INFLUENCE OF URBAN CANOPIES ON THROUGHFALL NUTRIENT COMPOSITION AND DOM OPTICAL PROPERTIES, AND THE DECOMPOSITION OF URBAN LEAF LITTER

A THESIS

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Abstract

Due to the rapid growth of large and densely populated cities, urban municipalities increasingly search for green solutions to manage urban air and water pollution. Expansion of urban tree cover has been popular among cities in an effort to mitigate air pollution and reduce stormwater volumes. While this growth of urban forests has had positive environmental impacts, little is known regarding the interactions between precipitation and canopy cover and the resulting nutrient fluxes particularly to stormwater. Previous studies have shown variability in atmospheric deposition onto tree canopies between urban and forested areas where canopies closer to anthropogenic sources have increased nutrient fluxes in throughfall. In addition, throughfall composition has been shown to differ by tree species and canopy structure. To address research gaps centered around the nutrient fluxes present in throughfall, I collected throughfall under multiple Fraxinus sp.(ash) trees in four St. Paul public parks for one growing season and analyzed for nutrients to determine rates of wet deposition under tree canopies. Optical properties of dissolved organic matter (DOM) were analyzed using excitation emission matrices (EEMs) to determine forms of organic matter present within urban throughfall. Leaf litter was also collected during autumn from various locations within an urban environment such as directly below canopies, parking lots, streets, and storm drains to determine the changes in nutrient composition along the pathway to storm drains. Leaf litter was analyzed for percent total carbon and nitrogen. I designed collections around trees as part of the Minneapolis-St. Paul Long Term Ecological Research Program (MSP LTER) with the goal of better understanding the role of urban forests in the hydrologic cycle and the nutrient pathways to stormwater and surface water.

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Chapter 1. INTRODUCTION

1.1 Introduction

Expansion of urban tree cover has been popular among municipalities to mitigate urban heat islands, manage stormwater, enhance carbon sequestration, and serve as an aesthetic enhancement (Berland et al., 2017). While many cities have had positive results from adding canopy cover, there are still many unknowns regarding the interactions between trees and the surrounding area, which ultimately leaves the role of canopies in an urban ecosystem unknown. Specifically, the interactions between urban tree canopies and precipitation have only been somewhat studied. It is known that within forests, canopy processing of constituents within precipitation is essential for transport of nutrients to soils (Van Stan et al., 2021), however, in an urban environment where impervious surface coverage is high, this process is disrupted, and contents are ultimately transported directly into urban surface waters. Precipitation can be thought of as a process that transports water and chemicals (dissolved or particulate), making it an important transport pathway that needs to be better understood within urban ecosystems (Ponette-Gonzalez et al., 2016). Throughfall, the precipitation that passes through the canopy, is a component of the transport of nutrients from the atmosphere back to soils (Ponette-Gonzalez et al., 2016). When the rainfall penetrates the canopy, various interactions occur that change the chemical makeup of the precipitation, resulting in greater fluxes of nutrients and heavy metals in throughfall samples. Due to throughfall being dynamic in ecosystems depending on the vegetation cover and environmental characteristics, it is often difficult to predict fluxes, which highlights the need for widespread data across various environmental conditions (Dunne & Leopold, 1978).

Throughfall can also be measured to determine the influence of the canopy on stormwater, especially in urban areas where impervious surface cover is high and flooding is likely (Berland et al., 2017). With an increasing volume of runoff that flows directly into lakes, streams, and rivers, the importance of water quality, based on the contents of the water inputs, need to be analyzed to properly diagnose various issues. The chemical composition of throughfall can be analyzed to determine the ion exchanges that occur when rainfall passes through a canopy. This type of analysis is important to determine atmospheric deposition rates of major pollutants on urban canopies, to monitor and manage surrounding water quality, and to answer questions that still remain about the water cycle. Monitoring various sources of major pollutants is essential to properly manage stormwater and protect urban surface waters. Specifically, excess inputs of nutrients such as nitrogen (N), phosphorus (P), and carbon (C) are often monitored due to their relationship with algal blooms that ultimately reduce dissolved oxygen availability which is harmful to aquatic ecosystems (Schindler, 1974). Currently, there are only a handful of papers discussing the chemical composition of urban throughfall and gaps in knowledge remain that necessitate further research.

Understanding how the canopy interacts with precipitation in forested environments is key to building knowledge of this interaction and applying the same scenario in an urban setting. Numerous studies have been conducted regarding the flux of nutrients and heavy metals in throughfall in forested areas (Henderson et al., 1977; Lovett and Lindberg, 1984; Germer et al., 2007). There has been evidence that throughfall is more chemically concentrated with common nutrients such as nitrogen, phosphorus, and carbon than open precipitation due to the interactions between the canopy and precipitation (Ponette- González et al., 2016; Van Stan & Allen, 2020) and often increases in nutrient concentrations and flux when sampled closer to an urban environment (Lovett et al., 2000; Chiwa et al., 2003; Forti et al., 2005; Carsartelli et al., 2008; Ponette-Gonzalez et al., 2017). Urban environments tend to have greater fluxes of nutrients in throughfall due to the ability of tree canopies to filter air pollutants like particulate matter (PM) from the air that will ultimately be washed off the canopy and enter the hydrologic cycle via throughfall or can be blown off to the soil or a completely new area from wind (CCTG, 2008). This trend is not universal, where Juknys et al., (2007) compared throughfall concentrations on an urban-rural gradient within Scots pine stands in Lithuania and found higher concentrations in the suburban site compared to rural and urban sites. This difference was ultimately attributed the difference in wind direction where pollutants from industrial activities were being blown onto canopies within the suburban site (Juknys et al., 2007). Several studies have reported nutrient concentrations in throughfall in forested environments, (Henderson et al., 1977; Lovett and Lindberg, 1984; Germer et al., 2007), but the knowledge of this in urban areas is limited and needs to be explored due to rapid urbanization, increasing impervious surface coverage, and an overall interest regarding the role of canopies as green infrastructure within urban environments.

Many studies have compared the throughfall concentrations in urban and rural or forested areas (Aikwaka et al., 2005; Decina et al., 2018; Forti et al., 2005; Lovett et al., 2000). However, there are comparisons of suburban and urban sites (Zaltauskaite and Juknys, 2009) as well as mountain facing and urban facing sites (Chiwa et al., 2013). While each study conducted was different in methodology and canopy characteristics, most found that atmospheric deposition of pollutants onto the tree canopy was the main source of carbon, phosphorus, and nitrogen species found in throughfall. Forms of organic nitrogen, carbon, and phosphorus are deposited onto the canopy through dry deposition and eventually washed out by precipitation as throughfall (Decina et al., 2018; González-Benitez et al., 2009; Matsumoto et al., 2014; Chiwa et al., 2013; Zaltauskaite and Juknys, 2009). This aspect of the hydrologic cycle is a major pathway for nutrients to be taken up by the canopy or leached into the surrounding soil or water bodies. Some studies also found that there were larger fluxes of nutrients during spring (Bettez and Groffman, 2013; Kopacek et al., 2011; le Mellec et al., 2011; Stadler and Michalzik, 1998; Templer et al., 2015a, 2015b; Decina et al., 2018). Spring fluxes are thought to be due to higher inputs of pollen, microbial activity, and increased precipitation during spring. Many studies also found difficulties in understanding the atmospheric deposition rates of NH^{+}_{4} due to absorption by the canopy (Decina et al., 2018; Chiwa et al., 2013) but this is still an important piece of understanding canopy processes. While there is some merging information that has guided researchers through understanding canopy processes when interacting with precipitation, there is not enough research across urban environments with varying climates and species to fully quantify the changes that occur. Filling these gaps can provide a better understanding of hydrologic pathways of pollutants, nutrients, and particulate matter in a system and can provide better management practices for urban forests. Specifically, throughfall chemical compositions is important as a useful tool to monitor air pollution and signal possible water quality issues. To contribute this growing area of research, this literature review will cover existing literature that analyzes the nutrient contents of urban throughfall.

1.2 Throughfall Chemical Composition

1.2.1 Nitrogen

Nitrogen is an essential nutrient for plant growth but problems with nitrogen distribution have risen in recent years and include various forms such as nitrate and ammonium. Nitrogen is typically a limiting nutrient in forested ecosystems, however, with increasing anthropogenic pollution it has become a major pollutant when deposited in large amounts (Galloway et al., 2008). This makes nitrogen an extremely important nutrient to study and understand its pathways to better manage inputs into soils and water bodies. Large inputs of nitrogen can lead to eutrophication of lakes and algal blooms; this is an especially widespread problem in urban areas due to high impervious surface coverage that provides a direct route for nutrients into lakes and streams (Conley et al., 2009; Howarth and Marino, 2006). These areas are also likely to have high inputs of nitrogen due to use of lawn fertilizers and pesticides, as well as inputs from failing to clean up pet waste (Lusk et al., 2020; Baker et al., 2014) and burning of fossil fuels (Sutton et al., 1995). These pollutants are often deposited onto urban canopies via atmospheric deposition creating potential for precipitation to wash off pollutants and enter urban surface waters.

Analysis of NO^{-}_{3} in urban throughfall is not uncommon due to high exposure of common anthropogenic sources of nitrogen within urban environments and has even been shown to produce nitrogen deposition hotspots (Fenn et al., 2003; Du et al., 2015) often due to vehicular emissions (Baker et al., 2001; Decina et al., 2017). It has been shown that throughfall fluxes can be eight times higher in urban areas when compared to forests (Fenn and Bytnerowicz, 1993) supporting the idea increased nitrogen deposition is closely related to emissions from industrial and urban sources. Nitrogen fluxes in throughfall has also been shown to be related to tree age where young trees in nitrogen limited environments are more likely to retain nitrogen species such as ammonium (NH^{+}_{4}) deposited onto the canopy to support plant growth (Hall and Matson, 2003; Lohse and Matson, 2005), specifically, it has been shown that NH_{4}^{+} is a preferential nutrient and will often be retained by the canopy (Adriaenssens et al., 2012). In tropical forested environments, it has also been shown that nitrogen fluxes in throughfall are related to the availability of nitrogen within soils (Cusack et al., 2016; Ponette-Gonzalez et al. 2017). Ultimately, it is known that nitrogen fluxes in throughfall are relative depending on the environment and nitrogen availability within the area but there is a need for more widespread research to fully understand canopy processes with regard to nitrogen in urban forests.

1.2.2 Phosphorus

Phosphorus is another important nutrient to monitor because like nitrogen, it is a vital nutrient for life and is also a common limiting nutrient, especially in lake ecosystems, where it can also cause eutrophication. Most natural phosphorus comes from weathering and erosion; however, it is also commonly found from inputs of organic matter like leaf litter and pollen (Grahm and Duce, 1979; Newman, 1995). Phosphorus also has anthropogenic sources such as burning of fossil fuels and heavy usage of fertilizers for lawns or agricultural purposes (Ponette Gonzalez et al., 2006) and has been shown to create local hotspots of phosphorus deposition (Du et al.,2016). However, unlike nitrogen, phosphorus has been found to be incredibly variable and remains somewhat difficult to predict fluxes below canopies (Neal et al., 2003). There is evidence that phosphorus concentrations in stormwater are related to canopy cover (Waschbusch et al., 1999; Janke et al., 2017) which supports the concept that throughfall is enriched with nutrients. Although throughfall acts as a medium to transport phosphorus, Decina et al., (2018) analyzed urban throughfall under mixed deciduous stands in Boston, MA and found that phosphorus concentrations in throughfall were higher than in sewage effluent indicating that throughfall is a major source of phosphorus for aquatic systems. It is unknown from the study if there was the opportunity for throughfall to be infiltrated (i.e by stormwater ponds, or buffer zones) before entering sewage systems, but could be supportive of research suggesting that soils are extremely effective at filtering and processing nutrients (Groffman et al., 2004; McPhillips et al., 2016; Wollheim et al., 2005).

1.2.3 Carbon

Much of the DOM in aquatic systems is present as dissolved organic carbon (DOC) (Dittmar and Stubbins, 2012). While there are several ways for DOC to enter aquatic systems, atmospheric deposition of carbon is one of the most common pathways for atmospheric carbon to enter the landscape (Dachs et al., 2005; Goldstein and Galbally, 2007) and ultimately runoff into nearby water bodies. It is known that canopy cover is the primary interceptor of precipitation, making tree-derived DOC an important area of research in forested ecosystems (Angelini et al., 2011). Much of the research regarding DOC in throughfall has been done in forested ecosystems and has shown variability across different forest types, specifically forests where there are changes in canopy cover and seasonal leaf shedding, had the greatest range of DOC values (Van Stan and Stubbins, 2018). It has also been found that DOC concentrations are related to storm intensity where larger storms are able to wash off more contaminants on the canopy surface, but the DOC concentration is diluted by the large amount of precipitation (Goller et al., 2006; Levia et al., 2012).

In addition to monitoring fluxes and concentrations of tree-derived DOC, the characteristics of carbon can be identified by using excitation-emission matrices (EEMs) on DOM. The evaluation of carbon forms within throughfall is valuable to understand the availability of carbon sourced from throughfall, and to monitor inputs to drinking water sources due to evidence of disinfection byproducts formed due to interactions with DOM and chemical disinfectants (Chen et al., 2019). Monitoring DOM using EEMs is also essential for determining the freshness or lability of DOM present, which can determine the availability of DOM as a ready food source within urban surface waters (McClain et al., 2003; Qualls, 2020). There are very few studies that characterize DOM in forested throughfall (Inamdar et al., 2011, 2012; Singh et al., 2015; Van Stan et al., 2017; Ryan et al., 2022) and at the point of this review, there have been no studies conducted in urban environments. Within the forested environments, it has been found that there are differences in DOM quality amongst tree species (Levia et al., 2012; Stubbins et al., 2017; Van Stan et al., 2017). DOC and DOM in throughfall is somewhat understood in forested environments, however, due to its strong relationship with atmospheric deposition, there is a widespread need for this research to be conducted in urban forests due to its direct transport across impervious surfaces to aquatic systems.

1.2.4 Heavy Metals

Increasing industrial processes in urban areas have led to an increase in emissions of heavy metals which ultimately increase research on urban forests due to its ability to filter pollutants and lower the pH of precipitation (Slamet et al., 2018). In addition, there are various public health concerns with water contamination of heavy metals such as arsenic, lead, and mercury that have a high toxicity in low concentrations (Tchounwou et al., 2012). Although there are numerous studies conducted in forested environments, the research has not been done as extensively in urban environments. It is already understood that the interaction between precipitation and the canopy can alter the chemical composition of throughfall (Gandois et al., 2010), but due to the spatial variation of atmospheric deposition, it is essential to conduct these studies in various environments.

In almost all the studies, it has been found that heavy metal concentrations increased in throughfall when compared to bulk precipitation due to increasing rates of atmospheric deposition (Shah et al., 1993; Alvia & Rodrigo, 2004; Hou et al., 2005). Zinc and lead have been shown in multiple studies to have the greatest flux in precipitation moving from the canopy to soil (Alvia &

Rodrigo, 2004; Hou et al., 2005), but there is evidence that these metals are retained within the canopy (Shah et al., 1993). From these studies, it is thought that much like nutrients, the main source of heavy metals in throughfall is due to atmospheric deposition (Alvia & Rodrigo, 2004; Hou et al., 2005).

Alvia and Rodrigo (2004) understood this threat and compared heavy metal fluxes in throughfall from an urban site and from a forested site. Under a holm oak forest, they reported greater concentrations of heavy metals in throughfall at the more urban exposed site, however, only copper, lead, and vanadium concentrations were found to be statistically different from the non-urban site (Alvia and Rodrigo, 2004). Regression analysis of cadmium, lead, and zinc concentrations indicated that dry deposition is the main cause for increases in concentrations (Alvia and Rodrigo, 2004). Manganese had the highest concentrations in throughfall at both sites which is attributed to leaching within the canopy, nickel and potassium were also thought to have the same effect (Alvia and Rodrigo, 2004).

Although the study was done in a suburban site, Hou et al. (2005) demonstrated that enrichment of heavy metals in throughfall is associated with leaching during canopy processes. Their results also showed greater enrichment of heavy metals within *C. japonica* in comparison to other species such as *P. denisflora, C. obtusa,* and *Q. myrsinaefolia*. Their throughfall measurements showed a flux of all metals in throughfall except for zinc, which was similar to results found in Alvia and Rodrigo (2006). The overall results of this study shows that zinc and antimony were more enriched in bulk precipitation while manganese and iron were enriched in throughfall (Hou et al., 2005).

1.3 Conclusion

It is clear that throughfall is a major pathway for dissolved ions and nutrients to enter the hydrologic system. In urban areas with high impervious surface coverage, this is a direct route to nearby aquatic systems due to lack of opportunity to infiltrate into soils. There are a number of factors that influence ion concentrations in throughfall such as season, tree species, exposure to anthropogenic emissions, and meteorological conditions such as temperature and storm intensity. Although research has been conducted in forested environments for decades, there is a need to understand this process in urban environments where concentrations are greater, and infiltration is limited. Future research requires the quantification of these ion fluxes beginning at an individual tree scale to further scale up to blocks, storm sewer shed, an entire urban watershed level.

Chapter 2. THROUGHFALL CHEMSITRY, DOM PROPERTIES, AND URBAN LEAF LITTER

2.1.0: Introduction

Increasing populations and the growth of urban environments throughout the world have led to increased urban land use, which ultimately comes with increased impervious surface coverage and pollution. The increased use of impervious surface coverage increases the likelihood of flooding due to increased stormwater runoff volumes and is a common issue that many municipalities face. In addition, due to the urban surroundings, much of this stormwater is polluted with nutrients and will flow directly into nearby lakes and streams with no opportunity for infiltration into soils (McGrane et al., 2016; Walsh et al., 2005). This rising problem of high impervious surface coverage leading to decreased water quality has initiated much of the current research regarding stormwater management and stormwater quality by development and improvement of green infrastructure. Green infrastructure includes engineered systems such as green roofs, rain gardens, and increased vegetation near sidewalks and roadways to emulate natural processes of filtration and ultimately reduce loading of pollutants to urban streams and lakes (Naumann et al., 2011). A popular and long-standing form of green infrastructure includes increasing canopy cover using boulevard trees and urban forests. There are several benefits such as filtration of air pollutants, mitigation of the urban heat island effect, carbon sequestration, interception of precipitation to reduce of stormwater volumes, mental health improvements, and its aesthetic value (Naumann et al., 2011; Zolch et al., 2016). While municipalities work to increase their canopy cover, the role of urban trees remains relatively unknown and unquantified in regard to the hydrologic system. Much of the previous literature has disproportionately focused on the nutrient inputs to waterways from forested sites. While there is an increasing need for and interest in green infrastructure and nature-based solutions in cities, many natural processes behave differently in urban watersheds. One important step involves quantifying the various aspects of nutrient inputs from urban canopies, primarily from throughfall and leaf litter, to stormwater and urban runoff. Such information is key to collaborations between stormwater practitioners and urban foresters to improve the placement and engineering of urban forests to best support its natural benefits.

2.1.1 Throughfall

While the full potential role of trees within the urban hydrologic system is not fully understood due to its complexity and variability across space and species, there are still some influences of canopies that are known. Within urban hydrology, trees play a major role in controlling the inputs and outputs of water through interception and uptake of precipitation, and evapotranspiration (Berland et al., 2017). Within urban environments, it has been shown that tree canopies are extremely efficient at reducing stormwater runoff. In a study conducted in Wisconsin, USA, it was found that the removal of 29 green ash and two Norway maple street trees within an urban environment increased stormwater runoff by 198 m^3 in a medium sized residential catchment (Selbig et al., 2022). This is extremely valuable in high impervious surface coverage environments to mitigate flooding due to the lack of opportunity for runoff to infiltrate into soils. In addition, there is evidence that tree canopies can change the chemical characteristics of precipitation which serve as a nutrient pathway from canopies to forest soils (Robertson et al., 2000), however, this process is less understood in urban environments. Many urban foresters and stormwater practitioners have questions regarding the stormwater reduction potential and nutrient fluxes due to urban canopies which has been a driver for much of the urban forest research conducted in the past decade. It is evident that there is a relationship between canopies and urban hydrology, however, quantification of this relationship is necessary for efficient planning and best management practices within dense urban environments.

One way we can quantify this relationship by analyzing throughfall, or the precipitation that passes through a canopy. The amount and chemical composition of throughfall differs from precipitation. Throughfall is often saturated with pollutants that were previously on or attached to the surface of the canopy then subsequently washed off by precipitation. This chemically enriched throughfall is a beneficial process in forested ecosystems by redistributing many of these nutrients to the soil under the drip line of the tree canopy (Van Stan et al., 2021), however, in urban environments, infiltration is less than in forested settings due to impervious surface coverage. In addition, urban environments are more susceptible to poor air quality, leading to increased pollutant trapping by the canopy, thus increased solute concentrations in throughfall compared to rural or forested environments (Weathers and Ponette-Gonzalez, 2011). It is important to understand tree canopy and throughfall processes in urban environments to fully gain all the benefits that urban canopies provide and to better support urban forest management.

2.1.2: Throughfall Chemistry Background

There is limited research regarding throughfall chemistry in urban environments. While research has been conducted on forested throughfall as far back as the 1960's (Voigt, 1959), to my knowledge, urban throughfall collections only began in 2000 (Lovett et al., 2000). Throughfall in urban environments are expected to have elevated concentrations of nutrients due to increased human activity. Atmospheric deposition of inorganic nitrogen (N) has been found to be greater in urban environments due to emissions from roadways (Decina et al., 2017; Fang et al., 2011; Rao et al., 2014; Templer & McCann, 2010) making street trees and urban forests a prime candidate for atmospheric deposition due to its high leaf surface area and surface roughness (Slinn, 1982). It has been found that N throughfall fluxes within urban environments can be 8 times greater than throughfall from forests with little exposure to urban sources of atmospheric deposition (Fenn and Bytnerowicz, 1993) which highlights the influence of the surrounding environment on throughfall chemistry. Responses to this increased level of atmospheric deposition can vary depending on the availability of N within the environment. For example, an environment where N is limited, canopies are more likely to hold much of the N deposited onto the canopy (Hall and Matson 2003; Lohse and Matson, 2005). Canopies have shown their ability to cycle N, specifically, NH_4^+ has been shown to be absorbed by the canopy to support growth and other canopy processes (Ponette-Gonzalez et al., 2010) but is dependent on the age of the tree and availability of N in the system (Hall and Matson, 2003; Lohse and Matson, 2005). These environmental differences that influence N in throughfall results in varying ranges of N concentrations in throughfall, making this area of research necessary to fully understand the influence of urban canopies on the urban hydrologic system.

Inputs of P from urban environments is understood to be a major cause of eutrophication in surface waters and is the leading cause of degradation within the United States (Schindler, 1977; EPA, 1990; Newman, 1995). There are a number of sources of P within urban environments including industrial activities, fertilizers, pesticides, and runoff over various surfaces mobilizing P into surface waters (Kleusner and Lee, 1974; Halverson et al., 1984; Newman, 1995; Waschbusch et al., 1999). Another contribution of P within the urban environment comes from throughfall. Like other nutrients found in throughfall, P is often deposited onto urban canopies via atmospheric deposition (Eisenreich et al., 1977; Hou et al., 2012). There is evidence that greater concentrations of P within stormwater runoff are found when percent street canopy is greater (Janke et al., 2017), supporting the idea that throughfall is likely a common pathway for P to enter surface runoff in urban environments. There is little research regarding P in urban throughfall although it is clear that urban canopies are likely a major non-point source of P within urban environments.

Much like N and P, organic carbon (C) has been found to be anthropogenically sourced, specifically from fossil fuel emissions (Huang et al., 2010; Santos et al., 2014; Siudek et al., 2015; Wang et al., 2016; Yan & Kim, 2012). In addition, organic C is also naturally sourced through shedding of dead leaves and decomposition of organic materials. A major input of carbon from throughfall include dissolved organic carbon (DOC) due to water washing and leaching carbon into throughfall (Ponette-González et al. 2020; Van Stan and Stubbins 2018; Van Stan et al., 2017). While there are several influencing factors that contribute to varying DOC concentrations such as precipitation amount and frequency, tree species, and canopy architecture (Levia et al., 2011), there are still questions regarding the seasonal changes of DOC and its sources, especially in urban environments. To understand the forms of carbon present in throughfall, we can analyze the dissolved organic matter (DOM) present in our sample, using excitation: emissions matrix spectra (EEMs). Previous characterization of tree-derived DOM using EEMs has shown that much of the DOM are extremely diverse and comes from various sources, processes, and degradation (Hernes et al., 2017; Inamdar et al., 2012; Levia et al., 2012; Stubbins et al., 2017; Van Stan et al., 2017). This method of DOM characterization has also been used to show that tree-derived DOM is a disinfectant byproduct precursor during drinking water treatment (Chen et al., 2019) making EEMs analysis of DOM an extremely beneficial tool for environmental research and improvement of anthropogenic processes. In addition, characterization of DOM is essential to understand the bioavailability, mobility, and degradability of the organic matter present in throughfall due to its direct transport to either soils in forested environments or its transition to stormwater runoff in urban environments that may ultimately enter nearby bodies of water (Kaushal and Lewis, 2005; Jaffe et al., 2008; Fellman et al., 2009, 2010; Inamdar et al., 2011).

Using absorbance and fluorescence indices, DOM can be characterized to determine cycling processes and sourcing. The Fluorescence Index (FI; McKnight et al., 2001) determines if the sample source is autochthonous (of microbial origin) or allochthonous (terrestrial) (Burns et al., 2016; Cory and Kaplan, 2012; Hood et al., 2003; Inamdar et al., 2011; McKnight et al., 2001; Miller and McKnight, 2010). The Freshness Index (BIX or β/α; Wilson and Xenopoulos, 2009) and Humification Index (HIX; Zsolnay et al., 1999) are used to determine the amount of decomposition the organic material has undergone (Cannavo et al., 2004; Gao et al., 2017; Su et al., 2021; Zsolnay et al., 1999; Rose et al., 2023). The specific UV absorbance at 254 nm ($SUVA_{254}$) defines the aromaticity of the sample (Coble et al., 2022; Fellman et al., 2009; Liu and Wang, 2021; Weishaar et al., 2003). The ratio of maximum absorbance at excitation wavelength of 275 nm and emission wavelength at 350 nm (T:C ratio) where T represents the tryptophan-like peak and C represents the fulvic-like peak (Coble, 1996; Baker, 2001). This index has been used to within rivers and other surface waters (Rose et al., 2023), but can provide insight for various sorts of hydrologic samples. While these are just a handful of the indices available for DOM optical properties, they provide extensive insight into the sourcing and degree of processing of the carbon present in our aquatic samples.

However, much of this work has been done in forested environments, leaving the role of urban canopies in DOM cycling less understood. Understanding this carbon cycling in an urban system better supports the paired management of urban hydrology and canopy cover and provides a more holistic approach to urban forest management.

2.1.3: Leaf Litter

Much like throughfall, leaf litter has been heavily studied in forested environments, but urban leaf litter is seldom studied in comparison. There are a variety of questions surrounding urban leaf litter such as its decomposition rates on impervious surfaces, nutrient fluxes to stormwater, differences between tree species, and the effect of street sweeping programs. Some research shows increased decomposition rates in urban environments likely due to increased temperatures (i.e urban heat island effect) and a greater number of earthworms found in urban environments (Pouyat et al., 1997; Pouyat and Carreiro, 2003). While others found slower decomposition rates in urban environments due to higher soil temperature (Pavao-Zuckerman and Coleman, 2005). However, on impervious surfaces it has been shown that leaf litter decomposes faster than forested environments, specifically leaf litter found in gutters decompose twice as fast than forested leaf litter (Hobbie et al., 2017). It is important to understand these rates of decomposition to better understand how these natural processes occur in heavily human-influenced urban environments.

2.1.4: Study Overview and Objectives

In this study, I analyze throughfall amounts, nutrient composition, and DOM optical properties from June 2022 to November 2022 from 5 urban park sites within St. Paul, MN. In addition, leaf litter samples were collected along the pathway to stormwater drains to determine changes in TOC contributions from leaf fallout. Each site has the presence of *Fraxinus* spp. (ash) that are scheduled to be removed according to the St. Paul Structured Ash Removal Program (SARP) in response to the spread of Emerald Ash Borer (EAB). By analyzing the nutrient composition of urban throughfall and other nutrient inputs from urban canopies, we can gain a better understanding of the role of individual trees in the larger urban hydrologic system. Within this study, I hope to visualize the nutrient changes of leaf litter within urban parks as it moves from below canopy to parking lots to storm sewers. By following the changes along this leaf litter pathway, we can better understand the effects of certain environments on leaching, decomposition, and quality of leaf material in urban environments.

The main objective of this study is to quantify nutrient contributions via urban throughfall and leaf litter and to report values for various optical property indices using EEMs. I monitored throughfall nutrient trends over one season and examine differences across an urban environment using the same tree species. In addition, I aim to monitor individual trees to compare species at the site level and monitor differences in tree placement and its influence on changing the characteristics in throughfall. Leaf litter is also analyzed from various sampling locations within our sample sites to determine changes in leaf litter nutrient composition along the pathway towards storm drains where urban leaf litter is often accumulated.

2.2.0 METHODS

2.2.1 Study Sites

With the spread of Emerald Ash Borer (EAB) throughout the Midwest, many municipalities are taking action to prevent the further destruction of ecosystems. Within the Minneapolis - St. Paul area of Minnesota, commonly referred to as the Twin Cities, municipalities have varying approaches to the management of EAB. Minneapolis conducted a clearcut method where all *Fraxinus sp.* (ash) trees are removed simultaneously. While this is effective at quickly removing the pathways for EAB to spread, Minneapolis residents rapidly lose canopy cover and its benefits. St. Paul took a different approach with the Structured Ash Removal Program (SARP) and is treating the ash trees until removal within 2-3 years. This program provides an opportunity for a natural experiment to collect hydrologic data before and after the canopies are removed to determine the influence of canopy cover on urban hydrologic systems.

St. Paul is located in Southeast Minnesota, within the Upper Mississippi River Basin and has a population of approximately 307,000 residents (U.S Census Beureau, 2022). Winter months range from November through March with an average temperature below 36 degrees F, where summer months range from May to September with an average temperature of 70 degrees F (MN DNR). The average annual precipitation in this area is 32 inches where in winter months it is accumulated as snow (MN DNR).

To determine the influence of an urban area on the nutrient composition of throughfall, four urban parks, Highland Park (HP), Dayton's Bluff (DB), Linwood Recreation Center (LW), and Orchard Park (OR), located within St. Paul, MN (Figure 1) were selected for sampling. Parks were selected based on its proximity to roadways, large infrastructure, and dense residential neighborhoods to best represent a typical urban environment. In addition, parks were required to have the presence of *Fraxinus sp.*(ash) that has been scheduled to be removed by the St. Paul Structured Ash Removal Program. This program, in response to the spread of Emerald Ash Borer (EAB), is designed to remove public ash trees throughout St. Paul over 3 years to maintain canopy cover while planting plans are being implemented. These ash trees are also treated to support tree health and public safety until their scheduled removal. Some ash trees that were initially planned to be sampled were removed from the project due to poor health and limited canopy cover. At each site, I sampled throughfall under approximately 4-5 ash trees. An additional species was sampled at two of the four park sites – maple (*Acer platanoides*) at HP and honey locust (*Gleditsia triacanthos*) at DB (Fig. 1).

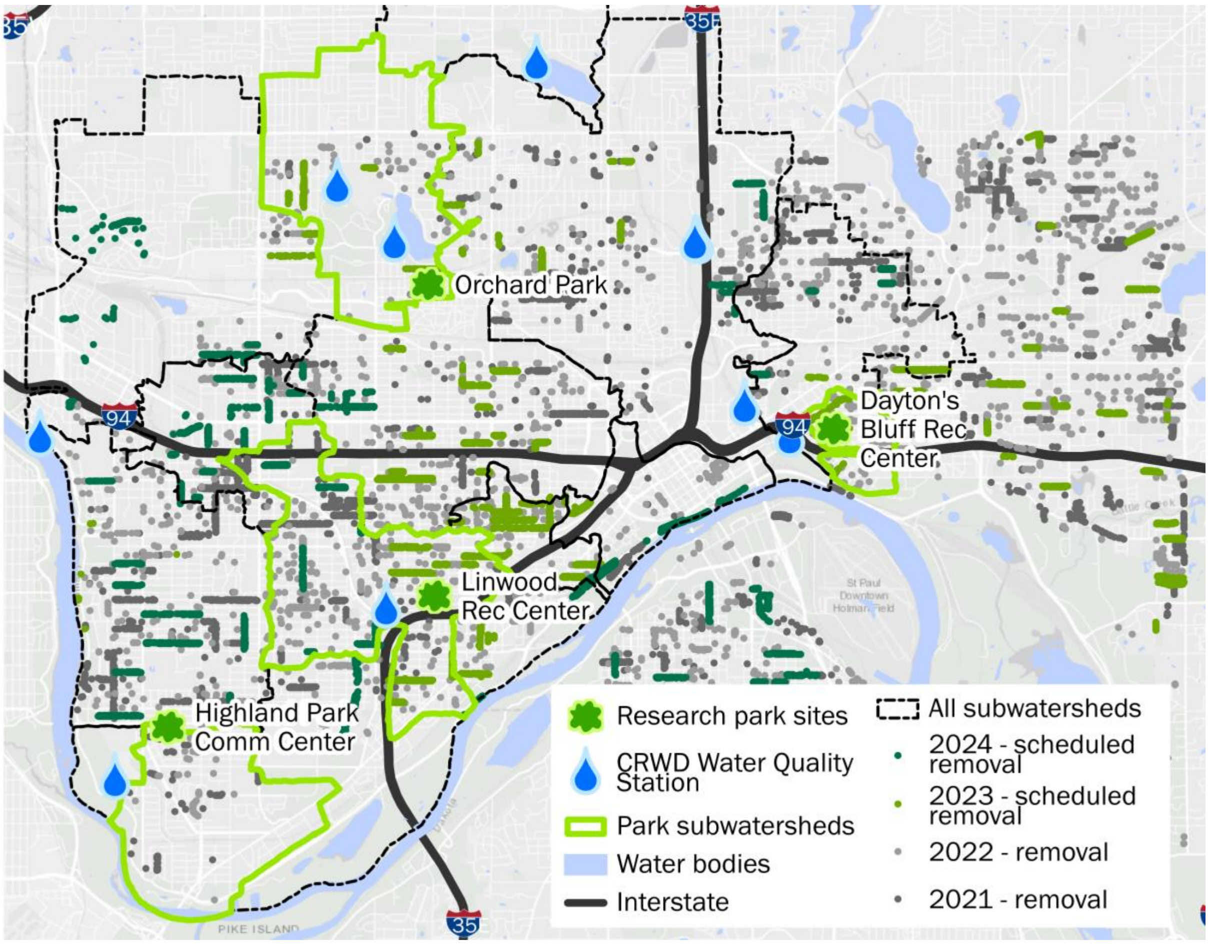

Figure 1: Locations of selected park sites within St. Paul, MN. Points on the map represent ash trees that are scheduled to be removed and park subwatersheds are outlined in green. Rain drop symbol represents municipal water quality monitoring stations.

2.2.2 Throughfall

Throughfall samples were collected from June to November of 2022 and analyzed for nitrate/nitrite, phosphorus, ammonium, total organic carbon (TOC) in mg/L, and the various forms of OM present were analyzed using Excitation Emission Matrixes (EEMs). Samples were collected using 79 cm long and a 7.62 cm diameter PVC pipe elevated approximately 35 cm above the ground and tilted downwards to promote flow (Figure 2). Collectors were placed directly below the canopy approximately 30 cm from the trunk. Samples were then funneled into a 1-2L plastic collection bottle that was changed weekly. To collect throughfall volumes below the canopy, HoboWare and RainWise tipping bucket rain gauges were placed below one tree at each site. To compare precipitation volumes to throughfall volumes, open precipitation data was collected using the WeatherUnderground data source where precipitation measurements are taken at the St. Paul Airport. For additional environmental site information, soil moisture, and air temperature sensors were also placed below the canopy.

Throughfall samples were first filtered through a 0.45-micron syringe filter and refrigerated until analysis. Soluble reactive phosphorus (here on referred to as P) concentrations were measured colorimetrically with a Thermo Scientific Genesys 150 UV-Vis spectrophotometer at 650 nm using a 1 cm quartz cell (U.S. EPA, 1978). Samples were then sent to the University of Minnesota's Research and Analytical Laboratory (RAL) to be analyzed for ammonium, nitrate, nitrite, and dissolved organic carbon. Analysis for ammonium utilizes colorimetric analysis by the salicylate/nitroprusside method on a Lachat 8500 FIA at 660 nm (RFA Methodology, 1989). Nitrate and nitrite analysis were performed using colorimetric analysis by the cadmium reduction method on a Lachat 8500 FIA at 520 nm (Henriksen and Selmer-Olsen, 1970; RFA Methodology, 2007). To measure total organic carbon, inorganic carbon was first removed by sparging with N2 gas before being measured on a Phoenix-Dohrmann 800 Tic/Toc Analyzer (RFA Methodology, n.d).

Measurements of absorbance and fluorescence spectra of dissolved organic matter were conducted with a Horiba Aqualog fluorescence spectrophotometer. For each sample, excitation-emission matrices (EEMs) were measured using a 1-cm quartz cell and included a reference sample of ultrapure water (18 MΩ cm1 at 25 ◦C) in each run. Corrections for the inner filter effects and normalization by the Raman scattering area at an excitation wavelength of 350 nm. After corrections, the sample EEMs data were used to calculate DOM indices common to environmental water samples, including the Fluorescence Index (FI;McKnight et al., 2001), Humification Index (HIX;Zsolnay et al., 1999), Freshness Index (BIX or β/α; Wilson and Xenopoulos, 2009), and Fluorescence Peak Ratio (T:C; Coble, 1996). Detailed descriptions of indices and their calculations are included in Table 1.

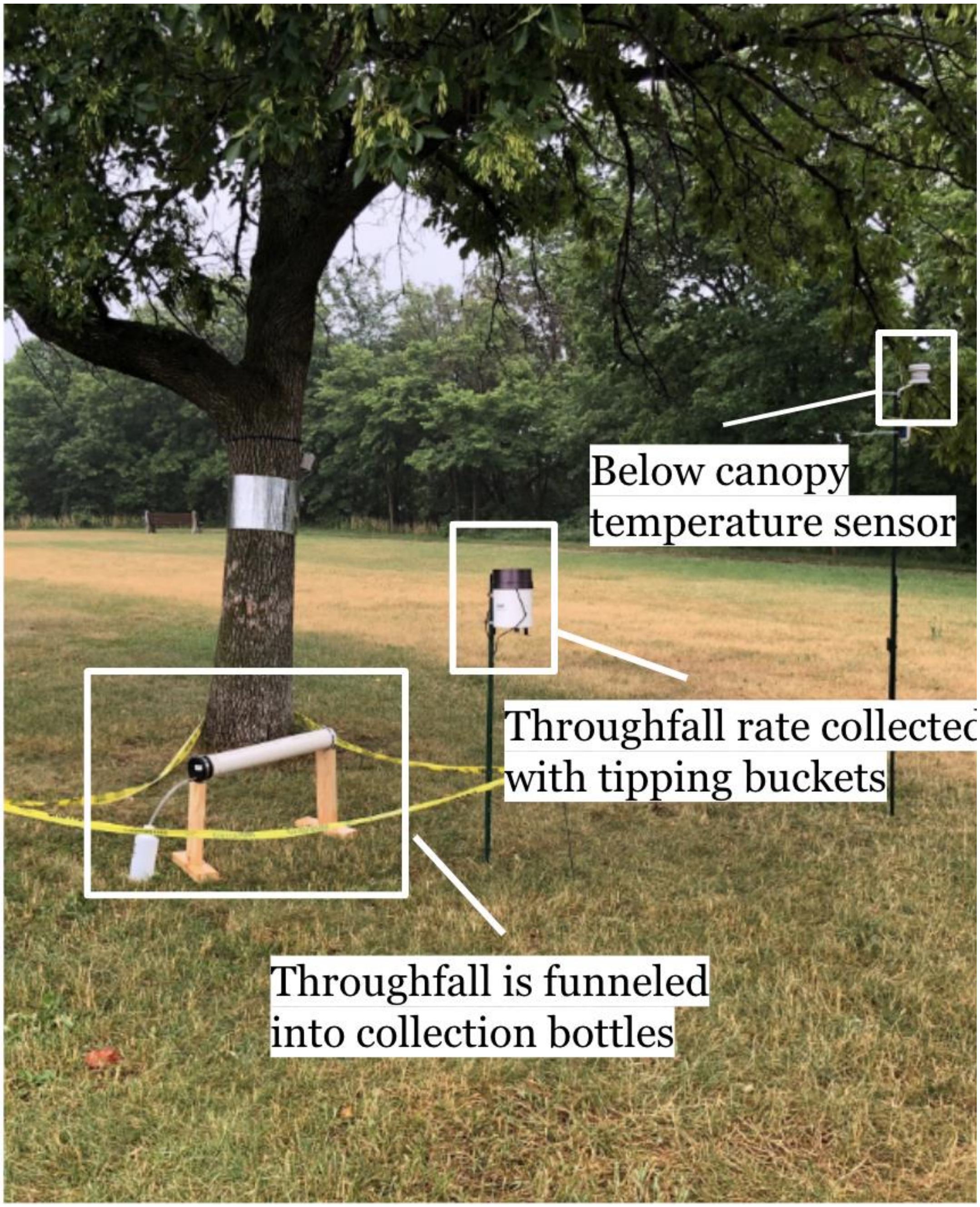

Figure 2: Example of instrumentation from LW site to display general layout of instruments at each study site. One rain gauge and temperature sensor were included at each site below the ash trees with the exception of HP where an additional throughfall tipping bucket was added for the maple tree cluster.

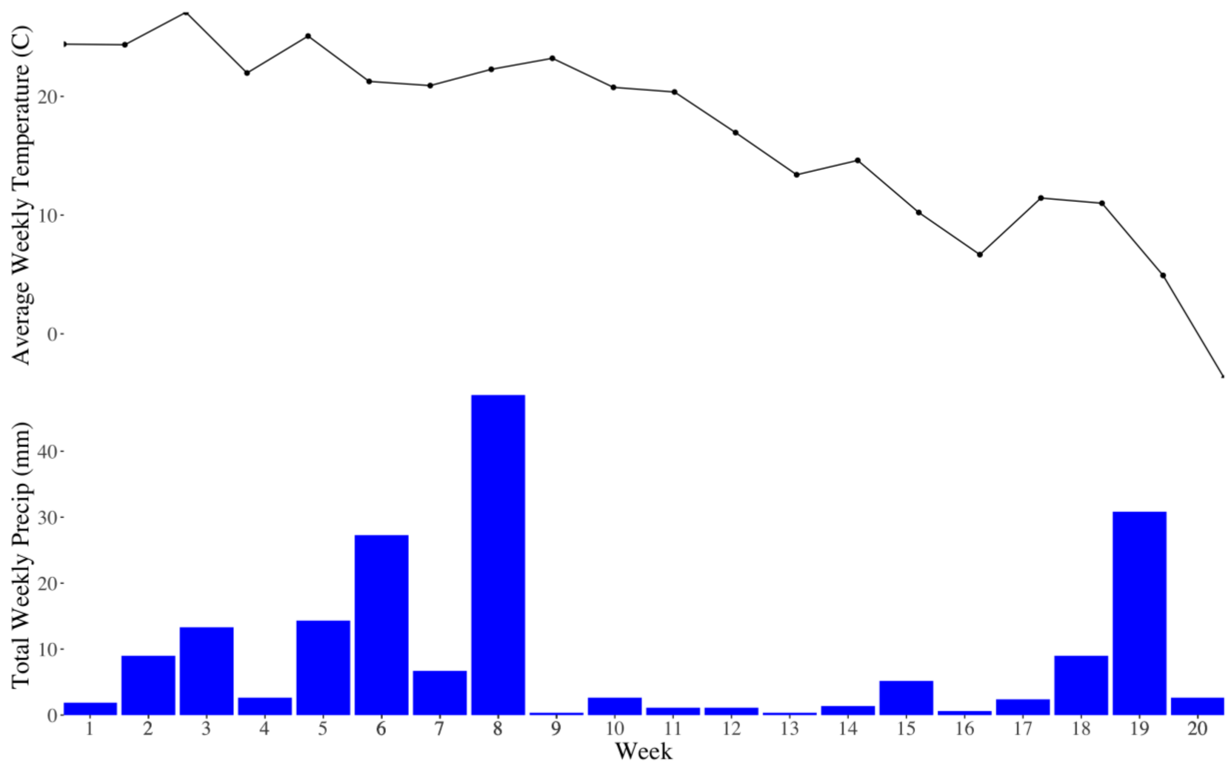

Figure 3: Total weekly precipitation volumes in millimeters and average weekly temperature in Celsius for the 2022 growing season from publicly available data from Weather Underground historical data taken at the St. Paul Airport.

Table 1: Description and calculations for indices of DOM optical properties included in this study.

Index	Calculation	Description	Reference
FI (Fluorescence Index)	470 nm emission intensity / 520 nm emission intensity at an excitation wavelength of 370 nm	Indicates potential sourcing of organic material. Values greater than 1.7 indicate microbial sources (directly from the canopy) while values less than 1.4 indicate allochthonous sources of OM	McKnight et al., 2001
BIX (Freshness Index)	380 nm emission intensity / 420 to 435 nm max emission intensity at an excitation wavelength of 310 nm	Indicates proportion of freshly derived DOM to DOM that has had opportunity to decompose. Higher values indicate more recently derived DOM.	Wilson and Xenopoulos, 2009
HIX (Humification Index)	435 nm and 480 nm fluorescence intensity / 300 nm 345 nm at an excitation wavelength of 254 nm	Indicates degree of humification of DOM where higher values are associated with more humic DOM.	Zsolnay et al., 1999
T:C Ratio	Peak T (ex275/em304) / Peak C (ex340/em440)	Ratio of fresh (tryptophan-like) to recalcitrant (humic-like) DOM. Higher values indicate more tryptophan-like DOM and lower values indicate more humic-like.	Coble, 1996 ; Baker et al., 2008

2.2.3 Leaf Litter

To analyze the nutrient inputs to stormwater systems from leaf litter fall, leaf litter samples were also collected at the end of the growing season (October - November). Leaf litter from various sources including leaves that were freshly fallen from the canopy, piled in parking lots, and built up on storm drains. Samples were subsequently dried at 60 degrees C and ground in a Thomas Scientific Laboratory Mill before analysis. Dried and ground leaf litter was sent to the University of Minnesota's Research and Analytical Laboratory for analysis of total nitrogen and total carbon using the dry combustion method on an Elementar varioMAX cube following standard methods (Simone et al., 1994; Matejovic, 1995).

2.2.4 Data Analysis

Throughfall concentration and flux data were analyzed and plotted using R Statistical Software. Standard deviation and means were calculated using standard R functions. All data was tested for normality assumptions using the Shapiro-Wilk test and Kruskal Wallis test followed by a one-way ANOVA and Tukey's HSD test when assumptions are met. The level of significance for all statistical tests were $p < 0.05$. Relationships between concentration and precipitation volumes were analyzed using linear regression.

To better understand the inputs to an area of land from urban canopies, concentrations of analytes are converted to flux values. Flux was calculated using (Eqn. 1).

$$Flux = (Cs * Vtf)/Ac \qquad \text{(Eqn. 1)}$$

Where Cs is the concentration of the analyte from lab analysis, V_{tf} is the measured volume of throughfall for a given event using a combination of tipping buckets and volumetric rain gauges, and A_c is the area of the opening of the collector.

2.3.0: RESULTS

Throughout the 5-month sampling period, ~100 throughfall samples were collected across all sites and species. It was expected to have a greater number of samples, but many samples were lost due to contamination (i.e. pet waste) or vandalism. Vandalism of throughfall collectors was apparent across all study sites, however, Dayton's Bluff experienced consistent vandalism and collection at this site was ultimately suspended after week 10. After contaminated samples were excluded, 91 throughfall samples were included for analysis. 28 samples were included from site OR, 23 from LW, 20 from HP, and 19 at DB. Vandalism or manipulation of tipping buckets was also observed resulting in loss of some throughfall rate data. Data was then supplemented with garden style rain gauges attached to throughfall collectors or by data recorded by tipping buckets from the nearest site (Figure 1).

Average weekly total precipitation rates excluding weeks with no rainfall is 22.86 millimeters (Figure 4). It is important to note that the sampling period occurred during a drought in the area resulting in 9 weeks without precipitation events or where any precipitation was so small (22.86 mm in total) and did not generate throughfall (weeks 10-18, Sept 5 - Nov 6). During pre-drought conditions (weeks 1-9, July 7 - Sept 4) 123.19 mm of precipitation occurred and during post-drought conditions (weeks 19 – 20, Nov 7 – Nov 20) 33.27 mm of precipitation occurred.

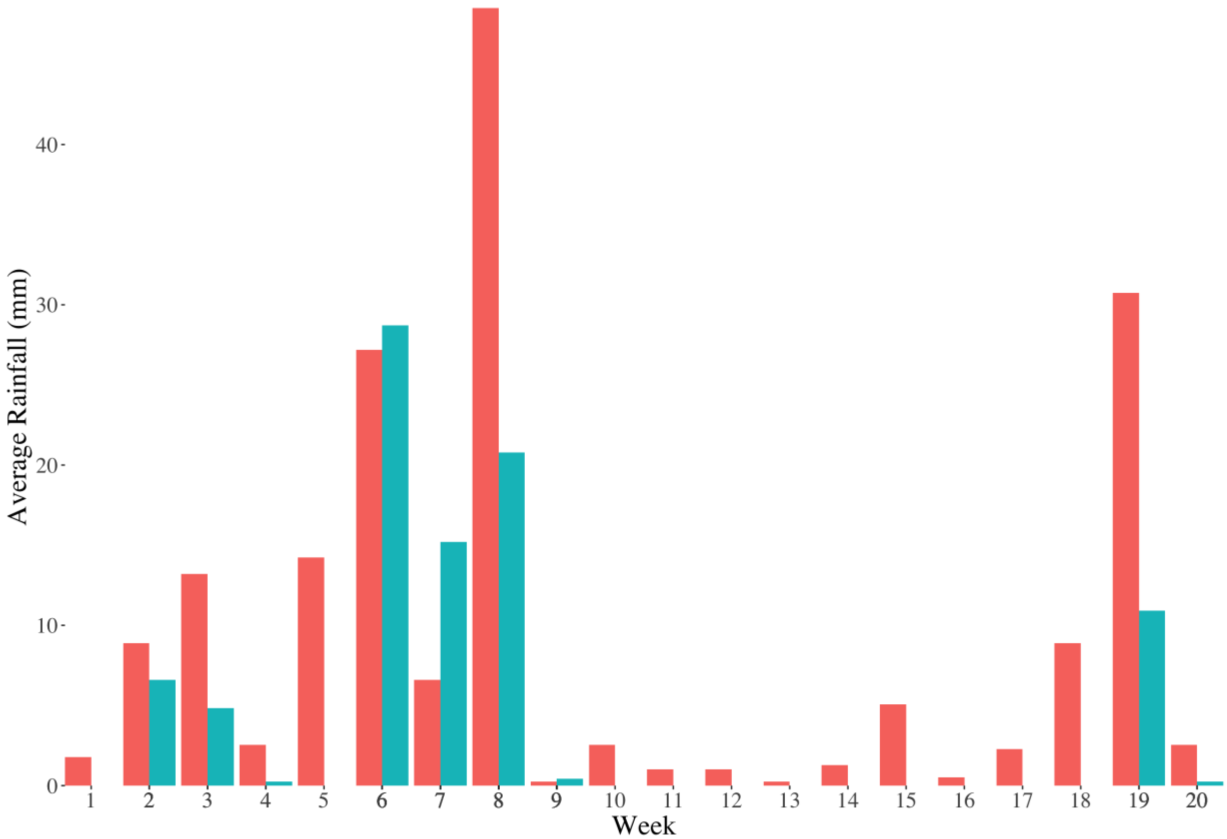

Figure 4: Average precipitation (red) and throughfall (green) rates across all sites and species. Open precipitation values are taken from the St. Paul Airport. Throughfall values are average weekly throughfall volumes using a combination of tipping buckets and volumetric rain gauges.

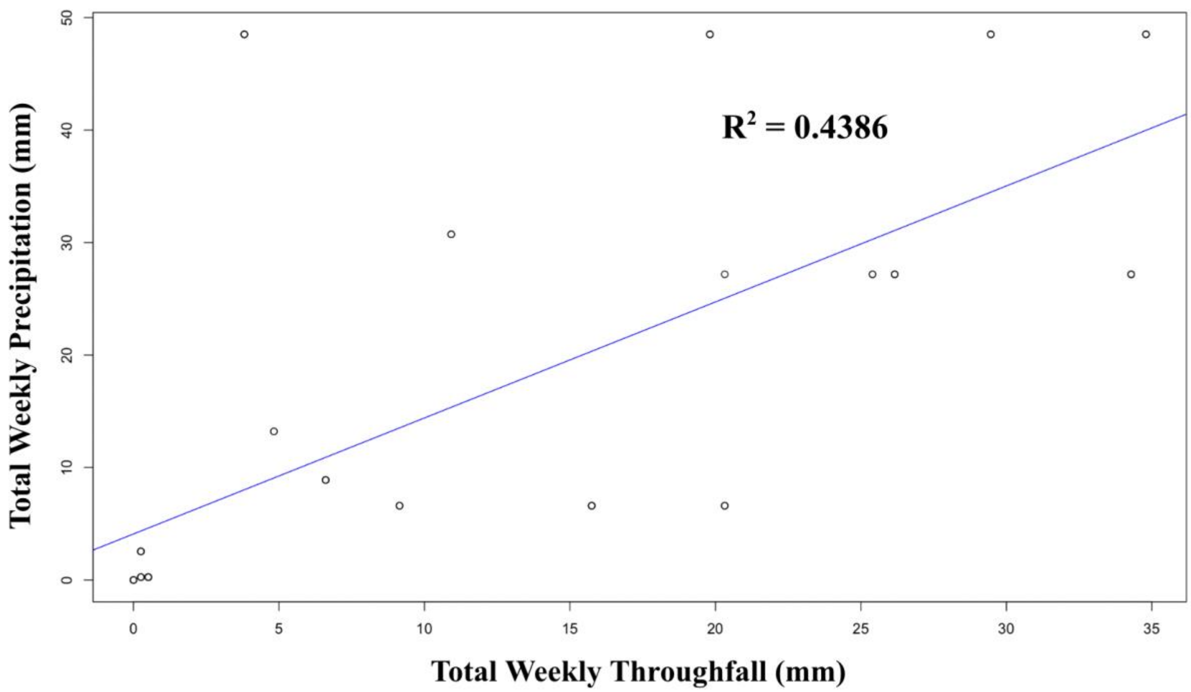

Figure 5: Linear regression of total weekly throughfall and total weekly precipitation (mm).

Throughout most of the study period, weekly open precipitation values exceed weekly throughfall volumes (Figure 4, 5). Average throughfall volumes throughout the study period excluding weeks where no throughfall was generated is 11.4 mm, which is about half of the average precipitation reported in this study period. There are weeks present where throughfall volumes exceed open precipitation volumes, but this is attributed to drip from the previous precipitation event carrying over into the next week. Weeks where precipitation is below 5 mm did not generate any throughfall (Figure 4).

2.3.1: Throughfall Nutrient Concentrations

Throughfall samples were collected for 8 rain events across all 4 study sites and analyzed for nitrate/nitrite, phosphorus, total organic carbon, and ammonium concentration (Table 2). Our results indicate that throughfall concentration does not significantly differ among measured nutrient species across sites and/or species (Figure 7, 8). No differences between sites were found for N, NH_4, or P, however significant differences were found for TOC between Dayton-Linwood ($p<0.05$) and Dayton-Orchard ($p<0.01$) (Figure 7). There were also no differences found between species at the sites where species could be compared (DB and HP) across all analytes included in this study (Figure 7). Relationships between analytes were also investigated, however, there were no consistent relationships to establish any influence from the concentration of one analyte to another. All analytes reported concentrations within range of previous research (Table 3, Figure 6).

TOC was the only analyte found to have a significant difference between pre-drought (July 7 – Sept 4) and post-drought (Nov 7 – Nov 20) conditions ($p = 0.00012$) where in weeks 19 and 20, mean concentrations are greater than mean concentrations from weeks 1-9. It is also noted that for ash only species, week 2 was found to be significantly different from weeks 7, 8, and 9 ($p = 0.009$) across all sites.

Phosphorus concentrations were the most variable over time of the analytes included in this study. Concentrations range from <0.01 to 1.2 mg/L with an average of 0.403 mg/L across all sites and species. This consistent variability throughout the sampling period resulted in no significant differences between weeks, sites, or species. Linear regression shows a weak negative relationship between weekly precipitation volumes and phosphorus concentrations ($R^2 = 0.06832$) however, with a low number of points, it cannot be concluded that phosphorus concentrations are influenced by precipitation volumes.

Ammonium concentrations remained within the same range (0.01 – 2mg/L) for most of the study period. There is some variation in the early season and after large rain events where ammonium values reach up to 4 mg/L, however, the variability is much lower than other analytes. Relationships between ammonium and temperature were investigated due to its correlation with microbial activity, however, no significant relationships were found.

Linear regression analysis of nitrate/nitrite concentrations prior to drought events show a correlation between time and concentration where concentrations of nitrate/nitrite decrease over the growing season ($R^2 = 0.6507$, Figure 10). These results indicate that factors such as site or species are less influential on nitrate/nitrite concentrations when compared to its relationship with time/seasonality.

Table 2: Average concentration (mg/L) and standard deviations for each analyte grouped by sites and species

Site	Species	P	P SD	NH_4^+	NH_4^+ SD	*N*	N SD	TOC	TOC SD
Orchard	Ash	0.63	0.42	0.60	0.78	1.13	0.99	28.34	25.63
Linwood	Ash	0.35	0.28	0.80	0.74	1.29	1.00	19.07	10.36
Highland	Ash	0.33	0.29	0.41	0.37	1.05	0.59	17.30	11.61
Highland	Maple	0.38	0.25	0.77	0.65	1.17	0.64	11.48	6.73
Dayton	Ash	0.21	0.18	0.55	0.28	0.88	0.59	8.68	2.60
Dayton	Honey Locust	0.18	0.10	0.56	0.29	0.86	0.62	11.62	7.53

Table 3: Average concentrations (mg/L) of throughfall and stormwater runoff from various sampling locations.

Analyte	Concentration (mg/L)	Standard Deviation	Sample Type	Sampling Location	Season	References
NO^-_2 / NO^-_3	1.12	0.85	throughfall	urban	growing season	Breeden, 2023
TOC	17.63	12.90	throughfall	urban	growing season	Breeden, 2023
NH^+_4	0.66	0.65	throughfall	urban	growing season	Breeden, 2023
SRP	0.40	0.24	throughfall	urban	growing season	Breeden, 2023
NO^-_3	2.47	0.71	throughfall	urban, upstream	summer	Mgelwa et al., 2022
	1.38	0.05	throughfall	urban, midstream	summer	Mgelwa et al., 2022
	0.50	0.14	throughfall	urban, downstream	summer	Mgelwa et al., 2022
NH^+_4	0.94	0.54	throughfall	urban, upstream	summer	Mgelwa et al., 2022
	1.12	0.11	throughfall	urban, midstream	summer	Mgelwa et al., 2022
	0.50	0.06	throughfall	urban, downstream	summer	Mgelwa et al., 2022
NO^-_3	0.39	0.58	stormwater runoff	urban	summer	Lusk et al., 2020
NH^+_4	0.20	0.20	stormwater runoff	urban	summer	Lusk et al., 2020
TP	0.21		throughfall	mixed forest stand		Neal et al., 2003
TP	0.45	0.03	throughfall	residential		Walsh, 2010
SRP	0.34	0.03	throughfall	residential		Walsh, 2010
DOC	10.00	8.10	throughfall	mixed forest stand		Ryan et al., 2022
DOC	20.00	13.00	throughfall	bare cedar forest stand		Van Stan et al., 2017
DOC	17.00	13.00	throughfall	oak stand		Van Stan et al., 2017
TP	0.32	0.09	stormwater runoff	urban	growing season	Janke et al., 2017
TN	2.36	0.37	stormwater runoff	urban	growing season	Janke et al., 2017
NH^+_4	0.26	0.18	stormwater runoff	urban	growing season	Janke et al., 2017

Figure 6: Average concentrations (mg/L) from previous research where all studies are throughfall concentrations except for Janke et al., 2017 and Lusk et al., 2020 being urban stormwater runoff.

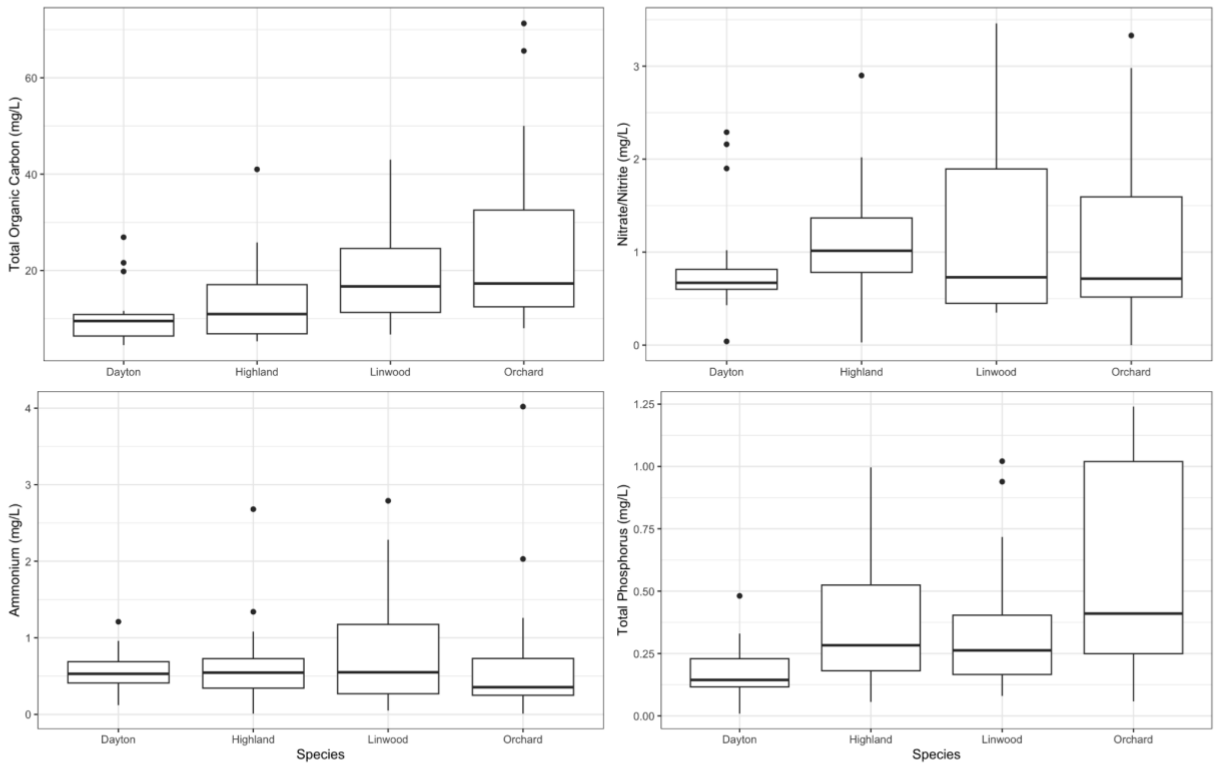

Figure 7: Boxplots of throughfall concentrations (mg/L) grouped by site. Data includes all species (sites DB and HP include two species) due to no significant differences between species.

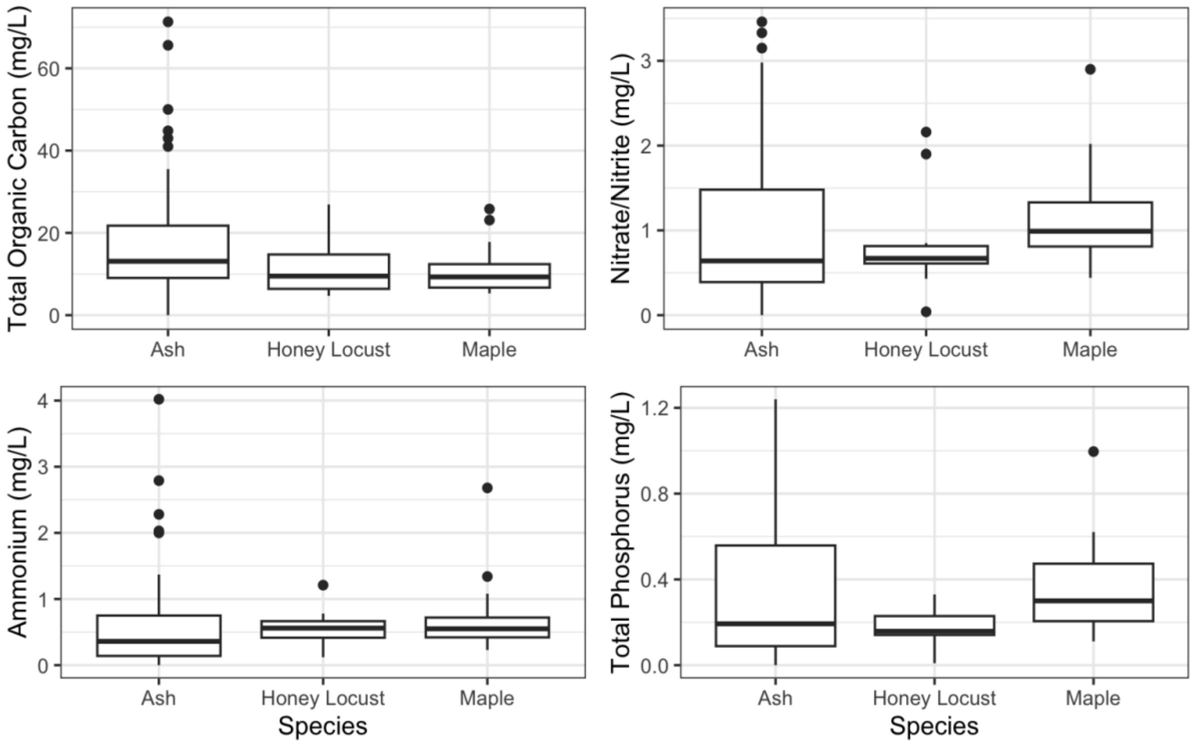

Figure 8: Boxplots of throughfall concentrations (mg/L) grouped by species. No significant differences were found between species.

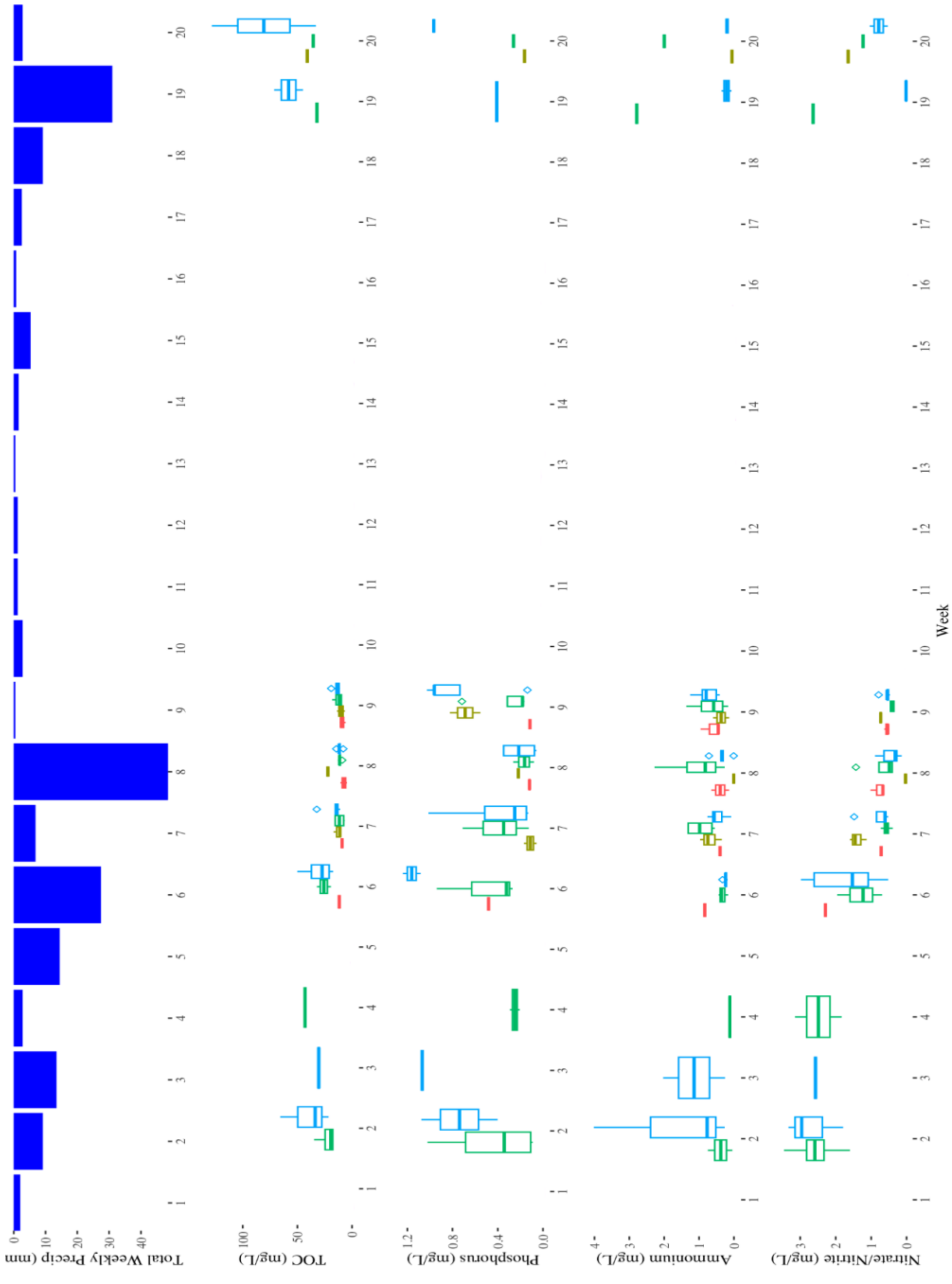

Figure 9: Boxplots of throughfall concentrations of TOC, N, NH4, and P in mg/L. Sites are distinguished by boxplot color where LW = green, HP = yellow, DB = red, OR = blue. Boxplots above represent the interquartile range of the dataset on a weekly basis. Week 1 begins on July 7th and week 20 ends on November 20th, 2022.

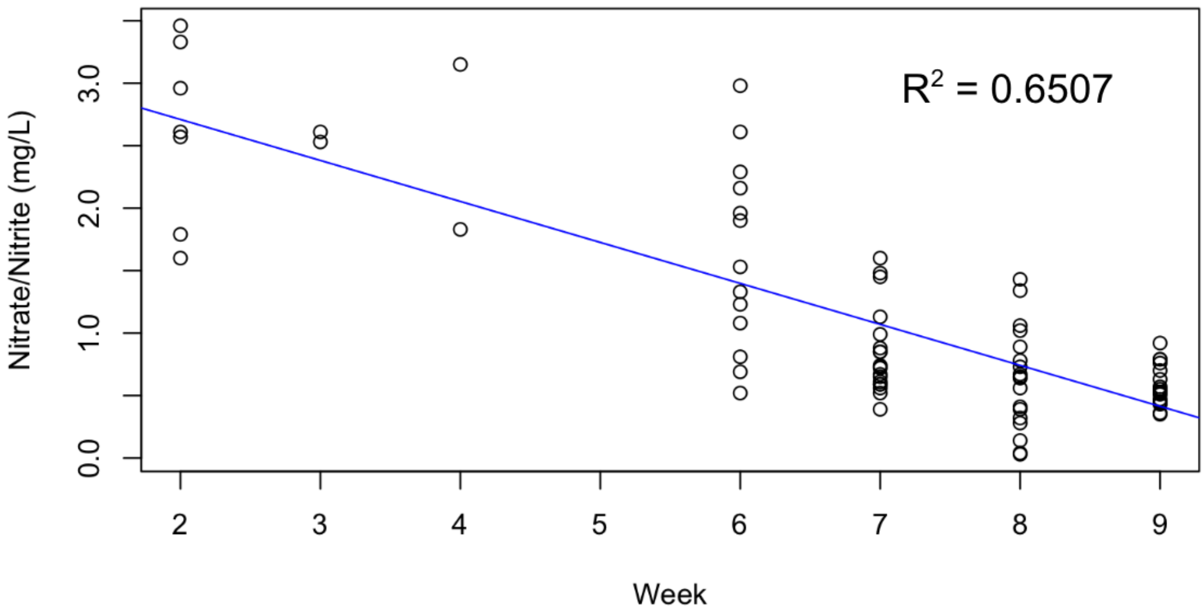

Figure 10: Linear regression of ash only nitrate/nitrite concentrations in throughfall across all sites. Data only consists of pre-drought concentrations to determine if seasonality was a potential pattern prior to lack of storm events.

2.3.2: Throughfall DOM Characteristics (EEMs)

All available throughfall samples were analyzed for DOM characteristics by Excitation Emission Matrices Some samples were not included due to limited volumes of throughfall, limiting the number of analyses available. Fluorescence-based characteristics of OM present in throughfall samples collected from our study sites did not vary across sites or species.

Average values for HIX, BIX, FI, and T:C across all sites and species were 0.689, 0.587, 1.368, and 0.628, respectively (See Table 4 for site and species mean). T:C had the greatest spread of all the indices ranging from 0.1985 to 3.6457. BIX and FI had similar ranges of 0.3826 to 1.6788 and 0.6571 to 2.1825, respectively, while HIX ranged from 0.2904 to 1.1778. No significant differences between sites or species were observed for any indices included in this study (Figure 12, 13).

Greater variability of all EEMs indices during weeks with greater volumes of open precipitation were also observed (Figure 12). Precipitation during week 8 (Aug 22 – Aug 28) reaches ~50mm while BIX, HIX, FI, and T:C show the widest range of values during week 9 (Aug 29 – Sept 4). This pattern is faintly observed in the post-drought samples. Week 19 showed greater volumes of precipitation and values of HIX, BIX, FI, and T:C are within a large range of values during week 20 (Nov 14 – Nov 20). Samples from Orchard (Figure 9, in blue) have a greater mean value for all indices when compared to samples from Highland and Linwood from the same week, however, it was not considered statistically significant ($p > 0.05$). It is also noted that indices BIX, HIX, and FI tend to reflect similar patterns and changes across time. For example, when BIX values increase or decrease, we tend to see a similar pattern in HIX and FI values.

Table 4: Average values of the Fluorescence Index (FI), Freshness Index (BIX), Humification Index (HIX), and T:C Ratio (T:C) and their standard deviation (unitless)

Site	Species	BIX	BIX (sd)	HIX	HIX (sd)	FI	FI (sd)	T:C	T:C (sd)
Orchard	Ash	0.65	0.14	0.78	0.08	1.64	0.13	0.66	0.23
Linwood	Ash	0.73	0.29	0.82	0.14	1.58	0.15	0.80	0.57
Highland	Ash	0.71	0.04	0.79	0.02	1.66	0.09	0.70	0.53
Highland	Maple	0.65	0.06	0.77	0.15	1.58	0.15	1.14	1.23
Dayton	Ash	0.65	0.07	0.79	0.04	1.44	0.34	0.63	0.26
Dayton	Honey Locust	0.67	0.12	0.82	0.11	1.62	0.21	0.92	0.55

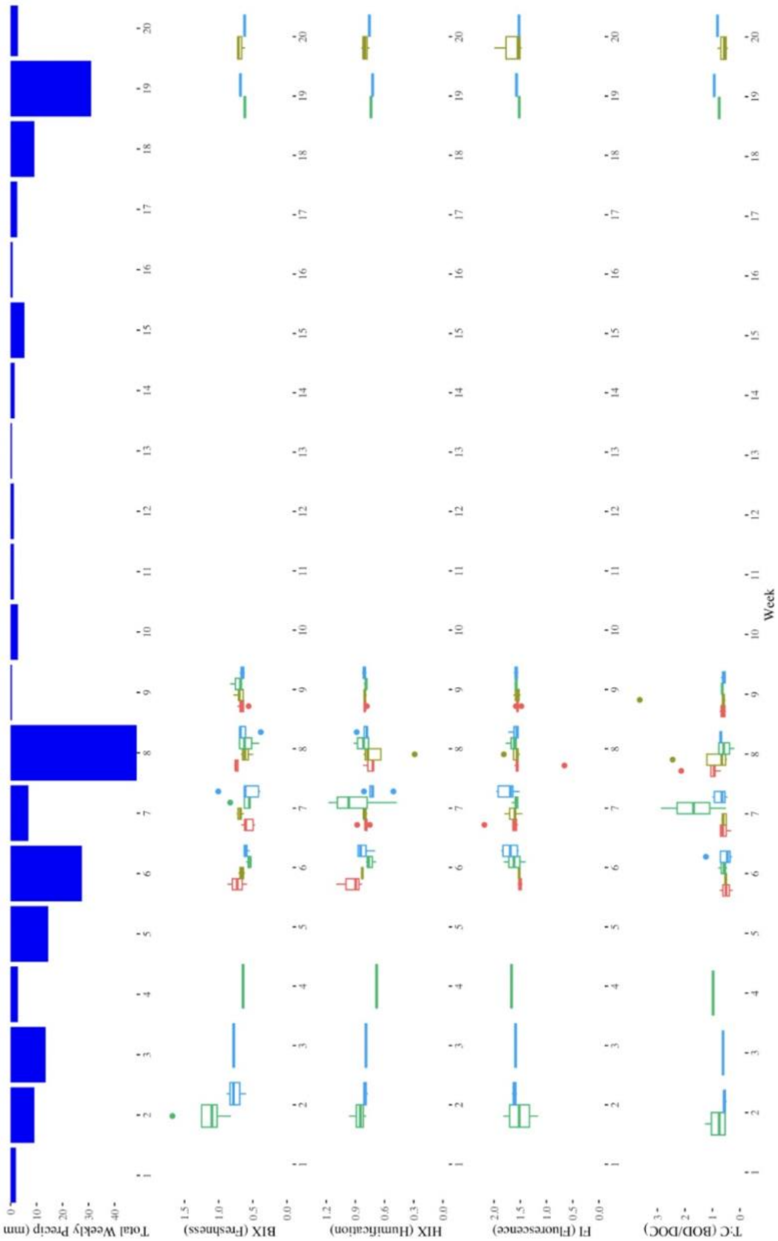

Figure 11: Boxplots of various DOC characterization indices BIX, HIX, FI, and T:C plotted against total weekly precipitation data in millimeters (barplot). Sites are distinguished by boxplot color where LW = green, HP = yellow, DB = red, OR = blue. Boxplots above represent the interquartile range of the dataset on a weekly basis. Week 1 begins on July 7th and week 20 ends on November 20th, 2022.

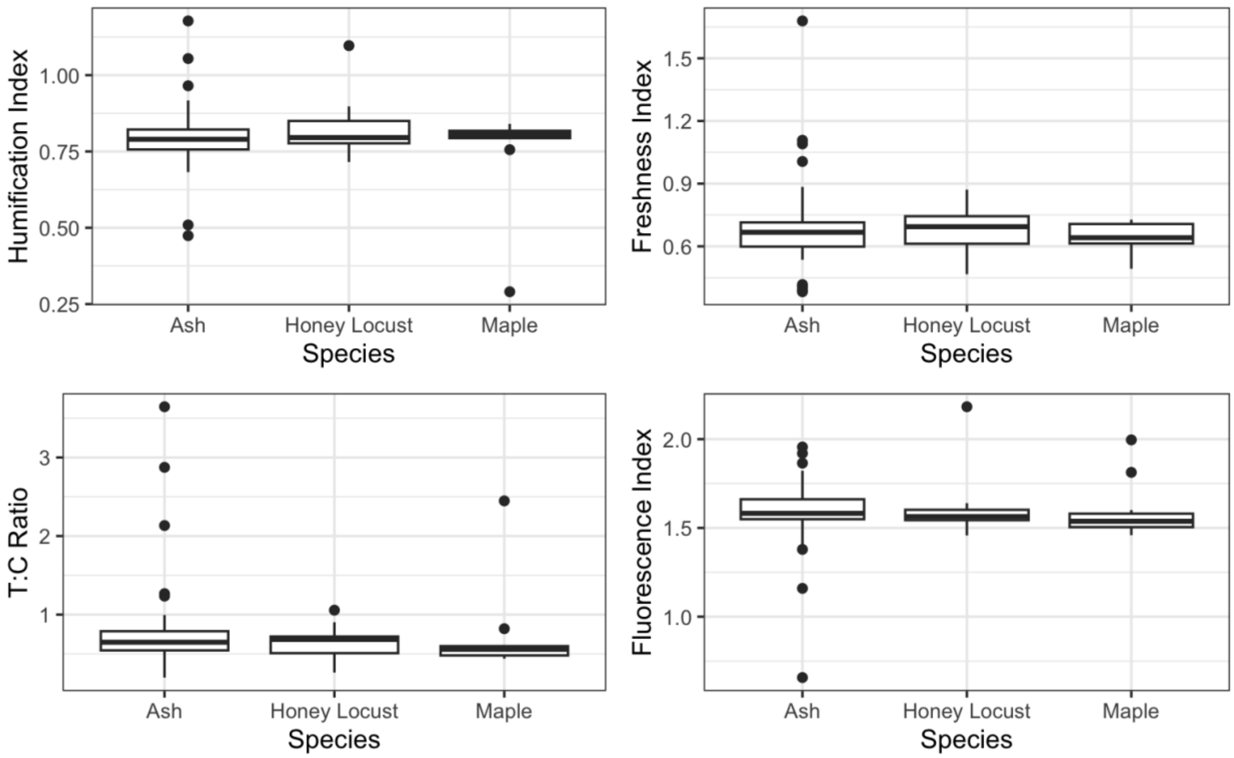

Figure 12: Boxplots of EEMs indices separated by tree species.

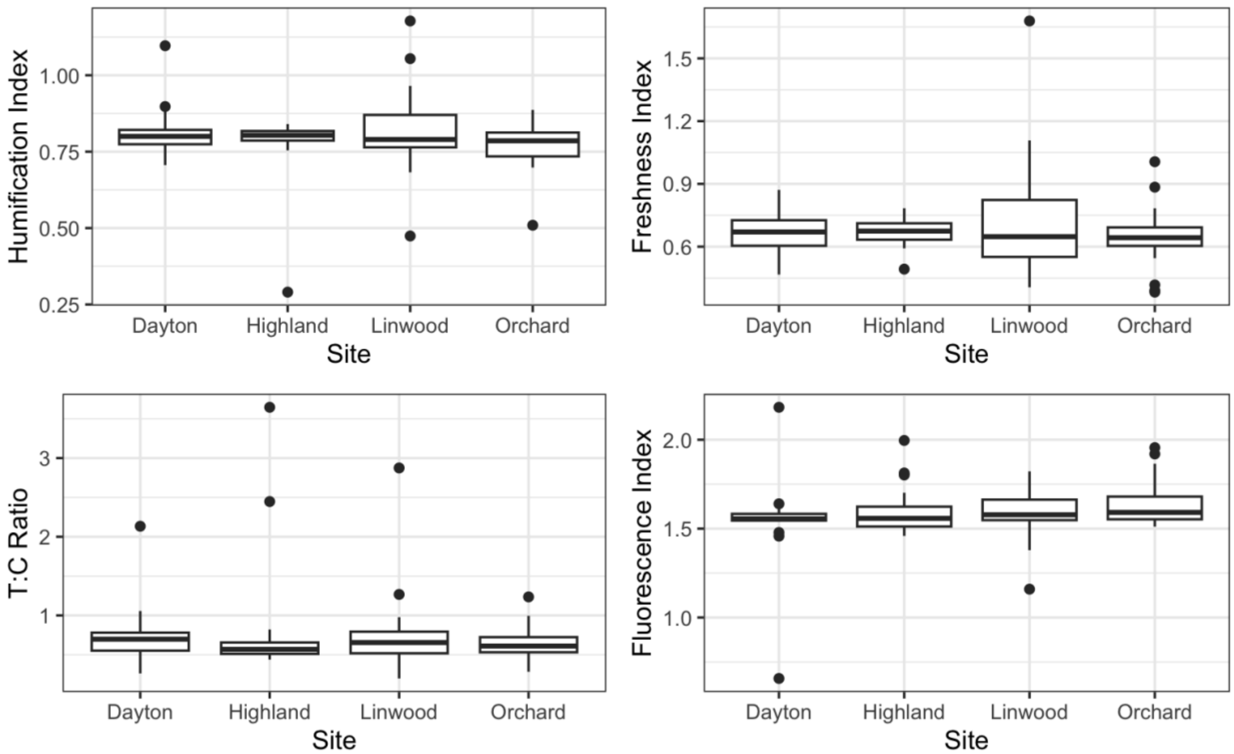

Figure 13: Boxplots of EEMs indices separated by study site.

2.3.3 Leaf Litter

From October to November 2022, 42 leaf litter samples were collected from beneath urban canopies, storm drains, parking lots, and along curbs on the street. Samples were collected beneath ash trees at all sites except HP due to the leaves already being cleared by the city. Average total carbon and nitrogen values across all sites, species, and sampling locations was 43.893 (SD = 5.04) and 0.897 (SD = 0.289) in percent, respectively. Average values separated by sampling location, tree species, and source are summarized in Table 5. Using a Kruskal-Wallis test and pairwise Wilcox test, I found no significant differences in TC and TN between sites, species, or sampling location ($p > 0.05$, Figure 14, 15).

Although no statistically significant differences were found between sites, tree species, or sampling locations, I observed overall trends in the leaf nutrient data for both TC and TN. I also observed that percent C is much lower in leaf litter collected from parking lots compared to leaves collected below canopies, however, there are a limited number of samples from parking lots with which to test the robustness of this comparison (Figure 16). In addition, LW had the greatest variability in leaf litter nutrient composition compared to other sites. In the early season, LW had two samples that were much higher in nitrogen percent than others and were collected beneath the canopy that did not lose its cover during the entirety of the sampling period (Figure 17).

Table 5: Average total Carbon and Nitrogen percent values by site, source, and species.

Site	Source	Species	Total N (%)	TN SD	Total C (%)	TC SD
Orchard	Storm Drain		0.94		45.64	
	Street		0.78	0.03	45.52	0.25
	Tree	Ash	0.89	0.04	46.11	0.64
Linwood	Storm Drain		0.77		43.40	
	Street		0.77		44.49	
	Tree	Ash	1.49	0.71	43.41	0.35
Highland	Parking Lot		0.89		43.52	
	Street		1.19	0.28	45.53	0.50
	Tree	Maple	0.88	0.11	43.92	2.76
Dayton	Street		0.80	0.24	41.52	6.82
	Parking Lot		0.54	0.04	24.50	3.55
	Tree	Ash	0.67	0.10	44.97	1.14
	Tree	Honey Locust	1.04	0.06	46.95	0.65

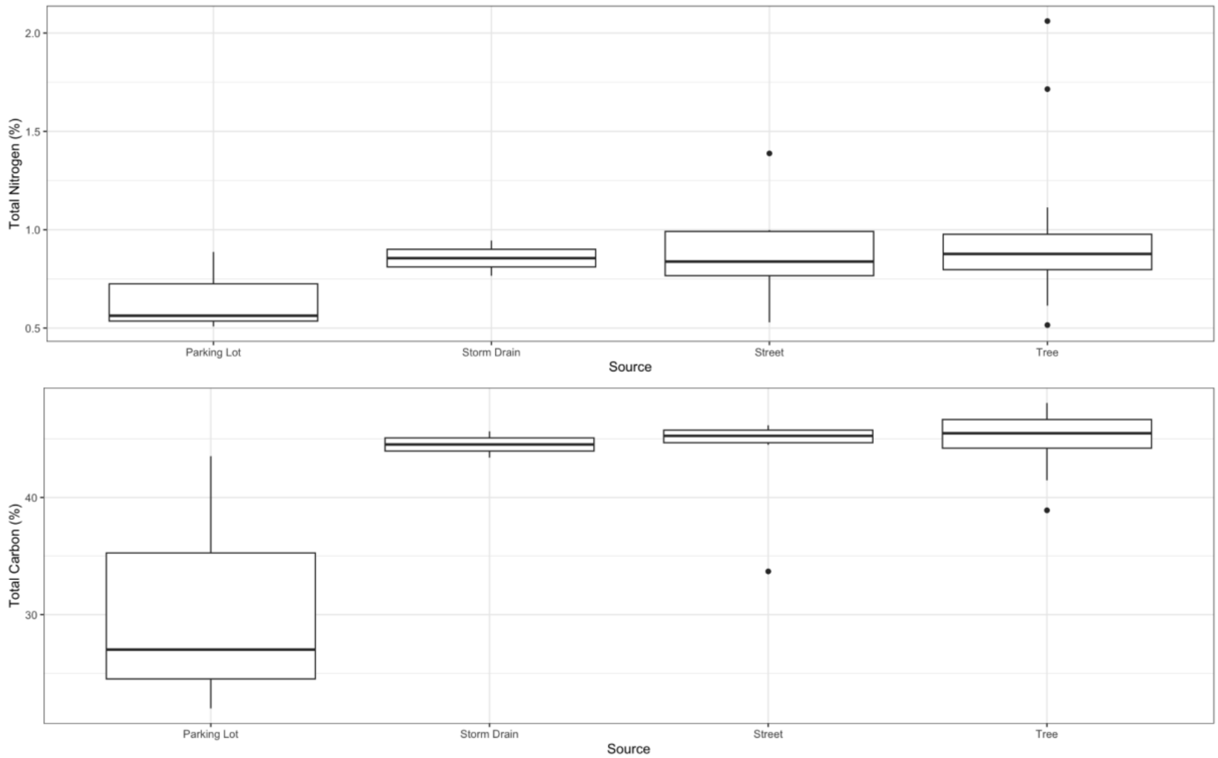

Figure 14: Boxplots comparing nutrient composition of leaf litter collected from parking lots (n = 3), storm drains (n = 2), streets (n = 8), and below canopies (n = 29).

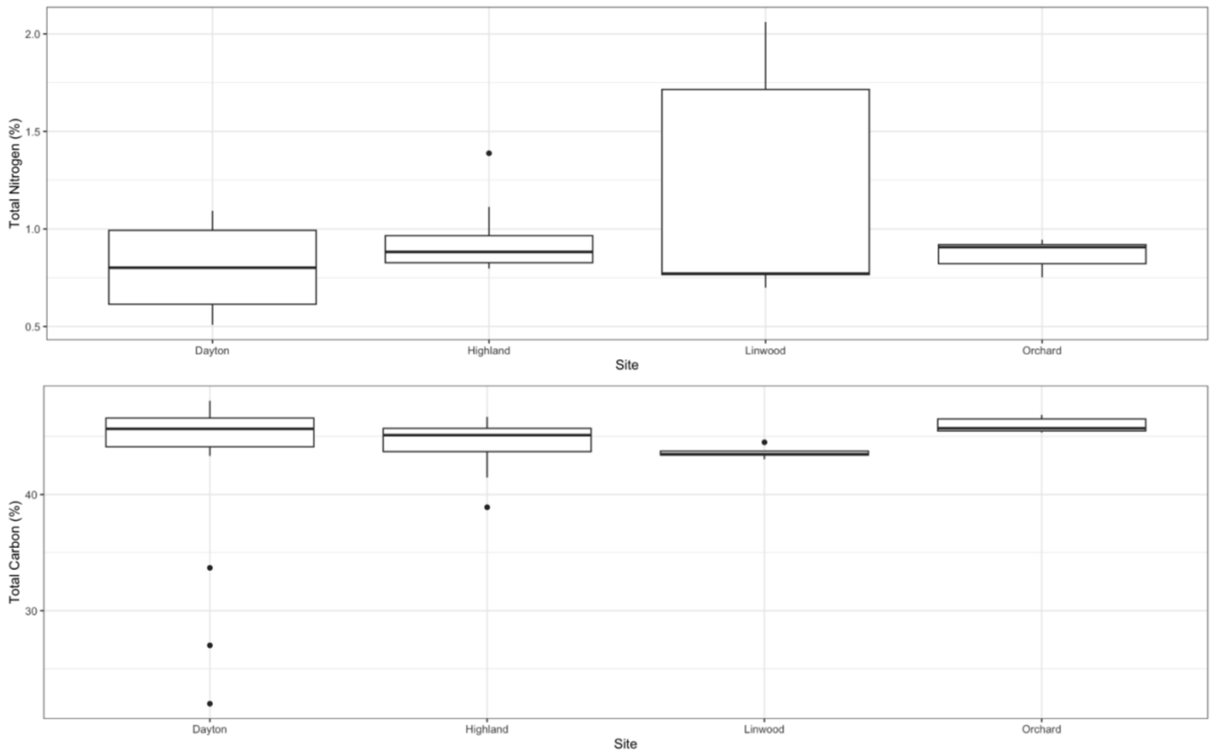

Figure 15: Boxplots comparing nutrient composition of leaf litter across all four study sites.

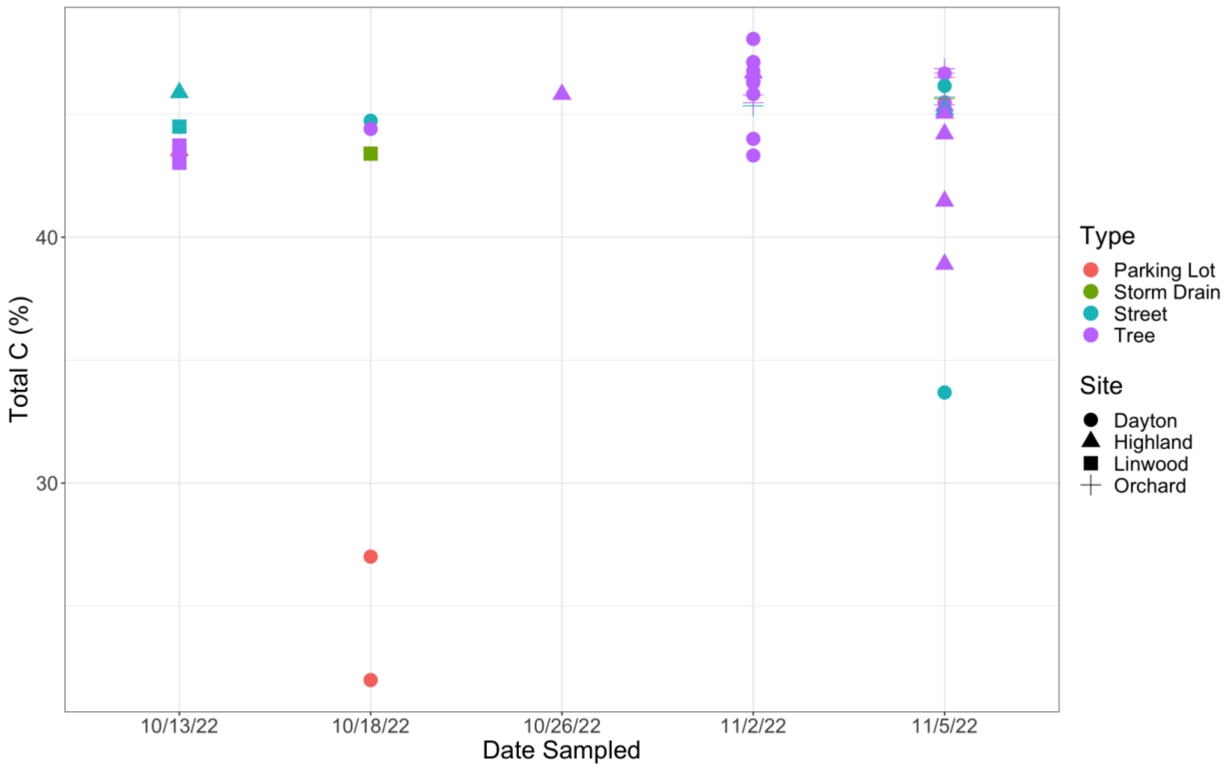

Figure 16: Scatter plots of total carbon (%) across time where different shaped points indicate study site and color represents source of leaf litter collection.

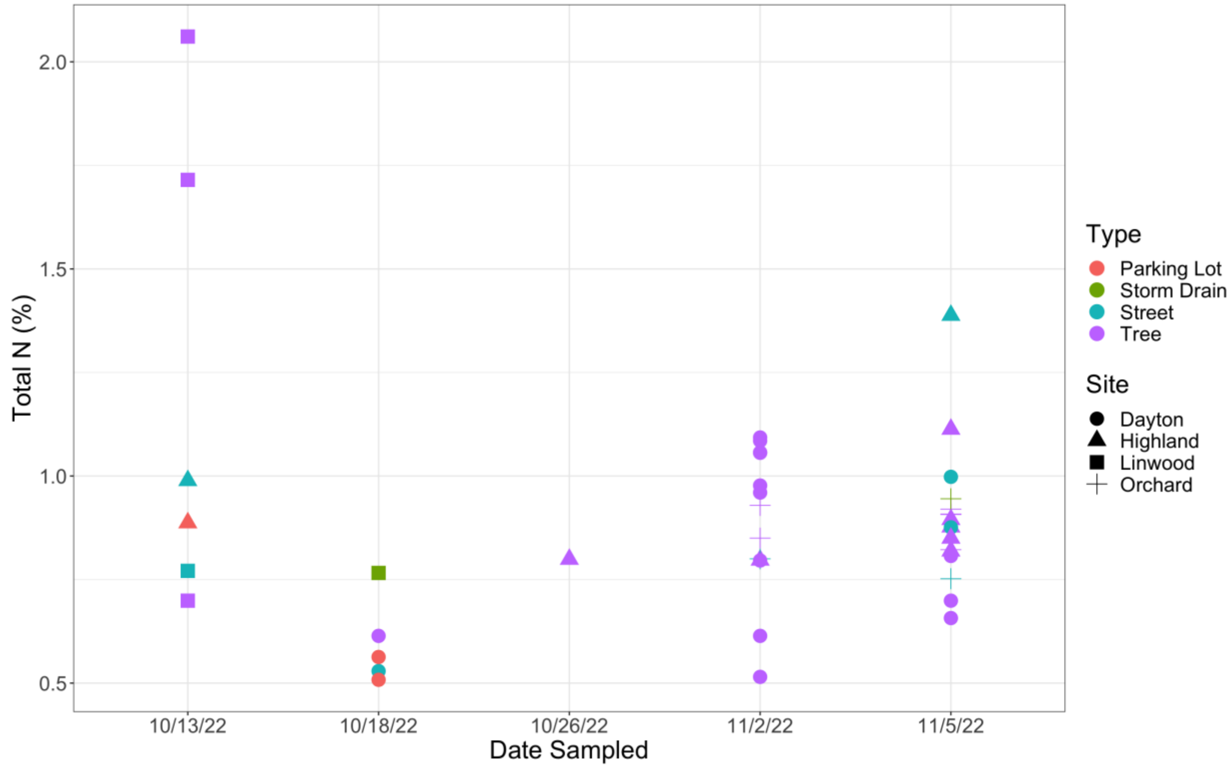

Figure 17: Scatter plots of total nitrogen (%) across time where different shaped points indicate study site and color represents source of leaf litter collection.

2.4.0 Discussion

2.4.1 Throughfall

2.4.1.1: Nitrate, Nitrite, and Ammonium

Within throughfall, fluxes of nitrogen species such as NO_3^- are closely related to distance the from an urbanized environment due to increased rates of anthropogenic sources of dry deposition (Lovett et al., 2000; Chiwa et al., 2003; Forti et al., 2005; Juknys et al., 2007; Du et al., 2015; Ponette-Gonzalez et al., 2017). Considering all 4 study sites are located within 7 miles of Downtown St. Paul and within 12 miles of Downtown Minneapolis, I expected greater fluxes of nitrogen ions via throughfall due to its proximity to common sources of atmospheric deposition. Within urban throughfall, N flux values during the growing season have been reported to be 1.40 kg/ha in a mixed deciduous forest stand in Boston, MA (Decina et al., 2017) and 2.4 kg/ha in a mixed tropical forest stand within a coastal urban site in Brazil (Ponette-Gonzalez et al., 2017). These values are much greater than values reported in this study, however, this is likely due to low rates of precipitation, drought conditions, climate, and differences in sampling periods (Appendix B - 4). Average concentrations of nitrate/nitrite for all sites and species across the growing season is 1.121 mg/L with a standard deviation of 0.849. My results are somewhat similar to those reported in previous literature (Table 3, Figure 6). Mgelwa et al., (2020) collected throughfall under 3 mixed forest stands in southern China with varying exposure to urban environments, reported average nitrate throughfall concentrations ranging from 0.50 to 2.47 mg/L collected from the more urban exposed forest stand during summer months.

There are many studies that have analyzed the seasonal patterns of nitrogen in throughfall in forested and urban environments (Ayars & Gao, 2007; Varenik et al., 2015; Izquieta-Rojano et al., 2016; Decina et al., 2017; Decina et al., 2018; Mgelwa et al., 2020) and report increased nitrogen fluxes during spring. Of these studies, Mgelwa et al., (2020) is the only paper to report autumn concentrations in throughfall and found increasing nitrogen concentrations, which is in contrast to the data reported in my study. My throughfall nitrate/nitrite concentrations show a decreasing trend when approaching autumn, however, my study period experienced a 9-week drought where no throughfall was collected mostly in September and October (Figure 9). Due to this, I do not fully understand the canopy fluxes that may occur during a typical growing season. It should also be noted that there was no significant difference found between nitrogen concentrations prior to the drought period and after the drought period, however, I expected to see greater concentrations after the drought due to buildup of particles within the canopy, yet concentrations are still lower. This is thought to be due to decreasing use of fertilizers in the surrounding neighborhoods as we approach winter months and an overall decrease in usage of the park (ie. less traffic from park visitors) (Yang and Lusk, 2018).

Ammonium concentrations remained consistent throughout the sampling period which is likely due to ammonium being a preferential nutrient and is often retained by tree canopies (Adriaenssens et al., 2012). The relationship between ammonium concentrations and temperature were investigated due to the relationship between temperature and microbial activity, however, no significant relationship was found. There is evidence that N-fixing microbes do exist in tree canopies in boreal forests (Moyes et al., 2016), Holm oak forests (Rico, Ogaya, Terradas, and Penuelas, 2014) and in Mediterranean forests (Guerrieri et al., 2020) and that these microbes are a component of the N fluxes seen in throughfall, in addition to atmospheric deposition. In contrast to previous studies that reported NH_4^+ to be the dominant form of N present in atmospheric deposition (Liu et al., 2008; Xiao et al., 2010), I found that NH_4^+ and NO_3^-/NO_2^- have comparable concentrations in throughfall, with more variability in NO_3^-/NO_2 species. This could be due to increased canopy uptake by our selected canopies due to the urban environment often being nutrient deficient.

2.4.1.2: Total Organic Carbon

It is not uncommon for forested throughfall studies to analyze for organic carbon. However, it is rare to find urban throughfall studies that include organic carbon, although it has been shown that urban environments are a source and sink for carbonaceous PM (Bond et al., 2013; Barrett et al., 2019; Xu et al., 2021). Urban throughfall-derived carbon in in Boston, MA, showed little flux variation of organic carbon between summer and fall and winter, but did report a major increase in spring (Decina et al 2017). Ponette-Gonzalez et al., (2022) also reported similar results in Denton, Texas, however, they show a larger decrease in organic carbon fluxes during fall and winter compared to spring. Within our dataset, TOC concentrations were significantly different ($p<0.05$, Appendix B - 2) between summer and fall, however it should be noted that much of the fall season was during the drought period, so no data is available for much of the season. The difference between pre and post drought conditions is likely due to a build-up of atmospheric deposition onto the canopy that is then washed off by precipitation and enriching fall throughfall concentrations.

Although there is limited information regarding TOC within urban throughfall, there are several studies that observe TOC in forests. Average TOC concentrations within our dataset across all sites and species is 17.63 +/- 12.90 mg/L. Ryan et al., (2022) reported average DOC concentrations between 10 to 50 mg/L in 3 types of forest stands (mixed, sugar maple, yellow birch) in Vermont. In a study conducted in Georgia, USA within a bare cedar and oak stand, average DOC concentrations were reported to be between 17 to 20 mg/L in the non-epiphyte forest stands (Van Stan et al., 2017). Within temperate continental forests, C concentrations in throughfall have been reported between 9 mg/L to 29 mg/L (Moore, 1987; Qualls et al., 1991; Currie et al., 1996; Chang and Matzner, 2000; Hagedorn et al., 2000). Although my data was collected from an urban environment, TOC concentrations are similar but there are samples present that are far above this range (Figure 9), which could be due to increased rates of atmospheric deposition from burning of fossil fuels (Huang et al., 2010; Santos et al., 2014; Siudek et al., 2015; Wang et al., 2016; Yan & Kim, 2012).

Amongst the two urban studies that reported organic carbon in throughfall, our fluxes are much lower and more variable than previous work (Decina et al., 2018; Ponette-Gonzalez et al., 2022). Within an urban mixed forest stand in Boston, MA, average C fluxes during the growing season were reported to be 42.41 kg/ha (Decina et al., 2018), while another study conducted under a tropical urban exposed forest stand reported mean C fluxes of 0.18 mg/m^2 per day (Ponette-Gonzalez et al., 2022). This difference in carbon fluxes in urban throughfall is likely due to a number of factors. First, our sampling period experienced a 9-week drought and even for weeks with precipitation, amounts were minimal. Second, much of their values include the spring spike of carbon in throughfall which would ultimately increase growing season carbon fluxes in comparison to this study which does not include spring throughfall measurements.

Differences between species has also been investigated in previous research. When comparing a sugar maple, yellow birch, and mixed forest stand in Vermont, USA, significant differences were found in C concentrations (Ryan et al., 2022). In contrast, when comparing a bare cedar and oak stand in Georgia, USA, significant differences not found (Van Stan et al., 2017). Although I found no significant differences between species within my dataset, there is evidence that there are differences in canopy processing across species (Eaton et al., 1973), but further research is required.

2.4.1.3: Soluble Reactive Phosphorus

The canopy influences on throughfall phosphorus fluxes cannot be fully determined from the data due to little to no relationship with the variables analyzed in this study. Across all sites and species our average total phosphorus concentrations were 0.341 mg/L (SD = 0.335), however, there were several samples that were below the detection limit for phosphorus and thus could not be included in the dataset. Of all the analytes included, phosphorus was the most variable over time throughout the entire study period. Due to this variability, there were no significant differences found between sites or species (Figure 7, 8). Forested sites in Wales have shown that phosphorus concentrations in throughfall can be extremely variable across tree species, which is likely due to differences in nutrient cycling between species, and variation between sites due to differences in local climate, atmospheric deposition, and canopy architecture/cover (Neal et al., 2003). Although I saw no significant differences between sites and species, my phosphorus concentrations within throughfall align with previous work (Table 3). Of the samples within detection limits, phosphorus concentrations ranged from 0.009 to 1.24 mg/L which is well within range of previous literature. A study conducted in Wales under a non-urban forest canopy reported average P concentrations of 0.21 mg/L (Neal et al., 2003). In an urban canopy study in Stevens Point, WI, investigating the relationship between canopy cover and P concentrations, soluble reactive phosphorus concentrations ranged from 0.02 to 3.73 mg/L with a mean of 0.34 mg/L (Wahl, 2010). Wahl (2010) found no significant differences between canopy coverage and P concentrations in throughfall and further suggests that species and canopy diversity are drivers in differing P concentrations. It is expected to see higher concentrations of phosphorus in throughfall from the urban canopies compared to forests due to increased atmospheric deposition rates from sources such as burning fossil fuels, roads, construction sites, and fertilizers (Eisenreich et al., 1977; Hou et al., 2012), however, more research reporting phosphorus in urban throughfall is necessary.

Relationships between open precipitation volumes and phosphorus concentrations had little to no relationship ($R^2 = 0.068$). Phosphorus fluxes were also calculated and much like the other analytes included in this study, fluxes were low but dilution effects from larger rain events were more apparent in phosphorus than other analytes during week 8 (Figure 9).

2.4.2 EEMs

There are limited optical studies that analyze throughfall organic carbon using EEMs analysis in forested environments (Wang et al., 2004; Inamdar et al., 2011, 2012; Stubbins et al., 2017; Chen et al., 2019; Ryan et al., 2022) and to my knowledge, there have been no previous studies analyzing organic carbon in urban throughfall. In addition, many of these studies do not investigate the same indices that I present in this study, so comparison of values is limited. Overall, it is somewhat unclear how canopies change the chemical properties of organic carbon in throughfall.

2.4.2.1: Humification Index (HIX)

HIX values amongst throughfall fall under a large range. Greater HIX values indicate more humic and aromatic organic carbon present (Fellman et al., 2008). Chen et al., (2019) reports average HIX values in forested throughfall as 2.25 under a pine stand and 3.38 under an oak stand.

My values are closer to Inadmar et al., (2012) which reports HIX values in throughfall between 0.7 and 0.9 under a mixed stand in Maryland. The mixed stand contained species such as red maple, American beech, and yellow poplar, which are species that are more like the species included within my study, which could indicate that species is a component influencing HIX values. From my data, it cannot be concluded that HIX values in urban throughfall are different than forested throughfall. It is clear that within my throughfall samples there is the presence of somewhat humic OM in comparison to throughfall collected under a pine and oak stand (Chen et al., 2019), however, it is unknown if this difference is related to species or environmental differences.

2.4.2.2: Freshness Index (BIX)

The freshness index (BIX or β/α) is an indicator of the level of decomposition that is present in the carbon sample where values above 1 indicate fresher material and values below 1 represent older materials (Wilson and Xenopoulos, 2009). Within our dataset, average values across all sites and species are 0.677 (SD = 0.174) suggesting that much of the carbon present in our samples are older or more processed. At the time of this study, only one other paper had reported average BIX values in throughfall, within two forest stands they reported values of 0.47 +/- 0.06 in an oak stand and 0.55 +/- 0.05 in a pine stand (Chen et al., 2019) and are quite similar to the average values that are seen in our study.

BIX values over our study period show a slight decline where week 2 (early July) we are seeing the highest BIX value. During this time is when leaves would have been more recently budded from the stem of the tree contributing fresher carbon to our throughfall samples. During week 2, I was only able to collect 2 samples so further research is necessary to determine if there is a true seasonal change of BIX values due to leaf out. Chen et al., (2019) found a similar trend where the least fresh throughfall samples were present in the fall, indicating that there is a relationship with season and carbon freshness.

2.4.2.3: Fluorescence Index (FI)

The Fluorescence Index (FI) is an indicator of carbon sourcing as either being more microbially sourced or allochthonous material (ie. from an external source) (McKnight et al., 2001; Cory and McKnight, 2005). Average FI values across sites and species range from 1.44 to 1.66, are between ranges of microbial sources (~1.8) and terrestrial sources (~1.2) (Gabor et al., 2014). Considering my values are in between these values, it is likely that throughfall is a mixture of allochthonous and microbially derived carbon. In addition, there is very little variability throughout the sampling period suggesting that meteorological conditions or seasonality plays a small role in FI values. There are also no differences between sites, species, or drought conditions.

Only one other study has reported FI values in throughfall but was conducted within a forested environment (Inadmar et al., 2012). Within their study, they reported FI values between 1.3 and 1.6 where their average was approximately 1.4 (Inadmar et al., 2012), which is quite close to the average FI value of 1.368. It was expected that I would have reported lower FI values due to increased atmospheric deposition of carbon onto urban canopies. However, the comparison of our data suggests that FI values from urban and forested canopies are not very different, however, more research is needed to fully understand the changes in FI that may occur between different exposures of anthropogenic sources.

2.4.2.4: Peak T/Peak C Ratio (T:C)

T:C ratios within our throughfall data showed little variability between sites, species, and over time. Average T:C ratio values is 0.663 (SD = 0.566) across all sites and species. Much of the previous research that report T:C ratios are done in streams (Rose et al., 2023; Dalzell et al., 2009; Hood et al., 2005) and to my knowledge has not been reported in throughfall. From our T:C values, it is apparent that the carbon present in throughfall samples has a greater range of values compared to stream samples (Rose et al., 2023). Throughfall carbon is likely much more fresh and less processed than carbon present in streams or soils, due to throughfall carbon having less of an opportunity for processing, resulting in in lower T:C ratios.

2.4.3 Leaf Litter

I have evidence that leaf litter collected from different locations associated with city parks have differing nutrient compositions. Of the four sampling locations (streets, parking lots, storm drains, and trees), leaf litter collected directly below canopies had the greatest percentage of total N and total C. It is expected to see more nutrients in leaf litter collected directly below canopies due to limited opportunities for decomposition and leaching. I expected to see the lowest nutrient loadings from storm sewer drains due to stormwater consistently passing through, resulting in leaching from leaf litter to stormwater. However, I found that that leaf litter collected from parking lots had the lowest nutrient contribution of all sampling locations. This is somewhat expected considering previous literature has established that a great amount of decomposition occurs on impervious surfaces (Kaushal and Belt 2012; Hobbie et al., 2014), however I did not expect to see parking lot nutrient totals to be far lower than leaf litter collected from storm drains. This contrast in our study is attributed to “fresher” leaf litter blown from below canopies directly into storm drains without a period of decomposition on pavements being a contributing factor to greater nutrient totals. In addition, it is unknown how long the leaf litter from parking lots had to decompose and leach nutrients, so it is difficult to determine if the contributing variable to differences in nutrient composition across space is time or contributions of allochthonous materials. It should also be noted that there were minimal samples collected from parking lots due to frequent street sweeping, which ultimately could be a signal of a lack of hydrologic connectivity between the parking lot and storm drains rather than external sources of N and C in leaf litter. Future work should aim for more collections from parking lots and nearby storm drains to further assess their nutrient contents.

Within my data, I also saw two points where leaf litter collected below trees at LW were almost two-fold greater in percent N than the other canopies at the same site (Figure 16). The two trees where the leaf litter were collected are located within 10 feet of each other and one of the trees had not lost its canopy cover for the entirety of the study period although other trees had already lost its leaves. This would have likely mixed older leaves that had fallen long before collection and leaves from the tree with canopy remaining, driving total N up within the two samples. In addition, one of the two ash trees sampled in this area was likely exhibiting a stress response where the tree rapidly produced seeds, which were likely mixed into the leaf litter contributing to higher values of total nitrogen. Although there are no studies to my knowledge that analyze the nutrient content of tree seeds, there is evidence that other forms of litter from trees such as fruits and blossoms can have varying nutrient content, specifically, blossoms were shown to have greater nutrient contents which could support the idea that seeds may have a higher nutrient content as well (Hill et al., 2022).

2.5.0 Conclusion

Within this study, I reported nutrient concentrations of TOC, NO_3^-/NO_2^-, NH_4^+, and P within throughfall collected from public parks within the urban environment of St. Paul, MN. I found that there were no significant differences in throughfall nutrient concentrations across sites or species. Although my study was conducted during a drought where the study sites experienced 9 weeks of no throughfall generation and little to no rainfall, I was able to observe some temporal trends within the dataset. First, NO_3^-/NO_2^- concentrations showed a weak relationship with time where concentrations decreased as autumn approached. NH_4^+ concentrations remained consistent over time and showed no relationship with environmental factors. The constant range of NH_4^+ concentrations suggest that the canopy was absorbing much of the NH_4^+ deposited onto the canopy, however, this cannot be fully concluded without measurements of NH_4^+ within stemflow. P concentrations also showed no relationship with environmental factors, but unlike NH_4^+, P concentrations fluctuations were greater and less predictable. TOC was the greatest nutrient contributor within throughfall. TOC showed a significant difference between pre and post drought conditions suggesting that there was accumulation of atmospheric deposition on the canopy during the drought or that a leafless canopy results in greater TOC concentrations in throughfall.

I also report optical properties of DOM found within urban throughfall using EEMs indices such as the Fluorescence Index (FI), Humification Index (HIX), Freshness Index (BIX), and the T:C Ratio. Although there are no other studies that report these values from urban environments to compare my values to, it is important to report these values within urban environments. Optical properties using EEMs show that DOM within urban throughfall is not very different from reports found in other studies in forested environments. Urban throughfall DOM showed to be a mixture of freshly derived DOM and older more processed DOM and much of this DOM is sourced from microbial activity, likely within the canopy.

Leaf litter collected along various points along the pathway to the storm drain showed varying nutrient compositions. Nutrient composition of TC and TN in leaf litter sourced from directly beneath trees, in gutters on streets, and in storm drains were not found to be significantly different from one another. However, leaf litter sourced in parking lots was found to have much lower percentages of TC and TN, suggesting accelerated rates of decomposition on pavements. I expected to see similar nutrient compositions of leaves from parking lots and storm drains due to leaching, however, it is unknown if leaves collected from the storm drain had an opportunity to leach nutrients due to frequent street sweeping.

It is clear from the data presented within this study that urban canopies are a non-point source of nutrient pollution and the factors that drive the changes in the composition of throughfall is complex. The presence of canopies within urban environments is an essential form of green infrastructure, however, there are implications for urban forest managers to consider when expanding urban canopy coverage. First, urban forest managers should consider expansion of under canopy vegetation to ensure the filtration and use of the nutrients present within throughfall, rather than throughfall moving directly into stormwater runoff. In addition, managers should also consider the placement of urban canopies. Ideally, canopies should be placed away from impervious surfaces, again to promote filtration of nutrients into soil. The yearly drop of leaf litter from urban canopies are also a major source of nutrient pollution, which highlights the need for frequent street sweeping to reduce the opportunity for leaching of nutrients present within urban leaf litter. Ultimately, this paper highlights the need for strategic planting to recreate the transfer of nutrients back to soils that is seen within forested environments to fully gain all the benefits that canopies can provide within urban environments.

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Appendices

Appendix A: Study site locations and locations of sampled canopies within study sites

Figure A - 1: Study site locations within St. Paul, MN

Figure A - 2: Study site Orchard Park and locations of sampled canopies and placement of rain gauge

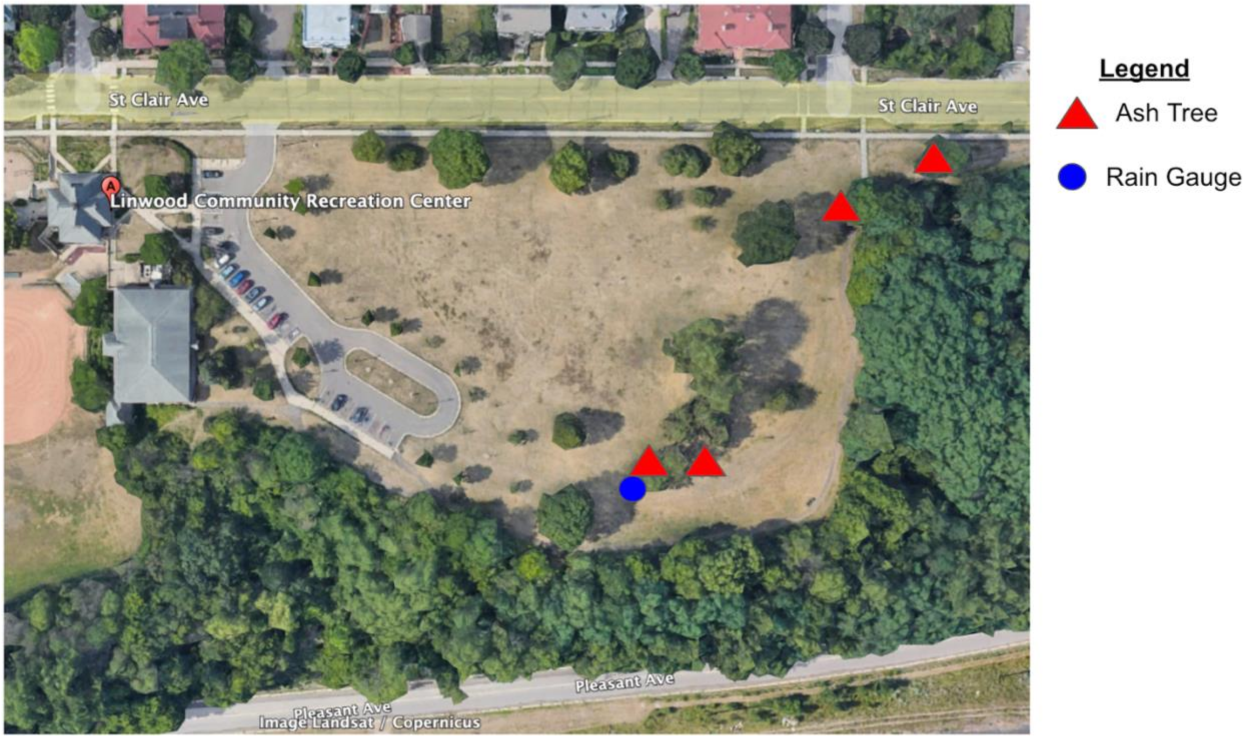

Figure A - 3: Study site Linwood Recreation Center and locations of sampled canopies and placement of rain gauge.

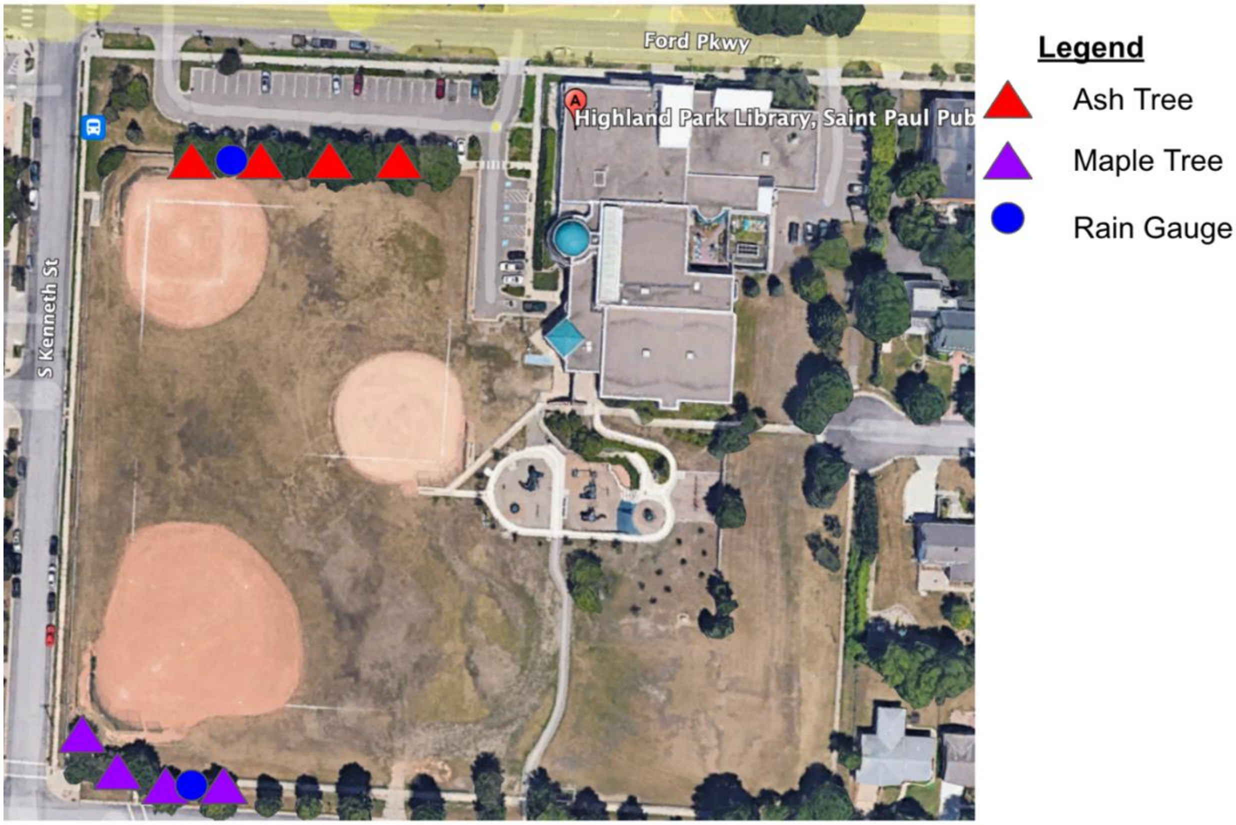

Figure A - 4: Study site Highland Park and Recreation Center and locations of sampled canopies and placement of rain gauge.

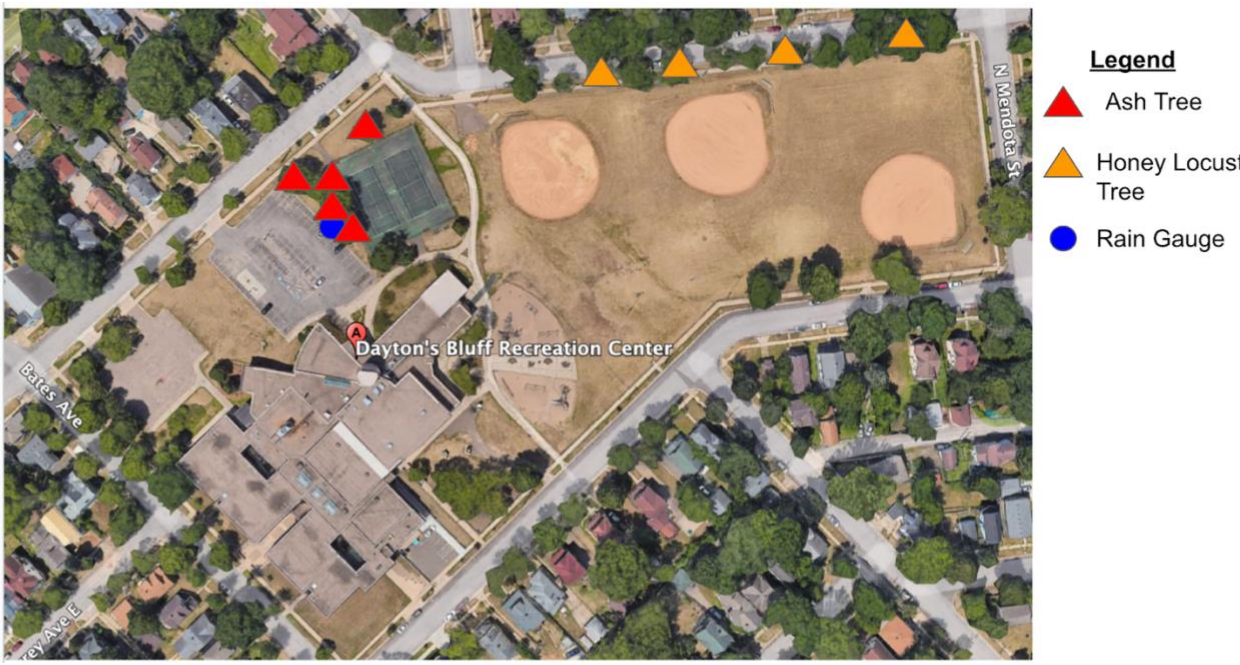

Figure A - 5: Study site Dayton’s Bluff Recreation Center and locations of sampled canopies and placement of rain gauge

Appendix B: Supplemental Figures

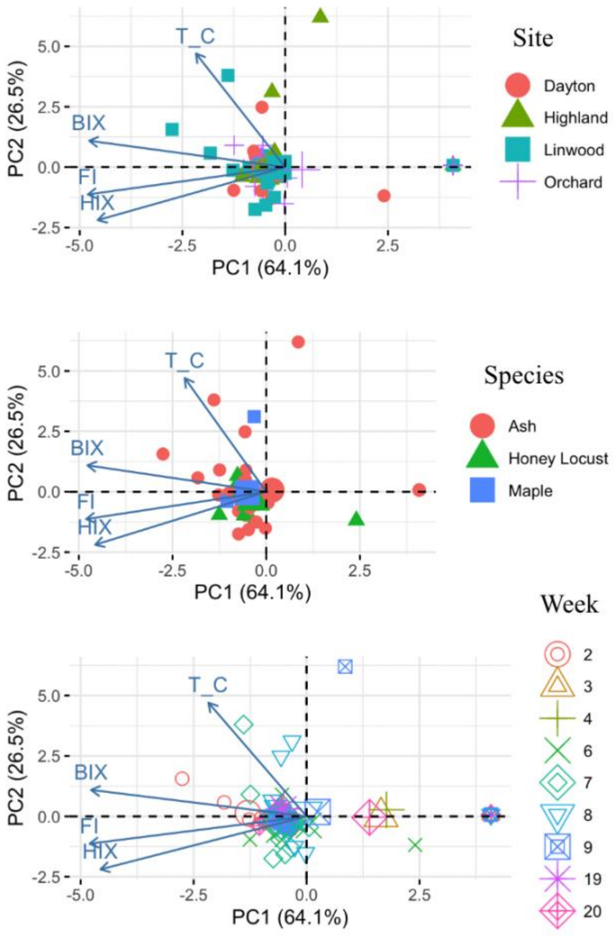

Figure B – 1: Principal component analysis scores (symbols) and loadings (blue arrows) of throughfall DOC composition during the 2022 growing season grouped by site, species, and week.

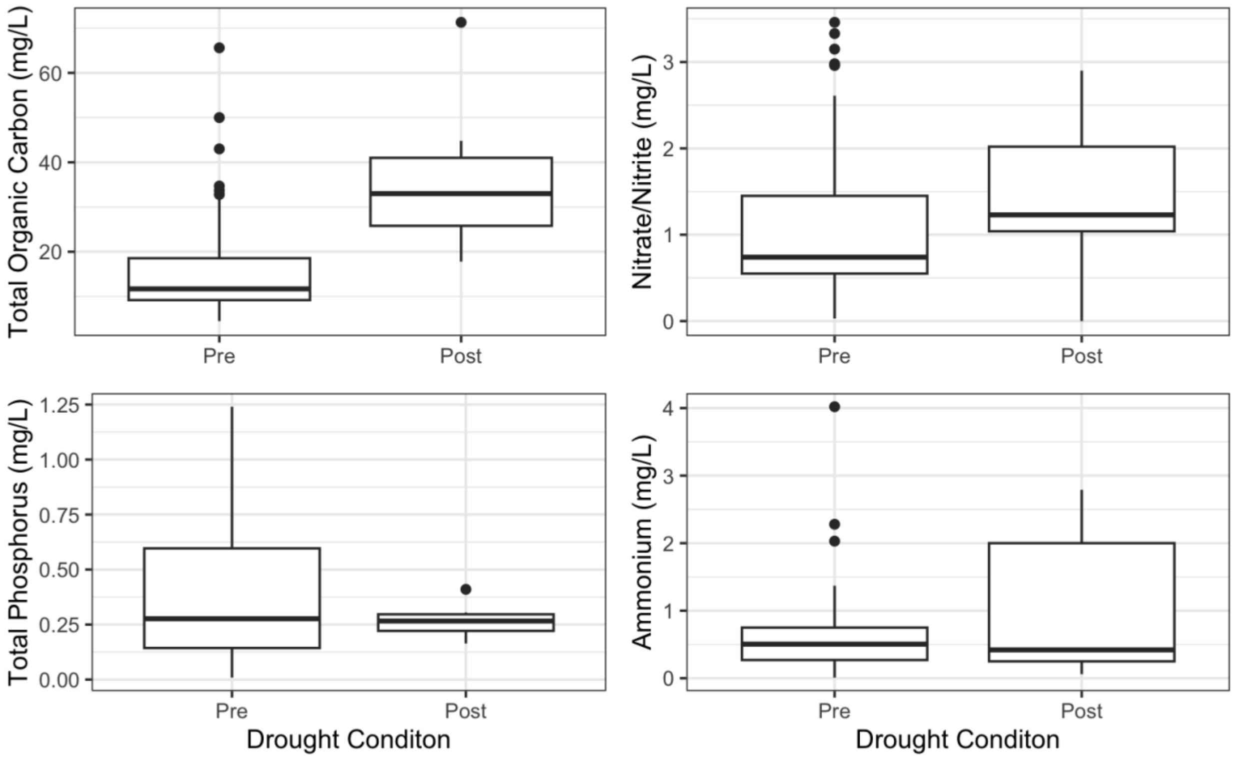

Figure B - 2: Boxplots of nutrient concentrations (mg/L) grouped by samples collected prior to 9 week drought and after 9 week drought. Total organic carbon was the only analyte to show a statistically significant difference between pre and post drought conditions.

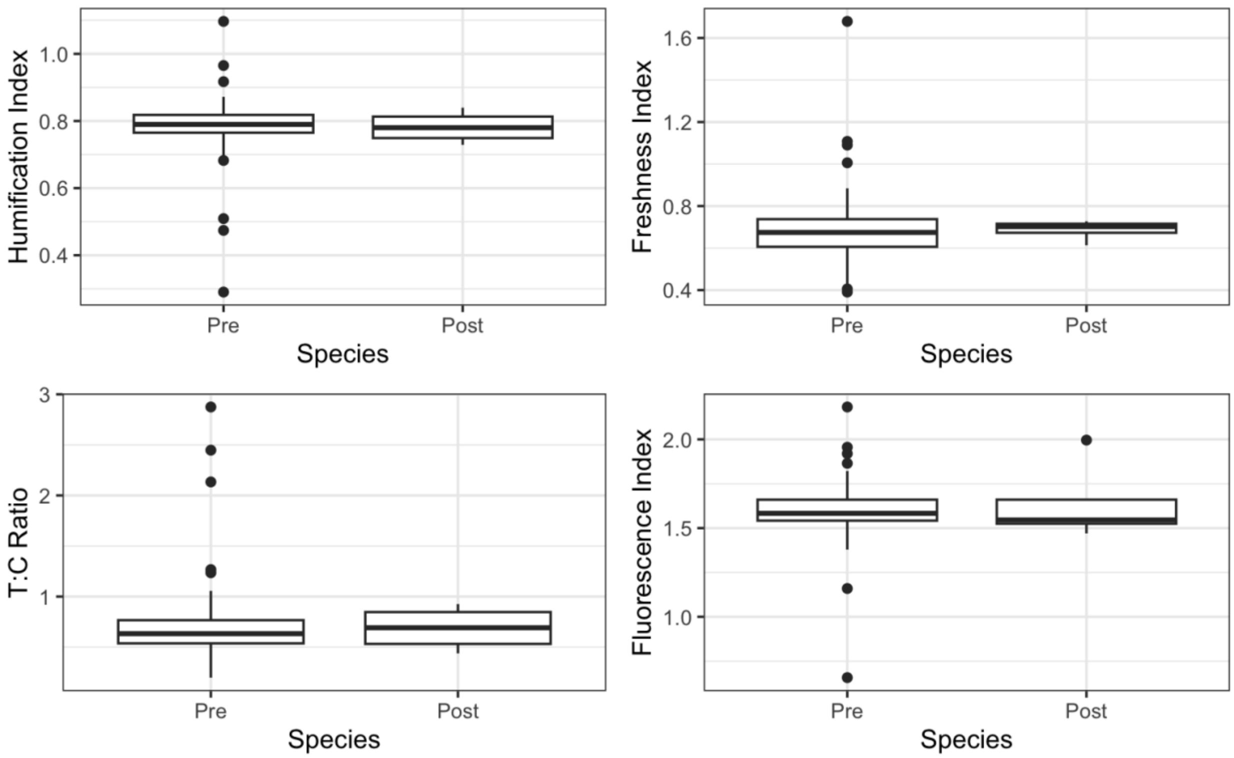

Figure B - 3: Boxplots of EEMs indices separated pre and post drought conditions.

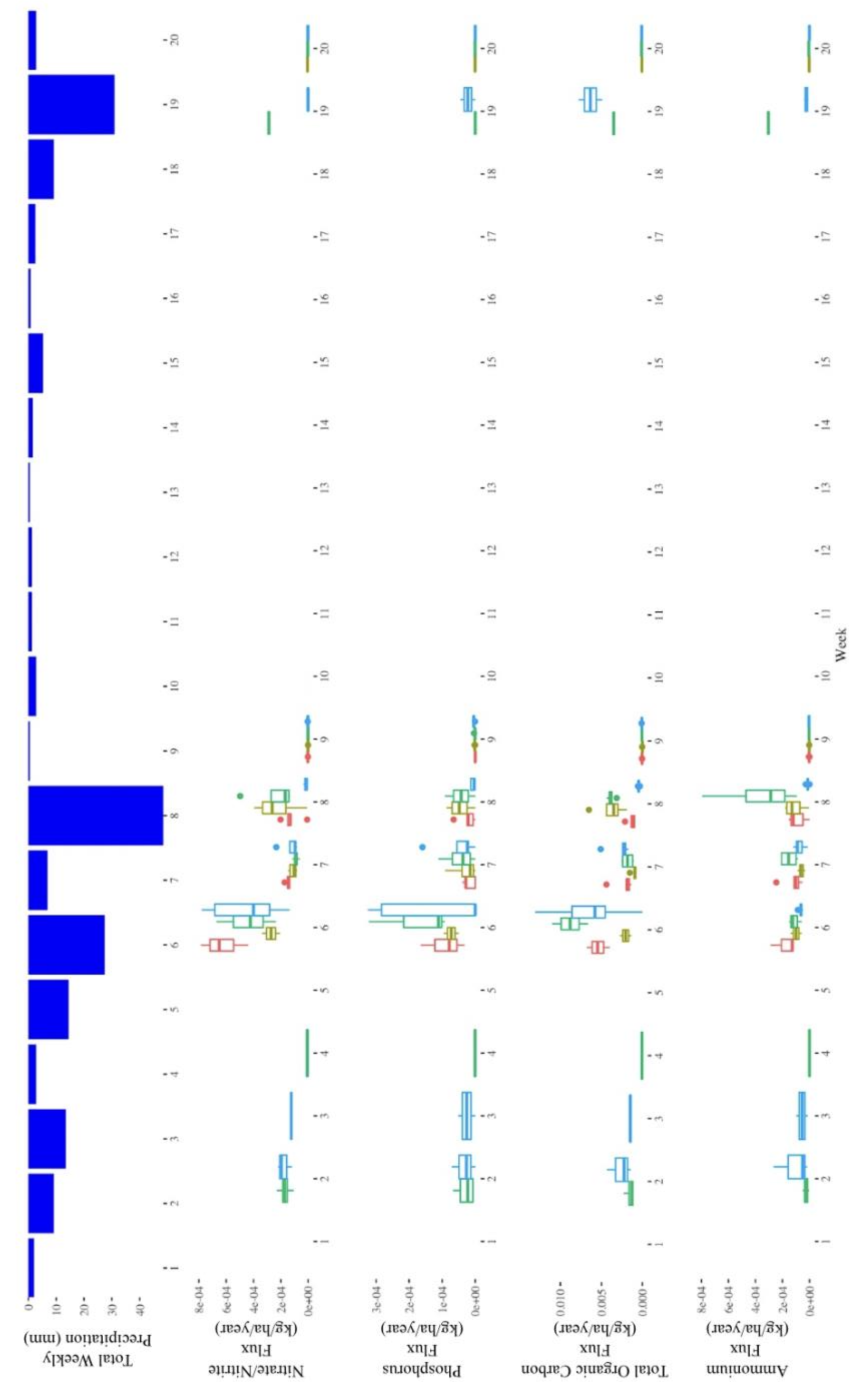

Figure B - 4: Boxplots of throughfall fluxes of TOC, N, NH4, and P in kg/ha/week. Sites are distinguished by boxplot color where LW = green, HP = yellow, DB = red, OR = blue. Boxplots above represent the interquartile range of the dataset on a weekly basis. Week 1 begins on July 7th and week 20 ends on November 20th, 2022.

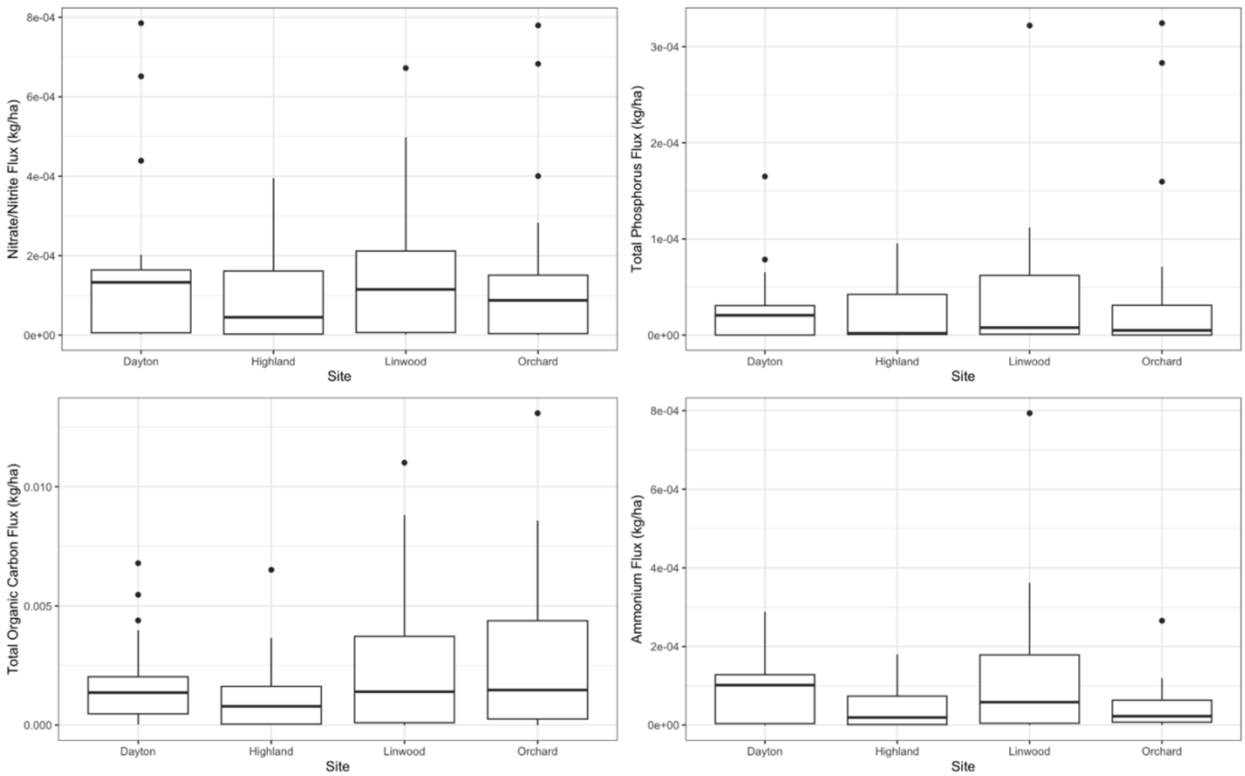

Figure B - 5: Boxplots of throughfall fluxes (kg/ha/week) grouped by site. Data includes all species (sites DB and HP include two species) due to no significant differences between species.

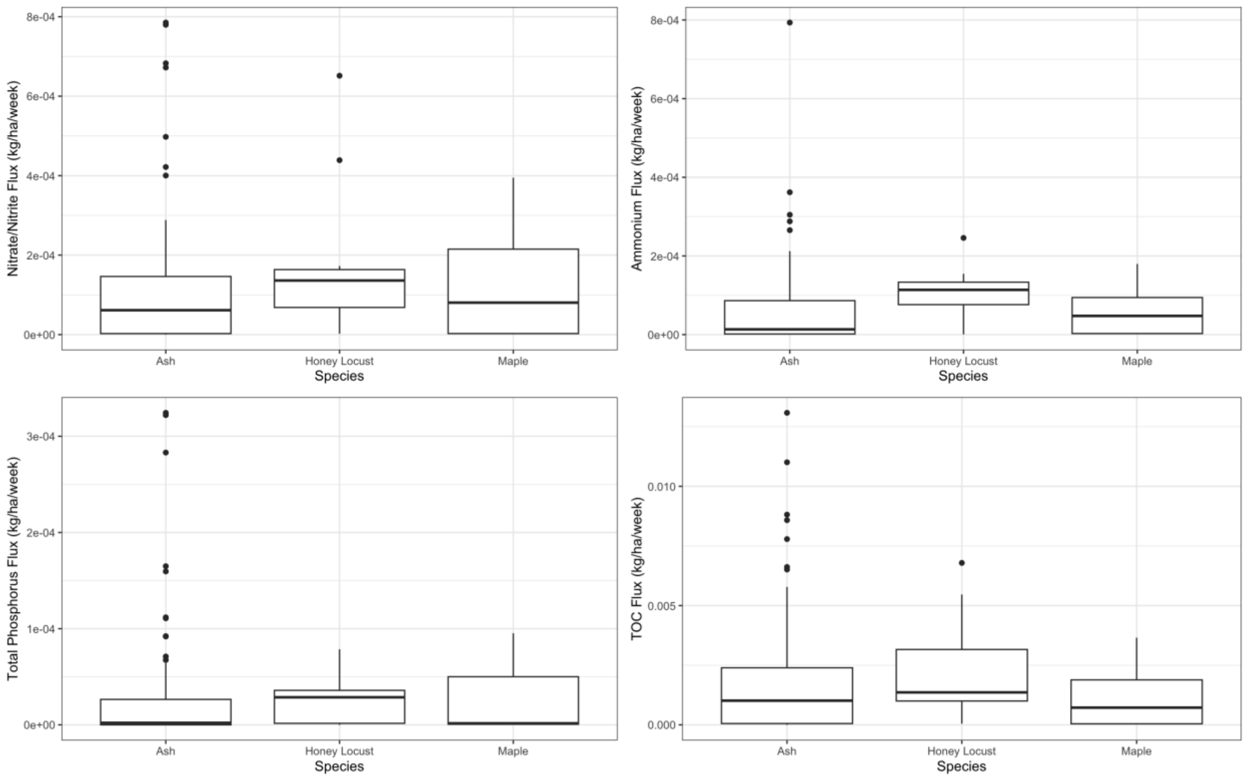

Figure B - 6: Boxplots of throughfall fluxes (kg/ha/week) grouped by species.

Appendix C: Raw Data

Table C – 1. Average and total weekly precipitation and temperature values (mm) with week numbers and associated dates.

Week	Week Start	Week End	Total Weekly Precipitation (mm)	Average Precipitation (mm)	Average Temperature (C)
1	7/3/22	7/9/22	10.16	0	24.40
2	7/10/22	7/16/22	12.446	1.778	24.35
3	7/17/22	7/23/22	0	0	27.08
4	7/24/22	7/30/22	7.366	1.016	21.97
5	7/31/22	8/6/22	4.064	0.508	25.08
6	8/7/22	8/13/22	58.166	8.382	21.26
7	8/14/22	8/21/22	17.018	2.54	20.91
8	8/22/22	8/28/22	0.508	0	22.28
9	8/29/22	9/4/22	28.702	4.064	23.21
10	9/5/22	9/11/22	2.794	0.508	20.76
11	9/12/22	9/18/22	1.016	0.254	20.37
12	9/19/22	9/25/22	2.032	0.254	16.95
13	9/26/22	10/2/22	0.254	0	13.40
14	10/3/22	10/9/22	0.762	0	14.61
15	10/10/22	10/16/22	3.302	0.508	10.22
16	10/17/22	10/23/22	0	0	6.67
17	10/24/22	10/30/22	2.032	0.254	11.44
18	10/31/22	11/6/22	6.35	1.016	11.00
19	11/7/22	11/13/22	24.892	3.556	4.92
20	11/14/22	11/20/22	9.144	1.27	-3.72
21	11/21/22	11/27/22	0	0	0.79
22	11/28/22	12/4/22	0.508	0	-4.26

Table C – 2. Raw data of weekly throughfall concentration values of nitrate/nitrite, ammonium, total organic carbon, and phosphorus in mg/L across the entire study period.

Week	Site	Species	Nitrate/Nitrite (mg/L)	Ammonium (mg/L)	TOC (mg/L)	Phosphorus (mg/L)
2	Linwood	Ash	1.6	0.27	17.3	0.091
2	Linwood	Ash	2.61	0.05	21.2	0.116
2	Orchard	Ash	2.96	0.77	21.4	0.401
2	Linwood	Ash	2.57	0.75	17.7	0.571
2	Linwood	Ash	3.46	0.49	34.7	1.021
2	Orchard	Ash	3.33	4.02	33.7	1.076
2	Orchard	Ash	1.79	0.27	65.6	
3	Orchard	Ash	2.61	0.26	31.2	1.068
3	Orchard	Ash	2.53	2.03	29.7	
4	Linwood	Ash	3.15	0.16		0.205
4	Linwood	Ash	1.83	0.08	43	0.293
6	Dayton	Honey Locust	2.16	0.63	26.9	0.158
6	Highland	Maple	1.33	0.23	10.8	0.197
6	Dayton	Honey Locust	1.9	0.34	19.8	0.229
6	Linwood	Ash	1.23	0.44	25.7	0.269
6	Linwood	Ash	0.69	0.36	19.3	0.323
6	Highland	Maple	0.81	0.55	5.3	0.375
6	Dayton	Ash	2.29	0.84	11.6	0.481
6	Linwood	Ash	1.96	0.17	32.1	0.939
6	Orchard	Ash	0.52	0.22	17.3	1.082

6	Orchard	Ash	1.08	0.25	32.8	1.24
6	Orchard	Ash	2.98	0.33	50	
6	Orchard	Ash	1.53	0.24	22.1	
6	Orchard	Ash	2.61	0.18		
7	Highland	Ash	1.13	0.35	11.1	0.056
7	Linwood	Ash	0.56	0.66	7.9	0.126
7	Orchard	Ash	0.61	0.76	10.9	0.131
7	Dayton	Honey Locust	0.74	0.25	21.6	0.141
7	Dayton	Honey Locust	0.67	0.56	9.5	0.144
7	Orchard	Ash	0.52	0.08	13.9	0.151
7	Highland	Ash	1.45	0.97	9.9	0.169
7	Dayton	Honey Locust	0.85	1.21	6.7	0.195
7	Linwood	Ash	0.73	1.31	15.1	0.348
7	Orchard	Ash	0.59	0.61	13.1	0.35
7	Highland	Maple	0.99	0.52	9.3	0.435
7	Linwood	Ash	0.59	1.32	16.1	0.71
7	Highland	Maple	0.88	0.72	7.9	0.996
7	Orchard	Ash	0.85	0.57	15.2	1.013
7	Orchard	Ash	1.48	0.35	32.3	
7	Highland	Ash	1.6	0.75	16.8	
7	Dayton	Ash	0.72	0.4	9.1	
7	Dayton	Honey Locust	0.65	0.5	7.9	
7	Linwood	Ash	0.39	0.55	6.7	
8	Dayton	Honey Locust	0.04	0.7	4.7	0.009
8	Orchard	Ash	0.14	0.01	11.7	0.058

8	Linwood	Ash	0.41	0.27	12.5	0.08
8	Orchard	Ash	0.64	0.31	11.7	0.082
8	Dayton	Honey Locust	0.65	0.56	6.1	0.104
8	Dayton	Ash	0.65	0.65	7.1	0.11
8	Highland	Maple	1.06	0.56	6.4	0.111
8	Dayton	Ash	1.02	0.14	10.7	0.129
8	Linwood	Ash	0.39	0.61	9	0.163
8	Highland	Ash	0.03	0.01	22.1	0.218
8	Linwood	Ash	1.43	1.04	11.3	0.264
8	Highland	Maple	0.73	0.32	12.4	0.295
8	Dayton	Honey Locust	0.78	0.78	5.4	0.33
8	Orchard	Ash	0.28	0.35	10.9	0.348
8	Orchard	Ash	0.32	0.37	8	0.348
8	Orchard	Ash	0.89	0.72	14.3	
8	Highland	Maple	1.34	0.61	11.4	
8	Linwood	Ash	0.56	2.28	11.3	
8	Dayton	Ash	0.67		4.5	
9	Dayton	Ash	0.53	0.44	11	0.116
9	Orchard	Ash	0.47	0.41	13.8	0.138
9	Linwood	Ash	0.45	0.38	9.8	0.167
9	Highland	Maple	0.79	0.54	5.4	0.175
9	Linwood	Ash	0.36	0.17	13.4	0.181
9	Linwood	Ash	0.35	0.79	9.7	0.181
9	Dayton	Honey Locust	0.43	0.12	9.5	0.284
9	Highland	Ash	0.7	0.14	13.8	0.554
9	Highland	Maple	0.44	0.39	6.7	0.588
9	Highland	Maple	0.92	1.08	6.9	0.621

9	Linwood	Ash	0.45	1.37	18.1	0.717
9	Orchard	Ash	0.79	0.8	19	0.734
9	Highland	Ash	0.76	0.6	6.4	0.823
9	Orchard	Ash	0.55	0.91	14.5	0.962
9	Orchard	Ash	0.55	1.26	11.8	0.962
9	Orchard	Ash	0.51	0.51	11.2	1.027
9	Dayton	Honey Locust	0.57	0.49	9.7	
9	Dayton	Ash	0.63	0.45	9.6	
9	Dayton	Ash	0.52	0.96	5.8	
19	Orchard	Ash	0.03	0.36	71.3	0.41
19	Orchard	Ash	0	0.07	44.8	
19	Linwood	Ash	2.64	2.79	32.1	
20	Highland	Ash	1.65	0.06	41	0.164
20	Highland	Maple	1.04	1.34	17.8	0.208
20	Linwood	Ash	1.23	2	35.5	0.261
20	Highland	Maple	2.9	2.68	25.8	0.271
20	Highland	Maple	2.02	0.42	23.1	0.305
20	Orchard	Ash	1.04	0.25	33	

Table C – 3. Raw data of weekly throughfall fluxes values of nitrate/nitrite, ammonium, total organic carbon, and phosphorus in mg/L across the entire study period.

Week	Site	Species	Nitrate/Nitrite Flux (kg/ha)	Ammonium Flux (kg/ha)	TOC Flux (kg/ha)	P Flux (kg/ha)
2	Linwood	Ash	0.000105664	1.78308E-05	0.001142492	6.00964E-06
2	Linwood	Ash	0.000172364	0.000003302	0.001400048	7.66064E-06
2	Orchard	Ash	0.000195478	5.08508E-05	0.001413256	2.6482E-05
2	Linwood	Ash	0.000169723	0.00004953	0.001168908	3.77088E-05
2	Linwood	Ash	0.000228498	3.23596E-05	0.002291588	6.74268E-05
2	Orchard	Ash	0.000219913	0.000265481	0.002225548	7.1059E-05
2	Orchard	Ash	0.000118212	1.78308E-05	0.004332224	0
3	Orchard	Ash	0.000125959	1.25476E-05	0.001505712	5.15417E-05
3	Orchard	Ash	0.000122098	9.79678E-05	0.001433322	0
4	Linwood	Ash	0.000008001	4.064E-07	0	5.207E-07
4	Linwood	Ash	4.6482E-06	2.032E-07	0.00010922	7.4422E-07
6	Dayton	Honey Locust	0.000438912	0.000128016	0.00546608	3.21056E-05
6	Highland	Maple	0.00033782	0.00005842	0.0027432	0.000050038
6	Dayton	Honey Locust	0.00065151	0.000116586	0.00678942	7.85241E-05
6	Linwood	Ash	0.000421767	0.000150876	0.00881253	9.22401E-05
6	Linwood	Ash	0.000236601	0.000123444	0.00661797	0.000110757
6	Highland	Maple	0.00020574	0.0001397	0.0013462	0.00009525
6	Dayton	Ash	0.000785241	0.000288036	0.00397764	0.000164935
6	Linwood	Ash	0.000672084	0.000058293	0.01100709	0.000321983
6	Orchard	Ash	0.000136042	5.75564E-05	0.004526026	0.000283073
6	Orchard	Ash	0.00028255	0.000065405	0.008581136	0.000324409
6	Orchard	Ash	0.000779628	8.63346E-05	0.013081	0

6	Orchard	Ash	0.000400279	6.27888E-05	0.005781802	0
6	Orchard	Ash	0.000682828	4.70916E-05	0	0
7	Highland	Ash	0.000103327	0.000032004	0.001014984	5.12064E-06
7	Linwood	Ash	8.81888E-05	0.000103937	0.001244092	1.98425E-05
7	Orchard	Ash	9.60628E-05	0.000119685	0.001716532	2.06299E-05
7	Dayton	Honey Locust	0.000150368	0.0000508	0.00438912	2.86512E-05
7	Dayton	Honey Locust	0.000136144	0.000113792	0.0019304	2.92608E-05
7	Orchard	Ash	8.18896E-05	1.25984E-05	0.002188972	2.37795E-05
7	Highland	Ash	0.000132588	8.86968E-05	0.000905256	1.54534E-05
7	Dayton	Honey Locust	0.00017272	0.000245872	0.00136144	0.000039624
7	Linwood	Ash	0.00011496	0.000206299	0.002377948	5.4803E-05
7	Orchard	Ash	9.29132E-05	9.60628E-05	0.002062988	0.000055118
7	Highland	Maple	9.05256E-05	4.75488E-05	0.000850392	3.97764E-05
7	Linwood	Ash	9.29132E-05	0.000207874	0.002535428	0.000111811
7	Highland	Maple	8.04672E-05	6.58368E-05	0.000722376	9.10742E-05
7	Orchard	Ash	0.000133858	8.97636E-05	0.002393696	0.000159527
7	Orchard	Ash	0.00023307	0.000055118	0.005086604	0
7	Highland	Ash	0.000146304	0.00006858	0.001536192	0
7	Dayton	Ash	0.000146304	0.00008128	0.00184912	0
7	Dayton	Honey Locust	0.00013208	0.0001016	0.00160528	0
7	Linwood	Ash	6.14172E-05	0.000086614	0.001055116	0
8	Dayton	Honey Locust	7.9248E-06	0.000138684	0.000931164	1.78308E-06
8	Orchard	Ash	0.000005334	0.000000381	0.00044577	2.2098E-06
8	Linwood	Ash	0.000142672	9.39546E-05	0.00434975	2.78384E-05
8	Orchard	Ash	0.000024384	0.000011811	0.00044577	3.1242E-06

8	Dayton	Honey Locust	0.000128778	0.000110947	0.001208532	2.06045E-05
8	Dayton	Ash	0.000128778	0.000128778	0.001406652	2.17932E-05
8	Highland	Maple	0.000312318	0.000164998	0.001885696	3.2705E-05
8	Dayton	Ash	0.000202082	2.77368E-05	0.002119884	2.55575E-05
8	Linwood	Ash	0.000135712	0.000212268	0.00313182	5.67207E-05
8	Highland	Ash	8.8392E-06	2.9464E-06	0.006511544	6.42315E-05
8	Linwood	Ash	0.000497611	0.000361899	0.003932174	9.18667E-05
8	Highland	Maple	0.000215087	9.42848E-05	0.003653536	8.69188E-05
8	Dayton	Honey Locust	0.000154534	0.000154534	0.001069848	6.53796E-05
8	Orchard	Ash	0.000010668	0.000013335	0.00041529	1.32588E-05
8	Orchard	Ash	0.000012192	0.000014097	0.0003048	1.32588E-05
8	Orchard	Ash	0.000033909	0.000027432	0.00054483	0
8	Highland	Maple	0.000394818	0.00017973	0.003358896	0
8	Linwood	Ash	0.000194869	0.000793394	0.003932174	0
8	Dayton	Ash	0.00013274	0	0.00089154	0
9	Dayton	Ash	2.6924E-06	2.2352E-06	0.00005588	5.8928E-07
9	Orchard	Ash	2.3876E-06	2.0828E-06	0.000070104	7.0104E-07
9	Linwood	Ash	0.000002286	1.9304E-06	0.000049784	8.4836E-07
9	Highland	Maple	2.0066E-06	1.3716E-06	0.000013716	4.445E-07
9	Linwood	Ash	1.8288E-06	8.636E-07	0.000068072	9.1948E-07
9	Linwood	Ash	0.000001778	4.0132E-06	0.000049276	9.1948E-07
9	Dayton	Honey Locust	2.1844E-06	6.096E-07	0.00004826	1.44272E-06
9	Highland	Ash	0.000001778	3.556E-07	0.000035052	1.40716E-06
9	Highland	Maple	1.1176E-06	9.906E-07	0.000017018	1.49352E-06
9	Highland	Maple	2.3368E-06	2.7432E-06	0.000017526	1.57734E-06
9	Linwood	Ash	0.000002286	6.9596E-06	0.000091948	3.64236E-06
9	Orchard	Ash	4.0132E-06	0.000004064	0.00009652	3.72872E-06

9	Highland	Ash	1.9304E-06	0.000001524	0.000016256	2.09042E-06
9	Orchard	Ash	0.000002794	4.6228E-06	0.00007366	4.88696E-06
9	Orchard	Ash	0.000002794	6.4008E-06	0.000059944	4.88696E-06
9	Orchard	Ash	2.5908E-06	2.5908E-06	0.000056896	5.21716E-06
9	Dayton	Honey Locust	2.8956E-06	2.4892E-06	0.000049276	0
9	Dayton	Ash	3.2004E-06	0.000002286	0.000048768	0
9	Dayton	Ash	2.6416E-06	4.8768E-06	0.000029464	0
19	Orchard	Ash	3.2766E-06	3.93192E-05	0.007787386	4.47802E-05
19	Orchard	Ash	0	7.6454E-06	0.004893056	0
19	Linwood	Ash	0.000288341	0.000304724	0.003505962	0
20	Highland	Ash	0.000004191	1.524E-07	0.00010414	4.1656E-07
20	Highland	Maple	2.6416E-06	3.4036E-06	0.000045212	5.2832E-07
20	Linwood	Ash	3.1242E-06	0.00000508	0.00009017	6.6294E-07
20	Highland	Maple	0.000007366	6.8072E-06	0.000065532	6.8834E-07
20	Highland	Maple	5.1308E-06	1.0668E-06	0.000058674	7.747E-07
20	Orchard	Ash	2.6416E-06	0.000000635	0.00008382	0

Table C – 4. Raw data of EEMs index values for the Freshness Index (BIX), Fluorescence Index (FI), Humification Index (HIX), and the Peak T/Peak C Ratio (T:C).

Week	Site	Species	BIX	FI	HIX	T:C
2	Linwood	Ash	1.678849704	1.378950377	0.828735625	1.266848819
2	Linwood	Ash	1.107728567	1.822113508	0.789810555	0.959287929
2	Orchard	Ash	0.884362089	1.658210385	0.771407201	0.580983992
2	Linwood	Ash	1.09025396	1.159480235	0.965253103	0.509663453
2	Linwood	Ash	0.820615147	1.662270545	0.866561468	0.54443877
2	Orchard	Ash	0.783476392	1.604544576	0.812758585	0.57284153
2	Orchard	Ash	0.597769414	1.563980731	0.806780106	0.482826059
3	Orchard	Ash				
3	Orchard	Ash	0.780305785	1.588338165	0.791443313	0.610553243
4	Linwood	Ash				
4	Linwood	Ash	0.643179135	1.665367201	0.682410887	0.977156774
6	Dayton	Honey Locust			0.897659297	
6	Highland	Maple	0.611946201	1.50464614	0.840404938	0.467581879
6	Dayton	Honey Locust	0.871208109	1.457676153	1.096690549	0.262560173
6	Linwood	Ash	0.599661128	1.398529306	0.790052711	0.464883939
6	Linwood	Ash	0.535747006	1.814067772	0.68745867	0.785645096
6	Highland	Maple	0.711731596	1.5375238	0.817384188	0.558151009
6	Dayton	Ash	0.584889308	1.54853404	0.830347083	0.740193977
6	Linwood	Ash	0.538029088	1.617712218	0.764547304	0.579358407
6	Orchard	Ash	0.636420366	1.526177219	0.698113705	1.23531293
6	Orchard	Ash	0.600605815	1.865015792	0.871912957	0.382600674
6	Orchard	Ash	0.620689625	1.564573375	0.820779254	0.531156939
6	Orchard	Ash	0.544866555	1.815843206	0.877098012	0.283678968
6	Orchard	Ash				

7	Highland	Ash	0.669953739	1.701751016	0.818570024	0.492171864
7	Linwood	Ash	0.830866763	1.665206541	0.474103859	2.874544585
7	Orchard	Ash	0.417106509	1.919944849	0.715289142	0.655030188
7	Dayton	Honey Locust	0.604346963	1.608388527	0.881843076	
7	Dayton	Honey Locust	0.466625967	2.182593263	0.782113516	0.320382528
7	Orchard	Ash	0.390743037	1.640779266	0.751167711	0.544738891
7	Highland	Ash	0.717731349	1.600468656	0.777574867	0.67185844
7	Dayton	Honey Locust	0.494237671	1.639702666	0.795605301	0.720713434
7	Linwood	Ash	0.542813309	1.572803119	1.177746825	
7	Orchard	Ash	0.613296426	1.687626722	0.723095574	0.928360647
7	Highland	Maple	0.680137647	1.60056355	0.79375498	0.606601453
7	Linwood	Ash	0.536983679	1.551439764	1.054453458	
7	Highland	Maple	0.628644219	1.458972945	0.826357434	0.480105681
7	Orchard	Ash	1.006037309	1.955672361	0.509265258	0.995112238
7	Orchard	Ash	0.623077763	1.511251264	0.812020846	0.446867368
7	Highland	Ash	0.734506538	1.801741552	0.797552476	0.639604871
7	Dayton	Ash	0.620006569	1.57089185	0.752142358	0.699464047
7	Dayton	Honey Locust	0.670297639	1.545497446	0.798571733	0.553281639
7	Linwood	Ash	0.553637074	1.536381424	0.881063323	0.501959063
8	Dayton	Honey Locust	0.749936755	1.571912161	0.715461479	1.056379288
8	Orchard	Ash	0.382640168	1.727749657	0.886763731	
8	Linwood	Ash	0.405670927	1.77755469	0.917161726	0.198583408
8	Orchard	Ash	0.690305873	1.583434585	0.783250623	0.638215791
8	Dayton	Honey Locust	0.772537215	1.555431034	0.719441994	0.902644123
8	Dayton	Ash	0.749006256	0.657164426	0.822366404	2.133552887
8	Highland	Maple	0.492668917	1.812962184	0.290393239	2.44751012
8	Dayton	Ash				
8	Linwood	Ash	0.554024246	1.639289545	0.865459435	0.432349526
8	Highland	Ash	0.674438313	1.56500284	0.754301749	0.783245985

8	Linwood	Ash	0.705635015	1.569439226	0.765739499	0.749851813
8	Highland	Maple	0.591958808	1.550569666	0.817715183	0.469462216
8	Dayton	Honey Locust	0.717678469	1.543030308	0.771745871	0.696342822
8	Orchard	Ash	0.68267921	1.54100424	0.777848579	0.723745136
8	Orchard	Ash				
8	Orchard	Ash	0.684344585	1.532483362	0.778642074	0.700843561
8	Highland	Maple	0.641268183	1.505493429	0.791319337	0.536938333
8	Linwood	Ash	0.689543769	1.580730653	0.76310661	0.796114453
8	Dayton	Ash	0.711117025	1.61195936	0.706042902	0.932625802
9	Dayton	Ash	0.665416712	1.550287511	0.803132781	0.619119919
9	Orchard	Ash	0.649347659	1.536970499	0.807978148	0.568621673
9	Linwood	Ash	0.830866763	1.575318397	0.788410903	0.64128488
9	Highland	Maple	0.707025458	1.531138853	0.803195108	0.598404317
9	Linwood	Ash	0.678473636	1.611162232	0.783407193	0.669002181
9	Linwood	Ash				
9	Dayton	Honey Locust	0.726282074	1.583103989	0.781771585	0.683374758
9	Highland	Ash	0.783639992			3.645777121
9	Highland	Maple	0.63803617	1.496028348	0.817329002	0.530040132
9	Highland	Maple	0.641268183	1.580314013	0.805731843	0.568548371
9	Linwood	Ash	0.652371869	1.574266154	0.811335184	0.611251912
9	Orchard	Ash	0.618358378	1.577834917	0.830380558	0.50685187
9	Highland	Ash	0.698493	1.631336857	0.784650197	0.63318951
9	Orchard	Ash	0.692656822	1.618791813	0.787933286	0.689211312
9	Orchard	Ash				
9	Orchard	Ash				
9	Dayton	Honey Locust	0.636174882	1.478272947	0.818194572	0.50906674
9	Dayton	Ash	0.685547671	1.560810058	0.80928805	0.547668444
9	Dayton	Ash	0.561269648	1.548547741	0.801495021	0.73315892
19	Orchard	Ash	0.692673799	1.548547741	0.729013547	0.925745347

19	Orchard	Ash	0.667227696	1.594227877	0.715934141	0.939508011
19	Linwood	Ash	0.616992189	1.519793729	0.739573621	0.754676074
20	Highland	Ash				
20	Highland	Maple	0.711731596	1.99599797	0.804368417	0.563132071
20	Linwood	Ash				
20	Highland	Maple	0.613400563	1.470178058	0.839551237	0.438739457
20	Highland	Maple	0.727558581	1.542975434	0.755834657	0.820560036
20	Orchard	Ash				

Table C – 5. Raw data of total nitrogen and total carbon (%) of leaf litter collected throughout study period

Date Sampled	Site	Type	Species	Total N (%)	Total C (%)
10/13/22	Highland	Parking Lot		0.887	43.517
10/13/22	Linwood	Tree	Ash	2.061	43.471
10/13/22	Linwood	Tree	Ash	1.715	43.726
10/13/22	Linwood	Tree	Ash	0.699	43.026
10/13/22	Highland	Street		0.989	45.878
10/13/22	Linwood	Street		0.771	44.495
10/18/22	Linwood	Storm Drain		0.766	43.397
10/18/22	Dayton	Street		0.529	44.734
10/18/22	Dayton	Tree	Ash	0.614	44.402
10/18/22	Dayton	Parking Lot		0.563	27.013
10/18/22	Dayton	Parking Lot		0.508	21.994
10/26/22	Highland	Tree	Maple	0.799	45.810
11/2/22	Dayton	Tree	Honey Locust	1.056	46.280
11/2/22	Dayton	Tree	Honey Locust	0.960	47.114
11/2/22	Dayton	Tree	Honey Locust	0.977	48.061
11/2/22	Highland	Tree	Maple	0.797	46.677
11/2/22	Dayton	Tree	Ash	0.614	45.816
11/2/22	Dayton	Tree	Honey Locust	1.057	46.757
11/2/22	Dayton	Tree	Honey Locust	1.085	47.120
11/2/22	Orchard	Street		0.800	45.337
11/2/22	Orchard	Tree	Ash	0.929	45.778
11/2/22	Dayton	Tree	Ash	0.796	43.999
11/2/22	Orchard	Tree	Ash	0.850	45.462
11/2/22	Dayton	Tree	Ash	0.515	43.323
11/2/22	Dayton	Tree	Honey Locust	1.093	46.347
11/5/22	Highland	Tree	Maple	0.819	41.465

11/5/22	Highland	Tree	Maple	0.895	45.339
11/5/22	Dayton	Tree	Ash	0.699	45.117
11/5/22	Highland	Tree	Maple	1.113	44.203
11/5/22	Orchard	Tree	Ash	0.822	45.385
11/5/22	Orchard	Tree	Ash	0.920	46.497
11/5/22	Highland	Tree	Maple	0.877	38.900
11/5/22	Dayton	Tree	Ash	0.657	45.482
11/5/22	Orchard	Tree	Ash	0.907	46.669
11/5/22	Orchard	Tree	Ash	0.908	46.857
11/5/22	Highland	Street		1.388	45.176
11/5/22	Dayton	Street		0.876	33.687
11/5/22	Orchard	Storm Drain		0.945	45.639
11/5/22	Dayton	Tree	Ash	0.807	46.653
11/5/22	Dayton	Street		0.998	46.153
11/5/22	Highland	Tree	Maple	0.850	45.045
11/5/22	Orchard	Street		0.752	45.697