

## ABSTRACT

Title of Document: DISSOLVED AND GASEOUS FLUXES OF CARBON AND NITROGEN FROM URBAN WATERSHEDS OF THE CHESAPEAKE BAY

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Carbon and nitrogen loading to streams and rivers contributes to eutrophication as well as greenhouse gas (GHG) production in streams, rivers and estuaries. My dissertation consists of three research chapters, which examine interactions and potential trade-offs between water quality and greenhouse gas production in urban streams of the Chesapeake Bay watershed. My first research project focused on drivers of carbon export and quality in an urbanized river. I found that watershed carbon sources (soils and leaves) contributed more than in-stream production to overall carbon export, but that periods of high in-stream productivity were important over seasonal and daily timescales. My second research chapter examined the influence of urban storm-water and sanitary infrastructure on dissolved and gaseous carbon and nitrogen concentrations in headwater streams. Gases ( $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2\text{O}$ ) were consistently super-saturated throughout the course of a year.  $\text{N}_2\text{O}$  concentrations in streams draining septic systems were within the high range of

previously published values. Total dissolved nitrogen concentration was positively correlated with CO<sub>2</sub> and N<sub>2</sub>O and negatively correlated with CH<sub>4</sub>. My third research chapter examined a long-term (15-year) record of GHG emissions from soils in rural forests, urban forest, and urban lawns in Baltimore, MD. CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O emissions showed positive correlations with temperature at each site. Lawns were a net source of CH<sub>4</sub> + N<sub>2</sub>O, whereas forests were net sinks. Gross CO<sub>2</sub> fluxes were also highest in lawns, in part due to elevated growing-season temperatures. While land cover influences GHG emissions from soils, the overall role of land cover on this flux is very small (< 0.5%) compared with gases released from anthropogenic sources, according to a recent GHG budget of the Baltimore metropolitan area, where this study took place.

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URBAN WATERSHEDS OF THE CHESAPEAKE BAY

By

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## Dedication

This work is dedicated to my entire family for their unyielding support over the years.

## Acknowledgements

I would like to thank my committee, Drs. Sujay Kaushal, Jake Beaulieu, Paul Mayer, Karen Prestegard, and Jay Kaufman for their support and guidance. I would like to especially thank Dr. Sujay Kaushal for his continued mentorship, patience, and insights throughout the process. Dr. Beaulieu provided indispensable guidance and expertise for Chapter 3, provided key insights, and analyzed all of my dissolved gas samples at EPA in Cincinnati, OH. Dr. Claire Welty helped select field sites, site access permissions, and maintained headwater stream gaging stations for my Chapter 3. My former lab mates, Drs. Michael Pennino and Tamara Newcomer Johnson deserve special thanks for all of the knowledge passed down, as well as the hours of fieldwork spent helping me get my research off the ground. Michael additionally shared data from his own work in Baltimore streams to help with gas flux calculations. Dr. Peter Groffman additionally provided guidance and support in preparing my final chapter using data collected by his lab and the Baltimore Ecosystem Study. Drs. Andrew Miller and Arthur Gold provided thoughtful guidance and advice over the years as well.

This work was supported by numerous grants and research programs. Work in the Anacostia watershed was leveraged on data collected at USGS gages maintained by the Maryland Water Sciences Center. This project was additionally supported by grants from the NSF-funded Washington D.C. ULTRA-Ex project, and NASA carbon cycle and ecosystems program. Work in Baltimore was part of the Baltimore Ecosystem Study LTER project, and leveraged upon the past research, as well as physical and digital infrastructure supported by the LTER. Work in Baltimore streams

was funded by a collaborative project funded by NSF Water, Sustainability and Climate program. Fellowships from Maryland Sea Grant, the Graduate School at UMD, and Maryland Water Resources Research Center helped support my work over the years. I was able to present my work at several conferences, thanks to the Earth System Science Interdisciplinary Center at UMD, the UMD Graduate School's Jakob K. Goldhaber fellowship.

Finally, this work would not have been possible without the Geology Department as a whole, and numerous labmates, interns, and friends who proofread papers, helped in the lab, and joined me in urban fieldwork adventures. These individuals include but are not limited to Evan Smith, Evan McMullen, Tom Doody, Tess Van Dorn, Sofia D'Ambroiso, Shahan Haq, Julia, Gorman, Metthea Yeppsen, Dan Dillon, Dan Jones, Melissa Grese, Palma Jarboe, Grant Jiang, Steve Hohman, Sze Wing Yu, Jon Urban, Carolyn Plank, and Rosemary Fanelli.

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# Chapter 1: Introduction

## 1.1. Statement of Purpose

### 1.1.1. Introduction

Nitrogen is an essential nutrient for organisms, which is naturally limiting to plant growth in many ecosystems.  $N_2$  gas is abundant in the atmosphere, but unavailable for plants unless converted to biologically reactive forms (Schlesinger et al. 1997). Fossil fuel combustion, bacterial nitrogen fixation, and fertilizer are all processes by which  $N_2$  can be converted into available forms (Figure 1.1; UNEP 2007). Human activities have more than doubled the amount of reactive N in the biosphere through these processes (Vitousek et al. 1997; Galloway et al. 2003). The advent of synthetic fertilizer *via* the Haber-Bosch process has alleviated major limitations to agricultural productivity over the past century (Galloway 2003; Vitousek et al. 1997), however the current excess of reactive nitrogen has many negative consequences for natural ecosystems (Vitousek et al. 1997).

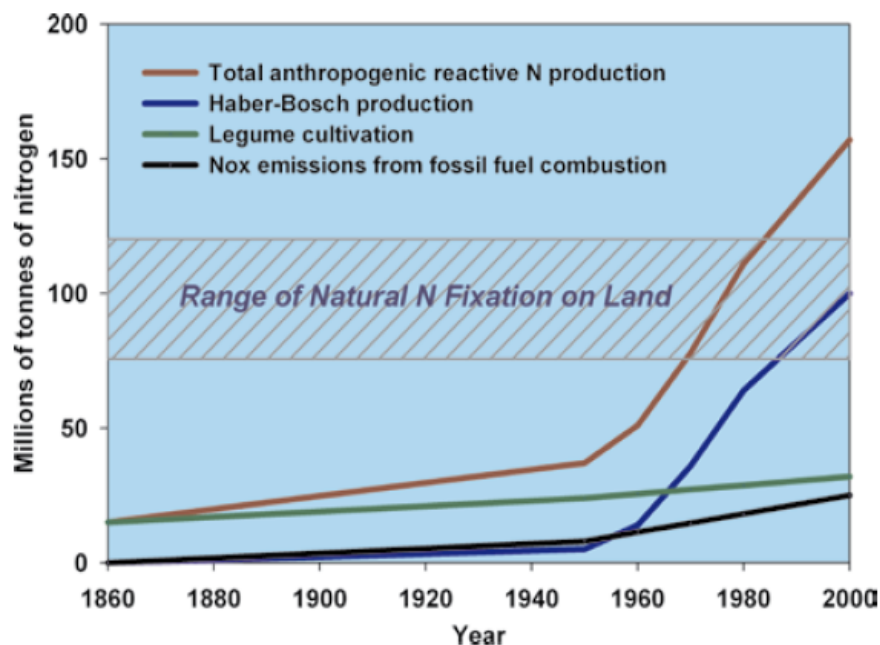


Figure 1.1 Comparing the range of natural N fixation in the biosphere with N fixed from various human activities globally, from UNEP 2007 report entitled 'Reactive Nitrogen in the Environment'.

Estuaries are especially sensitive to nutrient loading, or eutrophication, because the removal of N limitation can lead to algal blooms (Prepas and Charette 2003). When blooms die off, heterotrophic microbes break down the organic matter and consume oxygen in the water column. This process results in very low oxygen levels (hypoxia) at depth in estuaries. In the United States, 64% of estuaries experience seasonal hypoxia due to algal blooms; the extent, duration and number of these events has increased over the past three decades (Rabalais et al. 2009). Watershed nitrogen loading is the primary driver of algal blooms. Nitrogen in terrestrial organic matter exported by rivers is often assumed to be too recalcitrant to contribute to coastal hypoxia, however this assumption is largely un-tested in coastal rivers with significant urbanization. Carbon export can increase due to wastewater leakage or effluent (Daniel et al. 2001; Sickman et al. 2007; Kaushal et al. 2014a), or altered soil chemistry (Aitkenhead-Peterson et al. 2009), and

these sources may be more labile than natural waters as well (Newcomer et al. 2012; Duan et al. 2014). Relatively few studies have quantified carbon export from urbanized watersheds, or examined processes controlling carbon quantity and quality. Because carbon quantity and quality in streams can influence 1) oxygen consumption 2) greenhouse gas ( $\text{CO}_2$ ,  $\text{N}_2\text{O}$  and  $\text{CH}_4$ ) production, and 3) microbial N uptake processes, my first project focused on understanding the drivers of carbon cycling in a highly urbanized watershed.

Urban areas can contribute significantly to coastal N loading (Castro et al. 2003) and potentially to aquatic GHG emissions. N sources include deposition from vehicle exhaust, sanitary infrastructure, and residential fertilizer (Bernhardt et al. 2008; Kaushal et al. 2011). Castro et al. 2003 estimated that N loading was dominated by urban sources in 11 out of 34 major estuaries in the United States. The same study attributed between 1 and 86% of total N loading to sewage, depending on the extent of urbanization. The role of N loading on urban aquatic GHG emissions remains under-studied.  $\text{N}_2\text{O}$  emissions from non-point source N loading contributes between 0.23 and 11.9 Tg N  $\text{yr}^{-1}$  globally, with a wide range of estimates due to significant uncertainty in 1) the rate of N loading from watersheds, and 2) the proportion of N converted to  $\text{N}_2\text{O}$  (Mosier et al. 1998a; Nevison 2000).  $\text{N}_2\text{O}$  is produced *via* microbial processes of nitrification and denitrification within groundwater or along the stream network (Seitzinger and Kroeze, 1998). Denitrification requires anoxic conditions, while nitrification requires oxygenated conditions (Schlesinger 1997). Variations in redox state and hydrologic connectivity may influence the conversion rate of dissolved N to  $\text{N}_2\text{O}$  across and within watersheds (Beaulieu et al. 2011; Turner et al. 2015). Eutrophication can further influence GHG



production by contributing to a favorable redox state for N<sub>2</sub>O and CH<sub>4</sub> production in both freshwater (Baulch et al. 2011; Harrison and Matson 2003) and estuarine environments (Naqvi et al. 2010). CH<sub>4</sub> is produced anaerobically but can be consumed by methanotrophic bacteria in oxygen-rich environments. Rivers and estuaries may therefore switch from sink to source of methane as oxygen availability changes. Given the widespread nature of coastal eutrophication and GHG emissions globally, it is clear that managing N is an important challenge. My second project focused on understanding the role of urban infrastructure on GHG dynamics in headwater streams.

While urban areas are hot spots of N loading, a significant portion of N inputs can also be retained and/or removed within urban watersheds. For instance, Groffman et al. 2004 estimated that 75% of watershed N inputs were retained in a suburban Maryland watershed, compared to 77 and 95% in nearby agricultural and forested sites respectively. Evidence of N accumulation in urban soils has been documented in Baltimore (Raciti et al. 2008; 2011) and Phoenix (Zhu et al. 2006), suggesting that lawn fertilizer inputs are retained over annual timescales. The longevity of this N sink remains uncertain, however. Riparian zones are also potential hot spots of N retention in urban areas. For this reason, my third project focused on long-term (15-year) GHG emissions from urban lawns, in order to determine whether the role of urban soils as GHG sources or sinks has changed over time and across different vegetation classes.

## 1. 2 Overview of Research Chapters

### 1.2.1 Role of Aquatic Ecosystems in Urban GHG Budgets

*Chapter 2 examined the role of hydrologic variability and in-stream biota on gaseous (CO<sub>2</sub>) emissions and dissolved carbon export from streams across the Anacostia*

*Watershed.* The influence of urban aquatic ecosystems on aquatic carbon cycling warrants further research both in terms of N removal and GHG budgets. Recent estimates of greenhouse gas emissions from streams and rivers have demonstrated that these ecosystems contribute significantly to global CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O budgets (Cole et al. 2007; Butman and Raymond 2011; Bastviken et al. 2011). Major uncertainties surrounding GHG emissions from freshwater persist despite the relatively significant size of these fluxes. IPCC methodology currently assumes that lateral transport of carbon from terrestrial ecosystems to the ocean has remained relatively constant since pre-industrial times (Ciais et al. 2013). A growing body of work has shown that this assumption may not be valid (Regnier et al. 2013; Bauer et al. 2013). Inland waters are currently assumed to transport 0.9 Pg C yr<sup>-1</sup> of terrestrially sourced carbon to the ocean, and release 1.0 Pg C yr<sup>-1</sup> of this terrestrial pool to the atmosphere. These fluxes together are equal to approximately half of the annual atmospheric CO<sub>2</sub> increase (4.0 Pg C yr<sup>-1</sup>). Changes in the magnitude and fate of terrestrial carbon in freshwater (oceanic burial vs. CO<sub>2</sub> vs. CH<sub>4</sub>), therefore may have large impacts on the net terrestrial carbon sink (Ciais et al. 2013). Quantifying CO<sub>2</sub> emissions from flowing waters involves separating out the influence of in-stream respiration/mineralization of autotrophic (algae) biomass vs. terrestrially sourced organic matter. A conceptual figure of this approach can be found in Figure 1.1.

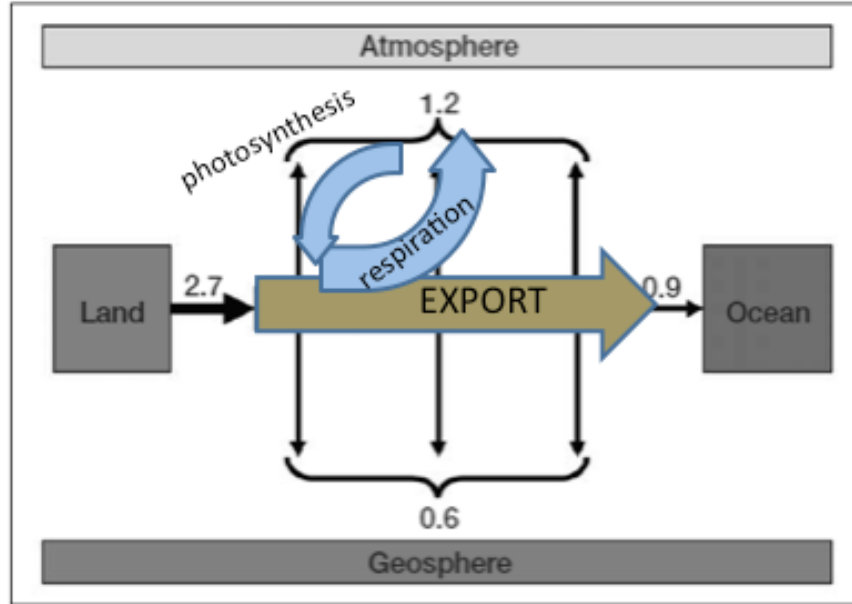


Figure 1.2 Figure adapted from Cole et al. 2007 with values in  $\text{Pg C yr}^{-1}$  describing the significance of inland waters to the global carbon cycle. The brown arrow describes lateral export of terrestrially derived carbon between land and the ocean. While  $2.7 \text{ Pg C yr}^{-1}$  is exported from the terrestrial biosphere, only  $0.9$  reaches the ocean. The remaining  $1.8 \text{ Pg C yr}^{-1}$  is either stored in sediment ( $0.6 \text{ Pg C yr}^{-1}$ ) or released as gases ( $\text{CO}_2 + \text{CH}_4$ ) along river networks. When measuring these fluxes in a watershed, it is crucial to take into account for the role of in-stream respiration (photosynthesis + respiration) on lateral and gaseous carbon export.

### 1.1.2 Role of Urban Infrastructure on Aquatic GHG Dynamics

*Chapter three examines the role of watershed management on  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{CH}_4$  emissions from urban headwater streams in Baltimore, MD.* In urban watersheds, streams and rivers are subject to a variety of stressors, which may influence biogeochemical cycling and contribute to hot spots of GHG emissions. At the watershed scale, managing excess nitrogen is a major challenge for water quality and  $\text{N}_2\text{O}$  production from excess N is likely. Leaking gravity-fed sewers are a key source of N in aging cities (Kaushal et al. 2011; Pennino et al. 2015; Fig. 1.2). Conversion of this excess N to  $\text{N}_2\text{O}$  is not accounted for in current IPCC methodology in the same way that indirect agricultural emissions are (Short et al. 2014; Strokal and Kroeze 2014; UNEP 2013). In addition to aging sanitary and stormwater pipes, many cities have also implemented

newer forms of stormwater management including wetland creation. Stormwater wetlands have been shown to reduce watershed N loading in numerous studies (e.g. Newcomer Johnson et al. 2014) however questions remain about both direct and indirect emissions of CH<sub>4</sub> and N<sub>2</sub>O *via* groundwater. The motivation for my second chapter was to understand how variations in urban infrastructure (wetlands vs. N loading) might influence aquatic GHG loads.

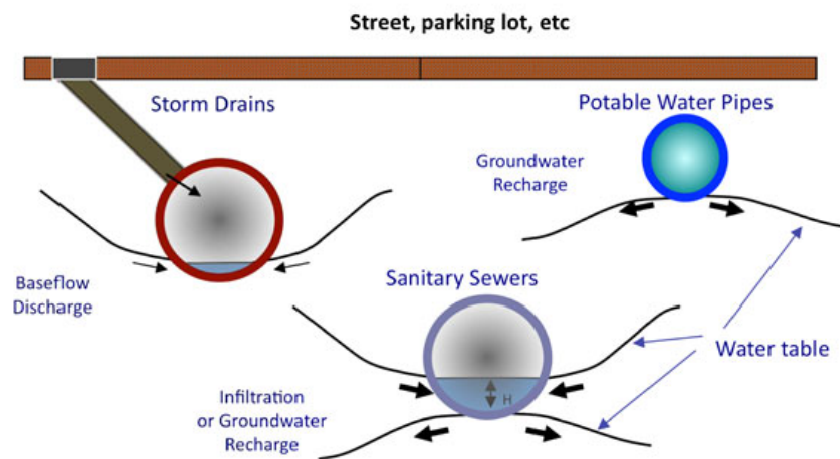


Figure 1.3 Adapted from Kaushal and Belt. 2012: Subsurface infrastructure alongside urban stream channels may influence N inputs.

### 1.2.3 Role of Climatic Variability and Vegetation Cover on Urban Soil GHG Emissions

*Chapter four examines the role of temperature, soil moisture, and vegetation cover on CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O emissions from urban soils in Baltimore, MD.* Urban lawns cover more area than any single irrigated crop in the United States (Milesi et al. 2005). Urban lawns are subjected to a suite of site- specific (nitrogen deposition, fertilizer, vegetation management) and climatic (drought, heat island) factors, which may influence carbon and nitrogen storage. Several studies (Raciti et al. 2011; Townsend-Small and Czimczik 2010; Kaye et al. 2004) have shown that urban lawns can accumulate carbon and nitrogen over time, however it is not clear what controls the duration and stability of these C and N sinks. By storing N, urban lawns are an important buffer for water quality.

Reductions in C and N storage may contribute to GHG emissions and/or significant N leaching into groundwater over time. The Baltimore Ecosystem Study Long Term Ecological Research station has monitored soil respiration, CH<sub>4</sub> consumption, and N<sub>2</sub>O fluxes from urban and rural forests as well as lawns for 15 years. Prior work at these sites has shown that CH<sub>4</sub> and N<sub>2</sub>O (Groffman and Pouyat 2009; Groffman et al. 2006; Costa and Groffman, 2013), however the overall global warming potential of these soils over annual timescales has not been fully examined for the entire record. This study examined the role of temperature sensitivity and soil moisture on fluxes in order to develop regional-scale estimations of annual soil GHG fluxes over time.

### 1.3 Study Questions

1.3.1 What is the role of seasonal and event-based hydrologic variability on transport downstream vs. transformations (metabolism) of carbon in a highly urbanized river?

1.3.2 Does urban infrastructure influence GHG fluxes and production in headwater streams, and how do emissions/production vary over space and time?

1.3.4 Does vegetation cover and warming alter temperature sensitivity, and GHG emissions from urban soils?

### 1.4 Scientific merit and contributions

Chapter two, '*Carbon Cycle of an Urban Watershed*', demonstrated that the contribution of in-stream productivity to aquatic CO<sub>2</sub> emissions is can be as high as 100% during seasonal low-flow conditions, but remains a smaller percentage (0-10%) during medium to high flow events. The remainder of CO<sub>2</sub> and DIC is from watershed sources, including weathering products, soil and root respiration transported *via* groundwater and

in-stream breakdown of terrestrial organic matter. These results further the scientific community's understanding of how terrestrial organic matter is transported and transformed carbon in urban waterways. Based on the results of this study, I developed a conceptual framework in which an increase in discharge causes urban streams to switch from 'transporters' to 'transformers' of terrestrial inputs and how this inflection point may vary among seasons.

Chapter three, *Influence of urban infrastructure on water quality and greenhouse gas dynamics in streams*, I found that nitrogen loading and wetland creation in watersheds influences CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O emissions from headwater streams. Streams with high NO<sub>3</sub><sup>-</sup> concentrations were located in watersheds with aging stormwater and sanitary infrastructure, and corresponded with high N<sub>2</sub>O. Headwaters draining new stormwater management and sanitary sewers had the lowest NO<sub>3</sub><sup>-</sup>, the highest DOC, and the highest CH<sub>4</sub> concentrations overall. Additionally, CO<sub>2</sub> was highly correlated with N<sub>2</sub>O and NO<sub>3</sub><sup>-</sup> suggesting that nitrogen additions may stimulate CO<sub>2</sub> production in waterways. This chapter shows how human activities can influence GHG emissions from streams, which contradict the current IPCC protocol for assuming that aquatic GHG fluxes have remained constant since pre-industrial times.

Chapter four, *Interactions between land cover and climate influence CO<sub>2</sub> CH<sub>4</sub>, and N<sub>2</sub>O fluxes from urban soils*, examined controls on GHG emissions from upland soils in the Baltimore region. I evaluated the role of various drivers (temperature, soil moisture, seasonality, and year) on CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O emissions from urban forests, rural forests, and suburban lawns. I modeled annual emissions and found that, in terms of net CH<sub>4</sub> and N<sub>2</sub>O emissions, suburban lawns had significantly higher global warming

potential than both rural and urban forests. CO<sub>2</sub> emissions were also significantly higher in lawns than rural forests, however, prior studies in Baltimore have shown that lawns accumulate organic carbon over time (Raciti et al. 2011). If this rate of carbon accumulation remains constant it would offset any global warming potential of lawns caused by increased N<sub>2</sub>O and CH<sub>4</sub> emissions. I scaled up soil GHG emissions and carbon accumulation estimates using spatial land cover data of forests and lawns, and estimate that soils store the equivalent of 0.33 Mg CO<sub>2</sub> ha<sup>-1</sup> yr<sup>-1</sup> on average throughout Baltimore County. This carbon sink is equivalent to 0.5% of anthropogenic emissions from the same county estimated during the study period (Brady and Fath 2008). I conclude that, while urban land cover and warming does to influence GHG budgets of lawns, the role of lawns as GHG sinks or sources is largely overshadowed by anthropogenic emissions.

## Chapter 2: Carbon Cycle of an Urban Watershed: Exports, Sources, and Metabolism

### 2.1. Previous publication of research

This research chapter was published in the journal, Biogeochemistry in October, 2015 (Smith and Kaushal 2015).

### 2.2. Abstract

Rivers transport and transform significant quantities of carbon to coastal zones globally. Urbanization and climate change impact the transport and transformation of carbon by altering hydrology, water temperatures, and in-stream metabolism rates. Changes in exports, sources, and metabolism of carbon influence ecosystem processes, food webs, and greenhouse gases. The present study characterized exports, sources, and metabolism of carbon in four urban watersheds using a combination of discrete stream chemistry measurements and continuous water-quality sensors. Over three years, watershed DOC exports in the Baltimore-Washington D.C. metropolitan area ranged from 9 to 23 kg ha<sup>-1</sup>yr<sup>-1</sup>. DIC exports ranged from 19 to 59 kg ha<sup>-1</sup>yr<sup>-1</sup>. Daily contributions from in-stream metabolism varied between -65 and 90% of DIC export depending on stream size and streamflow conditions. Negative contributions from metabolism occur on days when streams were autotrophic. All streams were heterotrophic during 60 to 87% of each year, but showed significant peaks in autotrophy during spring and summer. Differences in the timing and magnitude of peaks in springtime net ecosystem productivity were likely driven by varying light availability across streams of different sizes and riparian shading. CO<sub>2</sub> was consistently over-saturated with respect to the atmosphere on all sampling dates and was 0.25-2.9 mg C L<sup>-1</sup>.



Exports, sources, and metabolism of DOC and DIC showed strong predictable patterns across streamflow. These results support a new conceptual model for predicting carbon transport and transformation across changing streamflow and light availability (with impacts on sources and fluxes of DOC, DIC, and CO<sub>2</sub>). Overall, the results- based conceptual model suggest that urbanization accelerates the transition of streams from transporters to transformers of carbon across streamflow, with implications for timing and magnitude of CO<sub>2</sub> fluxes, river alkalization, and oxygen demand in downstream waters.

### 2.3 Introduction

Carbon transported by rivers provides a major source of energy for aquatic food webs, and is a significant component of the global carbon cycle (Perdue and Ritchie 2003; Cole et al. 2007; Battin et al. 2008; Moens et al. 2002; Middelburg and Nieuwehuize 1998). Approximately 2.7 Pg of carbon is exported from terrestrial to aquatic ecosystems globally. However, only 0.9 Pg of carbon reaches the ocean, while 1.2 Pg is respired as CO<sub>2</sub>, and 0.6 Pg is stored in sediments (Regnier et al. 2013). Changes in human activities related to agricultural liming, increased soil erosion, chemical weathering, and urban wastewater inputs have contributed significantly to accelerated transport of carbon from the land to ocean (e.g., Daniel et al. 2001; Raymond and Cole 2003; Cole et al. 2007; Tank et al. 2010; Kaushal et al. 2013; Regnier et al. 2013). Furthermore, riparian vegetation removal and nutrient loading from urban and agricultural landscapes may increase autochthonous carbon production (Mulholland et al. 2001; Bernot et al. 2010; Griffiths et al. 2013). Warming from climate change and urban heat islands has the potential to increase rates of organic carbon breakdown in rivers and

estuarine sediments (Neal et al. 1998; Daniel et al. 2001; Raymond and Cole 2003; Barnes and Raymond 2009; Kaushal et al. 2014b). The present study investigated how hydrologic variability and urbanization can alter the sources and metabolism of carbon exported by rivers.

Over decades, carbon cycling has been studied extensively in forested watersheds (e.g., McDowell and Fisher 1976; Sobczak et al. 2002). Controls on carbon export from forest watersheds can include climate, topography, soil carbon content, and the presence of wetlands (Hopkinson et al. 1998; Aitkenhead et al. 1999; Perdue and Ritchie 2003). These studies indicate that the quantity and quality of dissolved organic carbon (DOC) are important drivers of the ecological function of forest streams (Vannote 1980; Hopkinson et al., 1998). Streams naturally contain a mix of terrestrial (allochthonous) and in-stream (autochthonous) sources of dissolved organic matter (DOM), which contribute to watershed DOC export as particulate organic matter is leached or decomposed. Sources of terrestrial DOM include leachates or decomposed soil organic matter and leaf detritus. Autochthonous sources of DOM consist primarily of decomposed or leached algal, bacterial, and fungal biomass (Sinsabaugh et al. 1997; Webster and Meyer 1997). Previous studies have shown that hydrologic variability (e.g., Raymond and Saiers 2010) and stream metabolism (e.g., Tank et al. 2010) alter the relative proportions of terrestrial and in-stream-derived carbon in rural watersheds. However, impact of urbanization on exports, sources, and metabolism of terrestrial vs. in-stream sources of DOM remains unclear.

Urbanization increases the quantity of both natural (e.g., soil, leaves, algae) and anthropogenic (e.g., sewage, grass clippings) sources of organic matter, which may be

leached into DOM in streams and soils (Daniel et al. 2001; Newcomer et al. 2012; Kaushal et al. 2014a; Duan et al. 2014). Frequent flooding can increase inputs of natural particulate organic matter from riparian vegetation and soil erosion (Raymond and Saiers 2010; Imberger et al. 2011; Fraley et al. 2009), which also contribute to the DOM pool downstream through leaching and decomposition. Nutrient loading and tree canopy removal (which increases light availability) can stimulate autochthonous productivity (Mulholland et al. 2001). This contributes to the autochthonous DOM pool as this biomass decomposes over daily or seasonal timescales. Wastewater-derived DOM and nutrient inputs can enter streams *via* point sources such as wastewater treatment plant outfalls (e.g., Daniel et al. 2001; Barnes and Raymond 2009; Aitkenhead-Peterson et al. 2009; Edmonds and Grimm 2011) and nonpoint sources such as diffuse sewage pipe leakage and septic systems (Sickman et al. 2007; Kaushal et al. 2011). In addition, rising stream temperatures and salinization may influence rates of DOM leaching from soils and benthic sediments (e.g., Kaushal et al. 2005a; Aitkenhead Peterson 2009; Kaushal et al. 2010, Duan and Kaushal 2015). For instance, Duan and Kaushal (2013) found that warming increased DOC fluxes from streambed sediments, and previous studies have shown that road salt additions increases DOM leaching from soils through sodium dispersion and pH suppression (Green et al. 2008, Duan and Kaushal 2013).

Dissolved inorganic carbon (DIC = carbonate+ bicarbonate + CO<sub>2</sub>) is the dominant form of carbon exported from many rivers and streams globally (Meybeck 2003). Annual riverine DIC fluxes are comparable in magnitude to the terrestrial carbon sink (Cole et al. 2007). Several studies have shown that alkalinity of running waters, largely controlled by bicarbonate, is currently increasing in many watersheds (Raymond

and Cole 2003; Kaushal et al. 2013). Recent work suggests that long-term alkalization of streams and rivers can be an indicator of evolving water quality in cities over time due to human activities (Kaushal et al. 2014c, Kaushal et al. 2015). Potential drivers of river alkalization include agricultural liming, weathering of urban building materials, and a time-lag response of increased weathering due to acid rain (Raymond and Cole 2003; Kaushal et al. 2013; Hossler and Bauer 2013). Patterns of DIC and alkalinity in urban watersheds warrant further study due to its potential role in buffering coastal ocean acidification, aquatic primary production, and global aquatic carbon budgets (Cole et al. 2007, Kaushal et al. 2013). Several processes that offset terrestrial carbon storage produce DIC in streams and rivers, including mineral weathering, terrestrial soil and root respiration, and in-stream DOC mineralization (e.g., Berner et al. 1983, Hotchkiss et al. 2015). Dissolved CO<sub>2</sub> from terrestrial (soil and root) respiration contributes to the in-stream DIC pool *via* groundwater or shallow soil flowpaths (Jones and Mulholland 1997). Bicarbonate is produced when carbonate rocks dissolve in the presence of carbonic (or other) acid and when carbonic acid interacts with silicate rocks (Berner et al. 1983; Schnoor and Stumm 1986). The rates of various terrestrial processes vary widely with climate, vegetation, and underlying geology (Meybeck 2003). In-stream DIC (CO<sub>2</sub>) production *via* ecosystem respiration (ER = heterotrophic + autotrophic respiration) also varies widely in streams and is largely controlled by temperature, organic carbon loading, stream biota, and nutrients (e.g. Mulholland et al. 2001; Bernot et al. 2010; Tank et al. 2010). Urbanization has been suggested to increase export of DIC from anthropogenic sources such as building materials and wastewater treatment plant effluent (Daniel et al. 2001; Barnes and Raymond 2009; Zeng et al. 2010; Hossler and Bauer 2013).

Urbanization may also influence production of DIC *via* in-stream ER through heat island effects and increased DOC loading (Tank et al. 2010; Kaushal et al. 2014b). As DIC fluxes from streams and rivers continue to change globally, the aim of this study was understand how urbanization alters sources and fluxes. Specifically, I investigated how light availability, temperature, streamflow conditions influence DIC sources and export in urbanized watersheds. I also estimated the relative contribution of stream metabolism and terrestrial (soil/root respiration + weathering) processes to total DIC export from three watersheds on daily time scales over three years.

The impacts of urbanization on export, sources, and metabolism of carbon can evolve over time as watershed development practices alter hydrologic flow paths (Kaushal et al. 2014c). For example, urbanization often dramatically increases hydrologic response and peak streamflow conditions during storms due to impervious surfaces, riparian development, and subsurface drainage systems (e.g., Paul and Meyer 2001; Walsh et al. 2005; Kaushal and Belt 2012). The net effect of all these hydrologic alterations raises questions about the relative influence of in-stream *vs.* terrestrial controls on carbon quantity and quality. The objectives of this study were 1) to quantify inter-annual and intra-annual fluxes of DIC and DOC, and DOM sources from urban watersheds, 2) identify key environmental variables influencing carbon fluxes using a combination of *in situ* sensor and discrete measurements, and 3) to propose a conceptual model integrating the hydrologic and biological controls on C cycling in urban watersheds across streamflow. An improved understanding of the processes controlling transport, and transformation of carbon in urban watersheds across annual streamflow cycles is necessary to anticipate changes brought on by climate and land cover changes.

The overarching hypothesis was that urban streams shift from carbon transformers to transporters as streamflow increases, with resulting impacts on sources and fluxes of DOC, DIC, and CO<sub>2</sub>. Based on this hypothesis, the following specific predictions were tested: (a) urbanized watersheds export more DOC than minimally disturbed watersheds in similar climatic zones, (b) gross primary productivity (GPP) in nutrient-loaded and un-shaded streams would be elevated, causing dissolved matter quality to resemble recent autochthonous inputs more than terrestrial carbon sources, and (c) in-stream respiration contributes a significant portion of daily DIC fluxes compared with terrestrial sources. The resulting patterns were then used to develop a new conceptual model illustrating how streamflow and light availability can influence in-stream vs. terrestrial controls on transport and transformation of DIC, DOC, and CO<sub>2</sub>. An improved understanding of anthropogenic impacts on the sources, fluxes, and metabolism of carbon is essential for management of the coastal carbon cycle, organic nutrient cycling, contaminant transport, and increased river alkalization (e.g., Raymond and Cole 2003; Stanley et al. 2012; Kaushal et al. 2013; Kaushal et al. 2014c; Middleburg and Nieuwenhuize 1998).

## 2.4 Methods

### 2.4.1 Overview

This study investigated the hydrologic and metabolic controls on carbon cycling in an urban watershed over three years using a combination of stream chemistry measurements and continuous water quality sensor data. Discrete chemistry samples were used to characterize the sources and export of carbon in streams. High-frequency sensor data was used to model daily stream ecosystem metabolism and CO<sub>2</sub> fluxes from streams.

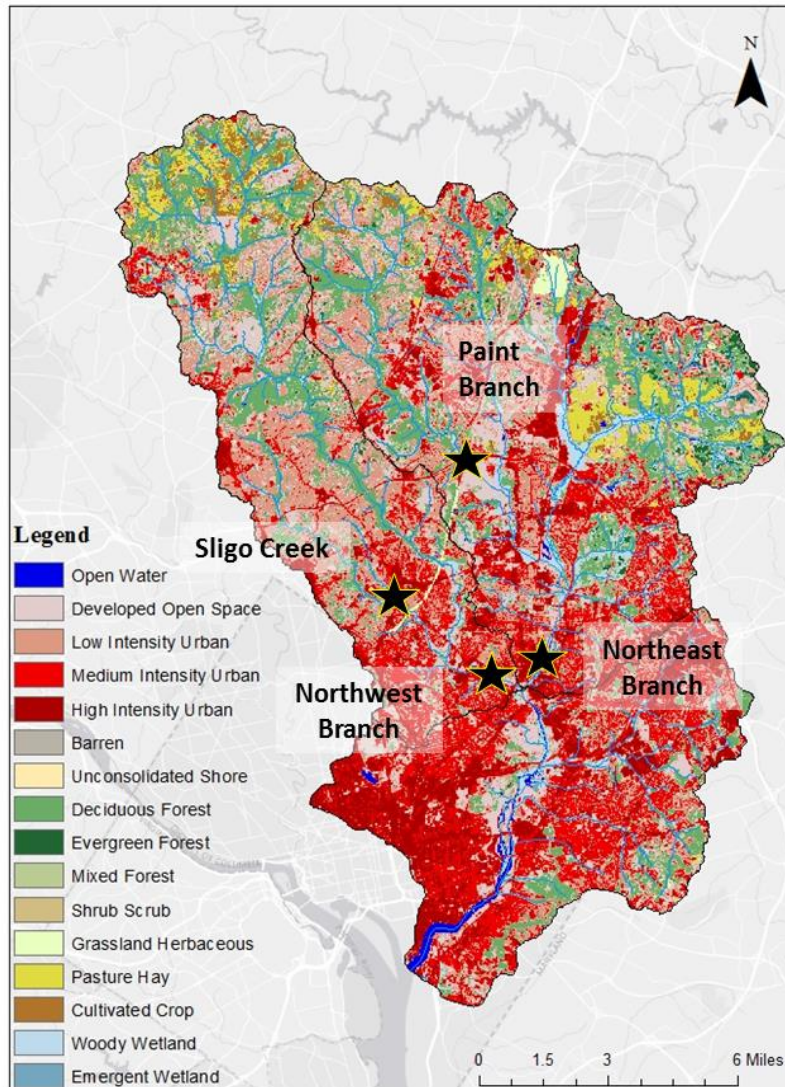


Figure 2.1 Map of the Anacostia watershed, located northeast of Washington D.C. Prominent red colors signify medium to high intensity urban cover, which dominates the lower reaches of the watershed. Greens and yellow signify forested and agricultural land. Stars denote the four U.S. Geological Survey gages sampled. Land cover data is from the 2006 National Land Cover Database (Fry et al. 2011).

#### 2.4.2 Site Description

The Anacostia River is a major tributary of the Potomac River, with a watershed draining 176 km<sup>2</sup> of the Piedmont and Coastal Plain geographic provinces in southeastern Maryland, USA and the northeastern portion of Washington D.C. (Fig. 2.1). Widespread clearing of forests and draining of wetlands for agriculture occurred between the 1700s and mid-1800s (Washington Council of Governments 2010), and urban land use spread quickly after the 1950s, with a major increase during the 1970s. The current land use distribution of the overall Anacostia watershed is: 45% residential, 30% undeveloped, 16% commercial or institutional, 4% agricultural, 4% industrial, and 1% mining (Fry et al. 2011). Efforts to reduce sediment and nutrient loads, biochemical oxygen demand, fecal coliform bacteria, trash, heavy metals, and organic contaminants are currently in progress as part of a comprehensive restoration initiative for the Anacostia. These efforts also contribute to progress toward meeting total maximum daily loads (TMDLs) for each sub-basin of the Chesapeake Bay (Maryland Department of Environment 2015). Numerous studies have taken place in this watershed evaluating nutrient dynamics and geochemistry (e.g., Huanxin et al. 1997; Langland et al. 2012; Miller et al. 2013; Connor et al. 2014), sediment sources (Devereux et al. 2010), suspended sediment loads (Yorke and Herb 1978; Miller et al. 2013), bacterial abundance (Miller et al. 2013), and organic contaminants (Foster et al. 2000).

The present study characterized sources and exports of carbon in four non-tidal tributaries of the Anacostia watershed in Maryland, which comprise 98% of river's flow at its convergence with the Potomac River. These tributaries include Paint Branch (PBCP), Sligo Creek (SLIGO), Northwest Branch (NWHV), and the Northeast Branch



(NERP). Paint Branch is nested within the Northeast Branch, and Sligo Creek is nested within the Northwest Branch. Sampling sites were co-located with continuous flow and water quality monitoring stations maintained by the U.S. Geological Survey (USGS). USGS maintains continuous flow data at all four sites, and water quality sensors at three of the four (SLIGO, PBCP, and NERP), which include dissolved oxygen, pH, specific conductivity, turbidity, and temperature. Water quality sensor measurements are collected at 5 or 15-minute intervals, and are continuously updated and available online (<http://waterdata.usgs.gov/nwis>). Details about sensor data collection, maintenance, and calibration are outlined in Miller et al. (2013). A summary of watershed characteristics is provided in Table 2.1.

**Table 2.1** Study sites including U.S. Geological Survey gage number, watershed name with 4-letter abbreviation below, watershed area, and percentage of each land use based on NLCD 2006 data (Fry et al. 2011). Watershed area and gage information can be found at <http://waterdata.usgs.gov/nwis>

| USGS Station ID | Station Name                  | Watershed Area (km <sup>2</sup> ) | Urban | Agriculture | Forest | Wetland |
|-----------------|-------------------------------|-----------------------------------|-------|-------------|--------|---------|
| 01649190        | Paint Branch<br>(PBCP)        | 21.1                              | 57    | 7.1         | 33     | 2.1     |
| 01649500        | Northeast<br>Branch<br>(NERP) | 117.2                             | 63    | 5.6         | 26     | 4.8     |
| 01651000        | Northwest<br>Branch<br>(NWHV) | 79.5                              | 66    | 7.6         | 24     | 1.5     |
| 01650800        | Sligo Creek<br>(SLIGO)        | 10.3                              | 88    | 0           | 12     | 0.29    |

#### 2.4.3 Water Chemistry Measurements

Discrete stream chemistry samples were collected every two weeks between October 2011 and October 2014. Samples were collected in acid-washed 500-mL high-density polyethylene bottles. Field samples were transported on ice to the laboratory where they were filtered through a pre-combusted Whatman 0.7-micron glass fiber filter. A subset of filtered water to be analyzed for optical properties of dissolved organic matter

(DOM) was stored into a pre-combusted glass amber vial and refrigerated until analysis within two weeks. Analyses of DOC, DIC, and total dissolved nitrogen (TDN) were performed on a Shimadzu Total Organic Carbon Analyzer (TOC-272 V CPH/CPN; Shimadzu, Columbia, Maryland, USA). I ran samples for DIC immediately after filtering following the Shimadzu IC method. I analyzed DOC and TDN following the Shimadzu NPOC (nonpurgeable organic carbon) and TN methods respectively (e.g., Kaushal and Lewis 2005). I selected the NPOC rather than the alternative TC-IC method because it is not sensitive to variations in DIC and thus less prone to significant overestimation of DOC than TC-IC (Findlay et al. 2010).

#### 2.4.4 Dissolved Inorganic Carbon Speciation

CO2SYS, a model of the inorganic carbonate system in freshwater and marine waters (Pierrot et al. 2006), was used to determine the abundance of individual dissolved inorganic carbon species ( $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{CO}_2$ ,  $\text{OH}^-$ , and alkalinity) using measured values of DIC, pH, and temperature.

#### 2.4.5 Estimation of Dissolved Carbon and Nitrogen Export

Discrete samples for DOC, DIC, and TDN concentrations were collected across a broad range of streamflow conditions in each stream during three years. Relationships between discrete concentration measurements and continuous discharge were optimized using a FORTRAN-based program, LOADEST, developed by (Runkel 2004). This approach allowed estimation of daily, monthly, and annual watershed exports ( $\text{kg ha}^{-1}\text{yr}^{-1}$ ) for each solute.

#### 2.4.6 Characterization of Dissolved Organic Matter Sources

Optical properties of stream water were measured in order to evaluate the contributions of terrestrial and aquatic sources of DOM. Upon filtering, samples were stored in pre-combusted amber vials at 4°C for up to two weeks prior to optical measurements. Many naturally occurring DOM compounds will fluoresce, or emit low-energy light following excitation by a higher energy light source. The emission spectra produced in response to a range of excitation wavelengths can be used to evaluate the relative abundance of DOM with terrestrial origin (humic soil/plant) and aquatic origin (periphyton/algae) (Zsolnay et al. 1999; Ohno 2002; Huguet et al. 2009). I used a FluoroMax-4 Spectrofluorometer (Horiba Jobin Yvon, Edison NJ, USA) to measure excitation-emission matrices (EEMs) of each sample. I then calculated the humification (HIX) and recent autochthonous contribution (BIX) indices of DOM quality from the EEM of each sample. HIX is defined as the ratio of emission intensity of the 435-480 nm region of the EEM to the emission intensity of the 300-345 nm region of the EEM at the excitation wavelength of 254 nm (Zsolnay et al. 1999; Ohno 2002). BIX is defined as the ratio of fluorescence intensity at the emission wavelength 380 nm to the intensity emitted at 430 nm at the excitation wavelength of 310 nm (Huguet et al. 2009). HIX and BIX are both used to differentiate between DOM with more humic/terrestrial character and DOM of more autochthonous character. HIX varies from 0 to 1, with higher values signifying high-molecular weight DOM molecules characteristic of humic terrestrial sources. Lower HIX values are driven by low molecular weight DOM of bacterial or aquatic origin (Zsolnay et al. 1999). Conversely, BIX values (<0.7) represent terrestrial sources, and higher BIX (0.8 to 0.1 and >0.1) represent algal or bacterial sources (Huguet et al. 2009).

HIX and BIX are calculated for each sample EEM after correcting the EEM for (1) emissions from a blank sample, (2) inner-filter effects from Raman scattering, and (3) absorbance of wavelengths 200-800 nm. Analyses of fluorescence indices were carried out using Matlab (version R2012a).

#### 2.4.7 Estimating Continuous Ecosystem Metabolism

Continuous ecosystem metabolism was measured for daily sensor data, using a Bayesian oxygen mass-balance model (BaMM) developed by Holtgrieve et al. (2010). The model is based on the principle that the amount of dissolved oxygen in a stream is a result of three main processes: (1) GPP, (2) ER, and (3) reaeration/gas exchange with the atmosphere (Odum 1956). Continuous monitoring of dissolved oxygen over diurnal cycles allows for estimation of daily stream metabolism based on the general mass-balance model of oxygen described by the following equation

$$\text{Eq. 2.1} \quad \frac{dO_2}{dt} = \frac{[k([O_{2,sat}] - [O_2]) - R + P]}{D}$$

where  $O_{2sat}$  is the oxygen concentration at equilibrium with the atmosphere ( $\text{mg O}_2 \text{ m}^{-3}$ ) and  $O_2$  is the measured  $O_2$  concentration. R and P are respiration and photosynthesis rates respectively ( $\text{mgO}_2 \text{ m}^{-2} \text{ hr}^{-1}$ ),  $k$  is gas transfer velocity ( $\text{m hr}^{-1}$ ) and D is water depth (m). GPP rates are modeled based on  $O_2$  saturation data and light availability, and ER is based on  $O_2$  under-saturation and temperature over diurnal periods.

Model input data included continuous measurements of dissolved oxygen, temperature, and discharge made available by USGS at the SLIGO, PBCP, and NERP gaging stations. Model time steps varied from 5 to 15-minute increments across sites. Photosynthetically active radiation (PAR) data was measured at the nearby USDA Beltsville Agricultural Research Center (USDA Agricultural Research Service 2014).

Daily rates of GPP, ER, and net ecosystem production (NEP=GPP-ER) were converted to  $\text{g C m}^{-2} \text{ day}^{-1}$  using respiration quotient of 1. Several studies have made this assumption in order to infer connections between carbon and oxygen cycling in stream metabolism studies (Jones and Mulholland 1998; Hall and Tank 2003; Demars et al. 2011).

#### 2.4.8. Gaseous and Dissolved Inorganic Carbon Fluxes

Multiple processes at both the stream channel and watershed-scale contribute to daily downstream DIC fluxes. In-channel processes include GPP, ER, and exchange of  $\text{CO}_2$  between the water surface and atmosphere. DIC from dissolution of carbonate minerals (e.g. calcite, aragonite) as well as soil and root respiration in upland soils are delivered to the stream *via* soil and groundwater flowpaths. A simplified mass-balance model of inorganic carbon fluxes from watersheds was used as follows:

$$\text{Eq. 2.2} \quad \text{WS} - \text{NEP} * \text{A} = \text{CO}_{2\text{F}} * \text{A} + \text{DIC}_{\text{F}}$$

where WS is the total flux of watershed sources (soil respiration + weathering) into the stream (grams/day), NEP is GPP-ER ( $\text{g C m}^{-2} \text{ day}^{-1}$ ). A is stream surface area ( $\text{m}^2$ ) above each stream gage.  $\text{CO}_{2\text{F}}$  is the flux of  $\text{CO}_2$  from stream to atmosphere ( $\text{g C m}^{-2} \text{ day}^{-1}$ ).  $\text{DIC}_{\text{F}}$  is the daily DIC flux ( $\text{g C day}^{-1}$ ) modeled using LOADEST. NEP,  $\text{CO}_{2\text{F}}$ , and  $\text{DIC}_{\text{F}}$  were estimated using measured data, and determined WS by difference. Surface area (A) was estimated based on flow lines using the EPA WATERS dataset (EPA WATERS, 2015), and measured mean wetted width from Google Earth imagery (Google Earth, 2015). Daily net consumption (or production) of DIC by NEP ( $\text{g C stream}^{-1} \text{ day}^{-1}$ ) was calculated by assuming that NEP rate was spatially consistent within the stream channel upstream of each gage. Positive daily NEP signified net DIC production and negative

NEP (or net respiration) signified net DIC production over a diurnal cycle.  $CO_{2F}$  ( $g\ C\ m^{-2}\ day^{-1}$ ) was calculated using equation 2.3

$$Eq. 2.3 \quad CO_{2F} = K_{CO_2}(CO_{2w} - CO_{2eq})$$

where  $CO_{2w}$  is the  $CO_2$  concentration in the water column ( $CO_2\ g\ C\ m^{-3}$ ) and  $CO_{2eq}$  is the  $CO_2$  concentration in water if it were in equilibrium with the atmosphere. Daily mean  $CO_{2w}$  concentration were estimated by running the LOADEST model separately with mean daily DIC concentration estimates. CO2SYS model was then used to estimate mean daily  $CO_{2w}$  with modeled DIC and measured daily temperature, depth and pH from each gaging station (Pierrot et al. 2006). I determined mean daily  $CO_{2eq}$  using equations in Weiss (1974) assuming barometric pressure of 1 atm and atmospheric mixing ratio of 350ppm  $CO_2$ .  $K_{CO_2}$  is the gas exchange velocity, with units of  $m\ day^{-1}$  for  $CO_2$  at ambient stream temperature. I estimated daily average gas exchange of oxygen at 20C ( $K_{20}$ ) using the BaMM model (Holtgrieve et al. 2010). I corrected daily oxygen  $K_{20}$  values for differences in solubility between  $CO_2$  and  $O_2$  using the ratio of their Schmidt numbers (Wanninkhof et al. 1992),

$$Eq\ 2.4 \quad K_{CO_2} = K_{O_2} (Sc_{CO_2} / Sc_{O_2})^n$$

where  $Sc_{CO_2}$  and  $Sc_{O_2}$  are Schmidt numbers for  $CO_2$  and  $O_2$  respectively. The exponent,  $n$  is set to  $-2/3$  because this value corresponds to smooth (rather than  $-1/2$  for choppy) water surfaces (Wanninkhof et al. 1992).  $K_{20}$  was converted to  $K_T$  based on relationships described in Elmore and West (1961).

$$Eq.2.5 \quad K_T = K_{20}*(1.0241)^{T-1}$$

Estimates of  $CO_2$  flux in this study are likely conservative because  $CO_2$  is based on DIC measured during daytime hours and do not account for diurnal lows in GPP. An

unknown portion of CO<sub>2</sub> from nighttime respiration may be lost to the atmosphere and thus unaccounted for with this analysis. In this case, this study would have also underestimated the contribution of DIC from watershed sources in the mass balance model (eq. 2.2). Another assumption was that CO<sub>2</sub> concentrations and flux rates estimated at each gage were representative of the total stream network upstream of that point. It must also be acknowledged that a small amount of CO<sub>2</sub> may have been lost prior to DIC analysis during filtration.

## 2.5 Results

### 2.5.1 Streamflow Variability

Study sites varied in mean annual discharge. Mean annual discharge across the three study years was lowest at SLIGO, with a range of 0.19 – 0.22 m<sup>3</sup> s<sup>-1</sup> during the study period, followed by PBCP (0.31 -0.38 m<sup>3</sup> s<sup>-1</sup>), then NWHV (1.22- 1.57m<sup>3</sup> s<sup>-1</sup>), and NERP (2.00- 2.76 m<sup>3</sup> s<sup>-1</sup>). Baseflow varied significantly among seasons (p<0.05), with the annual minimum occurring in early fall and maximum occurring during late winter/early spring, due to seasonal fluctuations in the water table with evapotranspiration (Fig. 2.2).

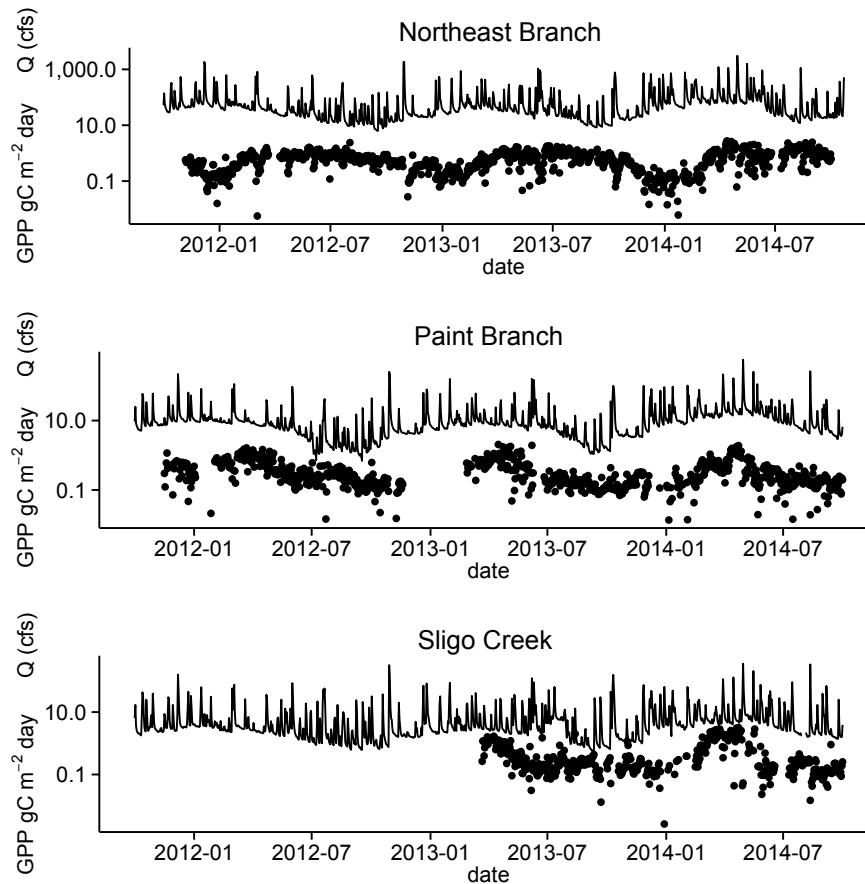


Figure 2.2 Time-series of continuous measurements of streamflow and Gross Primary Production (GPP) for Sligo Creek, Northeast Branch, and Paint Branch. Both streamflow and GPP show seasonal variability with leaf-out processes. Seasonal variations in GPP are driven by light availability during leaf-out and seasonal changes in discharge are driven by evapotranspiration following leaf-out.

### 2.5.2 Annual Exports of Carbon and Nitrogen

Carbon export varied widely across sites and years. The range of DIC export for all four sites and three years was 22-84 kg C ha<sup>-1</sup>yr<sup>-1</sup>, and the range of DOC exports was 8 - 40 kg C ha<sup>-1</sup> yr<sup>-1</sup> (Table 2.2). TDN export was less variable, with a range of 2.8 - 9.0 kg N ha<sup>-1</sup> yr<sup>-1</sup>. TDN export was also less responsive to changes in runoff (Fig. 2.3a) compared to DIC and DOC. PBCP had the lowest annual exports of: DIC (22-37 kg C



ha<sup>-1</sup> yr<sup>-1</sup>), DOC (8-16 kg C ha<sup>-1</sup> yr<sup>-1</sup>), and TDN (3-6 kg N ha<sup>-1</sup> yr<sup>-1</sup>). SLIGO had the highest annual DIC export in all years (50-84 kg C ha<sup>-1</sup> yr<sup>-1</sup>). DOC exports were variable across years for all sites. SLIGO had the highest DOC export in two out of three years. Concentrations of DOC and DIC were significantly correlated with mean daily discharge at three out of four sites (p-values = 2x10<sup>-7</sup>- 1x10<sup>-3</sup>, r<sup>2</sup>= 0.11-0.38). DOC showed a positive log-linear relationship with discharge, whereas DIC showed a log-linear negative relationship at three of the four sites (Fig. 2.3b).

Table 2.2 Annual area-normalized export (kg ha<sup>-1</sup>yr<sup>-1</sup>) of dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), and total dissolved nitrogen (TDN) by water year for four stream sites in the Anacostia watershed.

| Site  | Water year | DIC  | DOC  | TDN |
|-------|------------|------|------|-----|
| PBCP  | 2011-2012  | 22.5 | 8.4  | 3.3 |
|       | 2012-2013  | 23.2 | 12.3 | 2.9 |
|       | 2013-2014  | 37.7 | 17.0 | 6.0 |
| SLIGO | 2011-2012  | 50.1 | 17.3 | 3.9 |
|       | 2012-2013  | 57.4 | 24.1 | 4.2 |
|       | 2013-2014  | 83.6 | 40.1 | 9.0 |
| NWHV  | 2011-2012  | 28.5 | 13.8 | 3.1 |
|       | 2012-2013  | 43.3 | 23.2 | 3.8 |
|       | 2013-2014  | 64.3 | 38.8 | 6.6 |
| NERP  | 2011-2012  | 25.3 | 19.4 | 2.8 |
|       | 2012-2013  | 30.9 | 21.7 | 2.8 |
|       | 2013-2014  | 48.2 | 38.9 | 5.8 |

### 2.5.3 Carbonate System

CO<sub>2</sub> concentration was negatively correlated with TDN at SLIGO and positively correlated with DOC and SLIGO and NERP. CO<sub>2</sub> concentration was also positively correlated with temperature at SLIGO (p<0.01, r<sup>2</sup>=0.30). GPP and NEP were both negatively correlated with CO<sub>2</sub> concentration at SLIGO (p<0.01, r<sup>2</sup>=0.58 and 0.61), but

not at the other two sites (PBCP, NERP). CO<sub>2</sub> concentration was not correlated with discharge at any site.

#### 2.5.4 Spatial and Temporal Variability in Dissolved Organic Carbon Sources

The index of recent autochthonous inputs (BIX) was negatively correlated with discharge at all sites (p-values=  $1.2 \times 10^{-6}$  to  $2.0 \times 10^{-3}$ ,  $r^2 = 0.14$  to  $0.43$ ), which suggests a shift from

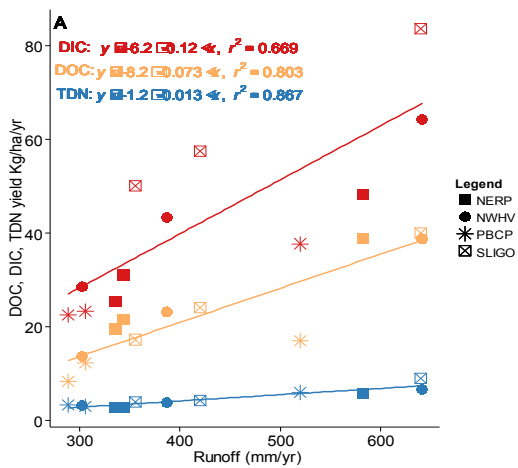
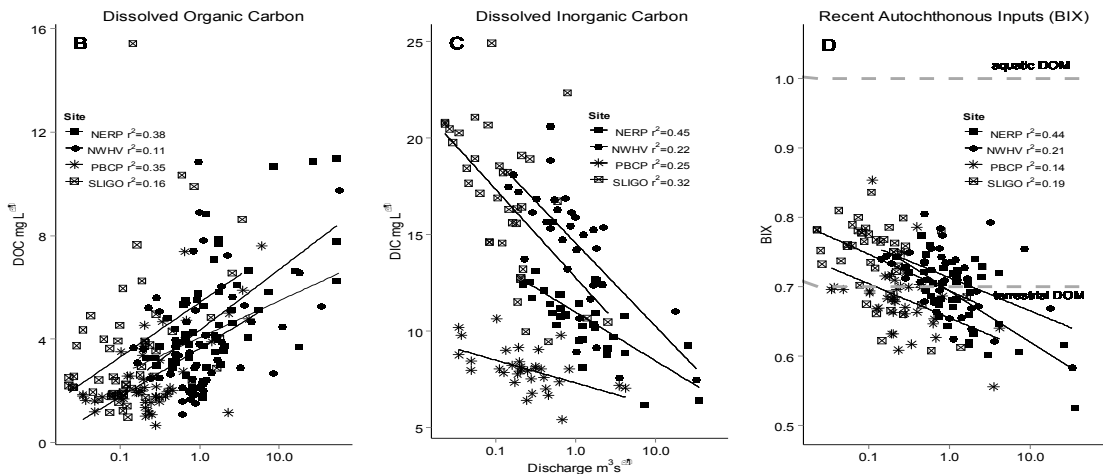


Figure 2.3 Scatterplots showing relationships between (a) DOC and DIC export ( $\text{kg ha}^{-1} \text{yr}^{-1}$ ) vs. total annual runoff ( $p < 0.01$  for all sites) and (b) mean daily discharge vs. DOC, DIC, and Index of Recent Autochthonous Inputs (BIX)



aquatic to terrestrial organic matter with increasing streamflow (b). The humification index (HIX) and SUVA<sub>254</sub> were not correlated with discharge at any site, however. BIX was also significantly different among sites, with the highest values at SLIGO and lowest median value at PBCP. Higher values of BIX ( $>1$ ) are expected to be indicative of

aquatic production, and low values (0.6-0.7) are expected to be indicative of terrestrial organic matter sources (Huguet et al. 2009). BIX values in this study mainly fell within the terrestrial range, with a minimum value of 0.52 and a maximum of 0.85 (Fig. 2.3b).

#### 2.5.5 Continuous Ecosystem Metabolism

Daily metabolism rates were estimated for 466 days at SLIGO (between March, 2013 and October, 2014), 785 days at PBCP (between October, 2011 and October, 2014), and 953 days at NERP (between October, 2011 and October, 2014). Mean daily GPP estimates for the entire period at SLIGO, PBCP, and NERP were 0.49, 0.38, and 0.66 g C m<sup>-2</sup>d<sup>-1</sup>, respectively. Mean daily ER (negative sign convention) estimates were -0.76 (SLIGO), -0.73 (PBCP), and -0.88 g C m<sup>-2</sup>d<sup>-1</sup> (NERP). NEP was < 0 for 75% of measured days at SLIGO, 84% of measured days at PBCP, and 71% of measured days at NERP. Peaks in GPP were evident at all sites, resulting in periods of autotrophy (NEP>0) during the spring and early summer (Fig. 2.2). Seasonal variability in GPP was primarily influenced by day length and light availability (Fig. 2.4). GPP was related to streamflow in a parabolic fashion, with the highest GPP rates corresponding with medium discharge conditions at each site (Fig. 2.5). There were short-term declines in GPP following storms including Hurricane Sandy, a major hydrologic event during the study period (Fig. 2.6); but day length and riparian shading availability appeared to be more important over longer seasonal and annual time scales (Fig. 2.4). The duration of springtime peaks in GPP were greatest in the stream with a large, open channel (NERP) and lower in the two more narrow streams, which had greater riparian vegetation cover (SLIGO and PBCP) (Fig. 2.3). ER was primarily influenced by seasonal variations in temperature and GPP (Fig. 2.7).

Daily GPP rates were positively correlated with TDN at two of the three sites (PBCP and SLIGO:  $p < 0.001$ ,  $r^2 = 0.37$ ,  $n = 21$ ; and  $p < 0.001$ ,  $r^2 = 0.76$ ,  $n = 9$  respectively). ER was also positively correlated with TDN at SLIGO ( $p < 0.001$ ,  $r^2 = 0.47$ ,  $n = 9$ ). DIC and DOC did not show significant relationships with GPP or ER for sampling dates with coinciding chemistry measurements and ecosystem metabolism ( $n = 19$ ).

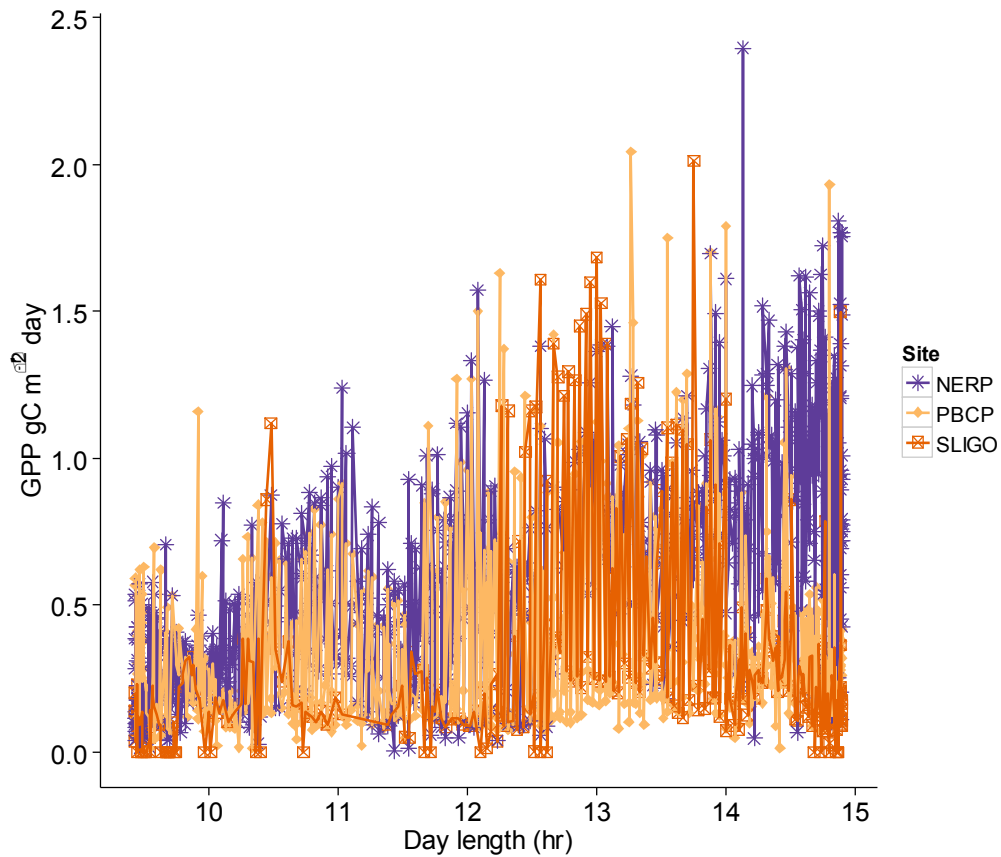


Figure 2.4 Continuous Gross Primary Production vs. day length for three stream sites. Orange and yellow colors show data from smaller shaded stream sites (SLIGO, PBCP), and purple lines are from open-channel river site (NERP)

#### 2.5.6 Gaseous and Dissolved Carbon Fluxes

Using a simplified mass balance model of the stream/watershed DIC budget, DIC inputs to the water column were separated into two categories: ‘net stream respiration’

and ‘watershed sources’ (Eq. 2.2). In this model, ‘net stream respiration’ was defined as ER-GPP, or -NEP. Net stream respiration accounted for less than 0% of DIC inputs on days when NEP was positive, and thus watershed inputs account for more than 100% of total export (downstream DIC + CO<sub>2</sub> emissions). The percent contribution of total DIC inputs from net stream respiration varied from -65 to 90% across streams and dates, and the percent contribution from watershed inputs also varied widely (10 to 165%). The mean percentage of inputs from net stream respiration across PBCP, SLIGO, and NERP were 13.4%, 13.2%, and 3.4% respectively. Percent inputs by net stream respiration had a significant negative, log-linear relationship with streamflow at both PBCP and SLIGO ( $r^2 = 0.22, 0.23$ ; p-values < 0.01) (Fig. 2.8). No such relationship existed at NERP, and NEP was generally positive during low-flow conditions at this site.

The percent of inorganic C outputs from gaseous (CO<sub>2</sub>) and fluvial (DIC) fluxes from the stream network was also estimated. Daily fluxes were dominated by fluvial DIC export which contributed between 93 and 102% of total export on all dates. Fluvial export exceeding 100% signifies dates when NEP > 0. The range of areal CO<sub>2</sub> fluxes was -2.67 to 25 g C m<sup>-2</sup> day<sup>-1</sup> across sites and dates, where negative values signifies uptake of CO<sub>2</sub> by the water column. These fluxes comprised the remainder of total inorganic carbon output (-2 to 7%) from the stream network.

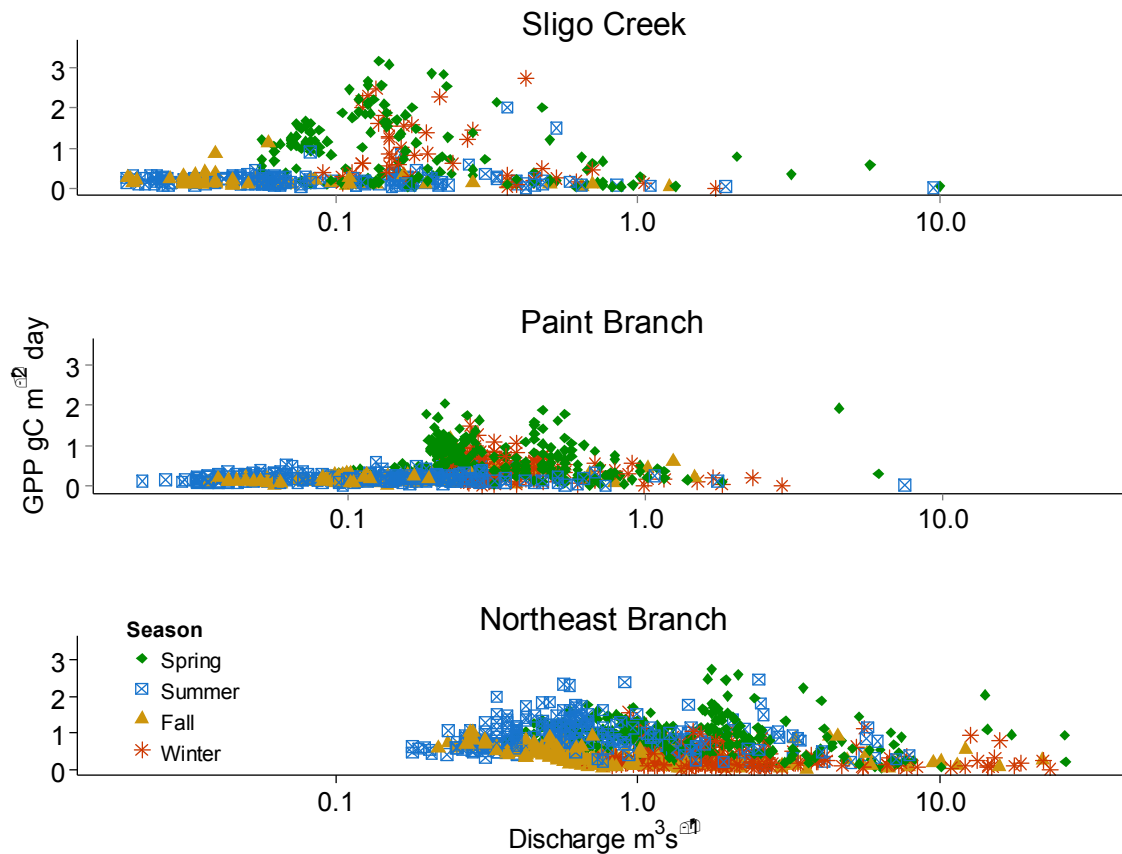


Figure 2.5 Relationships between Gross Primary Production (GPP) and streamflow across four seasons at three sites. Sligo Creek and Paint Branch are small streams with significant riparian shading, and the Northeast Branch is a larger, channelized tributary of the Anacostia River

## 2.6 Discussion

### 2.6.1 Urban Streams as Transporters vs. Transformers across Streamflow

The role of urban streams as biologically active ecosystems vs. passive hydrologic transporters of carbon and nutrients is an active source of investigation (Kaushal and Belt 2012). Urban streams have historically been characterized hydrologically by their flashy and frequent ‘transporting’ flow events (e.g. Leopold 1968; Paul and Meyer 2001).

However, a growing body of work has shown that urban streams are also dynamic

biological systems, which transform watershed carbon and nutrient inputs (Newcomer Johnson et al. 2014, Duan et al. 2014; Kaushal et al. 2014b). Globally, river and stream ecosystems act as both transporters of terrestrial organic matter to coastal areas (Middelburg and Nieuwenhuize 1998), and bioreactors that transform organic matter into CO<sub>2</sub> along their hydrologic flowpaths (del Giorgio and Pace 2008). As population growth continues, the extent to which urban aquatic ecosystems transform terrestrial organic matter inputs has direct implications for global and regional carbon budgets (Cole et al. 2007; Aufdenkampe et al. 2011), as well as water quality and ecosystem processes (Stanley et al. 2012; Newcomer et al. 2012).

Streamflow variability was the primary driver of carbon transport from urban watersheds in this study. Light availability also influenced the timing of peaks in net ecosystem production (NEP) and net stream respiration (-NEP). Based on the empirical results were used to develop a streamflow-based conceptual model. This conceptual model demonstrates the ways in which organic and inorganic carbon exports, sources, and metabolism can vary with streamflow across an urban watershed (Fig. 2.9). The model illustrates how the concentration of DOC increased and DIC decreased with increasing streamflow. The conceptual model demonstrates how dominant sources of DIC and DOC transition from in-stream to terrestrial sources at moderate to high flow conditions. Additionally, GPP varied expectedly with season as well as with streamflow. Periods of high GPP (corresponding with positive NEP) occurred during low to moderate streamflow conditions. GPP and ER were both at their lowest during high streamflow in all streams. In smaller streams with riparian canopies, GPP was also low during summer

baseflow. Low streamflow conditions are driven in part by seasonal evapotranspiration by riparian trees and thus correspond with shading and reduced in-stream GPP (Fig. 2.9).

#### 2.6.2 Urban Streams as Transporters: Terrestrial Inorganic Carbon Contributions

DIC was the dominant form of carbon exported in this study, which originated primarily from watershed sources (terrestrial weathering + soil respiration). Urbanization has been shown to influence terrestrial DIC loading to streams from both natural and anthropogenic sources (Barnes and Raymond 2009; Lu et al. 2014). Natural sources include dissolved CO<sub>2</sub> from soil respiration and products of chemical weathering. Novel anthropogenic sources may include building materials and wastewater. In the present study, the range in mean DIC concentrations (8, 10, 16 mg C L<sup>-2</sup>) from streams draining predominantly silicate-based lithology (quartz-feldspar schist) of the Atlantic Piedmont is high compared to pristine streams draining non-carbonate lithology (Dicken et al. 2008; Meybeck 2003).

Small portions of the Northeast Branch of the Anacostia watershed drain the Atlantic Coastal Plain, which may constitute additional DIC sources from carbonate deposits to downstream portions at the Northeast Branch site. Urbanization may also play a role in elevating DIC sources from the landscape through human-accelerated weathering of building materials and nonpoint sewage sources (Kaushal et al. 2013, 2014c). Several studies using carbon isotope tracers have shown correlations between urban land cover and DIC from bedrock (Zeng et al. 2010; Connor et al. 2014; Barnes and Raymond, 2009; Lu et al. 2014; Hossler and Bauer 2013), which suggest that urbanization may mobilize older, previously stable carbon reservoirs. For instance, Lu et al. (2014) found that DIC in urban headwater streams of Virginia originated primarily



from older bedrock weathering, compared to DIC in forested watersheds (which represented more recent primary production). Numerous studies have also shown that wastewater treatment plants contribute to watershed DIC fluxes (e.g. Hossler and Bauer 2013). The present study and others show that DIC can be elevated in urban streams without WWTPs as well, however. Additionally, previous work has shown long-term increasing alkalinity trends in the Anacostia watershed and other nearby urban watersheds, where there are minimal natural carbonate sources suggesting the importance of anthropogenic DIC sources (Kaushal et al. 2013; Prasad and Kaushal, 2013).

#### 2.6.3. Urban Streams as Transporters: Organic Carbon Contributions

Streamflow has a major influence on DOC concentrations and sources in both forested and urban watersheds (McDowell and Likens 1988; Hook and Yeakley 2005; Raymond and Saiers 2010; Stanley et al. 2012; Kaushal et al. 2014a). Forested streams often have positive concentration vs. discharge (C: Q) relationships as saturated soil and leaf leachates are delivered to the stream during precipitation events (Inamdar et al. 2013). Positive C: Q relationships as well as a decreased signal for ‘recent autochthonous inputs index’ (BIX) within increased flow suggest that terrestrial sources of DOC become more important with increasing streamflow, whereas in-stream organic matter may be more important at low streamflow. Impervious surfaces and storm drains may have an important role in delivery of terrestrial organic matter to urban streams. Hook and Yeakley (2005) found significantly higher DOC concentration in stormflow (median  $3.5 \text{ mg C L}^{-1}$ ) vs. baseflow (median  $2.0 \text{ mg C L}^{-1}$ ) in an urban stream in Portland, OR and estimated that 26 to 30% of DOC during came from storm drains. Additionally, Hope et al. (2004) found significant DOC loading from paved surfaces in Arizona, following long

periods of accumulation between rainfall events. In temperate watersheds, storm drains and gutters may be significant sources of organic matter (Kaushal and Belt 2012). Hobbie et al. (2013) found that this ‘gutter subsidy’ of leaf detritus contributes significantly to stormwater N and P loads in St. Paul, Minnesota. Results from the present study show evidence to support a similar mechanism in the Anacostia River, warranting further study on the role of storm drains as flowpaths impacting terrestrial carbon export from urban watersheds.

The processes that increase vs. decrease DOC fluxes from wastewater, soil, and vegetation management vary across cities. Fluxes and sources also vary spatially within watersheds along the continuum of light availability between headwaters and large open channels (Vannote et al. 1980; Kaushal et al. 2014a), and over time with changing streamflow conditions (Daniel et al. 2001; Duan et al. 2014). Currently, few studies have estimated DOC exports over annual timescales in urban watersheds. DOC exports in this study varied from 8.4 to 40.1 kg C ha<sup>-1</sup> yr<sup>-1</sup>, which is within the typical range estimated in temperate forests (i.e., 5 to 57 kg C ha yr<sup>-1</sup>) (e.g., McDowell and Likens 1988; Fahey et al. 2005a; Raymond and Saiers 2010 (and citations within); Hossler and Bauer 2013). Conversely, Sickman et al. (2007) found significant increases in TOC (DOC+POC) export (10 to 121 kg C ha<sup>-1</sup> yr<sup>-1</sup>) with urbanization in the Sacramento River watershed. Their study attributed 60% of urban C export to WWTP effluents, which were absent from the present study. Sickman et al. (2007) also attributed the remaining 40% of urban C sources to leaching of older soils in urban areas. Similarly, Aitkenhead-Peterson et al. (2009) reported exceptionally high mean annual DOC concentrations (20 to 52 mg C L<sup>-1</sup>) in urban streams with and without WWTP effluent in Texas, and attributed elevated DOC

to soil leachates from irrigated turf grass. These studies suggest that urban soils contribute significantly to urban DOC loads, regardless of wastewater inputs. Compared with other urban watersheds, the relatively low annual DOC concentrations and exports that reported here may be partially explained by the lack of WWTP outfalls.

#### 2.6.4. Stream Metabolism: Shifts in Urban Streams from Transporters to Transformers

The relative contribution of in-stream vs. terrestrial or anthropogenic sources to organic carbon fluxes is highly variable across watersheds of differing biomes and urban land cover (Hopkinson et al. 1998; Tank et al. 2010). In temperate forested streams, terrestrial sources often dominate DOM export (Fisher and Likens 1973), while in-stream processes have been shown to dominate DOM export in arid (Jones, 1997) and grassland streams (Young and Huyrn 1996). In the present study, indices of in-stream organic matter (BIX) decreased with streamflow, which suggests that terrestrial sources became more dominant as streamflow increased. Metabolism measurements show peaks of autotrophy during periods of seasonal light availability, suggesting that in-stream organic matter sources may be significant during low to moderate flow conditions. Nutrient enrichment and vegetation removal influence autotrophic productivity in urban streams (Taylor et al. 2004; Catford et al. 2007), and leached or decomposing algae may contribute to increased overall lability of the DOM pool. Duan et al. (2014) found this to be the case, as leached bacterial and algal-based carbon dominated the DOM pool of channelized urban streams in Texas. Even at high streamflow, Duan et al. (2014) found that channelized streams had reduced terrestrial organic matter loads due to the combination of increased autotrophic productivity and reduced hydrologic connectivity with floodplain soils and vegetation. Newcomer et al. (2012) also found significant

differences in diatom biomarkers and C: N ratios of DOM between nutrient-enriched urban streams and a forested reference in Baltimore, Maryland. Similarly, Kaushal et al. (2014) also found that export of protein-like DOM was correlated with increasing GPP. Empirical data from the present study and others suggest that in-stream productivity can contribute significantly to DOM export annually in urban streams with elevated nutrients and light availability.

One way to evaluate shifting contributions from in-stream vs. terrestrial organic matter sources is to compare DOC export to NEP. This comparison does not take into account time lags between primary production and biomass turnover, leaching, or biomass export in particulate form over annual timescales. However, it allows us to compare the magnitude of these two watershed carbon fluxes on a daily basis. Stream metabolism is defined as the capture of energy as GPP and release of heat by ER, which is commonly measured in units of dissolved oxygen production (GPP) and consumption (ER) in the water column (Odum 1965). Stream metabolism can also be evaluated in units of carbon uptake and production by assuming a constant ratio of O<sub>2</sub> consumption to CO<sub>2</sub> production during photosynthesis and aerobic respiration. By assuming that this ratio (respiratory quotient, RQ) was 1, the magnitude net CO<sub>2</sub> uptake from daily stream metabolism was compared with DOC export across a range of streamflow conditions. Berggren et al. (2012) tested the RQ assumption by measuring side-by-side CO<sub>2</sub> and O<sub>2</sub> production and consumption in 52 lakes and showed that RQ varies from 0.5 to 2 on average (depending largely on the most abundant carbon substrate being mineralized). An RQ of 1 was assumed with the caveat that this value is likely to vary in space and time. Additional assumptions used to scale NEP to the watershed-scale for comparison with

DOC export are outlined in the ‘Gaseous and Dissolved Fluxes’ subset of the methods section. NEP rates in study streams varied from  $-4.4$  to  $1.0 \text{ g C m}^{-2} \text{ day}^{-1}$ , within the high and low end of metabolism rates reported in the literature by single-day (Acuña et al. 2004; Bernot et al. 2010) and continuous methods (Izagirre et al. 2008; Beaulieu et al. 2013). Out of 1,557 daily NEP measurements across three streams, NEP was positive on 355 days and greater than daily DOC flux on 45 days. On average, daily NEP was lower than DOC by a factor of 0.66 with a minimum of 14.7 times lower and 3.3 times higher than DOC. Despite potentially significant time lags between autotrophic productivity and leaching/DOC production, this comparison shows that productivity is near equal to DOC flux on a substantial portion of the year. Of the days when  $\text{NEP} > 0$ , NEP is only greater than DOC during low to moderate streamflow conditions. Given the inter-annual importance of autotrophy in these urban streams, there was considerable potential for stream ecosystems to function as transformers of carbon.

#### 2.6.5. Urban Streams as Transformers: Gross Primary Production across Streamflow

Continuous sensor measurements allowed for the investigation environmental controls on stream metabolism across a variety of timescales and environmental conditions. These include storm events, seasonal light and temperature regimes, and varying carbon and nutrient loads. Patterns in stream metabolism show short-term decreases in GPP following major storms, similar to previous studies (Uehlinger 2006; Roberts and Mulholland. 2007; Beaulieu et al. 2013). Storm events caused GPP to decrease by approximately half, with a two-to three-week recovery period (Fig. 2.6). These effects are seen in both urban/suburban settings (Beaulieu et al. 2013) and non-urban streams (Acuña et al. 2004; Uehlinger 2006; Roberts and Mulholland. 2007).

Because urban areas tend to have greater flood frequency and intensity, it is possible that high streamflow events have a substantial effect on in-stream productivity (Beaulieu et al. 2013). One leading hypothesis explaining temporary decreases in GPP following storms is the scouring of in-stream benthic periphyton communities.

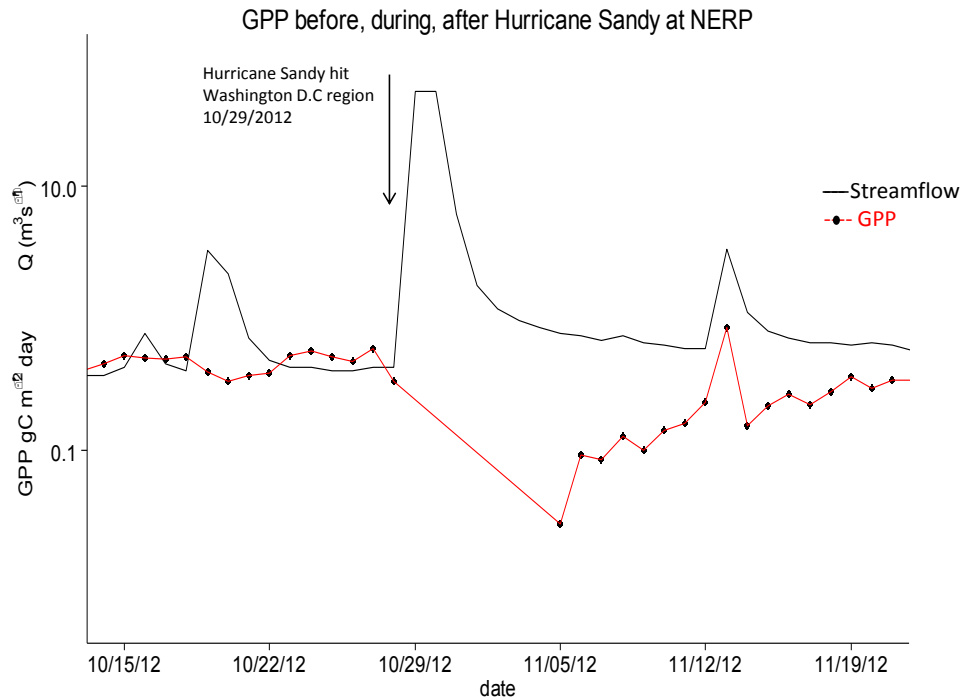


Figure 2.6 Gross Primary Production (GPP) and streamflow pre and post Hurricane Sandy at the NERP site. After storms there was a decline in GPP followed by rapid recovery over days and weeks

While storms influence GPP over shorter (weekly) timescales, other factors such as light availability appear to play a larger role across seasons. Light availability varied with stream size and adjacent vegetation, and these changes influenced the timing and magnitude of seasonal peaks in GPP and NEP. Across three streams of differing widths and shading in the Anacostia watershed, there were similar rates of daily growing-season GPP. However, there were notable differences in the timing and duration of seasonal peaks in GPP between the two smaller, shaded streams (PBCP, SLIGO) and the larger

non-shaded NERP. These variations contributed to overall differences in annual NEP for each stream (Fig. 2.4). While the importance of light availability for GPP is well established, the influence of riparian vegetation, stream size, and shading on annual GPP and NEP varies widely across stream reaches, watersheds, and biomes (Mulholland et al. 2001; Bernot et al. 2010). Results from this study highlight implications for the importance of spatial heterogeneity in riparian cover and stream order for influencing annual GPP rates, as well as potential management implications for reducing summer algal blooms by increased riparian shading.

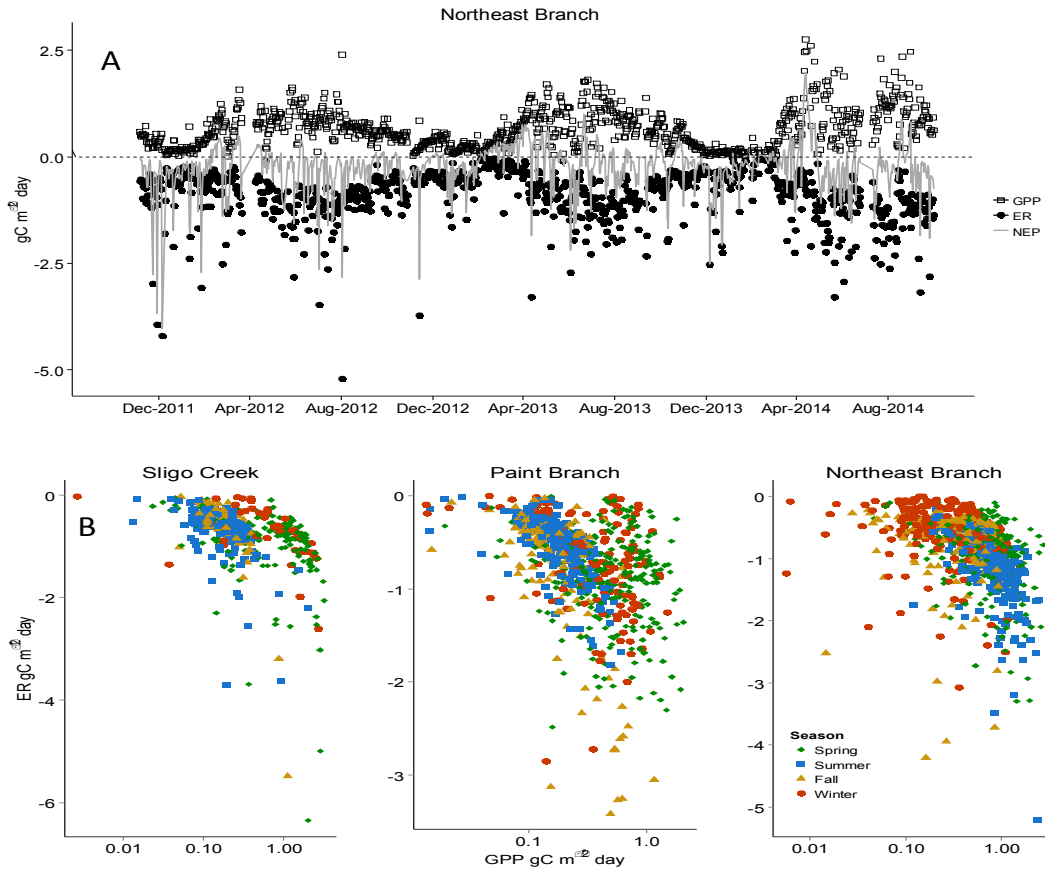
Along with light availability, nutrients can also be a limiting factor for in-stream productivity in streams (e.g., Mulholland et al. 2001; Bernot et al. 2010). Significant ( $P < 0.001$ ) correlations between TDN concentrations and GPP were present at two sites (SLIGO, PBCP). These relationships suggest that nitrogen is limiting, compared to phosphate, which showed no relationship with GPP (data not shown). However, these relationships are based only on a small subset (9 and 21) of days when metabolism and bi-weekly chemistry data coincide. More work is required to experimentally evaluate potential N limitation in these streams. Several studies have shown that coupling between nutrient (N and P) cycles and metabolism is highly variable. For instance, linkages between nutrient availability and GPP have been reported where large gradients in these variables exist as a result of: (1) large regional comparisons (Mulholland et al. 2001; Bernot et al. 2010), (2) sharp contrasts in land cover in small watersheds (Kaushal et al. 2014b), or (3) over very long (15-year) records of pollution reduction (Uehlinger, 2006). Alternatively, several studies of nutrient uptake and ecosystem metabolism have shown tight coupling between these processes both in pristine (Hall and Tank 2003; Roberts and

Mulholland, 2007; Heffernan and Cohen 2010; Cohen et al. 2013) and nutrient enriched streams (Pennino et al. 2014; Beaulieu et al. 2015). This suggests that stream ecosystem metabolism influences nutrient fluxes to some degree as well, particularly in urban streams with increased light availability and elevated nutrient loads (Kaushal et al. 2014b).

#### 2.6.6. Urban Streams as Transformers: Ecosystem Respiration across Streamflow

Stream metabolism in urbanized rivers can contribute significantly to increased DIC production and export (Martinelli et al. 1999; Daniel et al. 2001; Barnes and Raymond 2009; Andrade et al. 2011). Few studies have simultaneously evaluated variations in terrestrial and in-stream sources of DIC across variable streamflow conditions. However, the longstanding assumption that terrestrial sources dominate DIC export merits testing in urban areas. A recent study by Hotchkiss et al. (2015) estimated that 28% of CO<sub>2</sub> emissions from running waters in the U.S. are produced by stream metabolism, with the remainder from terrestrial or abiotic in-stream processes. In the present study, terrestrial sources of DIC (including CO<sub>2</sub>) were greater on average than in-stream sources. These results show that daily net respiration across three streams only contributed between 3.4 and 13% of total daily DIC inputs on average. Variability around these mean values was great, however, and DIC inputs from stream metabolism were often nearly 50% and approached 100% during low and moderate streamflow. The contribution of metabolism to daily DIC export varied with streamflow, with the greatest in-stream contributions at low and moderate flow conditions and the greatest terrestrial inputs during high flow (Fig. 2.8). Along with streamflow, variation in DIC production from net-respiration is also driven by temperature and organic matter substrate.





**Figure 2.7** (a) An example of time-series of gross primary production (GPP), ecosystem respiration (ER), and net ecosystem production (NEP) for the Northeast Branch. (b) GPP vs. ER for Sligo Creek, Paint Branch, and Northeast Branch in the Anacostia Watershed

Although there were significant relationships between ER and temperature, there was no relationship with DOC. This does not necessarily preclude a causal relationship between respiration and organic carbon, given that the bulk of stream respiration may take place in benthic sediments with particulate organic carbon rather in the water column. Additionally, growing evidence from previous studies suggests that lability of organic matter may be a stronger driver of metabolic rates and pathways than bulk DOC loading (Ballester et al. 1999; Martinelli et al. 1999). For instance, Newcomer et al. (2012) found that labile algae and grass leachates had a stronger effect on denitrification than leaf leachates in urban streams of Baltimore, Maryland. Similarly, Kaushal et al.

(2014) reported correlations between lability of organic matter and ecosystem respiration in similar sites. Additionally, Ballester et al. (1999) found that sewage inputs shifted riverine conditions from aerobic to anaerobic in a Brazilian river. Labile organic carbon sources can include decomposing microbial or phytoplankton biomass, urban wastewater inputs, or photo-oxidation of complex organic matter (Moran and Zepp 1997; Jarvie et al. 1997, Martinelli et al. 1999; Zhang et al. 2009). These studies provide evidence that a small rapidly cycling fraction of the overall DOC pool may be the main source of organic carbon mineralized within streams (Mayorga et al. 2005; Hall and Beaulieu 2013; Hofmann et al. 2008; Van den Meersche et al. 2009).

While stream metabolism has been shown to contribute to DIC fluxes in several cases (Jones and Mulholland 1998; Acuña et al. 2004), results from the present study demonstrate that the magnitude of metabolic contributions vary across streamflow conditions. By assuming that daily in-stream DIC production was synonymous with net respiration ( $ER-GPP$ , or  $NEP^* -1$ ), this study shows that in-stream DIC contributed significantly to total inorganic carbon exports during low baseflow conditions. GPP and ER are tightly coupled across all sites throughout the year (Fig. 2.7), which suggests that much of ER is attributable to autotrophic respiration and/or mineralization of recently produced algal biomass (Hall and Beaulieu, 2013). Negative NEP was observed on the majority of days in this study, signifying heterotrophic conditions. By converting metabolism measurements to units of  $CO_2$  uptake and production, equated heterotrophic conditions were equated with DIC production. While autotrophic respiration makes up a significant portion of ER, continuously heterotrophic conditions such as those measured in the present study require outside inputs of organic matter. Microbial mineralization of

terrestrial organic carbon inputs is especially apparent when ER exceeds GPP (negative NEP), given that autotrophic respiration cannot exceed GPP. Heterotrophic conditions are common in shaded forest streams, where GPP is light-limited and terrestrial inputs are high. However, many open-canopied streams are autotrophic due to high light availability and lower terrestrial inputs (Bernot et al. 2010; Demars et al. 2011). Urban watersheds, such as the Anacostia have a mixture of shaded and open channels, and this drives spatial and temporal variability in NEP. One common pattern found in forested streams is an autumnal spike in ER, driven by pulses of labile carbon from fallen leaves (Mulholland et al. 2001; Stelzer et al. 2003). Despite the prevalence of terrestrial organic matter, metabolism data did not show a clear pulse of ER or a seasonal drop in NEP during the fall. This pulse of ER was also absent in agricultural streams measured by Griffiths et al. (2013), and suburban streams measured by Beaulieu et al. (2013). In the former, the lack of riparian trees may reduce autumnal leaf litter inputs. In the latter, the authors suggest that scouring of banks during frequent storms reduced the availability of in-channel storage of labile organic C from riparian trees.

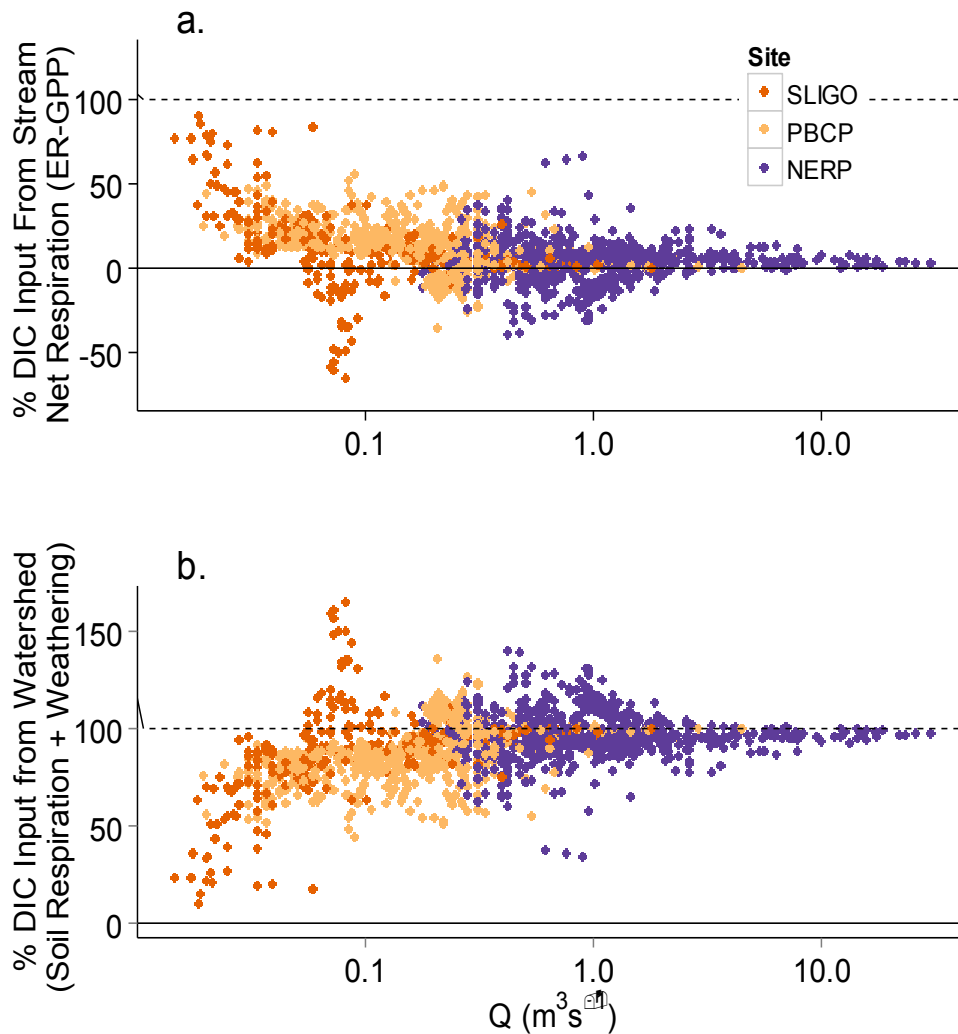


Figure 2.8 Daily estimates of terrestrial vs. in-stream DIC sources across variations in flow conditions. Source contributions are based on daily measurements of net respiration,  $\text{CO}_2$  fluxes, and DIC load estimates. Three separate colors signify three different study sites across the Anacostia watershed

## 2.7 Conclusions

Urban and agricultural land use has contributed to significant increases in DOC, DIC, and  $\text{CO}_2$  export by streams and rivers globally (Raymond and Cole 2003; Barnes and Raymond 2009; Zhang et al. 2009; Andrade et al. 2011; Bianchi et al. 2013; Kaushal et al. 2013; Kaushal et al. 2014a). As urbanization increases globally, it is critical to

understand the factors that influence transformations and transport of carbon in nutrient-enriched streams and rivers. In the present study, transport and transformation were both significant processes that influence the carbon cycle in urban streams. These results document the importance of streamflow variability on exports, sources, and metabolism of carbon over annual periods. DIC was the predominant form of carbon transported from these urban watersheds. There were major shifts between carbon transport and transformation and net ecosystem carbon production across variable streamflow conditions, which can impact river alkalization and biological oxygen demand in downstream receiving waters. Future work is necessary to test hypotheses regarding transport and transformation of carbon across hydrologic variability in order to better understand and manage stream ecosystem functions such as denitrification and primary production and water quality issues related to river alkalization and oxygen demand.

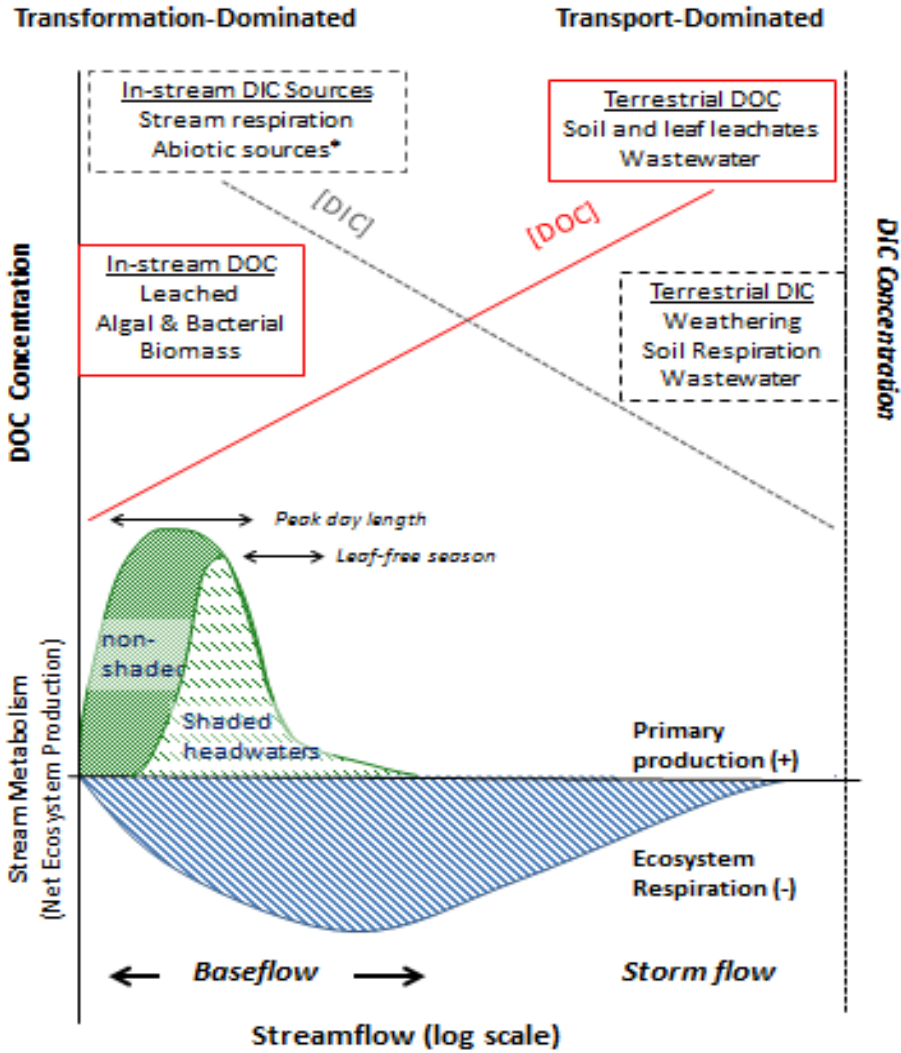


Figure 2.9 Streamflow-based conceptual model of processes that mediate carbon transport and transformation in urban streams. Streamflow is on the x-axis, and the y-axis is shared between the top: DOC (left) and DIC (right) concentrations, and bottom: Stream metabolism (GPP and ER). As streamflow increases, [DOC] increases and [DIC] decreases. In-stream metabolism dominates DIC sources at baseflow, and may contribute significantly to DOC as well, as seen during peaks in GPP. The proportion of each (DOC and DIC) contributed from terrestrial sources (vs. in-stream) increases with streamflow. Peaks in GPP are more pronounced and occur during a wider range of flow conditions in larger non-shaded rivers. GPP in smaller streams peaks during seasonal periods of intermediate baseflow in early spring. It can be hypothesized that this is the case because leaf-out corresponds to riparian shading and baseflow drawdown. Carbon export processes measured in this study include dissolved and gaseous fluxes. Gaseous  $\text{CO}_2$  export from the stream network (not pictured) was very low compared with fluvial DIC (mean = 0.33%, S.D. = 0.28%) with the majority of inorganic carbon export (including  $\text{CO}_2$ ) leaving the watershed in dissolved form.

## Chapter 3: Influence of urban infrastructure on water quality and greenhouse gas dynamics in streams

### 3.1 Abstract

Streams and rivers are significant sources of nitrous oxide ( $\text{N}_2\text{O}$ ), carbon dioxide ( $\text{CO}_2$ ), and methane ( $\text{CH}_4$ ), and watershed management can alter greenhouse gas emissions from streams. GHG emissions from streams in agricultural watersheds have been investigated in numerous studies; however, less is known about urban watersheds. This study hypothesized that urban infrastructure significantly influences GHG dynamics along the urban watershed continuum, extending from engineered headwater flowpaths to larger streams. GHG concentrations and emissions were measured across streams draining a gradient of stormwater and sanitary infrastructure including: 1) complete stream burial, 2) in-line stormwater wetlands, 3) riparian/ floodplain preservation, and 4) septic systems. Infrastructure categories significantly influenced drivers of GHG dynamics including carbon to nitrogen stoichiometry, dissolved oxygen, total dissolved nitrogen (TDN), and water temperature. These variables explained much of the statistical variation in nitrous oxide ( $\text{N}_2\text{O}$ ), carbon dioxide ( $\text{CO}_2$ ), and methane ( $\text{CH}_4$ ) saturation in stream water ( $r^2 = 0.78, 0.78, 0.50$  respectively).  $\text{N}_2\text{O}$  saturation ratios in urban streams were among some of the highest reported in the literature, varying from 1.1 - 47 across all sites and dates. The highest  $\text{N}_2\text{O}$  saturation ratios were measured in streams draining nonpoint N sources from septic systems and were strongly correlated with TDN.  $\text{CO}_2$  was highly correlated with  $\text{N}_2\text{O}$  across all sites and dates ( $r^2=0.84$ ), and  $\text{CO}_2$  saturation ratio varied from 1.1 - 73.  $\text{CH}_4$  was always super-saturated by factors of 3.0 to 2,157.

Differences in urban stormwater and sewer infrastructure influenced water quality, with significant implications for enhancing or minimizing stream CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O emissions based on watershed management.

### 3.2 Introduction

Streams and rivers are globally significant sources of nitrous oxide (N<sub>2</sub>O), carbon dioxide (CO<sub>2</sub>), and methane (CH<sub>4</sub>) (e.g., Seitzinger et al. 2000; Beaulieu et al. 2011; Bastviken et al. 2011; Raymond et al. 2013). The interactive effects of climate and land cover change have increased greenhouse gas emissions from streams and rivers by altering biogeochemical controls of ecosystem metabolism (i.e., nutrient stoichiometry, organic matter quality, redox state, and temperature), (e.g. Kaushal et al. 2014a; Beaulieu et al. 2009; Dinsmore et al. 2009; Baulch et al. 2011a; Harrison and Matson 2003). Urban stormwater and sewer infrastructure – including stormwater wetlands, stream burial, gravity sewer lines, and septic systems – influences nutrient loading (Shields et al. 2008; Kaushal and Belt 2012; Newcomer et al. 2012; Pennino et al. 2014; Beaulieu et al. 2015) and may have implications for GHG production as well. Numerous studies have examined the role of WWTPs on urban N<sub>2</sub>O emissions in (Foley et al. 2010; Townsend-Small et al. 2011; Stokal and Kroeze 2014). The nonpoint source N loads from gravity sewers and septic systems, however, may contribute substantially to urban N<sub>2</sub>O emissions (Beaulieu et al. 2010; Short et al. 2014). Aquatic N<sub>2</sub>O production and emissions have been linked to microbial transformations of excess N loading, as well as reduced oxygen availability (Beaulieu et al. 2011; Rosamond et al. 2012). Stormwater-control wetlands and other forms of green infrastructure may reduce N<sub>2</sub>O by removing excess N inputs, or increase both N<sub>2</sub>O and CH<sub>4</sub> to streams and groundwater due to anoxic conditions and



incomplete transformations to  $N_2$  gas (Søvik et al. 2006; VanderZaag et al. 2010). Despite considerable funds and efforts spent on restoring aging infrastructure in cities globally (Doyle et al. 2008), the role of urban water infrastructure on biogeochemical cycles and GHG production is a major source of uncertainty.

The International Panel on Climate Change (IPCC) considers emissions from agricultural, but not urban streams, into global GHG budgets based on nitrogen inputs from fertilizer and manure (Nevison 2000; Ciais et al. 2013; UNEP 2013; Stokal and Kroeze 2014; Short et al. 2014). Urban streams can receive similar watershed N inputs, but the relationship between N and  $N_2O$  emissions in urban vs. agricultural watersheds may differ substantially. Some key differences include: 1) the source and quantity of anthropogenic N in streams, 2) the C:N ratio of stream and groundwater, 3) the degree to which surface and groundwater flowpaths are altered by infrastructure. These factors are likely to be influenced by stormwater and sewer infrastructure designs (Søvik et al. 2006; Collins et al. 2010; Kaushal et al. 2011). Stormwater management may promote anoxic conditions and increase C:N ratio of stream water, if wetlands are created along the urban watershed continuum (e.g. Søvik et al. 2006; Newcomer et al. 2012). Stormwater management can reduce C:N ratios, if streams are buried in storm drains (Elmore and Kaushal 2008; Pennino et al. 2015; Beaulieu et al. 2014). Sewer infrastructure may additionally contribute to GHG emissions in urban streams, either by direct leakage of gases or from sewer lines (Yu et al. 2013; Short et al. 2014).

Inverse relationships between dissolved organic carbon (DOC) and nitrate ( $NO_3^-$ ) concentrations persist across a wide variety of ecosystems ranging from soils to streams to oceans (e.g., Aitkenhead-Peterson and McDowell 2000; Dodds et al. 2004; Kaushal

and Lewis 2005; Taylor and Townsend 2010). Recently, inverse relationships between DOC and  $\text{NO}_3^-$  have also been reported for urban environments from ground water to streams to river networks (Mayer et al. 2010; Kaushal and Belt 2012; Kaushal et al. 2014a). A suite of competing biotic process may control this relationship, by either: 1) assimilating or reducing  $\text{NO}_3^-$  in the presence of bioavailable DOC, or 2) producing  $\text{NO}_3^-$  regardless of DOC status (Hedin 1998; Dodds et al. 2004; Kaushal and Lewis 2005; Taylor and Townsend 2010). The former category includes heterotrophic denitrification, which oxidizes organic carbon to  $\text{CO}_2$  and reduces  $\text{NO}_3^-$  to  $\text{N}_2\text{O} + \text{N}_2$  (Groffman et al. 2000), and microbial assimilation of inorganic N (Wymore et al. 2015; Caraco et al. 1998; Kaushal and Lewis 2005). In the second category, nitrification is a chemoautotrophic process that produces  $\text{NO}_3^-$  by oxidizing  $\text{NH}_4^+$ , and consumes  $\text{CO}_2$ . Nitrification also yields  $\text{N}_2\text{O}$  as an intermediate product, and has been shown to dominate N cycling processes in low-DOC environments (Taylor and Townsend, 2010). In urban watersheds, denitrification is often limited by DOC due increased N loading and/or decreased connectivity with carbon-rich soils in the riparian zone (Mayer et al. 2010; Newcomer et al. 2012). The interactive effects of increased anthropogenic C and N loading and biogeochemical transformations have the potential to alter GHG production and emissions from streams (Kaushal et al. 2014c).

The goal of the present study was to identify patterns and potential drivers related to GHG dynamics in urban headwater streams draining different forms of infrastructure (stream burial, septic systems, in-line SWM wetlands and Riparian/Floodplain preservation). Although less considered, GHG emissions may be an unintended consequence of urban water quality impairments and biogeochemical processes occurring

within and downstream of urban infrastructure. An improved understanding of the relationship between infrastructure type and biogeochemical functions along the urban watershed continuum is critical for minimizing unintended consequences of water quality management (Kaushal and Belt 2012). Additionally, a better understanding of the contribution of urban watersheds to global GHG emissions will be critical, given that urbanization is the fastest form of land-use change and urban areas contain greater than 60% of Earth's population (Foley et al. 2006).

### 3.3. Sampling Methods

#### 3.3.1 Study Sites

Eight headwater streams were sampled every other week for water chemistry and dissolved gases at the Baltimore Long-Term Ecological Research (LTER) site ([www.beslter.org](http://www.beslter.org)). Sampling sites were located in the Red Run and Dead Run subwatersheds; these two subwatersheds of the Gwynn Falls watershed were developed at different times (Figure 3.1). Previous work at the Baltimore LTER site has extensively characterized the hydrology, biogeochemistry, and geomorphology of the Gwynns Falls stream network (*e.g.*, Groffman et al. 2004, Nelson et al. 2006; Meierdiercks et al. 2010; Kaushal et al. 2008, Shields et al. 2008, Sivorichi et al. 2011, Newcomer et al. 2012; Newcomer Johnson et al. 2014; Pennino et al. 2014; Pennino et al. 2015).

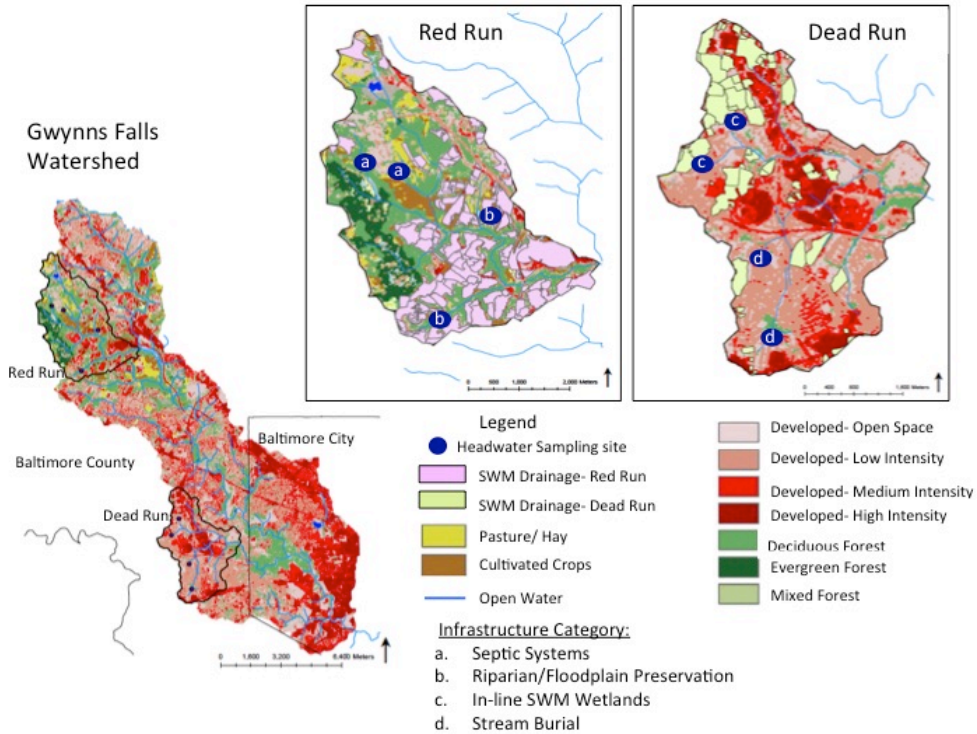


Figure 3.1 Site map of headwater stream sites within Red Run and Dead Run. Colors within the larger Gwynns Falls watershed signify land cover, whereas green and purple coloring in Dead Run and Red Run maps signify the area drained by stormwater management structures (detention basins, wetlands, sand filters, etc.). Blue dots signify headwater stream sampling sites, with letters for the paired infrastructure categories across Red Run and Dead Run.

Study sites were selected based on differences in sewer and stormwater infrastructure within each of eight headwater watersheds. Dead Run (15 km<sup>2</sup>) and Red Run (17 km<sup>2</sup>) were both dominated by medium to high-density residential and commercial land. Dead Run was developed between the 1950s and 1970s, with primarily channelized or buried stormwater infrastructure and ubiquitous, aging sewer lines. Stormwater wetlands and ponds drain a portion of the Dead Run watershed and are located in-line with stream channels. Red Run experienced intensive development in the 2000s and stormwater infrastructure reflects more infiltration-based designs such as stream buffer zones, infiltration wetlands, and bio-retention cells throughout the landscape (Baltimore County Department of Planning, 2010). Sanitary sewers were constructed in this watershed between 2000 and 2010 (Baltimore County Department of

Planning, 2000). Small areas with low-density development and septic service are located in the northern part of Red Run (Figure 3.1).

Infrastructure was grouped into categories based on the extent of existing infrastructure across Baltimore County. Four distinct categories of stormwater and sanitary infrastructure emerged including: 1) complete stream containment in pipes and burial, 2) in-line stormwater wetlands, 3) riparian/floodplain preservation, and 4) septic systems. Two streams were selected for each category (Table 3.1).

Table 3.1. Summary of site characteristics including drainage area (DA, km<sup>2</sup>), percent impervious cover in watershed and percent of the watershed drained by stormwater best management practices (i.e. non-buried pipes).

| <b>Category</b>                  | <b>Site</b> | <b>DA</b> | <b>% IC</b> | <b>% SWM</b> | <b>Description</b>  |
|----------------------------------|-------------|-----------|-------------|--------------|---|
| Septic Systems                   | RRSD        | 0.23      | 7.9         | 0.00         | Low-density residential development with septic systems, minimal stormwater management, and some stream burial.   |
|                                  | RRSM        | 0.68      | 3.78        | 13.97        |   |
| Riparian/Floodplain Preservation | RRRM        | 0.63      | 16.4        | 100.00       | Suburban and commercial low-impact development converted from agriculture in early 2000s. Many stormwater wetlands in upland + wide riparian buffer zones around each stream and sanitary sewer infrastructure. |
|                                  | RRRB        | 0.21      | 22.81       | 54.67        |   |
| In-line SWM Wetlands             | DRKV        | 0.31      | 39.16       | 100.00       | Older suburban development (circa 1950s) with a mixture of dry stormwater detention basins and stormwater sewer lines. Entire watershed is serviced by sanitary sewers  |
|                                  | DRGG        | 0.6       | 36.68       | 47.60        |   |
| Buried Streams                   | DRAL        | 0.26      | 41.9        | 1.10         | Older suburban and commercial development (circa 1950s) with completely buried headwaters upstream of the sampling point. Entire watershed is serviced by sanitary sewers.                                      |
|                                  | DRIS        | 0.18      | 30.57       | 0.00         |   |

### 3.3.2 Temporal Sampling of Dissolved Gases and Stream Chemistry

Dissolved gas samples were collected bi-weekly from eight headwater sites (first order streams) draining the categories of ‘Complete Stream Burial,’ ‘In-Line SWM Wetlands,’ ‘Riparian/Floodplain Preservation’ and ‘Septic Systems.’ Five replicate samples were collected per stream on each date. Samples were collected by submerging a 140 mL syringe with a 3-way luer-lock and pulling 115 mL of stream water into the syringe. Next, 25 mL of ultra-high purity helium was added to a syringe, and shaken for 5 minutes to promote the equilibration of gases between the aqueous and gas phase. After equilibration, 20 mL of the headspace was transferred into a pre-evacuated vial capped with screw-top rubber septa (LabCo Limited, Lampeter, UK) and stored at room temperature for up to four weeks prior to analyses. Water temperature and barometric pressure during the equilibration were recorded and three blank samples were taken at each field site.

Water samples were collected in 250 mL high-density polyethylene bottles at each site. Single samples were taken at each site, with one rotating site duplicated on each sampling date. Dissolved oxygen (DO) concentration and pH were measured at the upstream end of each study reach using a handheld YSI 550-A dissolved oxygen meter (YSI Inc. Yellow Springs, OH) and an Oakton handheld pH meter (Oakton Instruments, Vernon Hills, IL).

### 3.3.4. Longitudinal Sampling of Dissolved Gases along the Urban Watershed Continuum

Longitudinal surveys were conducted along the two main paired watersheds of Red Run and Dead Run. Longitudinal sampling started near the headwater study sites where temporal sampling occurred and typically extended several kilometers downstream

to the confluence with Gwynns Falls (Figure 3.1). During spring and fall months, solute and gas samples were collected along all major tributaries (>5% main stem flow) as well as every 500 m along the main stem of Dead Run and Red Run. Stream discharge was measured at each sampling point using a Marsh-McBirney Flo-Mate hand held velocity meter (Marsh McBirney Inc., Frederick, MD, USA). Discharge measurements were made by taking cross-sectional measurements of stream velocity and water depth at each site. A minimum of 10 points was measured along each cross section. Where sampling points were co-located with USGS gaging stations, discharge data was provided by USGS.

Locations for each sampling site were either recorded with a handheld GPS or estimated using Google Earth software. The watershed contributing area above each sampling point and flow length from each sampling point to the watershed outlet (Dead Run or Red Run respectively) were calculated using ArcMap 10 using a 2 x 2m digital elevation model of the Baltimore region. These surveys were used to determine whether or not the patterns in GHG's and solute concentrations within headwater streams were present along the broader urban watershed continuum encompassing engineered headwater flowpaths to higher order streams. Reach-scale hydrologic mass balances were calculated along the main stem of Red Run and Dead Run from these synoptic surveys following methods detailed previously (Kaushal et al. 2014a, Newcomer Johnson et al. 2014). Along each reach of the main stem, relative contributions of inflow were calculated following equation 3.1,

Eq. 3.1 
$$Q_{DS} = Q_{US} + Q_{TRIB} + Q_{GW}$$

where:  $Q_{DS}$  is discharge measured the main stem ( $m^3 s^{-1}$ ) at the bottom of a reach,  $Q_{US}$  is discharge in the main stem at the top of a reach,  $Q_{TRIB}$  is inflow from major tributaries,

and  $Q_{GW}$  is groundwater input.  $Q_{GW}$  was estimated by difference using field measurements of  $Q_{DS}$ ,  $Q_{US}$ , and  $Q_{TRIB}$ .

### 3.4 Laboratory Methods

#### 3.4.1 Dissolved Gas Concentrations

$CO_2$ ,  $CH_4$ , and  $N_2O$  concentrations were measured using a Bruker 450 (Billerica, MA, U.S.A) gas chromatograph equipped with a methanizer and flame ionization detector (FID) for  $CO_2$  and  $CH_4$  measurement. An electron capture detector (ECD) was used to measure  $N_2O$  concentrations. Instrument detection limits were 100 ppb for  $N_2O$ , 10 ppm for  $CO_2$ , and 0.1 ppm for  $CH_4$ .

#### 3.4.2 Solute Concentrations

Water samples were transported on ice to the University of Maryland and filtered using pre-combusted 0.7  $\mu m$  glass fiber filters within 24 hours. A Shimadzu analyzer (Shimadzu Scientific, Kyoto Japan) was used to measure total dissolved nitrogen (TDN) and dissolved organic carbon (DOC). The non-purgeable organic carbon (NPOC) method was utilized for DOC, despite potential under-estimates of volatile compounds because it is insensitive to variations in DIC (Findlay et al. 2010). Nitrate ( $NO_3^-$ ) concentrations were measured *via* colorimetric reaction using a cadmium reduction column (Lachat method 10-107-04-1-A) on a Lachat flow injection analyzer (Hach, Loveland, CO).

#### 3.4.3 Dissolved Organic Matter Characterization

Filtered water samples were analyzed for optical properties in order to characterize differences in the sources of organic matter spatially and temporally. Filtered water samples were stored in amber glass vials at 4°C for a maximum of two



weeks prior to analyses. Detailed methodology for optical properties and fluorescence indices can be found in Smith and Kaushal (2015). Briefly, fluorescence and absorbance properties of dissolved organic matter (DOM) were measured in order to evaluate the relative abundance of terrestrial (high molecular weight plant/soil –derived humic acids) and aquatic (low molecular weight bacterial or planktonic compounds) sources to the overall organic matter pool.

A FluoroMax-4 Spectrofluorometer (Horiba Jobin Yvon, Edison NJ, USA) was used to measure the emission spectra of samples in response to a variety of excitation wavelengths. Excitation-emission matrices (EEMs) were used for characterizing indices of terrestrial vs. aquatic DOM sources. For example, the humification index (also known as HIX) is defined as the ratio of emission intensity of the 435-480 nm region of the EEM to the emission intensity of the 300-345 nm region of the EEM at the excitation wavelength of 254 nm (Zsolnay et al. 1999; Ohno 2002). The humification index varies from 0 to 1, with higher values signifying high-molecular weight DOM molecules characteristic of humic terrestrial sources. Lower humification index values indicate low molecular weight DOM of bacterial or aquatic origin (Zsolnay et al. 1999). The autochthonous inputs index (also known as BIX) is defined as the ratio of fluorescence intensity at the emission wavelength 380 nm to the intensity emitted at 430 nm at the excitation wavelength of 310 nm (Huguet et al. 2009). Lower autochthonous inputs index values (<0.7) represent terrestrial sources, and higher autochthonous inputs index values (>0.8) represent algal or bacterial sources (Huguet et al. 2009).

### 3.5 Greenhouse Gas Calculations

#### 3.5.1 Gas Concentrations

Dissolved gas concentrations were calculated from the measured headspace concentration, Henry's law, and the Bunsen solubility coefficient (Stumm and Morgan 1981). The molar concentration  $[A_g]$  of gas in the headspace was calculated using the ideal gas law as follows

$$\text{Eq. 3.2} \quad [A_g] = \frac{n}{RT}$$

where  $n$  is measured partial pressure (atm),  $R$  is the universal gas constant (0.0821 L atm/mol K), and  $T$  is the temperature (K). The molar concentration of gas remaining in the aqueous phase following headspace equilibration was calculated using the temperature-corrected Bunsen solubility coefficient for each gas, total pressure, and the measured partial pressure (ppmv) of each gas using equation 3.3.

$$\text{Eq. 3.3} \quad [A_{aq}] = \frac{(n \cdot B_p \cdot \text{Bunsen})}{RT}$$

where  $B_p$  is the barometric pressure (atm) and Bunsen is the solubility coefficient in the vessel (L/L-atm). Calculations of the Bunsen coefficient were based on Weiss (1974) for  $\text{CO}_2$ , Weiss (1970) for  $\text{N}_2\text{O}$ , and Yamamoto et al., (1976) for  $\text{CH}_4$ . The original stream water gas concentration,  $[A_{str}]$  was determined *via* mass balance following equation 3.4, where  $V_{aq}$  and  $V_g$  were the volumes of water and gas respectively in a water sample with helium headspace.

$$\text{Eq. 3.4} \quad [A_{str}] = \frac{[A_{aq}] \cdot V_{aq} + [A_g] \cdot V_g}{V_{aq}}$$

Because gas solubility is temperature-dependent, it was useful to display gas concentrations as the % saturation, or the ratio of the measured dissolved gas

concentration to the equilibrium concentration. To determine gas saturation, the equilibrium concentration ( $[A_{eq}]$ ), was calculated based on water temperature, atmospheric pressure, and an assumed value for the current atmospheric mixing ratios of each gas following eq. 3.3. Saturation ratio is defined as a ratio  $[A_{str}] / [A_{eq}]$ , while excess (i.e.  $xsCO_2$ ) is described as a mass difference ( $[A_{str}] - [A_{eq}]$ ).

### 3.5.2 Apparent Oxygen Utilization

GHG concentrations in streams represent an amalgamation of sources including *in-situ* production, near-stream riparian zones and transport from soils through more regionalized groundwater flowpaths (e.g. Richey et al. 1988; Hiscock et al. 2003; Jahangir et al. 2012). Comparing gas saturation across streams can be misleading because variable gas exchange rates may obscure differences among sites. Using paired gas ratios within a stream is one way to explore differences in metabolic processes across sites. For example, relationships between  $CO_2$  and  $O_2$  can be used to examine aerobic *vs.* anaerobic gas production because these two gases are mechanistically linked *via* aerobic respiration and photosynthesis.

Equilibrium oxygen concentrations were calculated following equations 3.2-3.4 and oxygen saturation from field DO measurements. Apparent oxygen utilization (AOU) was calculated as the difference between  $O_2$  concentrations at equilibrium with the atmosphere and measured  $O_2$  concentrations. Positive values of AOU therefore signify net consumption of  $O_2$  along watershed flowpaths, and negative AOU values signify net production  $O_2$ . Similarly, excess  $CO_2$  was calculated as the difference between the measured and equilibrium dissolved  $CO_2$  concentration. Under aerobic conditions, respiration of organic matter consumes  $O_2$  and produces  $CO_2$  in approximately a 1:1

molar ratio (Richey et al. 1988). Therefore, 1 mole of AOU should result in 1 mol of CO<sub>2</sub> excess. This ratio was then used, with an offset to 1.2:1 to account for differences in diffusion constants for the two gases (Richey et al. 1988), to determine the proportion of CO<sub>2</sub> produced from aerobic respiration (Fig. S1). For instance, 1 mol of AOU would result in 1 mol of CO<sub>2</sub> excess if aerobic respiration were the only CO<sub>2</sub> source. A CO<sub>2</sub> excess value greater than 1 mol would be indicative of other CO<sub>2</sub> sources, namely anaerobic respiration, which produces CO<sub>2</sub> without consuming O<sub>2</sub>. This framework was used to calculate the percentage of CO<sub>2</sub> produced from anaerobic vs. abiotic processes. Anaerobic CO<sub>2</sub> concentrations were calculated as the difference between aerobically produced CO<sub>2</sub> (assumed equivalent to AOU) and measured CO<sub>2</sub> concentration.

### 3.5.3 Greenhouse Gas Emissions

Gas emissions were calculated using eq. 3.5, in which  $K_{\text{GHG,temp}}$  ( $\text{time}^{-1}$ ) is derived from  $K_{20}$  (see below),  $d$  is water depth, and  $F_{\text{GHG}}$  is the flux ( $\text{g m}^{-2}\text{d}^{-1}$ ) of a given GHG.

$$\text{Eq. 3.5} \quad F_{\text{GHG}} = K_{\text{GHG,temp}} * d * ([A_{\text{str}}] - [A_{\text{eq}}])$$

The air-water gas exchange rate was estimated using the energy dissipation model (Tsvoglou and Neal 1976), which predicts  $K$  as a function of water velocity, stream slope, and a constant called the escape coefficient. The escape coefficient ( $C_{\text{esc}}$ ) is derived from the slope of the relationship between  $K$  and velocity and streambed slope (eq. 3.6), where  $K_{20}$  ( $\text{units day}^{-1}$ ) is a function of  $C_{\text{esc}}$  ( $\text{units m}^{-1}$ ), velocity ( $V$ ) with units of  $\text{m day}^{-1}$ , and the change in depth ( $dH$ , m) over a reach with length,  $l$  (m).

$$\text{Eq. 3.6} \quad K_{20} = C_{\text{esc}} * \frac{dHV}{l}$$

$C_{esc}$  is a site-specific parameter related to additional factors that affect gas-exchange including streambed roughness and the relative abundance of pools and riffles.  $C_{esc}$  was estimated for this study using data from 22 direct measurements of  $K_{20}$  made using sulfur hexafluoride ( $SF_6$ ) as a tracer gas across six stream reaches located within 5  $km^2$  of the sites investigated in this study (Pennino et al. 2014). The six study reaches investigated by Pennino et al. (2014) were adjacent to USGS stream gages (#01589312, #01589317, and #01589316). Stream slope was needed to calculate  $C_{esc}$ . To estimate stream slope for these reaches, field measurements published by the USGS for these gaging stations were used to parameterize the continuity equation. The continuity equation, described in detail by Leopold and Maddock (1953), describes the relationships between discharge (Q), depth, velocity, and stream width for a given stream reach. Continuity parameters allowed us to estimate slope by rearranging Manning's equation (eq. 3.7):

$$\text{Eq. 3.7} \quad S = \frac{\sqrt{nQ}}{AR^{2/3}}$$

where n is Manning's n, a roughness parameter, was estimated to be 0.035 based on descriptions in the literature for similar streams (Arcement and Schneider 1989). Q refers to discharge ( $m^3 d^{-1}$ ) measured at a USGS gaging station. A refers to cross sectional area (m), calculated as depth multiplied by width from, and R is hydraulic radius (A divided by wetted perimeter). Wetted perimeter was estimated to be depth multiplied by 2 plus width based on field observations of channel morphology.

$C_{esc}$  was calculated to be 0.129 (n=22,  $r^2=0.79$ ,  $P<0.01$ ). The 95% confidence interval of this  $C_{esc}$  based on measured  $K_{20}$  values was  $\pm 0.031$  which corresponds to  $\pm 24\%$  of a given gas flux estimate. This estimate of  $C_{esc}$  from nearby sites was assumed

to be representative of the 8 stream reaches investigated in this study. The uncertainty associated with Cesc is small compared to the difference in estimated flux across sites. There were additional uncertainties associated with site-specific slope and velocity estimates and applicability of a generalized Cesc estimate. Areal flux data was thus interpreted with caution, and only examined in terms of the magnitude across all sites and in comparisons with literature values.

### 3.6 Statistical Analyses

#### 3.6.1 Role of Infrastructure and Seasonality

A linear mixed effects modeling approach was applied to evaluate temporal and spatial variability in gases and solutes in order to determine the significant drivers of each gas across streams in different headwater infrastructure categories. Due to data gaps at stream gaging stations and uncertainties in the gas flux parameters, GHG saturation ratios were used rather than GHG emissions to compare spatial and temporal patterns across sites. Mixed effects modeling was carried out using R (R Core Team, 2014) and the *nlme* package (Pinheiro et al. 2012) following guidance outlined in Zurr et al. (2009).

In order to determine the role of spatial and temporal variability on gases and solute concentrations, separate mixed effects models were examined for the role of infrastructure category and date on each response variable. Response variables included saturation ratios for each gas ( $\text{CO}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{CH}_4$ ) as well as solute concentrations (DOC, DIC, TDN,  $\text{NO}_3^-$ ) and organic matter source indices (humification index, autochthonous inputs index). Fixed effects were ‘infrastructure category’ and ‘sampling date,’ as well as an interaction term for the two. The effect of a random intercept for ‘site’ was included in each model.

Model assumptions of normality, independence, and equal variances were validated by visually inspecting the pattern of residuals. When necessary, variances were weighted based on infrastructure category to remove heteroscedasticity in model residuals (Zuur et al. 2009). Tests were run for temporal autocorrelation using the `corAR1()` function of *nlme*. The significance of random effects, weighting variances, and temporal autocorrelation was tested by comparing akaike information criterion (AIC) scores for models with and without each of these attributes. Additionally, pairwise ANOVA tests were run to determine whether the residual sum of squares was significantly reduced by each additional level of model complexity. Final model selection was based on meeting model assumptions, minimizing the AIC value, and minimizing residual standard error. Pairwise comparisons among infrastructure categories were examined using the Tukey HSD post-hoc test (*lsmeans* package, Lenth, 2016) for each response variable where ‘infrastructure category’ had a significant effect. Where ‘infrastructure category’ did not have a significant effect on a response variable after incorporating ‘site’ as a random effect, a separate set of linear models was run with ‘Site’ and ‘Date’ as main effects rather than ‘Infrastructure category’. The role of ‘Site’ was evaluated in these cases to determine the degree to which site-specific variability overwhelmed infrastructure category.

### 3.6.2 Role of Continuous Variables on Gas Saturation

A stepwise linear regression approach was used to examine the role of multiple variables on CO<sub>2</sub>, N<sub>2</sub>O, and CH<sub>4</sub> saturation across sites and dates. Predictor variables were selected *via* backward stepwise procedure, using the ‘Step’ function in R. This involves first running a model that includes all potential driving factors, then running

sequential iterations of that model after removing one variable at a time until the simplest and most robust combination of predictors was achieved. Model fit at each step was evaluated using the AIC score. Parameters that did not significantly reduce AIC were removed until the model had the best fit with only significant factors. The initial list of potential drivers included temperature, DO, DOC, TDN, DIC, humification index (HIX), and the autochthonous inputs index (BIX). Prior to the stepwise regression, a test for multicollinearity was run by calculating the variance inflation factor (VIF) for each response variable.  $VIF > 3$  was the cutoff for assessing multicollinearity (Zuur et al. 2010), and all response variables in this study were below this threshold.

Analysis of covariance (ANCOVA) was carried out to determine whether relationships among gases ( $\text{CO}_2$  vs.  $\text{N}_2\text{O}$ ,  $\text{CO}_2$  vs.  $\text{CH}_4$ ) and solutes (DOC vs.  $\text{NO}_3^-$ ) varied systematically across infrastructure categories. ANCOVA involved comparing two generalized least squares models. The first linear model included an interaction term between one of the predictor variables (i.e. DOC or  $\text{CO}_2$ ) and infrastructure category to predict the response variable ( $\text{N}_2\text{O}$  or  $\text{CH}_4$ ). The second was a linear model with the same two independent variables but no interaction term. When infrastructure category had a significant influence on both the intercept (first model) and slope (second model) of a relationship, this refuted the null hypothesis that infrastructure category had no influence on a relationship.



### 3.7 Results

#### 3.7.1 Effects of Urban Infrastructure on Water Quality and DOC: NO<sub>3</sub><sup>-</sup> Ratios

There were significant differences among TDN, NO<sub>3</sub><sup>-</sup>, and DOC: NO<sub>3</sub><sup>-</sup> ratios across infrastructure category (Table 3.2). TDN concentrations ranged from 0.12 to 8.7mg N L<sup>-1</sup> (Table 3.3). Pairwise comparisons yielded significantly higher TDN concentrations in sites with Septic Systems, compared with sites draining In-line SWM Wetlands and sites with Riparian/Floodplain Preservation. Sites with Complete Stream Burial fell within the mid-range of TDN concentrations and were not different from any other category. DOC concentrations varied widely from 0.19 to 16.89 mg L<sup>-1</sup>, but were not significantly predicted by infrastructure category (Table 3.2). DOC: NO<sub>3</sub><sup>-</sup> ratios varied over several orders of magnitude, from 0.02 to 112 (Figure 3.2). Infrastructure category was a significant predictor of DOC: NO<sub>3</sub><sup>-</sup>, with the lowest ratios in sites with Septic Systems and highest in sites with Riparian/Floodplain Preservation (Figure 3.2). DOC: NO<sub>3</sub><sup>-</sup> ratios did not differ between in the In-line SWM wetland and Complete Stream Burial categories (Figure 3.2).

#### 3.7.2 Effects of Urban Infrastructure on Dissolved Organic Matter Quality

Organic matter source metrics, humification index (HIX) and autochthonous inputs index (BIX) showed mixed results. Streams draining Septic System infrastructure had significantly lower humification index values than any other infrastructure category. The autochthonous inputs index (BIX) values showed no significant pattern across infrastructure categories (Table 3.2).

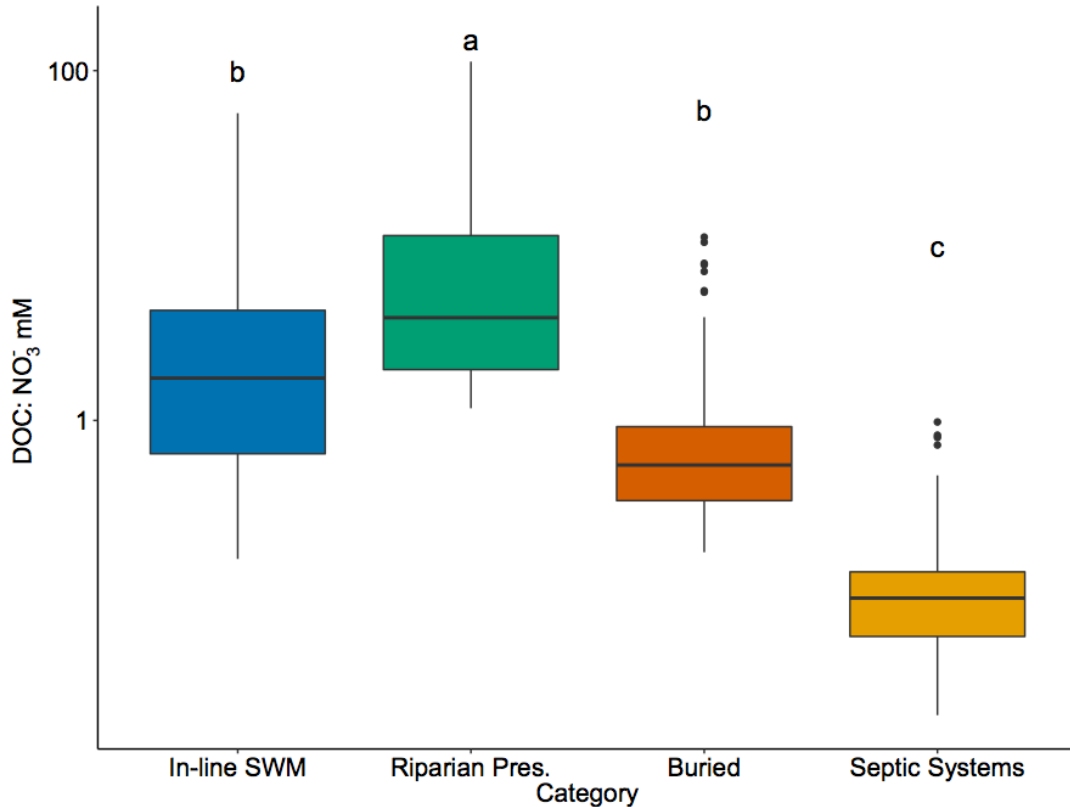


Figure 3.2 Boxplot of DOC: NO<sub>3</sub><sup>-</sup> ratio across sites in differing infrastructure categories

### 3.7.3. Effects of Infrastructure on Greenhouse Gas Saturation

Mixed effects models did not detect significant influence of infrastructure category alone on N<sub>2</sub>O, CH<sub>4</sub>, and CO<sub>2</sub> saturation in streams. There was, however, a significant interaction effect between sampling date and infrastructure category on the saturation ratios of all three gases (Table 3.2). This indicated that sampling date was important to GHG saturation for some infrastructure categories. The second set of linear models, which used site rather than infrastructure category as a main effect yielded significant differences across all sites for N<sub>2</sub>O. Similarly, for CO<sub>2</sub>, there were significant differences in 25 out of 28 pairwise comparisons. Pairwise comparisons across sites for CH<sub>4</sub> saturation were significant in 23 out of 28 cases. These patterns suggest that site-specific effects overwhelmed the role of infrastructure categories on GHG saturation.

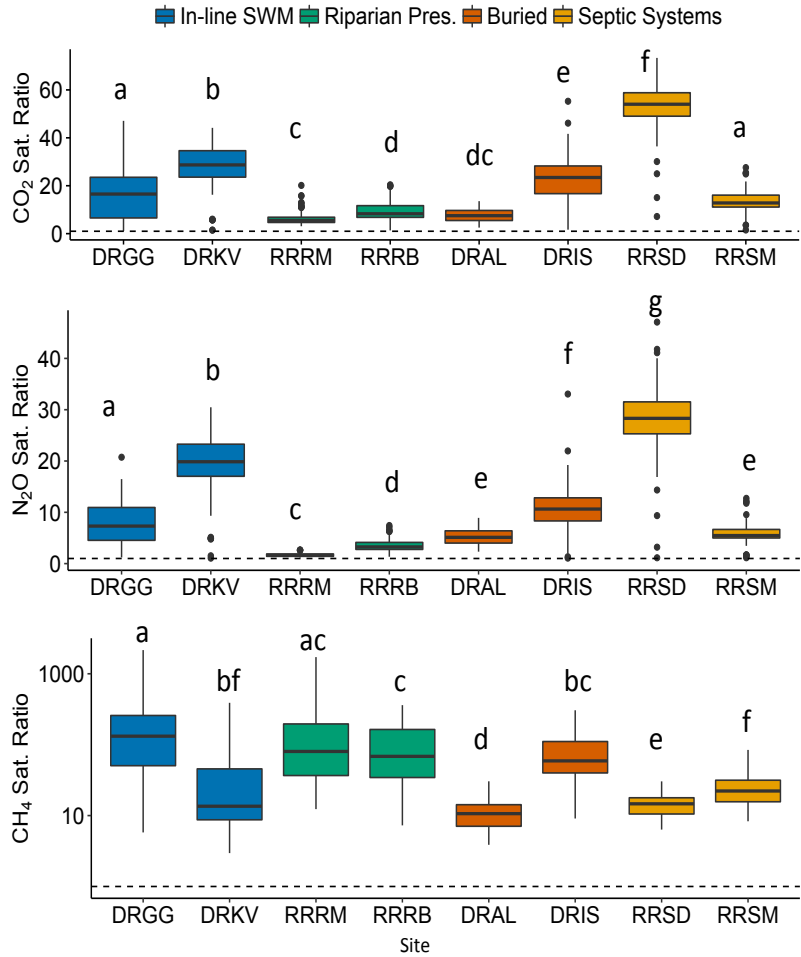


Figure 3.3 CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O saturation ratios across watershed sites in varying infrastructure categories. Letters denote significant pairwise differences across sites for a given gas.

Table 3.2 Summary of results (main effects p-values) from mixed effects models examining the role of infrastructure category and date on each response variable (CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> saturation ratios; TDN and DOC concentrations mg L<sup>-1</sup>, autochthonous productivity index (BIX) and humification index (HIX)).

| Infrastructure Category                            | CO <sub>2</sub> | N <sub>2</sub> O | CH <sub>4</sub> | TDN   | DOC   | BIX   | HIX   | DOC: NO <sub>3</sub> - |
|--|-----------------|------------------|-----------------|-------|-------|-------|-------|------------------------|
| Infrastructure Category p-value                    | 0.496           | 0.488            | 0.298           | 0.068 | 0.200 | 0.441 | 0.020 | <0.0001                |
| Date p-value                                       | 0.957           | <0.01            | 0.001           | 0.086 | 0.387 | 0.155 | 0.765 | 0.492                  |
| Date x Infrastructure Category Interaction p-value | <0.01           | <0.01            | 0.000           | 0.114 | 0.978 | 0.490 | 0.899 | 0.894                  |

Table 3.3. Mean (SE) GHG saturation ratios, TDN and DOC concentrations (mg L<sup>-1</sup>), autochthonous productivity index (BIX) values and humification index (HIX) values. P-values from mixed effects models examining the role of category and date on each variable. The bottom section of this table lists p-values for spatial and temporal variability across infrastructure categories and dates from mixed effects models.

| Infrastructure Category          | Site | CO <sub>2</sub> | N <sub>2</sub> O | CH <sub>4</sub> | TDN            | DOC            | BIX             | HIX              | DOC: NO <sub>3</sub> <sup>-</sup> |
|----------------------------------|------|-----------------|------------------|-----------------|----------------|----------------|-----------------|------------------|-----------------------------------|
| Septic Systems                   | RRSD | 52.9<br>(1.1)   | 28.0<br>(0.7)    | 14.9<br>(0.5)   | 6.40<br>(0.20) | 0.76<br>(0.12) | 0.89<br>(0.02)  | 0.74<br>(0.01)   | 0.06<br>(0.01)                    |
|                                  | RISM | 13.5<br>(0.5)   | 5.9<br>(0.2)     | 25.6<br>(1.5)   | 3.49<br>(0.13) | 1.40<br>(0.25) | 0.70<br>(0.02)  | 0.782<br>(0.015) | 0.27<br>(0.04)                    |
| Riparian/<br>Floodplain<br>Pres. | RRRM | 6.6<br>(0.3)    | 1.7<br>(0.04)    | 207.3<br>(36.2) | 0.59<br>(0.08) | 2.89<br>(0.27) | 0.67<br>(0.01)  | 0.85<br>(0.02)   | 12.16<br>(3.45)                   |
|                                  | RRRB | 9.6<br>(0.4)    | 3.6<br>(0.1)     | 103.6<br>(8.6)  | 0.35<br>(0.02) | 1.58<br>(0.18) | 0.716<br>(0.01) | 0.85<br>(0.01)   | 9.24<br>(2.43)                    |
| In-line SWM                      | DRKV | 28.1<br>(1.0)   | 19.1<br>(0.6)    | 50.8<br>(8.5)   | 2.52<br>(0.16) | 2.65<br>(0.24) | 0.75<br>(0.01)  | 0.86<br>(0.003)  | 2.38<br>(0.67)                    |
|                                  | DRGG | 16.3<br>(1.1)   | 7.9<br>(0.4)     | 225.8<br>(31.9) | 1.16<br>(0.07) | 5.32<br>(0.60) | 0.73<br>(0.02)  | 0.83<br>(0.01)   | 8.72<br>(2.23)                    |
| Complete<br>Stream Burial        | DRAL | 7.9<br>(0.3)    | 5.1<br>(0.2)     | 11.3<br>(0.6)   | 2.68<br>(0.09) | 2.64<br>(0.37) | 0.81<br>(0.01)  | 0.83<br>(0.01)   | 1.42<br>(0.40)                    |
|                                  | DRIS | 22.6<br>(1.0)   | 10.7<br>(0.5)    | 78.4<br>(5.8)   | 2.42<br>(0.09) | 2.51<br>(0.27) | 0.79<br>(0.01)  | 0.82<br>(0.01)   | 1.82<br>(0.44)                    |

### 3.7.4. Role of Continuous Variables on Gases and Solutes

Stepwise model parameter selection yielded several variables that correlate with each GHG (Table 3.4). TDN was the strongest predictor of N<sub>2</sub>O saturation, followed by DO. The final model for N<sub>2</sub>O ( $r^2=0.78$ ) also included temperature, HIX, BIX, %SWM, and DOC:NO<sub>3</sub><sup>-</sup>. CO<sub>2</sub> saturation had a similar pattern of predictors and nearly identical model fit ( $r^2=0.78$ ). DOC:NO<sub>3</sub><sup>-</sup> ratio was the strongest predictor of CH<sub>4</sub> saturation followed by DO and temperature. HIX, %IC, and %SWM also contributed to the predicting variance of CH<sub>4</sub> saturation, but TDN and BIX did not.

Table 3.4. Results of stepwise regression models examining continuous factors on CO<sub>2</sub>, N<sub>2</sub>O, and CH<sub>4</sub> saturation ratios. Predictors selected for the final model are listed with p-values. The absolute value of  $\beta$  signifies the relative contribution of each predictor, and sign signifies the direction of influence. \* Indicate the predictor with the greatest influence for each gas. 'N.A.' indicates that the predictor variable was not retained in the final model.

| Predictor                              | CO <sub>2</sub> |          | N <sub>2</sub> O |          | CH <sub>4</sub> |          |
|--|-----------------|----------|------------------|----------|-----------------|----------|
|  | $\beta$         | P-value  | B                | P-value  | $\beta$         | P-value  |
| TDN                                    | 1.08*           | < 0.0001 | 1.10*            | < 0.0001 | n.a.            | n.a.     |
| Temperature                            | -0.22           | 0.002    | -0.26            | 0.002    | 0.25            | 0.032    |
| DO                                     | -0.46           | < 0.0001 | -0.37            | < 0.0001 | -0.27           | 0.022    |
| HIX                                    | 0.09            | 0.054    | 0.13             | 0.054    | -0.15           | 0.090    |
| BIX                                    | 0.11            | 0.045    | 0.15             | 0.045    | n.a.            | n.a.     |
| %IC                                    | n.a.            | n.a.     | 0.14             | 0.036    | -0.16           | 0.063    |
| %SWM                                   | 0.18            | < 0.0001 | 0.31             | < 0.0001 | 0.16            | 0.100    |
| log(DOC:NO <sub>3</sub> <sup>-</sup> ) | 0.32            | 0.123    | 0.19             | 0.123    | 0.55*           | < 0.0001 |
| Overall Model Fit                      |                 |          |                  |          |                 |          |
| Adjusted $r^2$                         | 0.78            |          | 0.78             |          | 0.50            |          |
| P-value                                | <0.0001         |          | <0.0001          |          | <0.0001         |          |

### 3.7.5. Covariance among GHG abundance and C: N Stoichiometry

N<sub>2</sub>O and CH<sub>4</sub> were both correlated with anaerobic CO<sub>2</sub> concentrations, and these relationships varied significantly across infrastructure categories. The relationship

between anaerobic CO<sub>2</sub> concentrations and N<sub>2</sub>O saturation ratio (Figure 3.4a) was more consistent across land use categories than CH<sub>4</sub> saturation ratio vs. anaerobic CO<sub>2</sub> (Figure 3.4b). There was an overall inverse relationship between DOC and NO<sub>3</sub><sup>-</sup> across study sites. ANCOVA results showed that the slope of this relationship differed significantly with land use category (Figure 3.4c).

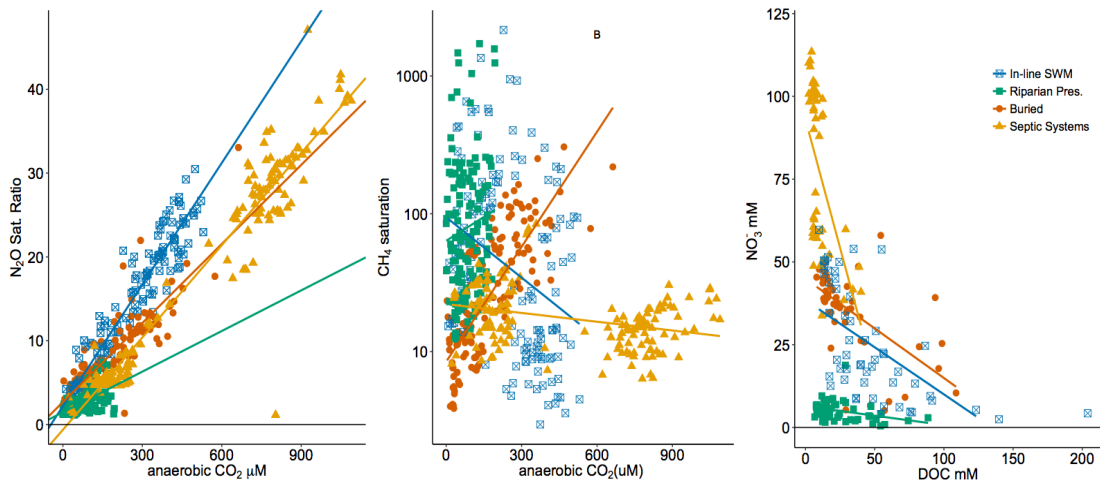


Figure 3.4 Scatterplots of a) N<sub>2</sub>O saturation vs. anaerobic CO<sub>2</sub>, CH<sub>4</sub> saturation vs. anaerobic CO<sub>2</sub>, and c) relationships between NO<sub>3</sub><sup>-</sup> and DOC. Lines show significant correlations among gas concentrations, which vary by infrastructure category.

### 3.7.6. Longitudinal Patterns in Water, Carbon, Nitrogen, and GHGs

Spatial variability in GHG abundance was examined in order to evaluate whether concentrations measured in tributaries were consistent along the drainage network for Red Run and Dead Run. Very high N<sub>2</sub>O saturation ratios were measured in headwaters of both Red Run and Dead Run, which were not representative of the remainder of the drainage network (Figure 3.5). Instead, a logarithmic decline was observed between the sites with highest N<sub>2</sub>O saturation and the main stem along hydrologic flowpaths from engineered headwaters to larger order streams. Headwater CH<sub>4</sub> saturation ratios were not markedly different from that in the main stem. Because the headwater sites were located

very close to their origin (either in natural springs, created SWM wetlands or storm drains), it is possible that the high GHG concentrations found in some headwater sites represent groundwater sources, which are released but not completely replenished along the stream network. The heterogeneous patterns found in gas concentrations both among headwater sites and along the stream network are likely a reflection of variations in dissolved N concentrations in ground water concentrations, incomplete denitrification, and differences in groundwater inflow volumes. Water balance estimates showed that groundwater inflow contributed up to 25% of reach flow in Red Run and up to 50% in Dead Run along the main stem. During early spring surveys, both watersheds also had a losing reach (groundwater outflow), which could have been due to evapotranspiration.

#### 3.7.7. Greenhouse Gas Emissions

Greenhouse gas emissions varied substantially across sites and dates. CO<sub>2</sub> and N<sub>2</sub>O emissions increased significantly ( $P < 0.01$ ,  $r^2 = 0.5$  and  $p < 0.01$ ,  $r^2 = 0.62$ , respectively) with discharge at the two sites with the greatest stream channel gradient (RRRB and DRKV). Sensitivity of emissions to discharge was in part due to the dependence of  $K_{20}$  on slope and velocity; however, CH<sub>4</sub> emissions were not correlated with discharge at any site. Emissions during three high-flow sampling dates (over  $0.015 \text{ m}^3 \text{ s}^{-1}$  for all sites) increased the variance of overall mean gas emission rates estimates. When these high emission rates were removed, average CO<sub>2</sub> emission rate ( $\pm$  standard error) was  $11.7 (\pm 2.9)$  and  $13.3 (\pm 2.38)$  at the two sites with higher channel gradient (RRRM and DRKV respectively) and  $0.64 (\pm 0.14)$  and  $0.27 (\pm 0.09)$  at sites with low channel gradient (DRGG and DRAL). Average site-specific N<sub>2</sub>O fluxes ( $\pm$  standard error)

excluding high flow samples varied from  $0.0003$  ( $1 \times 10^{-4}$ ) to  $0.016$  ( $0.003$ )  $\text{g N}_2\text{O-N m}^{-2} \text{d}^{-1}$

<sup>1</sup>.  $\text{CH}_4$  fluxes excluding high flows followed a similar pattern with site means ranging from  $1 \times 10^{-4}$  ( $4 \times 10^{-5}$ ) to  $0.02$  ( $1.2 \times 10^{-3}$ ).

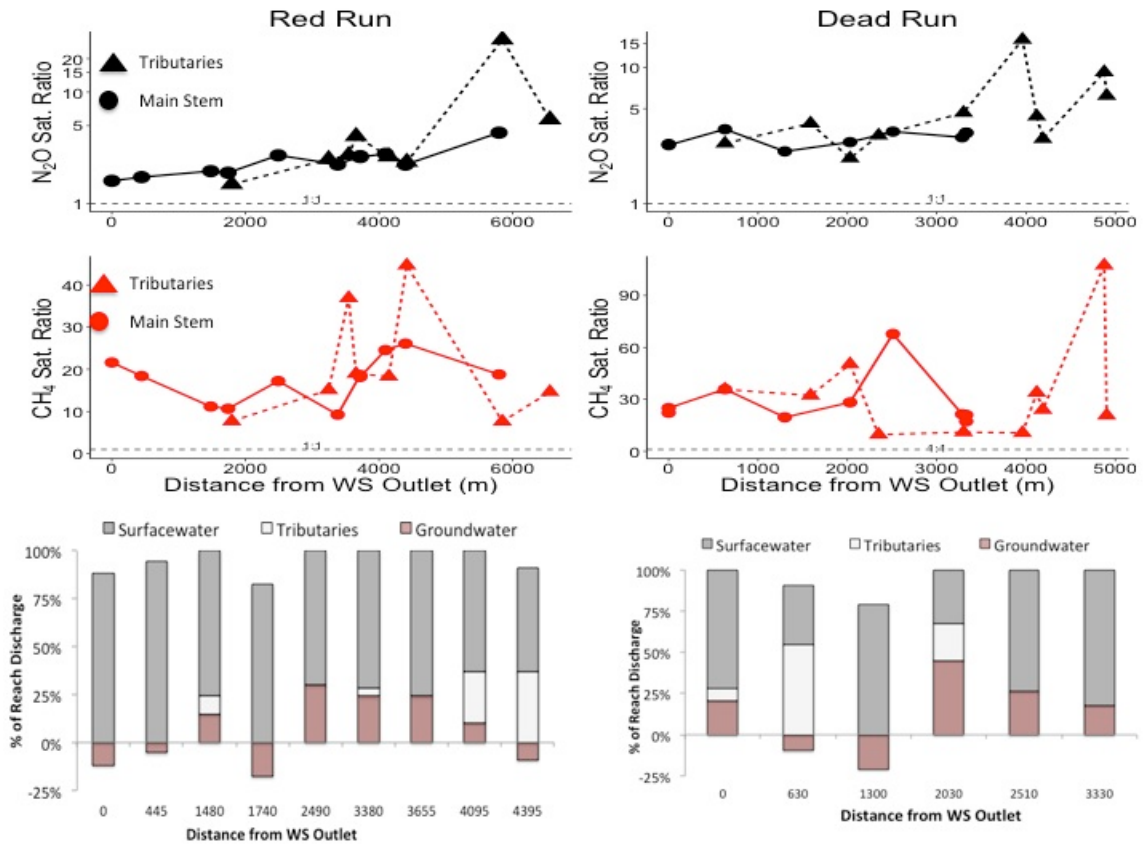


Figure 3.5 Longitudinal variability in  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{CH}_4$  saturation ratios from a spring synoptic survey in Dead Run and Red Run. The bottom panel shows the proportion of discharge at each sampling location from tributaries, surface water upstream of the reach, and groundwater inflow along the main stem reaches. Variable water sources along the main stem may contribute to  $\text{CH}_4$  and  $\text{N}_2\text{O}$  along the urban watershed continuum.

### 3.8 Discussion

#### 3.8.1. Overview

This study showed strong relationships between urban water quality and GHG saturation across streams draining different forms of urban infrastructure. Nitrogen concentrations were correlated with  $\text{N}_2\text{O}$  and  $\text{CO}_2$  saturation. Significant relationships



between infrastructure category and GHG saturation were not detected. However, the stark gradients in TDN, dissolved oxygen,  $\text{DOC}:\text{NO}_3^-$ , and other GHG predictors across the four categories suggest that infrastructure may have an indirect influence on biogeochemical processes in streams. Relationships between anaerobic  $\text{CO}_2$  and  $\text{N}_2\text{O}$  concentrations suggest that anaerobic metabolism contributes to  $\text{N}_2\text{O}$  production along hydrologic flowpaths.

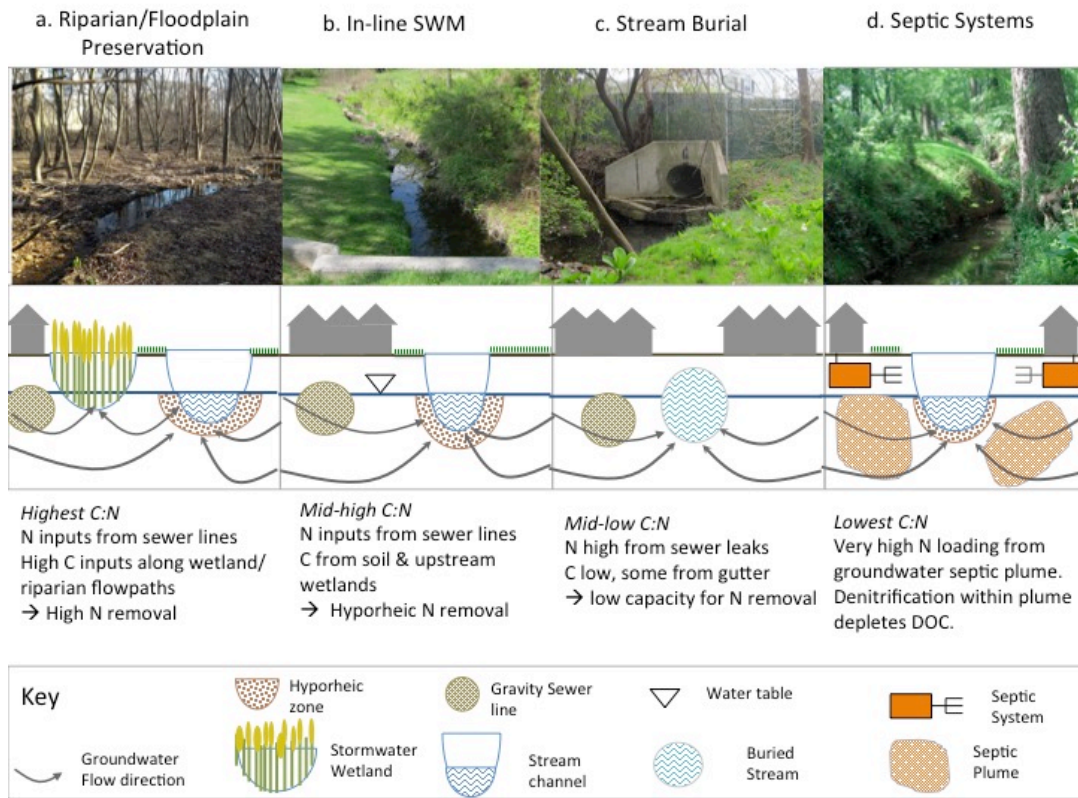


Figure 3.6 Conceptual illustrations of hypothesized ways in which headwater infrastructure can influence C and N delivery, processing and GHG production along highly altered subsurface flowpaths. Streams with preserved or restored floodplain/riparian zones (a) are likely to have high  $\text{DOC}:\text{NO}_3^-$  ratios due to C loading from saturated soils and ample opportunities for N removal in wetland and floodplain sediments. Streams with in-line SWM wetlands, but degraded riparian zones (b) are likely to have slightly lower  $\text{DOC}:\text{NO}_3^-$  if N inputs from leaky sewers are not attenuated in the riparian zone. Completely buried streams (c) may have N and C inputs form leaks in adjacent gravity sewers, or plant matter in street runoff, but reduced microbial processing due to higher velocities and lack of soil / water interaction. Finally streams draining septic systems (d) may be highly enriched in N relative to C, depending on the connectivity and concentration of septic  $\text{NO}_3^-$  plumes adjacent to streams.

### 3.8.2 DOC: Nitrate as a Potential Indicator of Microbial Metabolism

By comparing various forms of infrastructure, results from this study support a growing understanding of the biogeochemical consequences of expanded hydrologic connectivity in urban watersheds. Strong inverse relationships between DOC and  $\text{NO}_3^-$  were present across all four infrastructure categories (Figure 3.4), which suggests that organic carbon availability modulates nitrogen loading to streams. DOC availability has been shown to control  $\text{NO}_3^-$  concentrations across terrestrial and aquatic ecosystems through a variety of coupled microbial processes (Hedin et al. 1998, Kaushal and Lewis 2005, Taylor and Townsend 2010). Varying forms of urban infrastructure also influenced DOC:  $\text{NO}_3^-$  stoichiometry, which suggests that infrastructure influences C and N inputs and/or microbial metabolism along flowpaths (Figure 3.6).

Understanding the locations of “hot spots” and process responsible for  $\text{N}_2\text{O}$  production and  $\text{NO}_3^-$  removal in watersheds is useful for informing watershed management. Strong positive relationships between  $\text{N}_2\text{O}$  saturation and anaerobic  $\text{CO}_2$  concentrations suggest that denitrification was the source of  $\text{N}_2\text{O}$ . By contrast, very low DOC:  $\text{NO}_3^-$  ratios in stream water with highest  $\text{N}_2\text{O}$  saturation suggest that nitrification was the dominant process at these sites. Taylor and Townsend (2010) suggest that the ideal DOC:  $\text{NO}_3^-$  stoichiometry for denitrification is 1:1, and that persistent conditions below that are more ideal for nitrification. DOC:  $\text{NO}_3^-$  was consistently below 1 in streams with Septic System infrastructure and consistently above 1 at sites in Riparian/Floodplain Preservation category, which suggests that DOC and  $\text{NO}_3^-$  were limiting to in-stream denitrification in these two infrastructure categories respectively. Conversely, the mean stoichiometric ratio was consistently near 1 in sites with In-line

SWM Wetlands and Complete Stream Burial. While DOC:  $\text{NO}_3^-$  stoichiometry in some streams appeared more favorable for nitrification; the positive anaerobic  $\text{CO}_2$  vs.  $\text{N}_2\text{O}$  relationships in these streams suggest that these gases were produced anaerobically (by denitrification). One possible explanation for this discrepancy is that the  $\text{N}_2\text{O}$  and  $\text{CO}_2$  observed in the stream were produced under stoichiometric conditions more favorable for denitrification along groundwater flow paths prior to emerging in the stream channel. Because sampling took place very close to the origin of the stream network (either buried in pipes or stormwater management wetlands), it is not necessarily surprising that groundwater inputs would dominate the GHG signal.

### 3.8.3 Effects of Infrastructure on $\text{N}_2\text{O}$ along the Urban Watershed Continuum

The present study documents some of the highest  $\text{N}_2\text{O}$  concentrations currently reported in the literature for streams and rivers, ranging from 0.009 to 0.55  $\mu\text{M}$ , with a median value of 0.07  $\mu\text{M}$  and mean of 0.11  $\mu\text{M}$   $\text{N}_2\text{O-N}$ . This range of concentration is greater than reported for headwater agricultural streams in the Midwestern United States (0.03 – 0.07  $\mu\text{M}$ , Werner et al. 2012; 0.03 to 0.15  $\mu\text{M}$ , Beaulieu et al. 2008). A similar range of dissolved  $\text{N}_2\text{O}$  concentrations was reported for macrophyte-rich agriculturally influenced streams in New Zealand (0.06 to 0.60  $\mu\text{M}$ , Wilcock and Sorrell, 2008). The only report of higher dissolved  $\text{N}_2\text{O}$  concentrations in streams is from a subtropical stream receiving irrigation runoff, livestock waste, and largely untreated urban sewage (saturation ratio max of 60 compared with 47 in this study; Harrison et al. 2005). Average daily  $\text{N}_2\text{O}$  emission estimates varied across sites from 0.1 to 3.7  $\text{mg N}_2\text{O-N m}^{-2} \text{d}^{-1}$  and fell within the range of daily estimates reported for nitrogen enriched agricultural streams in the Midwestern U.S. (mean: 0.84, max: 6.4  $\text{mg N}_2\text{O-N m}^{-2} \text{d}^{-1}$ , Beaulieu et al. 2008)

and tropical agricultural streams in Mexico (mean = 0.4, max=5.9 mg N<sub>2</sub>O-N m<sup>-2</sup> d<sup>-1</sup>, Harrison and Matson 2003). Controls on N<sub>2</sub>O emissions from urban waterways warrant further study as a potentially significant contributor to global GHG.

N<sub>2</sub>O emissions from agricultural runoff are currently included in IPCC estimates, but emissions associated with urban ecosystems are not currently accounted for (Ciais et al. 2013). Urban and agricultural streams are similar in that they receive excess nitrogen inputs, including widespread groundwater N contamination. Key differences arise when considering N<sub>2</sub>O budgets. Whereas agricultural stream emissions are estimated based on annual fertilizer inputs, N in urban streams is derived from diffuse, spatially heterogeneous nonpoint sources. For instance, studies in Baltimore have found that atmospheric deposition and human waste contribute approximately 25 % and 50% of nitrate inputs, while the remainder is derived from soils and plant materials (Kaushal et al. 2011; Pennino et al. 2015). The proportion of these sources and others is likely to vary widely across and within watersheds. Recent reviews have suggested that N<sub>2</sub>O emissions from human waste (i.e. leaky sewer lines, septic system effluent, dug pits) are important globally but also largely unmeasured (Strokal and Kroeze 2014; UNEP 2013). Direct emissions from wastewater treatment plants (WWTPs) as well as indirect emissions from post-treatment effluent in rivers are currently accounted for in IPCC methodology. However, potential leaks from aging gravity fed sanitary sewers are not (UNEP 2013). Short et al. (2014) measured N<sub>2</sub>O concentrations in WWTP influent from gravity fed sanitary sewers in Australia and determined that gravity fed sanitary sewers are super-saturated with N<sub>2</sub>O, with concentrations in excess of equilibrium by as much as 3.5 μM. Average daily sewer pipe *xs*N<sub>2</sub>O concentrations were 0.55 μM, which is nearly

identical to the maximum  $x_s\text{N}_2\text{O}$  measured in the present study ( $0.54 \mu\text{M}$ ). While wastewater only contributes a portion of excess N in urban streams, further accounting for this source can likely improve urban GHG budgets substantially.

#### 3.8.4 Effects of infrastructure on $\text{CH}_4$ along the Urban Watershed Continuum

Methane was consistently super-saturated across all streams in this study, and varied significantly across headwater infrastructure categories. The highest  $\text{CH}_4$  abundance was measured in sites with riparian reconnection (RRRM and RRRB) followed by streams draining in-line SWS wetlands (DRKV and DRGG) (Figure 3.3). As with  $\text{N}_2\text{O}$  and  $\text{CO}_2$ ,  $\text{CH}_4$  saturation was negatively correlated with DO, however  $\text{CH}_4$  was positively correlated with  $\text{DOC}:\text{NO}_3^-$  while other gases had stronger relationships with TDN (Table 3.4). These patterns suggest that, along with redox conditions, carbon availability may modulate the relative proportion of different gases that occur in stream water. Measurements of  $\text{CH}_4$  saturation ratio (3.0 to 2157) fell within the lower range of previously measured values in agricultural streams in Canada (sat. ratio 500 to 5000, Baulch et al 2011a). Mean daily  $\text{CH}_4$  emissions estimates in this study varied from 0.1 to  $3.5 \text{ mg CH}_4\text{-C m}^{-2}\text{d}^{-1}$  and are an order of magnitude lower than measurements in agricultural streams of new Zealand (Wilcock and Sorrel, 2008;  $17\text{-}56 \text{ mg CH}_4\text{-C m}^{-2}\text{d}^{-1}$ ) and southern Canada ( $20\text{-}172 \text{ mg C m}^{-2} \text{d}^{-1}$ , Baulch et al. 2011). These prior studies also included ebullitive (i.e. bubble) fluxes, whereas the present study only examined diffusive emissions. Wilcock and Sorrel (2008) also measured plant transport where sedge plants with aerenchyma were found. These plant types were not present in this study, although they may be present in adjacent stormwater wetlands and floodplains. Measurements  $\text{CH}_4$  emission estimates in the present study have a large margin of

uncertainty due to factors related to gas flux parameters discussed above. Consistent variations in CH<sub>4</sub> abundance across headwater management categories, as well as negative relationships with TDN, suggest that CH<sub>4</sub> is susceptible to human activities such as wetland and floodplain reconnection in urban areas.

Results were consistent with prior studies, showing that streams are commonly super-saturated with CH<sub>4</sub> (e.g. Jones and Mulholland 1998; Wilcock and Sorrel 2008; Baulch et al. 2011a; Werner et al. 2012). In contrast with IPCC methodology (Ciais et al. 2013) there is growing evidence that human impacts on watersheds influence CH<sub>4</sub> emissions from streams (Kaushal et al. 2014c, Crawford and Stanley 2015; Stanley et al 2015). Prior studies have found CH<sub>4</sub> production tends to be elevated in streams with fine benthic sediments, an influx of organic matter, or significant wetland drainage (Dinsmore et al. 2009; Dawson et al, 2002; Baulch et al. 2011). Significant negative relationships between TDN and CH<sub>4</sub> were detected in this study, and elevated CH<sub>4</sub> concentrations in streams draining intact floodplains and/or stormwater management wetlands.

### 3.9 Conclusions

Urban watersheds are highly altered systems, with numerous hotspots of biogeochemical activity and GHG emissions. The present study demonstrates that GHG saturation and emissions from urban headwater streams can be similar in magnitude to those of agricultural streams, and warrant further study. Variations in urban infrastructure (i.e. SWM wetlands, riparian connectivity, septic systems) can affect C:N stoichiometry as well as redox state of aquatic ecosystems and significantly alter GHG production. Based on the observed temporal and spatial patterns in this study, variation

in nonpoint sources and flowpaths of nitrogen has potential to modify microbial metabolism of organic matter and may contribute significantly to urban GHG budgets.

An increasing number of scientific studies have compiled GHG budgets of anthropogenic and ecological emissions across cities (e.g., Brady and Fath, 2008; Hoornweg et al. 2011; Weissert et al. 2014). Understanding both the anthropogenic and ecological components of a regional GHG budget is crucial for setting GHG targets and managing ecosystem services (Bellucci et al. 2012). The role of human activities on GHG emissions from agriculturally impacted waterways is well recognized (Ciais et al. 2013; Nevison 2000). However, further studies examining the magnitude and variations in GHG emissions along the urban watershed continuum, which explicitly includes flowpaths from engineered infrastructure to streams and rivers (e.g. Kaushal and Belt 2012), are necessary. As cities and populations continue to expand globally, GHG emissions from wastewater are likely to rise. A greater understanding of the interplay between urban water infrastructure and biogeochemical processes is necessary to mitigate negative consequences of  $N_2O$ ,  $CH_4$ , and  $CO_2$ .

## Chapter 4: Interaction between Land Cover and Climate influence CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O fluxes from Urban Soils

### 4.1 Abstract

Urban lawns are widespread across the United States, and have been shown to accumulate carbon and nitrogen over time (Milesi et al. 2005; Pouyat et al. 2006; Raciti et al 2011). Recent studies have shown that, while soils accumulate carbon and nitrogen, they can also be significant N<sub>2</sub>O sources and weakened CH<sub>4</sub> sinks (Kaye et al. 2004; Groffman and Pouyat 2009; Townsend-Small and Czimczik 2010). The Baltimore Ecosystem Study LTER site maintains a 15-year record of soil greenhouse gas (GHG) emission measurements from urban lawns and forests. This study addresses 1) sensitivity of GHG fluxes from lawns and forests to temperature and soil moisture, 2) overall global warming potential of soils urban vs. rural soils, and 3) the role of soil emissions on a county-scale GHG budget. Temperature sensitivity of respiration was not significantly different across vegetation types. Lawns were net sources of CH<sub>4</sub> and N<sub>2</sub>O with an average flux of 0.03 Mg CO<sub>2eq</sub> ha<sup>-1</sup>yr<sup>-1</sup>. However, when net CO<sub>2</sub> consumption by soil organic carbon storage from in Baltimore (Raciti et al. 2011) was taken into account, lawns were much stronger GHG sinks (-0.78 Mg CO<sub>2eq</sub> ha<sup>-1</sup>yr<sup>-1</sup>). With 49% forest cover and 35% lawns, soil carbon storage and GHG sinks offset 0.5% of anthropogenic emissions from Baltimore County, MD (Brady and Fath 2008).



## 4.2 Introduction

Urban lawns are widespread and heavily managed ecosystems, covering three times the area of any other irrigated crop in the United States (Milesi et al. 2005; Polsky et al. 2014). There is growing interest in the biogeochemical function of turfgrass, especially regarding carbon and nitrogen storage, greenhouse gas emissions, and water usage (Pataki et al. 2011). Fertilization and irrigation facilitate high levels of primary productivity in urban grasslands despite regional or inter-annual climatic variability (Milesi et al. 2005; Hall et al. 2015). These organic matter pools accumulate over time and may serve as important sinks for nitrogen fertilizer in urban watersheds (Zhu et al. 2006; Raciti et al. 2008), and store more carbon than native soils as well (Kaye et al. 2005; Pouyat et al. 2006; Pouyat et al. 2009; Raciti et al. 2011). For instance, Kaye et al. (2005) found that irrigated, fertilized residential lawns in Denver had higher primary productivity and 2.5 times greater soil carbon density than agricultural soils. In Baltimore, Raciti et al. (2011) estimated significant C and N accumulation rates ( $0.083 \text{ kg C m}^{-2} \text{ yr}^{-1}$  and  $8.3 \text{ g N m}^{-2} \text{ yr}^{-1}$ ) across a 40-year chronosequence of residential urban grasslands, overlying formerly agricultural soils. Despite trends in carbon accumulation, urban soils can have the potential to be greenhouse gas sources, especially when indirect emissions from management practices are taken into account (Townsend-Small and Czimczik 2010). N-saturated soils can also be significant sources of  $\text{N}_2\text{O}$  (Eichner 1990; Mosier et al. 1998a; Bremer 2006), and urban lawn ecosystems are also regularly sources or weakened sinks of  $\text{CH}_4$  (Kaye et al. 2004; Groffman and Pouyat 2009). If N accumulation exceeds mechanisms for storage in soils, N leaching may increase over time as well (Groffman et al. 2009).

The global warming potential (GWP) of lawns remains uncertain due in part to a lack of long-term monitoring in urban areas. Existing studies have shown conflicting results regarding increased  $\text{N}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{CH}_4$  emissions. There is reason to expect increased  $\text{N}_2\text{O}$  from fertilized lawns, given that fertilized agricultural landscapes are substantial  $\text{N}_2\text{O}$  sources (Mosier et al. 1998a). Townsend-Small et al. (2011) and Kaye et al. (2005) found that  $\text{N}_2\text{O}$  emissions from lawns were comparable to or higher than in agricultural soils in California and Colorado respectively. By contrast, Raciti et al. (2008) did not find differences in  $\text{N}_2\text{O}$  between fertilized urban lawns and undisturbed forests in Baltimore. Reductions in methane consumption may additionally contribute to GWP of urban lawns. While upland forest and grassland soils are generally  $\text{CH}_4$  sinks (Castro et al. 1995), several studies have shown reduced  $\text{CH}_4$  consumption by urban lawns and agricultural fields, potentially due to ammonium inhibition of  $\text{CH}_4$  consumption following fertilization (Mosier et al. 1998b; Kaye et al. 2004; Groffman and Pouyat 2009; Costa and Groffman 2013). While it is clear that a suite of interacting biotic processes control GHG emissions from urban grasslands, the net influence of these varying biogeochemical processes on global warming potential (GWP) warrants further study.

I examined annual and seasonal trends in GHG emissions from urban soils Baltimore, MD, USA using data collected over 15 years, in order to better understand the magnitude and drivers and inter-annual variability in GWP of urban ecosystems. Prior studies in Baltimore (Groffman et al. 2009; and Groffman and Pouyat 2009) have shown significantly higher  $\text{CO}_2$  and  $\text{CH}_4$  emissions from fertilized lawns, compared with forest soils for earlier parts of this 15-year record. Along with potential ammonium inhibition, changes in physical environments of lawns may influence net GHG production as well.

For instance, vegetation cover (i.e. forest vs. grass) has been shown to influence soil temperature and moisture (Savva et al. 2010; Savva et al. 2013), with significantly higher soil temperatures in lawns compared to forests. The present study examines temperature sensitivity (Q10) for CO<sub>2</sub> as well as the interacting roles of temperature, moisture, seasonality, and land cover on gas emissions. Soil respiration is kinetically linked to temperature along with other factors such as organic carbon quality, and soil moisture, root biomass, and phenology (Davidson et al. 2006). While warming temperatures have been shown to increase soil CO<sub>2</sub> emissions (Melillo et al. 2011), temperature sensitivity may also differ between forests and grasslands due to differences in root turnover, phenology, and litter quality (Boone et al. 1998; Davidson et al. 2006; Contosta et al. 2013). I examined various controlling factors on GHG emissions over annual timescales, and additionally explored temporal and spatial variability in temperature sensitivity (Q10) of soil respiration across urban and rural landscapes in order to improve future predictions of global warming potential from temperate urban ecosystems.

#### 4.3 Methods

##### 4.3.1 Site Description

Soil gas emissions were measured as part of the Baltimore Ecosystem Study long-term ecological research program (BES LTER, [www.beslter.org](http://www.beslter.org)). Study sites included two forested urban parks, two forested rural parks, and two suburban/ institutional lawns. Urban and rural forest sites were located within Gwynns Falls watershed (76° 30', 39°15', 1,700km<sup>2</sup>), the main study area of BES LTER. The watershed is located in the Piedmont physiographic province, and is underlain by a mixture of crystalline granitic

bedrock (gneiss, micaceous schist) and mafic rocks (weathered amphibolite and diabase) (Dicken et al. 2008).

Long-term urban forest study plots were established in two Baltimore parks- Leakin and Hillsdale in 1998. Sites in Hillsdale Park were discontinued in 2005 due to vandalism. Rural forest sites were located across a slope transect in Oregon Ridge Park, in Cockeysville, MD in 1998 as well. Soil fertility is mixed across urban and rural sites, with the lower fertility soils overlying crystalline rocks and higher fertility overlying the more mafic bedrock (Groffman et al. 2006). Land use is predominantly medium to high-density residential development, with 34% impervious cover, 25% urban lawn, 40% tree cover, 0.5% barren, and 0.5% water. Groffman et al. (2006) describe soil and vegetation characteristics of the forested sites in great detail. All forested sites were mixed hardwood stands consisting mainly of *Liriodendron tulipifera* (tulip poplar), *Quercus rubra*, *Quercus velutina* (red and black oak), *Carya tomentosa* (black walnut), and *Acer rubrum* (red maple). Woody shrubs *Viburnum acerfolium* and *Lindera benzoin* dominated the understory at all four sites. Urban plots have higher herbaceous ground cover (12-28%) compared with rural forest plots (1-9%). Non-native species and vines were present at all sites, but did not contribute significantly to overall vegetation cover (Groffman et al. 2006).

Long-term turf grass study sites were established in 2001 at the University of Maryland Baltimore County (UMBC) in Catonsville, MD and McDonogh School (MCD) in Owings Mills, MD. Grasses were not irrigated at any site. Plots at MCD were periodically fertilized with manure and mowed infrequently. Plots at UMBC campus had either high or low-intensity management. Low-intensity plots were fertilized in spring

with  $9.7 \text{ g N m}^{-2} \text{ yr}^{-1}$  and mowed every one to two weeks. High-intensity plots were fertilized with  $19.5 \text{ gNm}^{-2} \text{ yr}^{-1}$  and mowed every two to three weeks (Groffman et al. 2009).

#### 4.3 2 Soil gas flux measurements

Soil fluxes of greenhouse gases, carbon dioxide ( $\text{CO}_2$ ), methane ( $\text{CH}_4$ ), and nitrous oxide ( $\text{N}_2\text{O}$ ), were measured monthly between 1998 and 2013. A summary of study sites and date ranges for each measurement can be found in Table 4.1.

Measurements took place across a total of 48 gas collars split amongst six sites- two rural forest (ORU, ORM), two urban forest (LEA, HD), and two urban lawns (MCD, UMBC), with two sub-plots at each site.

Table 4.1. Description of soil gas flux measurements

| Site           | Urban forest             |                       | Rural Forest               |                          | Lawn                    |                         |
|----------------|--------------------------|-----------------------|----------------------------|--------------------------|-------------------------|-------------------------|
|                | Leakin Park (LEA)        | Hillsdale Park (HD)   | OR Ridge Upper-slope (ORU) | OR Ridge Mid-slope (ORM) | UMBC campus (UMBC)      | McDonogh School (MCD)   |
| Plots          | 2                        | 2                     | 2                          | 2                        | 2                       | 2                       |
| Collars        | 4                        | 4                     | 4                          | 4                        | 3                       | 4                       |
| Gas Flux range | 11/10/1998<br>12/17/2013 | 5/5/2000<br>5/19/2004 | 11/10/1998<br>12/20/2013   | 11/10/1998<br>5/25/2010  | 6/25/2001<br>12/27/2013 | 11/18/1999<br>4/30/2001 |

Fluxes were measured using the static chamber method. Round collars were installed in quadruple or triplicate in each plot. Measurement involved placing an airtight lid with butyl stopper, and piercing the stopper with a syringe to pull 10 mL of headspace every 5 minutes. Flux rates were calculated based on the change in headspace concentration over 25 minutes. To account for long-term changes in soil accumulation in the gas collars, collar volumes were measured on each sampling occasion by measuring the depth from the top of collar to ground. Gas samples were stored in pre-evacuated

9mL vials and analyzed at the Cary Institute of Ecosystem Studies *via* gas chromatography. CO<sub>2</sub> was measured using a thermal conductivity detector, N<sub>2</sub>O with an electron capture detector, and a flame ionization detector was used for CH<sub>4</sub>.

#### 4.3.3 Soil temperature and moisture measurements

Continuous soil moisture and temperature sensors were deployed at the plot-scale. Both sensors were placed at 10cm depth. Data was collected and made available by the Baltimore Ecosystem Study LTER. In order to compare temperature and gas fluxes, I matched mean daily plot-scale temperature data (2 plots / site) to chamber –scale (3 or 4 chambers/plot) gas fluxes. On dates when plot-scale temperature data were not available, temperatures were gap-filled by linearly interpolating site-specific relationships between soil temperature and the historical record of mean daily air temperature from the nearby NOAA Meteorological Station at Baltimore Washington International Airport (<http://www.ncdc.noaa.gov/cdo-web/datasets>).

During the early part of the sampling record, soil moisture was recorded manually in conjunction with gas flux measurements, or within a few days. Where soil moisture measurements were not available on the same day as gas fluxes, the most recent measurement within 7 days was used. If no measurement was taken within a 7-day window of a flux measurement, that flux was excluded from the record.

#### 4.3.4 Statistical Analysis: Controls on GHG Emissions

Linear mixed effects models were used to examine the roles of land cover type, temperature, soil moisture, seasonality, and inter-annual variability on CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O emissions. Four predictive models for each gas were run and compared in order to address the following questions: 1) Does soil moisture significantly influence the

temperature sensitivity of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O emissions across land cover types? 2) Do emissions indicate seasonal or inter-annual associated with soil moisture or temperature? These models included four configurations of the following fixed effects: ‘Land Cover’, ‘Soil Temperature’, ‘Soil Moisture’, ‘Season’, and ‘Year.’ Models were run separately for each independent variable (CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O). The four configurations of fixed effects (Table 4.2) included Land Cover x Temperature, and Land Cover x Temperature x Soil Moisture, with an additional fixed effect of either Year or Season for each. Each of the four models predicted exponential relationships between soil fluxes and various fixed effects (Equation 4.1). Predicted fluxes were re-exponentiated in order to compare with observed values. Where doing so improved AIC score, random effects were included to take into account variability across sites within a land cover class, and plot within a site.

Models were compared using in AIC score, residual standard error (RSE) and sum of squared residuals ( $r^2$ ) for each model. RMSE and  $r^2$  were determined by performing linear regressions of predicted vs. observed gas flux values. All analyses were performed using R statistical language (R Core Team 2014), and package *nlme* for mixed effects modeling (Pinheiro and Bates 2012). Model comparisons were made with the restricted maximum likelihood estimation method. I additionally tested for the necessity of random effects in each model by running the same fixed-effects structure with and without random effects and compared AIC scores. Model assumptions of equal variances and normal distribution were evaluated by visually inspecting residuals of each model.

#### 4.3.5. Statistical Analysis: Temperature Sensitivity of Soil Respiration

Daily soil respiration was modeled for each site using the ‘prediction’ model in Table 4.2. Predictive models were based on log – transformed CO<sub>2</sub> fluxes, effectively making giving these models the exponential form seen in Equation 4.1,

$$\text{Eq. 4. 1} \quad \text{Resp} = \beta e^{kT}$$

where *Resp*= soil respiration (gCO<sub>2</sub>-C m<sup>-2</sup> hr<sup>-1</sup>),  $\beta$  is the site and year or season-specific regression intercept, and *k* the site, year and season- specific slope. The ‘predict’ function in R was used, in order to generate a vector of log-transformed values of *Resp*, as well as log-transformed values for each random effect, where applicable. Final *Resp* values for each site were determined for every season and year by re-exponentiating predicted values and adding random effects *Resp*. Q10 values for each site, season and year were calculated with following equation 4.2.

$$\text{Eq. 4.2} \quad Q10 = \frac{R(T10)}{RT}$$

where T is a reference temperature and T10 is the reference temperature (10 C) + 10 C.

Two-way ANOVAs were run to test for effects of season or year and land cover on Q10.

#### 4.3.5 Analysis: Modeling annual GHG fluxes

The ‘prediction’ model was used to interpolate each gas to examine annual and seasonal variability GHG emissions of CH<sub>4</sub> and N<sub>2</sub>O as well as CO<sub>2</sub>. Because continuous soil moisture was not available for the entire record, and did not substantially improve model fit (Table 4.2), it was not included in the prediction model. This temperature-based approach is commonly applied to CO<sub>2</sub> emissions over annual (Melillo et al. 2011) and seasonal (Fahey et al. 2005b; Contosta et al. 2011) timescales.



ANOVAs were run to test for the effect of land cover on annual CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O, emissions as well as 100-year global warming potential (GWP). Because flux measurements of CO<sub>2</sub> represent gross flux while N<sub>2</sub>O and CH<sub>4</sub> are net fluxes, I calculated GWP of N<sub>2</sub>O and CH<sub>4</sub> (GWP<sub>N<sub>2</sub>O+CH<sub>4</sub></sub>) without CO<sub>2</sub>. I then compared GWP to estimates of soil organic carbon (SOC) accumulation to evaluate the sensitivity of this carbon sink to non-CO<sub>2</sub> gases. Calculation of GWP<sub>N<sub>2</sub>O+CH<sub>4</sub></sub> followed IPCC 2007 methodology, in which CH<sub>4</sub> and N<sub>2</sub>O fluxes are multiplied by their estimated GWP compared to CO<sub>2</sub> of 21 and 310 respectively.

Table 4.2. Results from mixed effects models fitting exponential relationships between net soil- CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O fluxes and various Main Effects (temperature, site, year, soil moisture, and season). Random effects (P/C) signify which models incorporated effects of ‘Plot’ at each site and ‘chamber’ in each plot in a given model. AIC, residual standard error (RSE) and r<sup>2</sup> are reported for each model. Models A-D are used to examine the role of inter-annual *vs.* seasonal variability and temperature alone *vs.* soil moisture and temperature on gas fluxes. Prediction is the final model used for estimating annual flux.

|                  | Model ID   | Fixed Effects                 | Random Effects | AIC   | RMSE | r <sup>2</sup> |
|------------------|------------|-------------------------------|----------------|-------|------|----------------|
| CO <sub>2</sub>  | A          | Site*Temp + Yr *Temp          | n.a.           | 7632  | 0.57 | 0.59           |
|                  | B          | Site*Temp*Season              | P/C            | 8979  | 0.57 | 0.39           |
|                  | C          | Temp*SM*Site*Season           | P/C            | 9156  | 0.58 | 0.44           |
|                  | D          | Temp*SM*Site+Temp*Yr+SM*Yr    | P/C            | 7738  | 0.56 | 0.62           |
|                  | Prediction | Temp*Site*Season + Yr *Temp   | n.a.           | 5489  | 0.56 | 0.64           |
| CH <sub>4</sub>  | A          | Site*Temp + Yr *Temp          | P/C            | -3415 | 0.08 | 0.32           |
|                  | B          | Site*Temp*Season              | P/C            | -3188 | 0.07 | 0.28           |
|                  | C          | Temp*SM*Site*Season           | P/C            | -2687 | 0.08 | 0.31           |
|                  | D          | Temp*SM*Site+Temp* Yr +SM* Yr | P/C            | -3172 | 0.08 | 0.35           |
|                  | Prediction | Temp*Site*Season + Yr *Temp   | P/C            | -7709 | 0.08 | 0.34           |
| N <sub>2</sub> O | A          | Site*Temp + Yr *Temp          | n.a.           | 7410  | 0.85 | 0.47           |
|                  | B          | Site*Temp*Season              | n.a.           | 8437  | 0.61 | 0.15           |
|                  | C          | Temp*SM*Site*Season           | n.a.           | 8662  | 0.70 | 0.21           |
|                  | D          | Temp*SM*Site+Temp* Yr +SM* Yr | n.a.           | 7568  | 0.85 | 0.49           |
|                  | Prediction | Temp*Site*Season + Yr *Temp   | n.a.           | 5521  | 0.85 | 0.50           |

#### 4.3.5 Scaling up: regional GHG fluxes from soils

I estimated the average annual contribution of urban soils to GHG forcing (1998-2013) based on differences in GWP between forested (urban + rural) and other land covers. I utilized a fine-resolution ( $1\text{m}^2$ ) land cover map of Baltimore County procured for Baltimore Ecosystem Study project by the Spatial Analysis Laboratory at the University of Vermont. The map included layers for lawn, forest, impervious, barren, and water coverage and was made using imagery from 2007. Land cover datasets from 2004 and 2011 showed minimal change in vegetation cover for Baltimore County during the earlier and later parts of this record. After calculating  $\text{GWP}_{\text{CH}_4+\text{N}_2\text{O}}$  for lawns and forests (rural forest used rather than urban) countywide soil emissions in  $\text{CO}_2\text{eq}$  were estimated. This scaling exercise depended on the assumption that soil temperature and temperature sensitivity of GHG emissions were consistent within each land cover type for the entire spatial extent.

### 4.4 Results

#### 4.4.1 Controls on GHG Emissions

Soil temperature, moisture, year, site, and season all significantly influenced  $\text{CO}_2$  fluxes (Table 4.2). Model configuration A, which incorporated site, soil temperature, and annual variability and was a stronger predictor of gas fluxes than Models B-D, which incorporated seasonality and/or soil moisture (based on AIC). The second-best model for  $\text{CO}_2$  and  $\text{N}_2\text{O}$  was Model D, which incorporated soil moisture and inter-annual variability. Model D was also second- best for  $\text{CH}_4$  in terms of  $r^2$ , but third best in terms of AIC. Comparisons among models A-D signify that annual variability appears to have a stronger influence than seasonality on this dataset. Additionally, while soil moisture is

significantly correlated with all three gases, including it in the model did not necessarily improve model fit compared with temperature alone (Table 4.2). This result helps to justify the omission of soil moisture in the prediction model (due to lack of long-term continuous soil moisture data). The prediction model for each gas varied in model fit ( $r^2$ ) from 0.34 for CH<sub>4</sub>, 0.50 for N<sub>2</sub>O and 0.66 for CO<sub>2</sub>.

#### 4.4.2 Temperature sensitivity of respiration

Q10 values exhibited a wide range, both when estimated by season (0.61 – 7.9) and by year (1.2 - 5.6). Average Q10 values across the dataset were relatively consistent between seasonal and annual estimates (2.6 and 2.8 respectively) (Tables 4.3, 4.4).

ANOVAs results showed no significant groupings of Q10 across sites, seasons, or years.

Table 4.3. Summary of Q10 results for models varying by year

|      | Urban Forest |      | Lawn/Grass |      | Rural Forest |      |
|------|--------------|------|------------|------|--------------|------|
|      | HD           | LEA  | MCD        | UMBC | ORM          | ORU  |
| 1999 | 2.09         | 2.50 | n.a.       | n.a. | 2.18         | 2.88 |
| 2000 | 2.02         | 1.66 | 3.00       | n.a. | 2.32         | 2.59 |
| 2001 | 6.18         | 3.39 | 5.56       | 3.50 | 2.91         | 5.35 |
| 2002 | 1.27         | 1.58 | 2.33       | 2.21 | 2.07         | 1.81 |
| 2003 | 3.08         | 3.38 | 3.72       | 2.16 | 2.92         | 3.22 |
| 2004 | 2.51         | 2.02 | 1.50       | 1.18 | 2.07         | 2.71 |
| 2005 | 3.40         | 3.27 | 5.11       | 2.21 | 2.13         | 2.44 |
| 2006 | 1.73         | 1.62 | 2.76       | 1.52 | 1.98         | 2.11 |
| 2007 | 1.62         | 2.26 | 1.47       | 2.25 | 1.49         | 2.24 |
| 2008 | 3.23         | 4.09 | n.a.       | 1.31 | 4.45         | 4.37 |
| 2009 | 1.79         | 2.12 | n.a.       | 2.22 | 1.88         | 2.71 |
| 2010 | 3.64         | 3.20 | n.a.       | 2.79 | 4.02         | 3.22 |
| 2011 | 3.22         | 3.48 | n.a.       | 3.14 | n.a.         | 4.90 |
| 2012 | n.a.         | 3.41 | n.a.       | 2.49 | n.a.         | 3.15 |
| 2013 | n.a.         | 2.79 | n.a.       | 3.43 | n.a.         | 3.71 |

Table 4.4 Summary of Q10 values estimated seasonally

|        | Lawn/Grass |      | Rural Forest |     | Urban Forest |     |
|--------|------------|------|--------------|-----|--------------|-----|
|        | MCD        | UMBC | ORM          | ORU | HD           | LEA |
| Fall   | 3.2        | 3.1  | 2.1          | 3.8 | 2.2          | 2.4 |
| Spring | 1.5        | 1.7  | 2.3          | 3.2 | 2.6          | 3.9 |
| Summer | 2.9        | 7.9  | 5.1          | 1.0 | 0.6          | 2.1 |
| Winter | 2.1        | 1.8  | 1.4          | 1.5 | 2.3          | 1.3 |

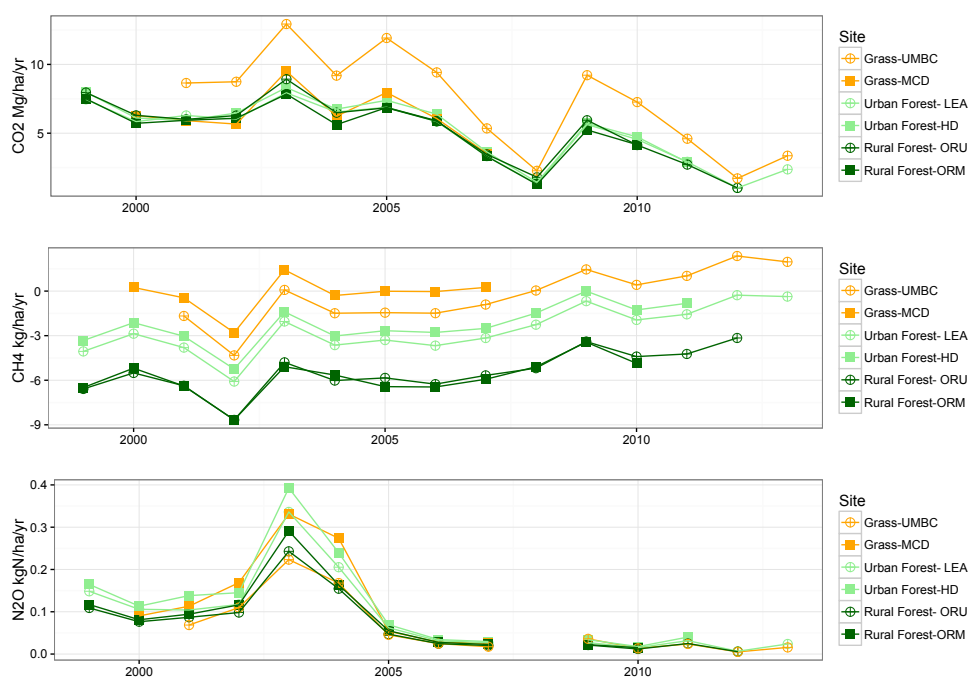


Figure 4.1 Predicted annual fluxes based on exponential models with fixed effects for site, season and temperature, and a random intercept for year. Overall  $r^2$  for  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2\text{O}$  models were 0.38, 0.32, and 0.21 respectively.

#### 4.4. 3 Annual GHG Emissions

Spatial and temporal variability in annual gas fluxes was apparent across urban forest, rural forest, and urban lawns. Gross soil  $\text{CO}_2$  fluxes were consistently highest at one of the lawn sites (MCD) compared with all forested sites (Figure 4.1). Across all sites, annual  $\text{CO}_2$  emissions varied from 4.8 to 19.6  $\text{Mg C ha}^{-1} \text{ yr}^{-1}$ . Net  $\text{CH}_4$  emissions

varied across sites. The overall range for all sites and years was  $-14.3$  to  $2.4 \text{ kg CH}_4 \text{ ha}^{-1} \text{ yr}^{-1}$  (positive= source to atmosphere, negative = net consumption by soil). Forested sites were consistently  $\text{CH}_4$  sinks or small sources, with annual mean fluxes of  $-11.4$  and  $10.8$  for the two rural forest sites, and  $-4.2$  and  $-4.0 \text{ kg CH}_4 \text{ ha}^{-1} \text{ yr}^{-1}$  for the urban forest sites. Lawn sites were consistently either very small  $\text{CH}_4$  sinks or net sources ranging from  $-0.62$  -  $0.69 \text{ Kg CH}_4 \text{ ha}^{-1} \text{ yr}^{-1}$  for UMBC and MCD sites respectively (Figure 4.1). Mean annual  $\text{N}_2\text{O}$  fluxes were significantly higher in urban forests than rural, and fluxes from lawns were not significantly different from either forest type. Average fluxes ranged from  $0.10$  to  $0.21 \text{ Kg N ha}^{-1} \text{ yr}^{-1}$ .

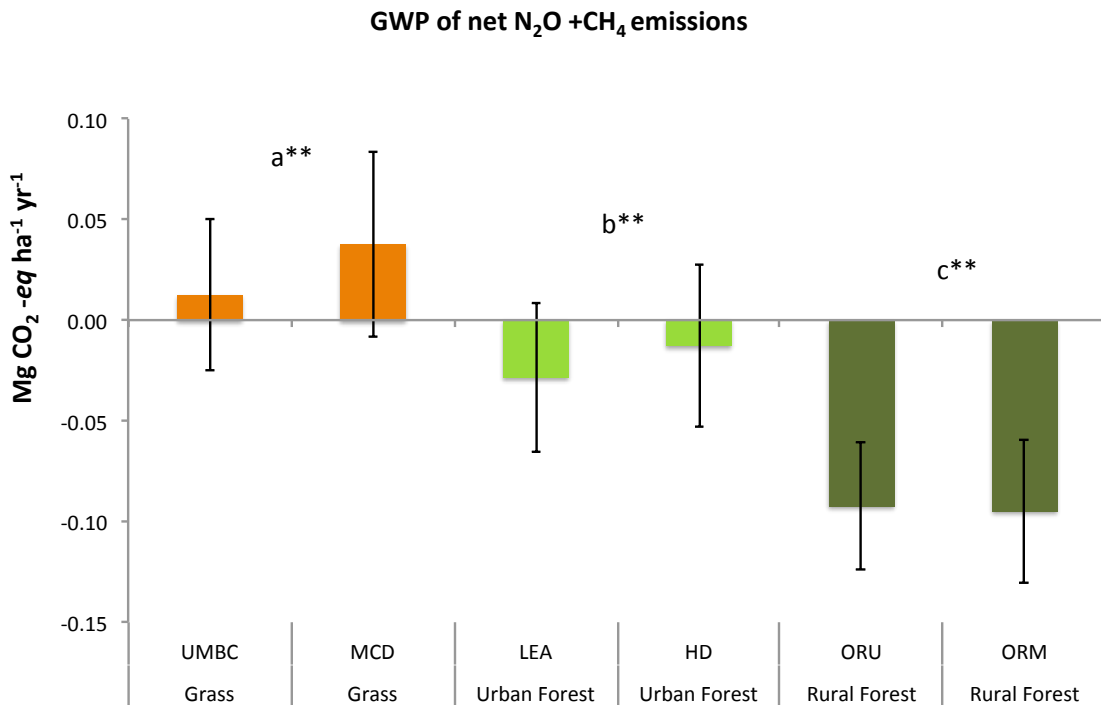


Figure 4.2 Average annual GWP of  $\text{N}_2\text{O} + \text{CH}_4$  across lawn, urban forest, and rural forest sites across the 15-year record. Error bars signify standard deviation of the mean. Letters show significant differences at

the 0.01\*\* or 0.05\* level between land cover types (grass, urban forest, rural forest) from a Tukey HSD pairwise test following one-way anova of GWP vs. land cover type.

Mean annual  $GWP_{N_2O+CH_4}$  varied as a function of land cover (Figure 4.2). Lawn soils were most often net sources of  $N_2O$  and  $CH_4$  with a range of -0.06 to 0.13  $Mg CO_2eq ha^{-1}yr^{-1}$ , while rural forests were consistently  $N_2O$  and  $CH_4$  sinks (-0.15 to -0.02  $Mg CO_2eq ha^{-1}yr^{-1}$ ). Urban forest sites fell in the middle, with a range -0.09 to 0.09  $Mg CO_2eq ha^{-1}yr^{-1}$ . This pattern was mainly driven by  $CH_4$ , which varied strongly across land cover types.  $N_2O$  emissions did not vary significantly with land cover type.

#### 4.4. Regional GHG Emissions from soils

Baltimore County encompasses a 1,700 $km^2$  area surrounding the city of Baltimore, MD. Based on 2007 imagery, forest cover composed 49% of county land cover and grass composed 35%. Impervious area was approximately 13% (Figure 4.3). When summed for the entire county, annual average  $GWP_{N_2O+CH_4}$  from lawn soils was 1,562  $Mg CO_2eq yr^{-1}$ , while  $GWP_{N_2O+CH_4}$  from forest soils was -8,156  $Mg CO_2eq yr^{-1}$ . The net effect of all forest and lawn soils in the county was a net sink of on non- $CO_2$  gases (-6,595  $Mg CO_2eq yr^{-1}$ ).

While gross  $CO_2$  emissions were elevated in lawns compared with rural forests (Figure 4.1), the net  $CO_2$  flux depends on organic matter production and storage. A recent study by Raciti et al. (2011) found that residential lawns accumulated carbon at a rate of 0.82  $Mg CO_2 ha^{-1} yr^{-1}$ , leading to higher carbon density in older lawn soils compared than in rural forests. When this potential  $CO_2$  sink is considered, lawns remain strong GHG sinks despite elevated  $GWP_{N_2O+CH_4}$ . Assuming this accumulation rate is consistent across lawns in the present study, the maximum annual  $GWP_{N_2O+CH_4}$  measured in this study would offset less than 16% of the  $CO_2$  sink from SOC accumulation, and the mean

$GWP_{N_2O+CH_4}$  would offset less than 4% (Figure 4.4). While forest soils may also accumulate carbon over time, these data were not available for comparison.

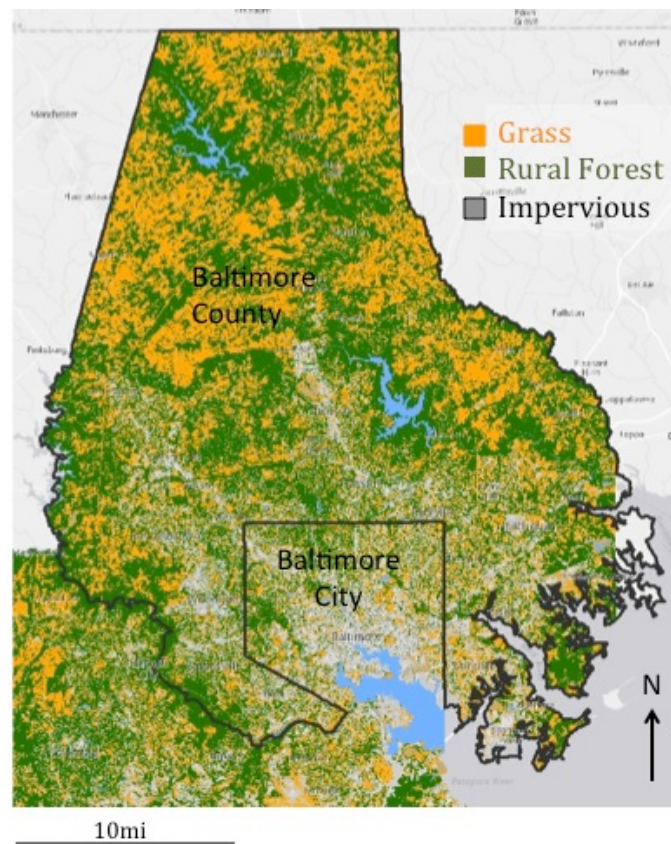


Figure 4.3. Map of lawn, forest, and impervious cover for Baltimore City and Baltimore County, MD.

#### 4.5 Discussion

##### 4.5.1 Spatial and Temporal Variability in soil GHG emissions

There were significant differences in net  $CO_2$  and  $CH_4$  fluxes across sites and land cover classes over the 15 –year study period. Modeled annual  $N_2O$  emissions were not significantly different across sites. Lawn sites had the highest  $CO_2$  and  $CH_4$  emissions throughout the study, while rural forests had the lowest. Carbon ( $CO_2$  and  $CH_4$ ) fluxes were intermediate from urban forest sites near downtown Baltimore. Temperature and soil moisture were both correlated with all three GHG fluxes across all sites, however

incorporating soil moisture into models with temperature did not significantly improve model fit (Table 4.2).

Annual estimated CO<sub>2</sub> emissions from urban lawns in this study varied from 0.5 to 1.1 kg C m<sup>-2</sup> y<sup>-1</sup> over 15 years and two sites. These estimates are very similar to measurements of residential lawns in Phoenix, AZ (1.1 kg C m<sup>-2</sup> y<sup>-1</sup>, Koerner and Klopatek 2002) but low compared with golf courses from the same study (6.9 kg C m<sup>-2</sup> y<sup>-1</sup>), or urban lawns in Fort Collins, CO (2.78 kg C m<sup>-2</sup> y<sup>-1</sup>, Kaye et al. 2005). Climatic differences such as water availability and growing season length may further explain differences between soil respiration fluxes in Baltimore and Arizona and Colorado.

Significant reduction in CH<sub>4</sub> uptake by soils was observed between lawns and rural forests, which led to increased GWP (Figure 4.2), and these results are consistent with Groffman and Pouyat 2009, as well as Costa and Groffman 2013 who examined methane dynamics at these sites. Costa and Groffman (2013) evaluated N sensitivity to CH<sub>4</sub> consumption *via* lab incubations and demonstrated a link between increased potential nitrification rates and reduced CH<sub>4</sub> consumption across urban and rural forests. Given these results, it is more likely that reductions in CH<sub>4</sub> consumption are being driven by microbial community dynamics than overt climatological forcing.

Trends in annual N<sub>2</sub>O emission estimates were surprisingly highest in urban forest soils, and there was no difference between fertilized lawn and rural forest soils. This result is consistent with prior studies in Baltimore (Groffman et al. 2009; Raciti et al. 2008), but remains surprising when compared with studies from highly fertilized lawns elsewhere (Kaye et al. 2004; Townsend-Small et al. 2011). For instance, Townsend-Small et al (2011) found that N<sub>2</sub>O emissions from fertilized urban lawns in California



were similar to or higher than nearby agricultural fields over 1 year of study. Kaye et al. (2004) also found similar fluxes between urban lawns and fertilized cornfields, both of which were ~10 times higher than native lawns. Measuring fluxes prior to and within several days of fertilizer applications is key to quantifying annual N<sub>2</sub>O emissions from managed lawns (Townsend-Small and Czimczik 2010). The temporal frequency of monthly N<sub>2</sub>O measurements is likely not sufficient for annual estimation, given the relative importance of extreme events following fertilization (Raciti et al. 2008). Extreme N<sub>2</sub>O fluxes also occur in undisturbed forest soils in this study, suggesting that large emissions occur in the absence of fertilization.

#### 4.5.2 Soil moisture and Temperature Sensitivity of GHG Emissions

CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> emissions were correlated with both temperature and soil moisture, however, model fits for each gas only improved slightly when moisture was incorporated into temperature-only model. This result is surprising, given that numerous studies have documented the interactive importance of soil moisture and temperature on CO<sub>2</sub> (Davidson et al. 1998; 2006). CH<sub>4</sub> and N<sub>2</sub>O are both produced anaerobically and thus require increased soil moisture for production (Groffman et al. 2000; Le Mer and Roger 2000). N<sub>2</sub>O can also be produced aerobically *via* nitrification, however, which contributes to difficulty in predicting N<sub>2</sub>O emissions. On the other hand, the majority of moisture conditions fell between 20 to 30% volumetric water content, ideal conditions for CO<sub>2</sub> production. Soil moisture fell below the 12% threshold for drought stress (Davidson et al. 1998) during 1.8% of the gas flux sampling record and above 40% during 0.7% of the record.

Temperature was a primary driver of soil respiration in this study, however, temperature sensitivity did not vary significantly across land cover types, seasons, or years. Because growing season soil temperature was consistently higher in lawn sites compared with forested sites, I sought to examine whether temperature alone could explain site-scale differences. It was hypothesized that sensitivity of respiration (Q10) might increase if labile carbon inputs from grass clippings and fine root turnover as well as synthetic fertilizer and watering stimulated microbial activity in lawn soils. Q10 is a useful though simplistic metric to examine changes in the role of temperature on fluxes before looking into more complex drivers of respiration across various soils (Davidson et al. 2006). Despite consistent differences in growing –season temperature and vegetation cover between forested and lawn sites in this study (Savva et al. 2010; Groffman et al. 2009), significant differences in Q10 across sites, seasons, or years were not detected (Tables 4.3, Table 4.4). The range of annual Q10 across sites in this study (0.6 to 7) encompasses the median expected Q10 of 2 to 2.4 for soils (Davidson et al. 1998; Schlesinger and Andrews 2000; Davidson et al. 2006). Q10 values much above 2.5 signify changes in substrate supply or water stress (Davidson et al. 1998). For instance, higher Q10 values would be expected in urban lawns, if grass clippings and dense fine root structures contributed to an overall more labile carbon pool. Conversely, a decline Q10 over time would be expected if soil carbon stocks decline or become more recalcitrant over time. Non-ideal soil moisture conditions (either too wet or too dry) would also decrease Q10.

Variability in seasonal and annual estimation of Q10 may be partially explained by differences in phenology across years, since seasons were delineated based on equinox

and solstice dates rather than observations of leaf-out. Root respiration can be more sensitive to temperature changes than bulk soil (Schlesinger and Anderson 2000), and inconsistencies in the definition of the growing season could skew the overall trend. Additionally, drought stress is most severe during summer months, and a severe drought early in the record (2002-2003) could influence seasonal Q10 estimates as well.

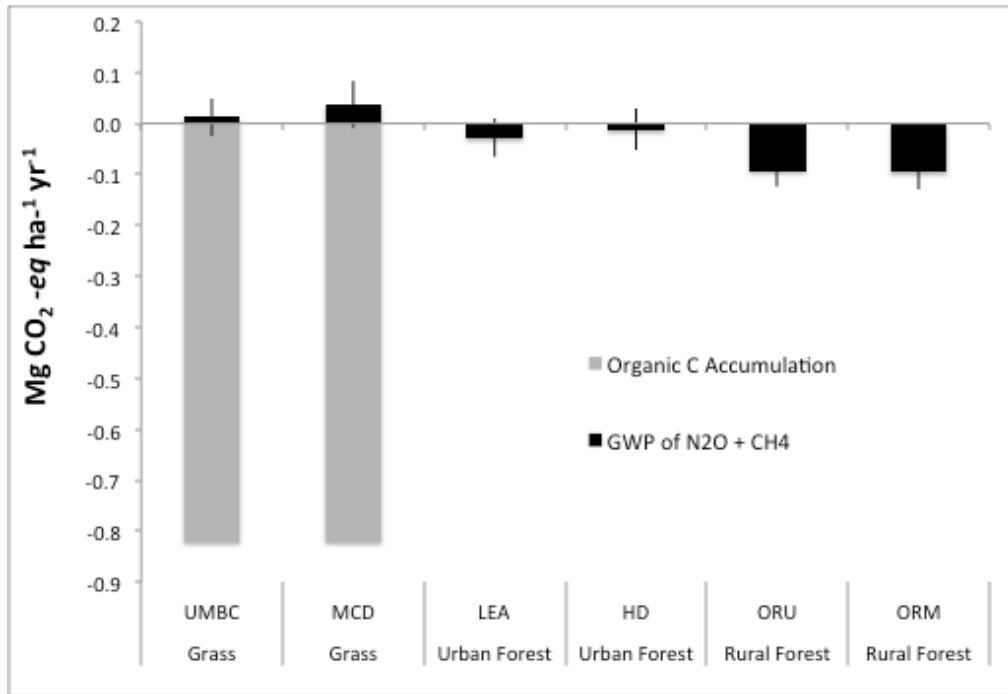


Figure 4.4. Black bars show average annual  $GWP_{N_2O+CH_4}$  with error bars for standard deviation. Gray bars show potential for  $CO_2$  uptake in lawns from chronosequence study by Raciti et al. (2011).

#### 4.5.3 Soil Respiration in the Context of Urban Carbon Budgets

Recent studies have focused on the role of urban ecosystems as potential carbon and GHG sinks (Nowak and Crane 2002; Weissert et al. 2014). There has been particular interest in lawns given their widespread nature, and conflicting studies regarding potential for significant long-term carbon storage (Weissert et al. 2014). Lawn and forest soil GHG fluxes were compared to a recent greenhouse gas inventory of Baltimore County (Brady and Fath, 2008) in order to evaluate the role of ecosystems on global

fluxes. The anthropogenic GHG flux from the county was  $1.1 \times 10^{-7}$  Mg CO<sub>2</sub> eq yr<sup>-1</sup> (Table 4.5). When SOC storage in lawns (Raciti et al. 2011) was considered, the soil GHG sink offset 0.5% of anthropogenic flux. If SOC storage was not considered, the GHG sink (mainly CH<sub>4</sub> consumption) offset less than 0.05% of annual anthropogenic emissions (Table 4.5). Additionally, if it were assumed that the entire county accumulated SOC at the same rate as lawns in Raciti et al. (2011), soils would still only offset 1.2% of yearly anthropogenic emissions. This accounting exercise did not include any carbon sinks (soil, or plant uptake), aboveground respiration, or aquatic GHG fluxes. Vegetation carbon storage is not likely to offset a significant percentage of anthropogenic and soil GHG emissions, however. On average, eastern temperate forests in the U.S. store 3.08 Mg C ha<sup>-1</sup> yr<sup>-1</sup> with a high-end estimate of 6.30 Mg C ha<sup>-1</sup> yr<sup>-1</sup> (e.g. Crawford et al. 2011 and refs within). This high-end estimate would still offset less than 1% of anthropogenic emissions from detailed local GHG budget estimate of 65 Mg C ha<sup>-1</sup> yr<sup>-1</sup> (Brady and Fath 2008).

#### 4. 6 Conclusions

Soil CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O emissions are sensitive to land cover and temperature. This study found significantly higher net combined GWP from CH<sub>4</sub> and N<sub>2</sub>O emissions from urban lawns, compared with rural forests. Temperature was a key driver of emissions, however site-specific variability in GHG emissions was also important. While land cover change has clearly altered these ecosystems, the role of this change on GHG emissions is small compared to prior estimates of soil carbon accumulation in lawns (Raciti et al. 2011). Additionally, the net carbon + GHG consumption by soils in the Baltimore metropolitan area was miniscule (0.5%) compared with anthropogenic

emissions. In recent decades, urban ecosystems have been managed for multiple ecosystem services. While carbon sequestration is a key function of forest and grassland ecosystems globally, it is not feasible to manage urban ecosystems to sequester local GHG emissions (Weissert et al. 2014; Pataki et al. 2011).

Table 4.5 Summary of anthropogenic GHG inventory of Baltimore County from Brady and Fath (2008) alongside scaled up soil N<sub>2</sub>O + CH<sub>4</sub> emissions from the present study. Total soil fluxes from Baltimore County were estimated based on the average annual lawn soil emissions from modeled fluxes during 15-years of monitoring (Mg CO<sub>2</sub>-eq). Lawn fluxes represent MCD and UMBC sites and forest represent rural forest' sites (ORU, ORM). Lawn area and tree canopy coverage was estimated from 2007 imagery (1m<sup>2</sup> pixel size).

\*\*SOC: Soil organic carbon accumulation rate in urban lawns from Raciti et al. 2011 chronosequence study, assuming the rate they found for post-agricultural lawns is consistent across Baltimore county lawns.

| Source   | Mg CO <sub>2</sub> eq yr <sup>-1</sup><br>Baltimore County | MgCO <sub>2</sub> eq<br>ha <sup>-1</sup> yr <sup>-1</sup> | % Of total<br>Anthropogenic |
|--|--|---|-----------------------------|
| Residential  | 3,195,697  | 18.1  | 27.7                        |
| Commercial   | 2,331,496  | 13.2  | 20                          |
| Industrial   | 956,473  | 5.4   | 8.3                         |
| Transportation   | 4,897,796  | 27.7  | 42.4                        |
| Waste  | 166,805  | 0.9   | 1.4                         |
| Total Anthropogenic emissions                              | 11,548,267   | 65.39   | 100                         |
| Soil CH <sub>4</sub> + N <sub>2</sub> O                    | -6,595   | -0.037  | -0.06                       |
| Lawn SOC accumulation **                                   | -51,227  | -0.28   | -0.44                       |
| Total Soil flux (SOM + CH <sub>4</sub> + N <sub>2</sub> O) | -57,822  | -0.33   | -0.50                       |

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