hydrochemical Analysis

Inductively coupled plasma – optical emission spectroscopy (ICP-OES) was used to determine solute concentrations for the macronutrients Ca, K, Mg, and S, and for the micronutrients Mn and Zn. A Thermo Scientific 215 iCAP™ 7600 ICP-OES Duo Analyzer was used to process all samples analyzed before 15 July 2016; a Thermo Scientific Iris Intrepid II XSP Duo View ICP- 216 OES Analyzer (Waltham, Massachusetts, USA) was used to process samples after 15 July 2016. NO_3-N concentrations were determined with a Bran+Luebbe AutoAnalyzer 3 flow injection analyzer. All hydrochemical analyses were performed by the University of Delaware Soil Testing Program.

Throughfall flux, TFF, was calculated as

$$TFF = V_{TF} * C_{TF} / A,$$

where V_{TF} denotes median throughfall volume for each transect (L), C_{TF} denotes throughfall solute concentration (mg L^{-1}), and A denotes the throughfall gauge orifice area (m^2), with use of the latter of these metrics allowing for the calculation of throughfall flux per unit ground area.

4.3.4 Geospatial Analysis

Land use surrounding each of the study sites was assessed using 2010-based census tract data from the United States Census Bureau (www.factfinder.census.gov) and aerial imagery. Each census tract was assessed for total population, population density, total housing unit count, and housing unit density. All geospatial analyses were completed using Esri ArcMap (version 10.1).

4.3.5 Statistical Analysis

All statistical analyses were performed with the Statistica software package (version 13.3, Tibco Software 2017). Neither the throughfall solute concentration nor flux data were normally distributed; thus Kruskal-Wallis tests were used to determine significant differences ($p < 0.05$) in throughfall chemistry and solute fluxes between the sites. *Post hoc* multiple comparisons tests were used to identify sources of variability when differences were found to be significant. For those cases in which the observed variability was significant and values at the suburban site exceeded those at sites within the city, Mann-Whitney u-tests were used to determine the significance of the observed variability between Banning and each of the city sites.

4.4 Results

4.4.1 Characterization of Land Use Surrounding Forest Fragments

Population and total housing unit count were highest in the census tract containing Banning Park (CT 129, Table 4.1). Both population density and housing density were largest in census tract 13, in which both Rockford and the Art Museum are located (Table 4.1). Census tract 117, which contains the Alapocas site, was largest in size but had the

lowest population, population density, housing unit count, and housing unit density of all census tracts included in the study.

Table 4.1 Population and housing density for census tracts in which the study sites are located. Rockford and the Art Museum are located within the same census tract. Bold population densities indicate urban classification according to the US Census Bureau's standard (urban classification as population ≤ 386 people km^{-2}).

Fragment	Census tract number	Census tract area (km^2)	Total population	Population density (km^{-2})	Total housing unit count	Housing density (km^{-2})
Alapocas	117	19.5	3974	204	1809	93
Rockford						
Art Museum	**13**	**2.28**	**3468**	**1519**	**1852**	**811**
Banning	**129**	**5.49**	**4720**	**920**	**2017**	**393**

4.4.2 Variability in Throughfall Hydrologic Flux and Chemistry

Variability in throughfall hydrologic flux was insignificant ($p < 0.05$) between the four sites. Relatively small differences were observed in the proportion of total rainfall partitioned into throughfall. For Alapocas, Banning, the Art Museum, and Rockford, throughfall accounted for 73.6, 73.7, 74.4, and 75.5% of total rainfall, respectively.

For all solutes and study sites, elemental concentrations in throughfall exceeded those observed in gross precipitation (Tables 4.2 and 4.3). Variability in throughfall solute concentrations was significant among the sites for Ca, Mg, Mn, NO_3-N, S, and Zn, but not for K (Table 4.3). Throughfall solute concentrations were highest for K, ranging from 3.50mg L^{-1} at Rockford to 4.52mg L^{-1} at Banning, and were lowest for Mn, ranging

from 0.003mg L^{-1} at the Art Museum to 0.017 mg L^{-1} at Banning. For Ca, Mg, and S, the highest median throughfall concentrations were observed within one of the Wilmington sites, while for K, Mn, NO_3-N, and Zn, throughfall concentrations were highest at Banning, the suburban site.

Table 4.2 Solute concentrations in bulk precipitation for each of the study sites. The same collector was used for bulk precipitation measurements for the Art Museum and Rockford sites. Solute concentrations are in mg L^{-1}.

Solute	Alapocas	Art Museum & Rockford	Banning
Ca	0.68	0.88	0.81
K	0.25	0.94	0.36
Mg	0.25	0.34	0.33
Mn	< 0.01	< 0.01	< 0.01
NO_3-N	0.14	0.15	0.23
S	0.24	0.31	0.41
Zn	0.22	0.04	0.02

Table 4.3 Median event-based throughfall concentration at each study site. The range of observed values is listed within parenthesis. Solute concentration is measured in units of mg L^{-1}. Bold values indicate significant variability in fluxes among all sites.

Site	**Ca**	K	**Mg**	**Mn**	**NO_3-N**	**S**	**Zn**
Alapocas	**2.83 (0.69-16.2)**	3.99 (1.13-27.8)	**0.67 (0.27-8.95)**	**0.004 (<0.001-0.09)**	**0.19 (0.02-1.83)**	**0.47 (0.16-1.40)**	**0.05 (0.01-0.31)**
Rockford	**1.62 (0.66-9.51)**	3.50 (0.95-22.0)	**0.52 (0.20-3.72)**	**0.003 (<0.001-0.18)**	**0.30 (0.03-1.95)**	**0.51 (0.17-1.49)**	**0.05 (0.01-0.53)**

Art Museum	**1.32 (0.54-4.13)**	4.15 (1.20-27.1)	**0.47 (0.19-1.88)**	**0.003 (0.001-0.10)**	**0.25 (0.01-4.91)**	**0.44 (0.18-1.81)**	**0.06 (0.03-0.22)**
Banning	**1.53 (0.66-7.6)**	4.52 (1.47-19.7)	**0.59 (0.29-3.00)**	**0.017 (0.001-0.32)**	**0.51 (0.06-2.77)**	**0.47 (0.25-2.25)**	**0.06 (0.03-0.61)**

4.4.3 Variability in Throughfall Solute Flux

Similar to the patterns observed with solute concentrations, throughfall flux was highest for K, ranging from 26.0 mg m^{-2} $event^{-1}$ at the Art Museum to 51.2 mg m^{-2} $event^{-1}$ at Alapocas (Table 4.4). Fluxes were lowest for Mn, with the lowest values observed at Alapocas (median = 0.04 mg m^{-2} $event^{-1}$) and the highest observed at Banning (median = 0.27 mg m^{-2} $event^{-1}$) (Table 4.4). The highest flux values for Ca, K, and Mg were observed at Alapocas; at the Art Museum for S; and at Banning for Mn, NO_3-N, and Zn. The variability in throughfall fluxes among the four sites was significant ($p < 0.05$) for Mn, NO_3-N, and Zn, but not for K, Ca, Mg, and S ($p > 0.05$). For Mn, NO_3-N, and Zn, the highest fluxes were observed at Banning, the suburban site. *Post hoc* multiple comparisons tests (not shown) determined that among the urban sites, throughfall NO_3-N fluxes were significantly different between Alapocas and the Art Museum, but not between Rockford and either of these two sites. Significant differences in throughfall solute fluxes between Banning and the urban sites are explored in section 3.4.

Table 4.4 Median event-based solute flux at each study site. The range of observed values is listed within parenthesis. Flux is measured in units of mg m^{-2} $event^{-1}$. Bold values indicate significant variability in fluxes among all sites.

Site	Ca	K	Mg	**Mn**	**NO_3-N**	S	**Zn**
Alapocas	36.8 (5.19-295)	71.0 (8.1-492.8)	12.0 (2.07-162)	**0.04 (0.01-2.13)**	**2.31 (0.08-6.49)**	4.35 (1.84-16.9)	**0.40 (0.09-13.4)**
Rockford	19.1 (5.12-174)	44.0 (6.79-403)	6.6 (1.61-68.0)	**0.05 (0.01-1.89)**	**3.29 (0.34-16.2)**	5.07 (1.39-27.3)	**0.62 (0.11-5.91)**
Art Museum	16.1 (3.84-73.5)	62.9 (7.56-493.3)	6.3 (1.59-26.0)	**0.05 (0.01-0.99)**	**4.86 (0.05-32.8)**	5.4 (2.31-24.1)	**0.70 (0.18-6.42)**
Banning	21.4 (5.61-97.5)	48.7 (14.2-285)	8.25 (2.47-35.9)	**0.27 (0.01-6.60)**	**6.95 (0.20-19.9)**	5.35 (2.14-41.7)	**0.78 (0.09-17.2)**

4.4.4 Solute Flux Comparisons between Banning Park and the Wilmington Sites

Mann-Whitney U tests determined that throughfall solute fluxes at Banning varied significantly ($p < 0.05$) from those observed at each of the three Wilmington sites for Mn and NO_3-N (Figure 4.2). For Zn, fluxes varied significantly between Banning and both the Alapocas and Rockford sites, but not between Banning and the Art Museum ($p = 0.16$). Mn fluxes at Banning exceeded those at each of the Wilmington sites by a factor of four or more (Table 4.4, Figure 4.2). NO_3-N fluxes at Banning were nearly twice as large as those at Alapocas, where the lowest fluxes for this solute were observed. For Zn, fluxes at Banning were nearly twice as large as those at Alapocas, with smaller differences noted between Banning and both the Rockford and Art Museum sites (Figure 4.2).

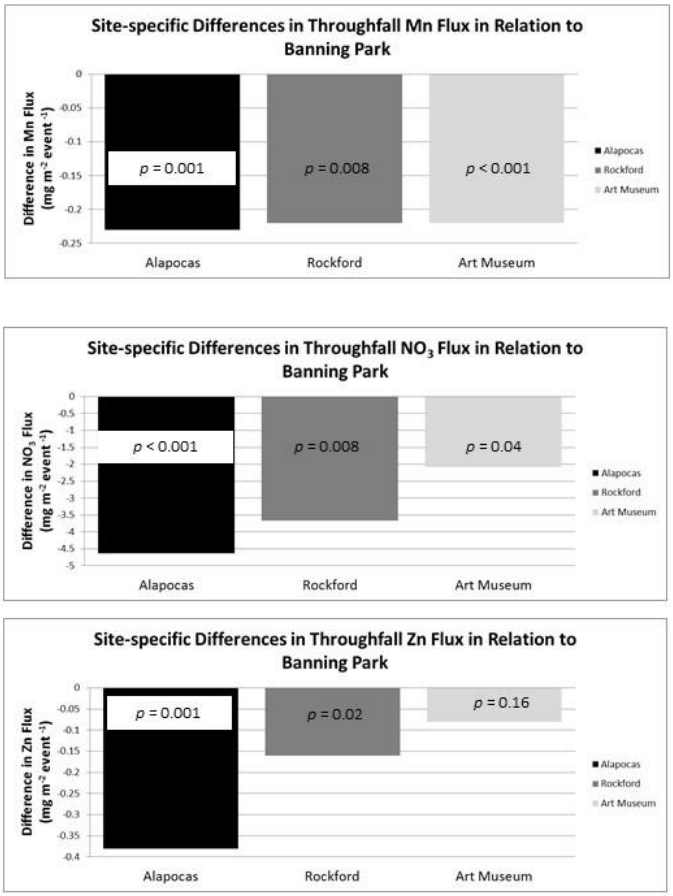


Figure 4.2. Differences in throughfall solute flux in relation to those observed at Banning Park. In each figure, the "0 line" indicates median event-based flux for each solute at Banning Park over the duration of the study period.

4.5 Discussion

4.5.1 Variability in Throughfall Solute Flux

In this study, throughfall solute concentrations consistently exceeded those of gross rainfall, indicating the chemical enrichment of throughfall due to the washoff and leaching of nutrients following its interaction with the canopy (Levia and Frost 2006). Chiwa et al. (2003), Forti et al. (2005), and Aikawa et al. (2006) noted similar amplifications of throughfall chemistry relative to that of open rainfall in urban forested ecosystems, with Chiwa et al. (2003) further noting throughfall concentrations in excess of those in gross rainfall by a factor of five or more for some elements. The maximum throughfall concentrations and fluxes for K found in this study can be attributed to the known high leachability of this element and agree with similar findings from Lovett et al. (1996), Van Stan et al. (2012), and Siegert et al. (2017), in which they all examined variability in subcanopy nutrient cycling. Our observations for minimum solute fluxes for Mn agree with those by Michalzik et al. (2016). The range of fluxes we observed were notably larger than Michalzik et al. (2016) for Ca, K, Mg, Mn, NO_3-N, and S (their study did not investigate Zn flux). This may likely be attributed to the fact that Michalzik et al. (2016) conducted their study in a controlled environment, with their vegetation not exposed to the same emissions and deposition loads as that in the current study.

4.5.2 Relationship between Adjacent Land Use and Throughfall Solute Flux

With the exception of K, solute fluxes for terrestrially sourced solutes (e.g., Ca, Mg) were consistently highest at Alapocas Park. This may be attributed to several local land use factors. Of the four sites, Alapocas occupies the largest expanse of

uninhibited natural green space, has the largest proportion of its border formed by a natural boundary (e.g., Brandywine Creek; Figure 4.3), and has the highest proportion of exposed rock surface. It is likely that weathering and resuspension of natural dust (i.e., dirt particles) at this location allows for higher deposition and subsequent solute flux of crustal elements there. Additionally, during the study period, several construction projects (e.g., one roadway and one demolition) were initiated in the land surrounding Alapocas. These projects likely resulted in the heightened emission of Ca, which is an important constituent element in concrete and other construction materials (Amato et al. 2009a), leading to the higher fluxes of Ca observed at Alapocas. Previous studies by (Amato et al. 2009a) and (Amato et al. 2009b) attributed high Ca concentrations of Ca in urban air masses to the suspension of construction materials in Barcelona. It is thus probable that the relatively high Ca levels observed in throughfall flux at Alapocas may be attributed to the ongoing construction occurring within close proximity to this urban remnant forest.

Figure 4.3 Aerial imagery of respective study sites. The left panel includes sites within Wilmington, while the right pane the suburban site, Banning Park.

For most of the solutes most commonly attributed to anthropogenic sources (e.g., NO_3-N, Mn, Zn), throughfall fluxes were consistently highest at the Banning Park site. While both population and housing density are lower for the census tract in which Banning Park is located than that which contains Rockford and the Art Museum, total population and housing unit count is higher in the former. That both population and housing density are lower in CT 129 is not solely based on the fact that this tract is larger in area than CT 13, but also on the fact that it contains a sizeable proportion of uninhabitable land, including both portions of the Christina River and marshland that borders the river's banks. This observation suggests that when developing a fundamental understanding of variability in solute fluxes within remnant forest fragments that occupy highly developed portions of a metropolitan area, census tract data alone may not serve as

the best proxy for atmospheric deposition and subsequent subcanopy fluxes. Rather, at a finer spatial scale, consideration must be given to the land use and associated emissions sourced by land parcels adjacent to these wooded lots.

The largest difference in throughfall solute fluxes observed between Banning Park and the sites within Wilmington was observed for Mn, as fluxes at Banning were exceeded those at the other sites by a factor of four or more. There are several anthropogenic emission sources for Mn, one of which includes railways (Gehrig et al. 2007, Bukowiecki et al. 2007). Both Gehrig et al. (2007) and Bukowiecki et al. (2007) attributed a proportion of the presence of Mn in aerosols to the abrasion of steel from the consistent movement of trains along railroad tracks in Zurich, Switzerland. Similarly, at the Banning Park site, the entirety of the fragments southern border is formed by tracks utilized by both the regional commuter rail and Amtrak's Northeast Corridor rail service (Figure 4.3). It is thus likely that the high flux of Mn in throughfall at this site can be attributed to the deposition of steel particles suspended by the frequent railway activity within close proximity to the site, and its subsequent deposition to and washoff from the canopy at Banning.

Like Mn, anthropogenically-sourced atmospheric Zn is known to have distinct emission sources, one of the most known of which is transportation corridors utilized by automobiles (Augusto et al. 2004, Herngren et al. 2006, Lin et al. 2011). Zn is often emitted into the atmosphere as a byproduct of bakeware and tires, and as such, has often been found in high concentrations in air quality samples taken adjacent to roadways (e.g., Lin et al. 2011). It is thus likely that the observed incremental increase in Zn throughfall

flux between the four sites may be attributed to incremental differences in roadway usage and traffic-sourced emissions.

As an example, though Rockford Park and the Art Museum are within the same census tract, Zn throughfall flux was found to be higher in the latter than in the former. The higher fluxes at the Art Museum may be attributed to the fact that two of the boundaries of this fragment are formed by roads that service both the local community and the institution, in comparison to Rockford Park, which is bordered on its eastern boundary by the Brandywine Creek and is transected by a park service road characterized by relatively low traffic volume (Figure 4.3 and c). The higher road traffic at the Art Museum may result in the higher emission, deposition, and subsequent washoff of Zn at this location than at Rockford. Similarly, the absence of an adjacent roadway at the Alapocas site may account for the lower Zn flux values observed there in comparison with the other two Wilmington sites.

4.5.3 Implications for Urban and Community Forest Management

The spatial variability in throughfall and solute fluxes observed in this study indicate that even within highly developed extents of the same metropolitan region, there can be markedly significant differences in the total deliver of nutrients to urban forest soils. These differences may likely be attributed to emissions from varying forms of land use in the areas adjacent to or near these urban ecosystems. These findings nay highlight important implications for urban and community forest management, as previous studies have indicated that both trees and plants of varying species display different tolerances to varying degrees of nutrient loading.

Nakaji et al. (2001) investigated the relationship between N-loading to the soil and tree productivity. They found that for Japanese red pine seedlings, dry matter production decreased with higher N delivery, while Japanese cedar seedlings were not impacted by this higher N loading. Yamaguchi et al. (2012) found that there is interspecific variability in tree response to nutrient exposure and loading. They determined that when N loading to forest soils is constant, some tree species experienced reduced growth when exposed to SO_2, while others did not. Further, Mao et al. (2018) found that for herbaceous vegetation, excess nitrogen deposition decreased photosynthetic capacity to varying degrees for three different understory species. Thus, as urban and suburban wooded lots are planned, expanded, and managed, care should be taken to select species that are tolerant to the anticipated levels of throughfall-sourced nutrient delivery that can be expected based on land use within close proximity to these metropolitan wooded areas.

4.6 Conclusion

Within highly developed portions of metropolitan regions, there exists some spatial variability in the forms of urban land use present. This consequently impacts elemental emissions, atmospheric deposition, and the subsequent flux of solutes via throughfall in remnant wooded ecosystems within the urbanized areas. Though located at a greater distance from the city center and characterized by lower population and housing densities than the Wilmington-based sites, the suburban Banning Park remnant forest consistently had the highest throughfall solute fluxes for NO_3-N, Mn, and Zn, which can be attributed to its proximity to intense forms of urban land use. The higher fluxes of solutes at this site can have direct impact on the total delivery of nutrients to the forest

floor; nutrient delivery in excess may have negative impacts on forest health and function, thus warranting future studies of throughfall fluxes and other forms of nutrient cycling within urban and suburban forested ecosystems. Though solute fluxes may generally be assumed to be notably lower in suburban sites, the current study underscores the importance of placing higher value on the impact of adjacent land use to nutrient fluxes within suburban wooded lots, rather than focusing solely on their distance from the regional major city, or on solely comparing fluxes between urbanized and non-urbanized forest ecosystems. Further, the observed variability in subcanopy solute fluxes highlight the importance of strategic tree selection when planning and managing urban and community forest initiatives, as trees of varying species may possess varying functioning capacities under different degrees of nutrient loading.

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Chapter 5

DISCUSSION

As development pressures increase in expanding metropolitan areas, so do efforts to maintain, and where possible, expand urban forest cover to mitigate the negative environmental impacts of urbanization. For optimized utilization of the urban forest in this capacity, it is imperative that future urban forest planning and management strategies be based on a sound understanding of the biotic and abiotic characteristics of the urban canopy that either aid or hinder its ability to provide these ecosystem services. This dissertation explored the relationships between urban forest structure, hydrologic, and nutrient cycling in metropolitan remnant forest fragments to broaden our current understanding of ability of these wooded ecosystems to capture and redistribute water and nutrients, and the related impacts on their ability to provide hydrologic and hydrochemical ecosystem services.

Two important ecosystem services provided by the urban canopy include stormwater mitigation via interception and infiltration, and acid neutralization. Canopy structural characteristics, to a large extent, govern the degree to which a given tree or total urban canopy is able to provide these ecosystem services. For example, rainfall interception by the urban canopy has been found to be significantly larger for trees characterized by high bark water storage capacity, plageophile branching structures, relatively hydrophilic leaf surfaces, and relatively high plant area index values.

Collectively, these characteristics aid in the effective capture and retention of precipitation by the urban canopy, and in reducing the proportion of gross precipitation that may potentially become stormwater.

Physical characteristics of the urban canopy also contribute significantly to the urban canopy's ability to neutralize acids. This ecosystem service is vital regarding maintaining a healthy nutrient load to urban forest soils, and in preventing the likelihood of aluminum toxicity or soil podzolization, both of which pose significant risks to urban forest health and function. Acid neutralization by the urban canopy is minimized by coniferous tree species, and maximized by the species that are characterized by bark of greater microrelief and complex morphology. The structural characteristics of the latter classification of trees increase the residence time of water interacting with the canopy, thereby allowing for a greater degree of canopy exchange processes in which hydrogen ions are taken up by the canopy in exchange of base cations, where are leached and subsequently transported to forest soils via throughfall and stemflow.

Utilizing knowledge of the complex relationships between canopy structure and the production of select hydrologic and hydrochemical ecosystem services, this dissertation provides a novel prescriptive guide for urban tree selection that may be utilized by urban land managers. This guide introduces an important, practical means by which advances in forest hydrology and biogeochemistry research may be used to inform urban forest practice in a sustainable manner. Future research should build upon this work by introducing additional prescriptive guides that inform tree selection to meet biodiversity standards, or to provide other valued ecosystem services by the urban canopy. Future guides should offer descriptions of both the structural characteristics that

will optimize provision of the intended services, in addition to recommended species for various climatic and hardiness zones (the former of which is of great importance for urban forests outside of the North American continent.

A second important contribution of this dissertation is its spatially representative quantification of subcanopy solute fluxes within urban remnant forest fragments. As there has been a predominant focus on the hydrology of urban street trees, this research has aided in filling a knowledge gap with a respect to assessing the transport of solutes within urban wooded ecosystems, which may exert significant influence on their respective capacities to provide ecosystem services.

Through the *in-situ* sampling of hydrologic and solute fluxes conducted for this dissertation, patterns of subcanopy solute fluxes within urban wooded lots were found. These solute fluxes vary spatially, which may be attributed to both biotic and abiotic fluxes. Several metrics were utilized to quantify these fluxes: traditional throughfall flux calculations, and flux-based enrichment ratios for stemflow. Regarding the latter, this study became the of its kind to utilize flux-based enrichment ratios for stemflow in relation to throughfall (introduced by Levia and Germer 2015) to quantify the relative contributions of both flux mechanisms to the delivery of solutes to the forest floor, and to the best of the author's knowledge, the first to quantify variability in solute fluxes occurring from multiple remnant wooded lots within the same city.

Use of the two flux-based enrichment ratios for stemflow (i.e., in relation to stemflow, throughfall) aided in the identification of drivers of spatial variability in solute flux within remnant urban forest fragments. For both enrichment ratio metrics, values were consistently higher for red oak trees than for white oaks. This significant

observation may be attributed to the marked differences in stemflow yield between the two species, with stemflow yield by red oaks found to be, for some events, an order of magnitude larger than that observed for white oaks. This interspecific variability in stemflow yield results from varying structural characteristics between the two species, with the linearly aligned and relatively smoother bark of red oaks helping to facilitate stemflow production, while the flaky bark of white oak impedes its generation. As such, while solute concentrations were found to be higher for white oaks due to the longer residence times, fluxes were generally higher for red oaks. This observation suggests that there is marked spatial variability in nutrient delivery to urban forest soils, which likely results in spatial variability in the presence of biogeochemical hotspots below urban canopies.

There are several promising future directions for research based on these findings. First, it may be helpful to utilizing geospatial analysis techniques to delineate zones of high nutrient deliver based on knowledge of the flux-based enrichment ratio data. Such mapping may be utilized to determine hot spots of microbial activity in urban forest soils, which may subsequently be utilized to identify subcanopy localities of increased forest resilience or vulnerability. Additional work should be done to develop a baseline quantifiable assessment of relative flux-based enrichment ratios for the urban tree species that most commonly occupy urban wooded lots within a given metropolitan region. Findings from such work can be used to further develop the capacity of urban forest modeling packages to incorporate simulation and predictions of solute fluxes and biogeochemical activity within the urban forest.

Finally, this dissertation explored the linkages between adjacent land use and subcanopy nutrient flux, as evidenced through solute fluxes via stemflow. This portion of the study was limited to those fragments that were present within highly developed extents of the metropolitan region. Findings from this research underscore the importance of considering adjacent land use when assessing nutrient flux within urban wooded lots, rather than basing such assessments (or assumptions) on the location of remnant fragment along an urban to rural gradient. For select elements investigated in this study, subcanopy solute fluxes were found to be significantly higher in the suburban fragment than in any of the urban fragments, in some cases by a factor of four or more (e.g., for Mn). These observations were likely caused by the intensity of urban land use in the areas adjacent to or near the study fragments, which changed in a notable fashion across the region. In this study, some of the most intense urban land use was actually found outside of the city. In conjunction with the elevated solute fluxes that were observed, this may be used to justify expanding future urban ecology, forestry, and biogeochemistry research in a direction that is not solely guided by the traditional urban-to-rural gradient perspective.

Collectively, findings from this research strongly suggest that as urban forests continue to expand, and as dependence on them for ecosystem service provision continue to increase, selection of the trees that will sustainably populate them must be based on a firm understanding of the biotic and abiotic characteristics that govern their ability to function and yield their intended services.

Chapter 6

CONCLUSIONS

This dissertation utilized a comprehensive review of the literature and in situ sampling to quantify the hydrologic and hydrochemical fluxes that occur within metropolitan remnant fragments. Key outcomes and findings from this research include:

- A prescriptive guide for urban tree selection to optimize stormwater mitigation and acid neutralization by the urban canopy was developed.
- Flux-based enrichment ratios for stemflow were consistently higher for red oak trees than for white oak trees within remnant forest fragments.
- Flux-based enrichment ratios for stemflow were consistently higher for those sites within the city of Wilmington than those outside of the city.
- This study was the first to quantify subcanopy solute fluxes for closed-canopy remnant metropolitan forest fragments using the flux-based enrichment ratio for stemflow in relation to throughfall, thereby quantifying spatial variability in throughfall flux within these wooded ecosystems are three spatial scales: intra-fragment, intra-urban, and trans-regional.
- Within highly developed portions of a metropolitan region, whether within the city limits or in the suburban extents of the region, surrounding land use is a key factor in subcanopy flux, likely of equal or greater importance than location along an urban to rural gradient.
- It is intended that use of the advances in urban forestry research provide helpful insights for advances in urban forestry practice.

Appendix A

PERMISSIONS

The following pertains to chapters 2, 3, and 4 of this dissertation, which were submitted to three Elsevier journals for review. The manuscripts herein contained are in the form of their initial submission, rather than the finalized publication. As declared by Elsevier Permissions, as author of this work, I retain the right to include these manuscripts within this dissertation.

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