

Temporal Variation in Greenhouse Gas Emissions Among Four Different Riparian Land-Use Types in Southern Ontario, Canada

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Statement of Contributions

4.0 Results contributions: Primary in situ collection and analysis of soil organic carbon (SOC) data was performed by Enoch Efosu, PhD candidate at the University of Guelph from the School of Environmental Sciences.

Abstract

Forested riparian buffers (RBs) provide various environmental services, such as reducing streambank erosion and sedimentation, creating wildlife habitat, enhancing carbon (C) sequestration, enhancing streamside microclimate, and filtering contaminants and pollutants from surface agricultural runoff. However, RBs located downslope of agricultural areas have high water tables, increased nitrogen (N) due to surface runoff, and high C inputs from vegetation, creating a potential hot spot for soil greenhouse gas (GHG) emissions. Despite this concern of RBs as a GHG source, there are few comparative analyses of GHG emissions from different riparian land-use systems (e.g. grassed vs forested) in temperate regions. This information is crucial as it will provide insight into which riparian buffer is the most effective in mitigating GHG emissions, as this has future implications for contributions to climate change. The goal of this study was to quantify and compare temporal trends in soil GHG (N_2O , CO_2 , CH_4) emissions, as well as the soil physical and chemical characteristics that influence emissions, from a rehabilitated forest riparian buffer (RH), a grassed riparian buffer (GRS), two undisturbed natural riparian forests (UNFA and UNFB), and an agricultural field (AGR) located in southern Ontario, Canada.

Mean annual soil temperature and moisture from the AGR, GRS, RH, UNFA and UNFB sites were 17, 17, 16, 15, and 16°C, and 22, 32, 35, 52 and 38 % volume, respectively. The highest soil temperatures were seen at the AGR and GRS sites. There was little variation among land-use types, but soil temperature followed a strong seasonal trend. Soil moisture was highest at the UNFA site, as it had wetland-like soil conditions. The mean annual concentration of NH_4^+ and NO_3^- for the AGR, GRS, RH, UNFA and UNFB sites were 4, 6, 5, 7 and 9 mg $\text{NH}_4^+\text{-N kg}^{-1}$ dry soil, and 23, 18, 14, 11 and 11 mg $\text{NO}_3^-\text{-N kg}^{-1}$ dry soil, respectively. There was little

variation in NH_4^+ among the land-use types. The strongest seasonal trend was seen between spring 2018 and summer 2018, where there was a significant drop in NH_4^+ concentration as a result of the spring freeze-thaw conditions. Highest NO_3^- concentration was seen at the AGR site, likely due to the fertilizer this soil receives when on a corn rotation.

Mean annual soil N_2O emissions from the AGR, GRS, RH, UNFA and UNFB sites were 34, 17, 16, 14, and 10 $\mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$, respectively. The mean emissions were consistently higher at the AGR site compared to all the other land-use types, but this observation was not significant according to a Tukey's post hoc test of significance. This trend can likely be explained by the fertilizer treatments added to the soil, contributing sources of N to fuel N_2O production. Mean annual CO_2 emissions from the AGR, GRS, RH, UNFA, and UNFB sites were 120, 276, 131, 120, and 117 $\text{mg CO}_2\text{-C m}^{-2} \text{ h}^{-1}$, respectively. The GRS was significantly ($p < 0.05$) higher than all the other land-use types, and this can likely be attributed to the high density of root matter fueling soil respiration. Mean annual CH_4 emissions from the AGR, GRS, RH, UNFA, and UNFB sites were -37, -61, -17, 756, and 55 $\mu\text{g CH}_4\text{-C m}^{-2} \text{ h}^{-1}$, respectively. The UNFA site was the only site that consistently acted as a CH_4 source, and was significantly ($p < 0.05$) higher than all the other sites. For all three GHGs, season did not consistently have a significant ($p < 0.05$) impact on emissions. Soil CO_2 emissions were significantly positively correlated to soil temperature in most land-uses, with the highest emissions for all sites in the summer. N_2O emissions were also significantly positively correlated to soil temperature at most land-uses, with the highest emissions for all sites in the summer. It was expected that there would be a significant correlation between N_2O emissions and soil nitrate (NO_3^-), but this was only true for the AGR site where NO_3^- concentrations were the highest. Both CO_2 and N_2O emissions were significantly negatively correlated to soil moisture, as they both have an optimal level of soil

oxygen before it becomes too limiting for the microbes responsible for the production of these GHGs. The opposite was true for CH₄ emissions where soil moisture was the most significant influencing factor, with the highest emissions in the wetter seasons (spring and autumn). CH₄ production is an anaerobic process, and the wetland-like conditions at the UNFA site likely fueled methanogenesis in the soil. Soil ammonium (NH₄⁺) concentration and photosynthetic photon flux density (PPFD) did not have significant correlations to any of the GHGs at any of the land-uses.

The results of this study are significant, as they show that forested riparian buffers have lower emissions than grassed buffers and agricultural fields. For all the GHGs analyzed, the RH site had similar or lower emissions compared to the other land-use types. This suggests that riparian buffers are not acting as a hot spot for GHG emissions, despite the ideal environmental conditions for GHG production. Therefore, forested riparian buffers should be suggested as a best management practice over conventional grassed buffers for protecting water courses in agriculturally-dominated landscapes, due to their reduced impact on GHG production and the additional ecological services trees provide when present in buffers. Further, soil physical characteristics (soil temperature and moisture) seemed to play the largest role in influencing emissions, rather than the soil chemical characteristics (NO₃⁻, NH₄⁺, SOC). These results are highly dependent on the environmental conditions of the site, including the presence of a tile drainage system, the location of the water table, and the abundance of understory vegetation. Further long-term research (>3 years) should be undertaken to identify GHG emissions under varying environmental conditions (e.g. interannual climate variation).

Dedication

This work is dedicated to the memory of my grandparents:

Joan Monique White

and

Gordon Lawson Baskerville

My Meme was always a major support network for me, and I attribute a lot of my strong will and tenacity to her. She taught me that sometimes it is okay to ask for help, but also to try my best to persevere. She experienced hard times I will never fully understand, but the way she faced adversity with strength and confidence will always make her a role model. Meme had a sense of humour when most people thought it couldn't be possible, and was always able to put a smile on my face. She was wise, caring, and truly selfless.

Gramps was the perfect balance between intellect and humour. He was full of short stories, limericks, and songs, but also had an impressive knowledge of forest ecosystems that led him to do great things. Although when he was alive I did not know it yet, he is my true inspiration for entering the world of forestry. His impressive contributions to both the academic world and to government policy has provided me with motivation to achieve the same. Gramps believed strongly in sustainable forestry, and that it is our responsibility to protect our forests. I look forward to following in his footsteps.

Although they have both passed away, the memories I hold of Meme and Gramps remain a regular part of my life. I miss them terribly, but they have taught me important life lessons. I look forward to the rest of my career, and my life, knowing I am well equipped with the knowledge they have provided me.

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1.0 Introduction

The intensification of agriculture has led to the degradation of both aquatic and terrestrial ecosystems (Lovell and Sullivan 2006). Industrial agriculture has significantly modified both environments, particularly in soil and aquatic sediments (Compton and Boone 2000). A negative impact of agricultural intensification of particular concern is the conversion of natural ecosystems to agriculture, which has negatively impacted the balance of the soil ecosystem, leading to increased greenhouse gas (GHG) emissions, loss of soil fertility and increases in soil erosion (Kim et al. 2009; Compton and Boone 2000). In 2016 alone, 12 300 ha of Canadian forests were converted to be used for agriculture (Natural Resource Canada, 2019). Land conversion has also harmed nearby water courses, as riparian ecosystems have been converted to crops or pastureland (Fortier et al. 2010). These areas are extremely important, providing numerous ecosystem services and protecting aquatic habitat (Gregory et al. 1991; Bourgeois et al. 2016). For instance, tree-based riparian buffers can be implemented in order to re-establish streamside habitat, as well as to intercept harmful pesticides and fertilizers running off adjacent agricultural fields (Tufekcioglu et al. 2001). However, there can be a potential environmental disservice of this riparian land-use in the form of enhanced GHG emissions.

The production of GHG emissions from the soil is highly dependent on environmental factors (e.g. soil moisture, soil temperature, vegetation type) (Smith et al. 2003). When a streamside is rehabilitated, the addition of woody vegetation to riparian zones significantly alters these soil environmental factors, particularly the microclimate, structure, and chemical make-up of the soil, all of which will significantly impact GHG emissions (Bourgeois et al. 2016; Tufekcioglu et al. 2001). Additionally, land management practices that frequently disturb the soil, such as forestry and agriculture, can also lead to enhanced GHG emissions. (Jandl et al.

2007; Al-Kaisi and Yin 2010). Subsequently, the land-use riparian zones are being managed under will have a direct impact on their potential to release GHGs (Smith et al. 2003). Of particular concern are riparian forest buffers located along agriculturally degraded streams (Tufekcioglu et al. 2001; Kim et al. 2009). The addition of carbon (C) in the form of litterfall, the presence of a high water table, and high amounts of incoming plant available nitrogen from nearby agricultural field has raised concerns over whether riparian buffers will be a hot spot for GHG emissions (Bailey et al. 2009; Kim et al. 2009). However, very little research has been conducted on the GHG emissions from temperate rehabilitated riparian forests where environmental factors are greatly altered, and how this compares to other land-uses typically found along agriculturally degraded streams (Shrestha et al. 2009; Teiter and Mander 2005). Further, few studies on GHG emissions exist using repeated measures over multiple days at select chambers to address between chamber (spatial variability) and over time (temporal variability) (Vidon et al. 2015). Therefore, the objective of this study are two-fold: (1) to quantify and compare temporal GHG (CO₂, CH₄, N₂O) emissions among a grassed buffer (GRS), two undisturbed natural forests (UNF), a 32-year old rehabilitated riparian forest buffer (RH), and an agricultural field (corn-soybean rotation) (AGR); and (2) to quantify and compare the relationship between temporal GHG emissions, soil moisture, soil temperature, SOC, and soil ammonium and nitrate in the GRS, UNF, RH and AGR land-uses.

2.0 Literature Review

2.1 Effects of Agricultural Practices on Streams and GHG Emissions

Society has pushed agricultural producers to provide more environmental and economic services due to rises in population and subsequent food demand (Ruddimann 2003). This increase in pressure has led to increased usage of fertilizer and pesticides (Albrechet and Kanji 2003). Intensification has also lead to other environmentally detrimental management practices, leading to severe soil erosion, large-scale livestock operations producing huge quantities of nutrient-loaded manure, and increases in homogenous cropping systems resulting in decreased functional diversity (Yates et al. 2007). These intensive agricultural practices have detrimental impacts on aquatic ecosystems, particularly streams where stressors are focused and aggregated on a landscape scale (Yates et al. 2007). Some stressors to aquatic systems due to agricultural practices include high volumes of sediments, nutrients, and pesticides, each of which are forms of non-point source pollution and negatively impact stream health (Yates et al. 2007; Zhang et al. 2017).

In addition to decreases in environmental quality, agricultural intensification has contributed significantly to increases in atmospheric GHG concentrations. On-farm agricultural production accounts for approximately 10-12% of total global GHG emissions (Jones and Sands 2013; Smith et al. 2009). Additionally, the conversion of pastureland and forests to cropland accounts for 12-20% global GHG emissions by releasing soil and biomass carbon (Jones and Sands 2013). Increases in income and population are raising the demand for agricultural goods, so regulation of agricultural GHG emissions is essential in order to meet the GHG reduction goals set by Canada's commitment to the Paris Accord (Jones and Sands 2013). An approach that is frequently utilized to combat agricultural GHG emissions is to design the agroecosystems

to sequester soil carbon (Smith et al. 2009). This is due to CO₂ emissions often being the focus of agricultural GHG discussions (Jones and Sands 2013). However, recently there has been more concern over CH₄ and N₂O emissions from the livestock enteric fermentation and waste management, and from nutrient applications to crops, for these can increase on-farm GHG emissions five-fold (Jones and Sands 2013).

Intensive agriculture, particularly for crop production, requires a lot of external inputs of fertilizers and agrochemicals in order to maintain high productivity (Bourgeois et al. 2016). When the addition of these amendments exceeds uptake by plants and soil, they can reach water courses either through soil leaching or surface runoff, contaminating surface water and groundwater, or released as the potent GHG N₂O (Deslippe et al. 2014; Muñoz-Leoz et al. 2011; Yang et al. 2007). The release of N₂O from agricultural fields has become a significant concern in Canada, due to the sources of legacy soil N that fuels N₂O production (Yang et al. 2007). Therefore, intensive agriculture not only threatens nearby aquatic habitats, but makes farms significant contributors to climate change.

2.2 Riparian Zones and their Degradation

Until the 19th century, many agricultural lands featured riparian wetlands, hedges and forests (Gregory et al. 1991). These riparian zones are defined as the interface between terrestrial and aquatic ecosystems, and are considered integral to preserving aquatic systems due to the numerous ecological services they provide (Gregory et al. 1991; Bourgeois et al. 2016; González et al. 2017). However, as agriculture began to intensify, riparian zones were removed directly to be replaced with crops, or indirectly through the widespread implementation of clay tile drainage systems and excessive fertilizer/pesticide use (Lovell and Sullivan 2006; Fernández et al. 2014;

Audet et al. 2014; Correll 2005; Bourgeois et al. 2016). Tile drainage in particular is problematic, as it is implemented in order to lower the water table for agricultural activities (Audet et al. 2013). After the water table has been lowered, there is enough oxygen for rapid mineralization of soil organic matter, and the intensive use of fertilizers allows discharge of nitrogen (N) and phosphorous (P) into water courses, degrading the water quality and contributing to eutrophication (Audet et al. 2013; Deslippe et al. 2014). As a result of these intensive agricultural practices, it is estimated that 80% of riparian zones have been lost in the past 200 years within North America and Europe (Naiman et al. 1993). With growing, large-scale industrial agricultural production using many external inputs, riparian zones are even more critical in this current global environment (Bourgeois et al. 2016; Fernández et al. 2014).

2.3 Riparian Buffers and their Benefits

Riparian buffers have been frequently suggested as a best management practice in agriculturally-dominated landscapes (Zhang et al. 2017). This is because riparian buffers are able to intercept indirect sources of pollution from upland agricultural runoff, which enhances terrestrial and aquatic habitat along agriculturally degraded streams (Tufekcioglu et al. 1999; Correll 2005; Lovell and Sullivan 2006). They can provide many ecological services, particularly if trees are present. Trees enhance the functionality of these ecotones by improving soil aggregation, enhancing runoff water infiltration and retention of sediments, and intercept N and P more efficiently than herbaceous species (Bourgeois et al. 2016).

Riparian buffers enhance terrestrial and aquatic habitat for wildlife (Gregory et al. 1991). For example, they increase the amount of soil organic matter by providing leaf litter and dissolved organic matter for aquatic organisms, helping support the local food chain by adding

allochthonous and autochthonous food resources (Gregory et al. 1991; Correll 2005). Further, the addition of riparian vegetation increases the biodiversity of agricultural landscapes, not only by increasing the diversity of flora but by providing a habitat for fauna as well (Lovell and Sullivan 2006). This new-found habitat can act as a conservation corridor, connecting fragmented habitats allowing for increased travel by wildlife (Lovell and Sullivan 2006; Fernández et al. 2014).

Riparian woody vegetation creates a full canopy, which controls temperature, light, and humidity, creating a wide variety of microclimates that can support greater biological diversity (Lovell and Sullivan 2006; Gregory et al. 1991). Additionally, increasing terrestrial flora and fauna inadvertently provides an improved quality in aquatic habitats by providing a cooling effect, food, and habitat, as well as increasing oxygen availability (Lovell and Sullivan 2006).

Riparian buffers have shown to reduce the amount of fertilizers reaching water systems that originate from cultivated fields, and are particularly effective at removing P, N, and several pesticide compounds (Gregory et al. 1991; Lovell and Sullivan 2006; Correll 2005). These filtered contaminants are chemically transformed by riparian vegetation and soil microbes, reducing their environmental impact (Muñoz-Leoz et al. 2011). Phosphorous can be removed by vegetation, but removal rates vary substantially based on the form of P and the site conditions (Lovell and Sullivan 2006). Nitrogen is reduced by plant and microbial N-immobilization, or by denitrification, effectively reducing about 50% of agricultural nitrogen runoff (Lovell and Sullivan 2006; Deslippe et al. 2014; Correll 2005). Pesticides that are bound tightly to the soil are easily removed due the vegetation's ability to intercept travelling sediments (Correll 2005).

Erosion is a prevalent problem in agroecosystems, and leads to the subsequent sedimentation of nearby water courses (Lovell and Sullivan 2006). Riparian buffers, particularly when trees are present, enhance the functionality of these ecotones. The tree roots enhance

streambank stabilization and limit erosion by improving soil aggregation, resulting in enhanced runoff water infiltration and increased retention of sediments (Bourgeois et al. 2016; Lovell and Sullivan 2006).

2.3 Riparian Buffers in Government Policy

Tree-based riparian buffers are one of the most common agroforestry land-use types in Canada (Albrecht and Kanji 2003). Various government organizations, such as the Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA) and Agriculture and Agri-Food Canada (AAFC), promote the use of buffer strips as a best management practices in order to reduce nutrient runoff. However, at the provincial level, the buffers OMAFRA are promoting do not specify the integration of trees (OMAFRA 2017). On a federal level, AAFC lists riparian buffers as a best farming practice within the framework of agroforestry, and suggest a minimum of two vegetations types, including a mixture of grasses, trees and shrubs, compared to the more commonly used grassed buffer (AAFC 2017). In 2004, the Grand River Conservation Authority (GRCA) released the Watershed Forest Plan for the Grand River, in which they discuss the benefits of riparian buffers in agricultural landscapes, and outline their goal of establishing 75% forest cover along all streams within the Grand River watershed (GRCA 2018). The *Ontario Environmental Protection Act*, the *Ontario Nutrient Management Act*, the *Ontario Clean Water Act*, and the *Canadian Fisheries Act* all emphasize reducing pollution from agricultural areas (particularly runoff water) in order to protect habitat integrity (Government of Ontario 2017; McMcKague et al. 2017; Government of Ontario 2006; Government of Ontario 1985). However, none of these approaches promote the explicit use of riparian buffers, let alone tree-based riparian buffers.

2.4.0 Soil Greenhouse Gas Emissions

2.4.1 Carbon Dioxide Emissions

Global warming is the most prominent environmental issue affecting society on a global scale (IPCC, 2014). The primary driver of rising temperatures is the increase in atmospheric GHG concentrations, particularly carbon dioxide (Nair 2011). Our current atmospheric CO₂ concentration is approximately 1.4 times that of the pre-industrial period, at roughly 400 ppm (IPCC 2014; Udawatta and Jose 2012). Soil is a substantial source of CO₂, and is a greater contributor to atmospheric CO₂ than fossil fuels (Smith et al. 2003). Soil releases CO₂ through the processes of heterotrophic respiration of organic matter and autotrophic respiration from plant roots, causing soil respiration (Gritsch et al. 2015). The contribution to respiration by the microbial community depends on the availability of organic C in the soil, which holds about twice as much C compared to atmospheric CO₂-C (Raich and Potter 1995). Therefore, changes to the soil organic C (SOC) will result in significant impacts to the atmospheric CO₂ concentration (Raich and Potter 1995; Gritsch et al. 2015). There are a variety of other factors that also impact CO₂ release from soil. For example, temperature and moisture are the two biggest drivers of soil respiration. As long as no other factors are limiting, microbial and chemical reactions (including soil respiration) will increase exponentially with increasing temperatures (Gritsch et al. 2015; Schaufler et al. 2010; Smith et al. 2003). Moisture content determines oxygen availability and gas diffusivity in the soil, and subsequently whether reactions are aerobic or anaerobic (Gritsch et al. 2015; Schaufler et al. 2010). Highest CO₂ emissions are usually reported under intermediate moisture conditions (Gritsch et al. 2015). This is when the soil is saturated (50-80% water-filled pore space), at which point changes in temperature and soil moisture have little

effect on CO₂ emissions, since soil conditions are ideal for microbial community responsible for CO₂ emissions (Raich and Potter 1995). If moisture is too limiting, microbial activity declines and CO₂ emissions decline regardless of soil temperature (Smith et al. 2003). In saturated and oversaturated soils, oxygen is limiting because the majority of the pore space is filled with water (Smith et al. 2003; Gritsch et al. 2015). This reduces CO₂ emissions as respiration is restricted, but this is not as limiting as when moisture is low (Smith et al. 2003).

2.4.2 Methane Emissions

Methane (CH₄) concentration has been steadily increasing in the atmosphere accounting for 20% of the greenhouse warming effect and increasing at a rate of 0.4% per year (Butterbach-Bahl and Papen 2002; Wilcock et al. 2008). It also has a warming potential 25 times greater than CO₂ (Smith et al. 2003; Audet et al. 2013). CH₄ emissions and absorption are a result of methanogenesis and methanotrophy, respectively (Turetsky et al. 2014). Methanogenesis is a strictly anaerobic process, while methanotrophy is aerobic (Turetsky et al. 2014). CH₄ oxidizer communities that live near the surface are thought to carry out oxidation of CH₄ that originated from lower soil horizons (Turetsky et al. 2014). CH₄ emissions are most strongly related to water table level and soil temperature, due to their impact on microbial activity and where conditions are anaerobic or aerobic conditions. When the water table is lower (i.e. soil is drier near the surface) there are significantly less emissions (Liblik and Moore 1997). CH₄ release is often hindered in the summer months, and this is a result of drier soils allowing for increased aeration. Therefore, the higher the water-filled pore space (WFPS), the higher the released CH₄, especially when associated with a high bulk density (Smith et al. 2003). CH₄ emissions have a varied range of optimal moisture content, occurring around 20-60% water-holding capacity, and emissions are

positively correlated with increasing WFPS (Schaufler et al. 2010; Liblik and Moore 1997). The presence of vegetation also affects CH₄ release from the soil, mainly by supplying C based material that fuel substrate-based methanogenesis. As a result, occasionally CH₄ bypasses the aerobic layers of the soil and is instead emitted through plant tissues (Turetsky et al. 2014).

2.4.3 Nitrous Oxide Emissions

Along with CO₂ and CH₄, nitrous oxide (N₂O) is a significant contributor to GHG emissions. It has a global warming potential 298 time greater than CO₂, and also contributes to ozone stratospheric depletion (Smith et al. 2003; Bradley et al. 2011; Deslippe et al. 2014). Soil emissions of N₂O make up about a third of total global emissions (Smith et al. 2003), and atmospheric N₂O accounts for 5% of the greenhouse warming effect increasing by 0.3% per year (Wilcock et al. 2008)

N₂O is generated through the transformation of N by the processes of nitrification and denitrification in soils (Pilegaard et al. 2006). Denitrification is defined as the microbial respiration of soluble N oxides, which in a step-by-step reaction reduces aqueous nitrate (NO₃⁻) or nitrite (NO₂⁻) into a gaseous form (Deslippe et al. 2014). Heterotrophic bacteria carry out denitrification of NO₃⁻, and when it is fully reduced to N₂ gas this can have beneficial impacts on the environment (Bradley et al. 2011; Deslippe et al. 2014). However, under anaerobic conditions there can be incomplete reduction of NO₃⁻, resulting in denitrification and the release N₂O (Bradley et al. 2011; Audet et al. 2013; Deslippe et al. 2014). Denitrification favours three main environmental conditions: anoxic soil, high availability of NO₃⁻, and high amounts of reduced C (Bradley et al. 2011). Therefore, soil temperature and moisture have a strong impact on N₂O emissions (Pilegaard et al. 2006). Nitrification, in contrast to denitrification, is the

transformation of first ammonium (NH_4^+) to NO_2^- , to NO_3^- , and then finally to N_2O gas (Smith et al. 2003). Nitrification is an aerobic process, but oxygen is still limiting resulting in nitrifying bacteria using NO_2^- as the electron acceptor to reduce NO to N_2O (Smith et al. 2003).

N_2O emissions often have an exponential increase with increasing temperature. This is due to increased soil respiration increasing the size of anaerobic microsites by removing oxygen, creating a more favourable environment for N_2O production (Smith et al. 2003). Additionally, higher temperatures increase enzymatic activity increasing the rate of release of N_2O , provided no other factors (e.g. moisture and substrate) are limiting (Schindlbacher 2004). When there are well-aerated soils, nitrification is the predominant microbial process taking place. It will remain the predominant form of N_2O production until a WFPS of approximately 40% (Smith et al. 2003). In wet soils, as saturation increases the soil becomes increasingly filled with anaerobic microsites, resulting in denitrification as the predominant process leading to N_2O release (Schaufler et al. 2010). This maximum N_2O release occurs around 50-60% WFPS, but emissions diminish at 80% because N_2O is consumed by denitrifying bacteria that release N_2 (Smith et al. 2003; Schaufler et al. 2010).

2.5 Riparian Buffers and GHG Emissions

Although riparian buffers have the capacity to mitigate GHG emissions, they can also be emitters of GHGs through hot spots that dwell within the soil of the riparian zone (Bradley et al. 2011). First, riparian buffers are characteristic of high water tables and low oxygen content due to their close proximity to streams, frequently leading to anaerobic conditions (Figure 2.1) (Audet et al. 2013; Bradley et al. 2011). Second, riparian buffer soils contain high amounts litter and root exudates from the vegetation, leading to an increased availability of C (Bradley et al.

2011). Lastly, riparian buffer strips often occur downslope of agricultural fields, so they receive and trap a significant amount of NO_3^- from N-based fertilizers in the form of surface runoff (Bradley et al. 2011; Bailey et al. 2009). The NO_3^- is not only incorporated into the soil, but is involved in plant uptake creating N-rich vegetation and litterfall (Kim et al. 2009). The addition of trees to riparian buffers increases the availability of SOC, directly relating to increased CO_2 emissions (Bailey et al. 2009). Further, the lack of oxygen in riparian buffers slows decomposition resulting in sustained soil organic carbon (SOC) supplying constant fuel for CO_2 emissions (Bailey et al. 2009). This lack of oxygen also creates a higher potential for denitrification, leading to enhanced N_2O emissions (Audet et al. 2013; Deslippe et al. 2014; Muñoz-Leoz et al. 2011; Audet et al. 2014; Teiter and Mander 2005). This release of N_2O may act as a trade-off for the reduced non-point source pollution entering the water course (Kim et al. 2009). Further, the anaerobic conditions and high availability of SOC also favour the production of CH_4 , which causes riparian buffers to be a net source of CH_4 (Jacinthe and Vidon 2017; Audet et al. 2014). Therefore, the enhanced filtration of N by plant roots and availability of SOC from plant matter in riparian soil is a direct result of adding trees, making agroforestry riparian buffers a potential hotspot for GHG emissions (Bailey et al. 2009; Kim et al. 2009).

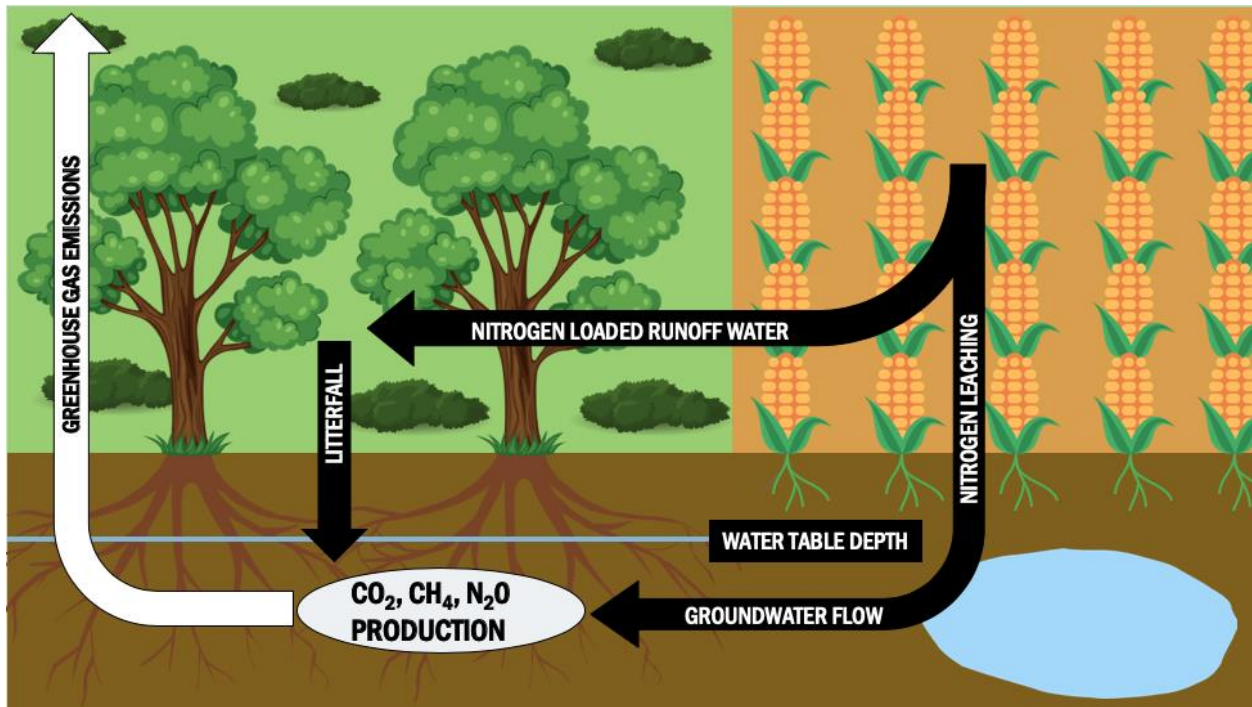


Figure 2.1. Diagram of the environmental conditions that influence greenhouse gas emissions in forested riparian buffers.

There are other factors outside of soil physical and chemical characteristics that contribute to the risk riparian buffers pose as a significant source of GHGs. Anecic earthworms are prevalent in riparian areas, and burrowing activity in riparian buffers can influence denitrification by creating preferential flow pathways, which increases water infiltration and nutrient leaching (Bradley et al. 2011). Although earthworms can enhance leaching of NO_3^- , earthworm casts, their burrow walls, and their gut can act as favourable environments for denitrifying bacteria, contributing to N_2O production (Bradley et al. 2011). Additionally, flood events are frequent in riparian buffers due to their close proximity to water courses. This can impact the material available and the moisture regime of riparian buffers, depending on the frequency and duration, therefore altering the production of GHGs (Jacinthe et al. 2012). It is thought that since poorly drained soils favour N_2O and CH_4 production, increased flood events

and flood-affected riparian buffers may have increased production of these GHGs (Jacinthe et al. 2012).

Further, floods not only change the amount of material available (sediment deposition, SOC accumulation, and redistribution of organic matter and nutrients) (Blazejewski et al. 2009), they also affect microtopography that creates semi-permanent wet soils causing the emission of CH₄ and CO₂ (Jacinthe et al. 2015). Landscape heterogeneity (e.g. microtopography) also impacts GHG emissions and creates hot spots within riparian buffers (Jacinthe et al. 2015), indicating that GHG emissions are highly variable spatially (Muñoz-Leoz et al. 2011). Similarly, temporal scales also impact GHG emissions depending on the environmental conditions, such as prolonged anaerobic conditions as a result of extensive flooding (Muñoz-Leoz et al. 2011; Jacinthe et al. 2015). There are also changes in emissions following rewetting of dry soils and the thawing of frozen soils, yet little is known how this impacts riparian buffers (Kim et al. 2009). However, changes in moisture heavily effect soil GHG emissions along with higher soil C and N, which are characteristic of riparian buffers (Audet et al. 2014).

Due to their greater global warming potential than CO₂, the augmented transfer of N₂O and CH₄ to the atmosphere should be regarded as a significant concern as their concentration in the atmosphere is expected to continue to increase (Jacinthe and Vidon 2017). This emphasizes the risk riparian buffers adjacent to agricultural fields pose to stable atmospheric GHG concentrations (Audet et al. 2013). Despite this, there are significant knowledge gaps on GHG production potential of rehabilitated riparian zones in temperate regions, even after researchers have expressed concern with diverting N-rich waters towards riparian buffers (Jacinthe and Vidon 2017; Shrestha et al. 2009; Teiter and Mander 2005; Audet et al. 2013, 2014). There is particularly little research in an agroforestry setting, where trees were intentionally planted

(Bailey et al. 2009). Studies have either solely focused on CO₂, and studies that do include N₂O have focused on grassed buffers and agricultural fields, and studies that include CH₄ focused on the role that flooding plays in riparian forests (Tufekcioglu et al. 2001; Kim et al. 2009; Shrestha et al. 2009; Oelbermann and Raimbault 2015; Jacinthe 2015).

Few studies have focused on GHG emissions from temperate rehabilitated riparian forests in agriculturally dominated landscapes, as most studies have focused on reclaimed, mined riparian soils and constructed wetlands for wastewater treatment (Teiter and Mander 2005; Shrestha et al. 2009; Oelbermann et al. 2015). It is important to quantify GHG emissions from rehabilitated riparian forests in agricultural landscapes in order to determine their significance compared to other natural systems or anthropogenic sources to help fill the gap in this knowledge (Vidon et al. 2015). In the context of this study, in the Grand River watershed approximately 24km of streamside have treed buffers on at least on one side, and 11.5km have the potential to have trees added (either no buffer exists, or it is a grassed buffer) (A. Loeffler, 2019, pers. comm.). This is a significant amount of land that could potentially contributing to enhanced GHG emissions. Therefore, the goal of this study is to quantify and compare GHG emissions from 3 different riparian land-use systems in contrast to an agricultural field under conventional agronomic management

2.6 Research Objectives

The objectives of this research are two-fold:

1. To quantify and compare GHG (CO₂, CH₄, N₂O) emissions among a grassed buffer (GRS), two undisturbed natural forests (UNFA and UNFB), a 32-year old rehabilitated riparian forest buffer (RH), and an agricultural field (corn-soybean rotation) (AGR).

2. To quantify and compare the relationship between temporal GHG emissions, soil moisture, soil temperature, SOC, and soil ammonium and nitrate in the GRS, UNF, RH and AGR land-uses.

Hypotheses:

H₁: GHG emissions will be significantly different among land-use types, as well as over time.

H₀: GHG emissions will not be significantly different among land-use types, or over time.

H₂: Soil characteristics will be significantly correlated to GHG emissions within each land-use type.

H₀: Soil characteristics will not be significantly correlated to GHG emissions within each land-use type.

3.0 Materials and Methods

3.1 Study Site

This study took place using various land-use types found along Washington Creek, located in the Township of Blandford-Blenheim, Oxford County, Ontario, Canada. It is a 9-km long 1st-order spring-fed stream within the Grand River watershed, and flows into the Nith River south of Plattsville (43°18'N 80°33'W). The landscape in Oxford County is dominated by agricultural lands and there is very little streambank vegetation, causing a high degree of streambank and aquatic habitat degradation. Since Oxford County is in the peninsular region of southwestern Ontario, the Great Lakes have a substantial influence on climate (Wicklund and Richards 1961). The climate is temperate, which is defined by hot, humid summers and cold winters; a mean annual temperature of 7.3°C, a mean annual frost-free period of 208 days, and a mean annual precipitation is 919 mm (Environment Canada 2018).

The drainage basin Oxford County resides in has a soil parent material characterized as glacial till (Pleistocene) overlying limestone bedrock (Silurian) (Wicklunds and Richards 1961). Oxford County soils have a loamy texture with hilly areas consisting of silt loam and sand (Wicklund and Richards 1961). Plattsville is 304 m above sea level, and the soil was classified as a Grey Brown Luvisol (Mozuraitis and Hagarty 1996). The surface soil at each of the land-use sites is classified as silt loam (Oelbermann et al. 2015) and clay loam (Wicklund and Richards 1961).

Though most of the streambank is dominated by corn (*Zea mays L.*), soybeans (*Glycine max (L.) Merr.*), or pastureland, sections of the stream were under different management practices. For this study, four different land-use types along Washington Creek will be observed:

an agricultural field, a grassed buffer, 33-year-old rehabilitated forest buffer, and two undisturbed natural forests.

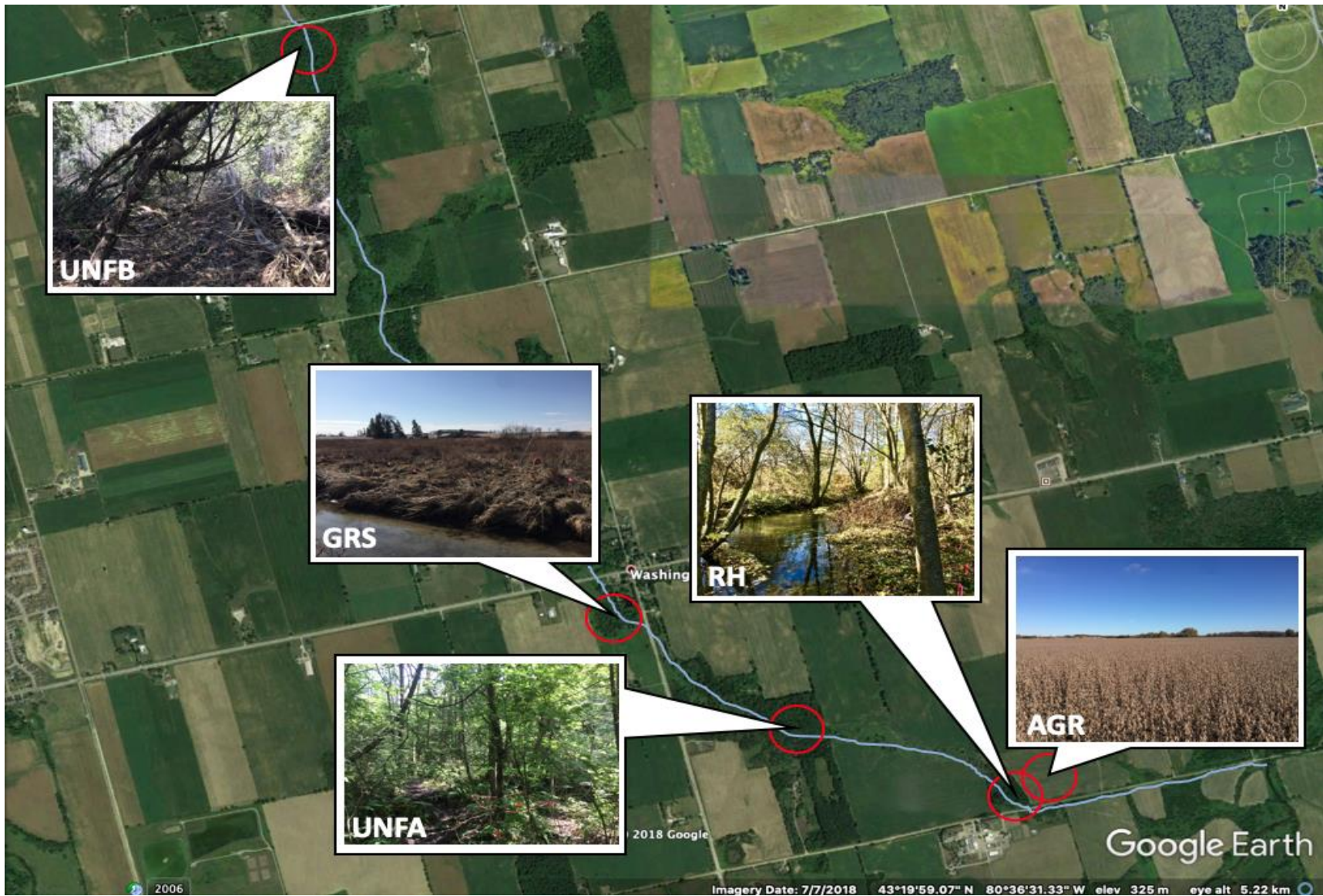


Figure 3.1 Aerial photograph of Washington Creek depicting the location of each of the land-use types (retrieved from Google Earth Pro).

3.1.2 Agricultural Field

The agricultural field is adjacent to the rehabilitated forest buffer on the east side. The field is on a corn-soybean rotation, with corn as the crop for the 2017 growing season and soybean for the 2018 growing season. The land is managed with conventional tilling, using manure and fertilizer, and tile drainage. The soil has a bulk density of 1.38 g cm^{-3} to a depth of 30 cm (Efosu, 2018).

3.1.4 Grassed Buffer

Approximately 3-km upstream of the rehabilitated forest buffer, is a grassed buffer. The buffer surrounds roughly 20-m of Washington Creek, and is comprised mostly of bentgrass (*Agrostis app.*), as well as panicled and purple-stemmed aster (*Symphotrichum puniceum*). The soil has a bulk density of 0.73 g cm^{-3} to a depth of 30 cm (Efosu 2018). The agricultural field adjacent to the buffer is on a corn-soy rotation, with corn grown in the 2017 season, and soybean in the 2018 season. The field uses conventional agricultural practices and was tile drained.

3.1.1 Rehabilitated Forest Buffer

As previously mentioned, Washington Creek has been negatively impacted by the agriculturally dominated landscape it resides in. Due to this, a 6-year long initiative began in 1985 to rehabilitate a 1.6-km long stretch of the streambank. The rehabilitated forest buffer was planted, mainly using woody vegetation, with a design comprised of blocks or 3 x 3 m spacing occupying the first 30-50 m from the stream edge (Gordon et al. 1992). The rehabilitated forest buffer was initially composed of a variety of alder [*Alnus incana* subsp. *Rugosa* (Du Roi) R.T. Clausen., *Alnus glutinosa* (L.) Gaertn., and *Alnus rubra* Bong.] and hybrid poplar (*Populus x*

Canadensis Moench) trees (Oelbermann and Raimbault 2015). Silver maple (*Acer saccharinum* L.) were planted as filler trees in 1986 and 1990, along with multiflora rosevine (*Rosa multiflora* Thunb.), Russian olive (*Elaeagnus angustifolia* L.), and red-osier dogwood (*Cornus sericea* subsp. *Sericea* L.) (Gordon et al. 1996). The soil has a bulk density of 1.06 g cm⁻³ to a depth of 30 cm (Efosu 2018).

3.1.3 Undisturbed Natural Forest A

The first undisturbed natural forest is located approximately 600-m upstream of the rehabilitated forest buffer. It covers a width of a minimum of 100-m, and has remained undisturbed for at least the past 150 years. The vegetation is predominantly comprised of American beech (*Fagus grandifolia* E.), American basswood (*Tilia americana* L.), American hophornbeam (*Ostrya virginiana* P.), sugar maple (*Acer saccharum* L.) and eastern hemlock (*Tsuga canadensis*) (Oelbermann et al., 2015). The soil has a bulk density of 0.56 g cm⁻³ to a depth of 30 cm (Efosu 2018). The land adjacent to the undisturbed natural forest is used for agriculture currently under a corn-soy rotation, with soy grown in the 2017 season and corn in the 2018 season, and therefore there is no 2017 data.

3.1.5 Undisturbed Natural Forest B

The second undisturbed natural forest is located approximately 5 km upstream of the rehabilitated forest buffer, and has been undisturbed for at least 100 years. This forest occurs at the start of Washington Creek, where the spring begins to feed into the creek. The dominant vegetation is Eastern White Cedar (*Thuja occidentalis*), and is characteristic of high amounts of deadwood with little to no understory vegetation. The soil has a bulk density of 0.63 g cm⁻³ to a

depth of 30 cm (Efosu 2018). Sampling at this study site did not begin until the second sampling year on May 22nd, 2018.

3.2 Study Design and Sample Analysis

3.2.1 Study Design

This study takes advantage of the diverse land-use types that all occur along the same agriculturally degraded stream. All four land-uses occur on both sides of the stream, and are situated within a 5km stretch of Washington Creek. To encompass temporal GHG emissions, sampling days occurred bi-weekly from June 30th, 2017 to November 14th, 2018 to capture spring, summer and autumn emissions. Winter emissions were not quantified due to inaccessibility of the sites during this season. Furthermore, a previous study at the RH and UNFA sites showed minimal emissions during winter (De Carlo et al. 2019). Seasons were divided using the following:

1. Summer 2017: June 30th – September 14th (n=6)
2. Autumn 2017: September 28th – November 14th (n=4)
3. Spring 2018: March 13th – June 6th (n=6)
4. Summer 2018: June 20th – August 30th (n=6)
5. Autumn 2018: September 18th – November 14th (n=5)

To accurately capture the average emissions from each treatment, four chambers were placed within each land-use (n=16). Although Parkin and Venterea (2010) recommend a minimum of two chambers per plot, four chambers were used to ensure spatial heterogeneity of the sites was captured given the intrinsic variability of microtopography within each site. The chambers were randomly distributed within a 5x30m plot in order to capture a significant

length of each land-use, as well as because farmers are usually only willing to give up the first 3m of productive land starting at the stream edge (Cardinali et al. 2014). Therefore, the plot began directly adjacent to the stream edge. Sampling took place from 10:00 h to 16:00 h, which corresponds with the time of day most consistent with the daytime average temperature (Parkin and Venterea 2010). During this time, emissions should be at their highest and more consistent (Petrone et al. 2008). Due to the unique landscape at Washington Creek, no other 1st order stream within the Grand River watershed with the same four land-use types with similar ages and composition. Therefore, this study is pseudoreplicated with a sample size of one, limiting the universality of results. To cope with this, a nested sampling design was used (Davies and Gray 2015).

3.3 Soil Sampling and Analysis

Soil samples were also collected bi-weekly at the time GHG sampling, and were taken randomly within a 1 m radius of each GHG chamber. This was done in order to avoid using constantly disturbed soil. Soil was extracted using a spade down to a depth of 10 cm as according to Estefan et al. (2013). Soil was placed in labelled plastic bags, which were then transported in a cooler to the Soil Ecosystem Dynamics Laboratory, University of Waterloo, Waterloo, Ontario. Soils were immediately frozen to preserve the available nitrogen (Carter and Gregorich 2008). Samples were collected for both the 2017 and 2018 sampling years.

3.3.1 Soil Physical Parameters

Soil moisture (%) and temperature (°C) were obtained from each soil sample location using an HH2-WET Sensor (Delta T Devices, Cambridge, UK). Measurements were taken to a

10 cm depth using where the soil samples were collected (i.e. within 1 m of the GHG chambers), and were collected bi-weekly at the time of GHG measurements. Ambient air temperature (°C) were determined using hourly data from the closest weather station in Kitchener-Waterloo (43°27'39.000" N 80°22'43.000" W). Photosynthetic photon flux density (PPFD) was determined using a quantum meter (Apogee Electronics Corporation, California, USA). Measurements were taken at ground height for each chamber at 15 seconds intervals for 90 seconds bi-weekly at the time of GHG sampling. Data was collected for both the 2017 and 2018 sampling years.

3.3.2 Soil Chemical Parameters

To determine the chemical characteristics of the soil, soil samples were allowed to thaw in a fridge overnight, set out to air-dry, grounded using a mortar and pestle, and then put through a 2 mm sieve. To determine available ammonium (NH_3^+) and nitrate (NO_3^-), 5 mL of air-dried soil was mixed with 25 mL of 2.0 M KCl. The solution was mixed for 15 minutes at 180 rpm using a reciprocating shaker. The solution was filtered through Whatman 42 filter paper into snap cap 50 mL containers. The extraction was then run through a Shimadzu 1800 UV-Vis Spectrophotometer (Shimadzu Corp., Kyoto, Japan) at 640 nm after 1 h of colour development to determine NH_3^+ (Verdow et al. 1978; Foster 1995), and then at 540 nm after 12 h of colour development to determine NO_3^- (Doane and Horwath 2003; Miranda et al. 2001).

3.4 Greenhouse Gas Sampling and Analysis

Greenhouse gases (CO_2 , CH_4 , and N_2O) were measured at each land-use type, and chambers were deployed 1 week before the first sampling date to allow soil to settle. Chambers consisted of white, non-reflective PVC piping (25 cm height, 10 cm radius), as well as ventilated

PVC caps, covered in an insulated reflective coating (Dyer et al. 2012; Lutes et al. 2016). When deployed, chambers permanently sat 10 cm into the soil throughout the sampling season, leaving 15-cm of headspace above the soil surface (Dyer et al. 2012; Lutes et al. 2016). Chamber caps will be fitted with a 1-cm diameter sampling port to fit a rubber septa in order to extract gas samples, and had a 10-cm long (9-mm diameter) ventilation tube to allow pressure to equalize when caps are on the chambers (Xu et al. 2006; Dyer et al. 2012; Lutes et al. 2016). Caps was removed after each sampling time, and soil were exposed to air between sampling dates (Hall et al. 2014). New vegetation growth and litterfall within permanent chambers will be removed 24-h before each sampling day to avoid their influence on emissions.

In order to capture emissions when vegetation and microbial communities are the most productive, sampling dates took place from the summer of 2017 to the autumn of 2018, excluding the winter season. As mentioned previously, to capture sinusoidal diurnal temperature variation (Smith et al. 2003), sampling takes place between 10:00-h and 16:00-h (Parkin and Venterea, 2010). To determine the emissions of GHGs, once the cap is placed on the chamber samples are taken at times 0, 10, 20 and 30 using a 60-mL air-tight syringe (Luer-Lock Tip. BD, Franklin Lakes, NJ, USA), and will be force-filled into evacuated 10-mL Exetainers (Labco Ltd., Lampeter, UK) (Parkin and Venterea 2010; Hall et al. 2014). Samples were collected for both the 2017 and 2018 sampling years.

GHG samples were analyzed using an Agilent 6890 Gas Chromatograph (Agilent Technologies, Inc., Santa Clara, CA, USA) housed in the Wetland Soils and Greenhouse Gas Exchange Lab, University of Waterloo, Waterloo, Ontario. Soil N₂O, CO₂, and CH₄ emissions will be expressed in ppm, and will be converted into emissions ($\mu\text{g GHG m}^{-1} \text{ h}^{-1}$) by determining whether the fluxes have linear or curvilinear curvature (Hutchinson and Mosier 1981). If the

fluxes follow a linear response, a linear regression slope will be used to determine GHG emissions. If the response is curvilinear, the Hutchinson and Mosier (1981) equation will be used. The result of these calculations will be in $\mu\text{L GHG m}^{-1} \text{ h}^{-1}$, so using the ideal gas law the results will be converted into $\mu\text{mol GHG m}^{-1} \text{ h}^{-1}$, and then by applying the molecular mass the fluxes can be expressed as $\mu\text{g GHG m}^{-1} \text{ h}^{-1}$ (Parkin and Venterea 2010; Lutes et al. 2016). All equations are based on Lutes (2016).

3.5 Statistical Analysis

GHG fluxes were tested for outliers, as well as tested for normality and homogeneity. Shapiro-Wilks test of normality and Levene's test of homogeneity was run first in order to deal with assumptions of normality and homogeneity associated with many statistical models. Non-normal data was transformed into a z-score to satisfy assumptions of normality (Crawford et al. 2006). However, if the distribution was still non-normal, parametric tests were still run in accordance with the central limit theorem as the sample sizes (e.g. seasonal and annual data) were larger than $n=30$, and should not substantially affect results (Elliott and Woodward 2011).

Linear mixed models (LMMs) were run in order to determine differences among GHGs for each land-use type, as well as for temporal changes in GHGs at each land-use and the soil characteristic data. Due to the chambers being in relatively close proximity and therefore not assumed to be independent, covariance among chambers within each land-use type must be accounted for. To accomplish this, chambers were assigned an ID from 1 to 16 and were used as the random effect (Arnau et al. 2010). To compare seasonal GHG emissions among and within the land-use types, land-use and season were used as the fixed effects (Maruyama 2008; Bates et al. 2015). To compare the annual changes in GHG emissions within land-use type and season,

land-use, season and year were used as fixed effects. The same random and fixed effects were used to analyze the soil characteristics. The Tukey's Test post hoc procedure was run on the LMMs to find significant differences among land uses and between seasons (Graham 2018).

Correlations between GHGs, soil temperature and moisture, inorganic nitrogen (NH_4^+ and NO_3^-), SOC, and PPFD were determined using the Spearman-Rank Correlation due to its robustness in the presence of outliers, non-normal distributions, and covariance (de Winter et al. 2016). Correlations were run between GHGs and soil and environmental characteristics at each land-use type. Further, correlations were run between all measured variables to see if there were significant correlations at the system level (De Carlo et al. 2019). To further identify which measured soil and environmental characteristics best predicted GHG emissions, stepwise regression models were run using all possible combinations of variables to create linear models (Seltman 2012). The best model was selected based on the lowest Akaike Information Criteria (AIC) and the Bayesian Information Criteria (BIC) (Seltman 2012). All tests will be run using R binary for OS X 10.11 (El Capitan). The Type I error rate for all statistical analyses was $p < 0.05$.

4.0 Results

4.1 Soil and Environmental Characteristics

4.1.1 Soil Temperature and Moisture

The mean annual air temperatures ($^{\circ}\text{C}$) for the AGR, GRS, RH, UNFA and UNFB sites were 14.97 ± 0.9 , 16.01 ± 0.79 , 15.07 ± 0.81 , 17.25 ± 0.76 , and 18.36 ± 1.17 , respectively (Figure 4.1a-e). Mean seasonal soil temperatures ($^{\circ}\text{C}$) in 2017 across all land-use types ranged from 9.33 ± 0.99 to 21.43 ± 0.8 (Table 4.1). In summer 2017, the AGR site ($21.43 \pm 0.8^{\circ}\text{C}$) had significantly (RH, $p < 0.0001$; UNFA, $p < 0.0001$) higher soil temperatures than the RH and UNFA sites ($18.04 \pm 0.81^{\circ}\text{C}$ and $17.52 \pm 0.81^{\circ}\text{C}$). The AGR and GRS ($18.67 \pm 0.81^{\circ}\text{C}$) sites were not significantly different. In autumn 2017, the GRS site ($11.22 \pm 0.99^{\circ}\text{C}$) had the highest soil temperature, and there were no significant differences among land-use types. For all land-use types, soil temperature was significantly (AGR, $p < 0.0001$; GRS, $p < 0.0001$; RH, $p < 0.0001$; UNFA, $p < 0.0001$) higher in the summer 2017 compared to the autumn 2017.

Mean seasonal soil temperatures ($^{\circ}\text{C}$) in 2018 across all land-uses ranged from 9.99 ± 0.99 to 24.29 ± 0.90 . There were no significant differences in soil temperature among land-uses within each season. However, there were differences within land-uses among seasons. The AGR site had significantly (spring, $p = 0.0025$; fall, $p < 0.0001$) higher soil temperatures in the summer 2018 ($24.29 \pm 0.90^{\circ}\text{C}$) season compared to the spring and fall 2018 seasons (16.65 ± 1.55 and $10.71 \pm 0.98^{\circ}\text{C}$). This trend was true for all land-use types for 2018, as the summer 2018 season was significantly higher than both the spring and fall 2018 seasons across all land-use types (Table 4.1). All land use types' seasonal differences had a p-value of < 0.0001 , except for the UNFA and UNFB sites both between spring and summer 2018 (UNFA, $p = 0.0003$; UNFB, $p = 0.0400$). For the within land-use, within season annual variation, the GRS and RH sites

experienced significantly (GRS, $p=0.0006$; RH, $p=0.0092$) higher soil temperatures in the summer 2018 season compared to the summer 2017 season. There were no other significant differences in annual variation for soil temperature.

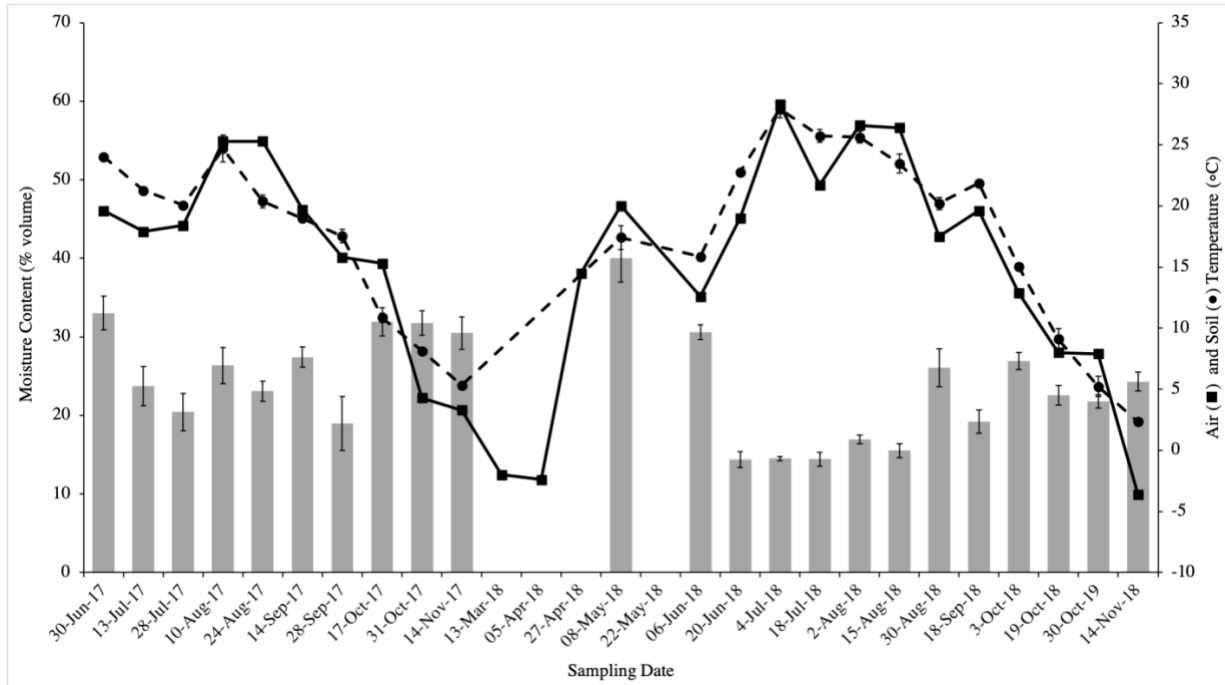


Figure 4.1a. Mean ambient air temperature, soil temperature and soil moisture for the agricultural field (AGR) found along Washington Creek in southern Ontario, Canada for all sampling dates from June 30th, 2017 to November 14th, 2018.

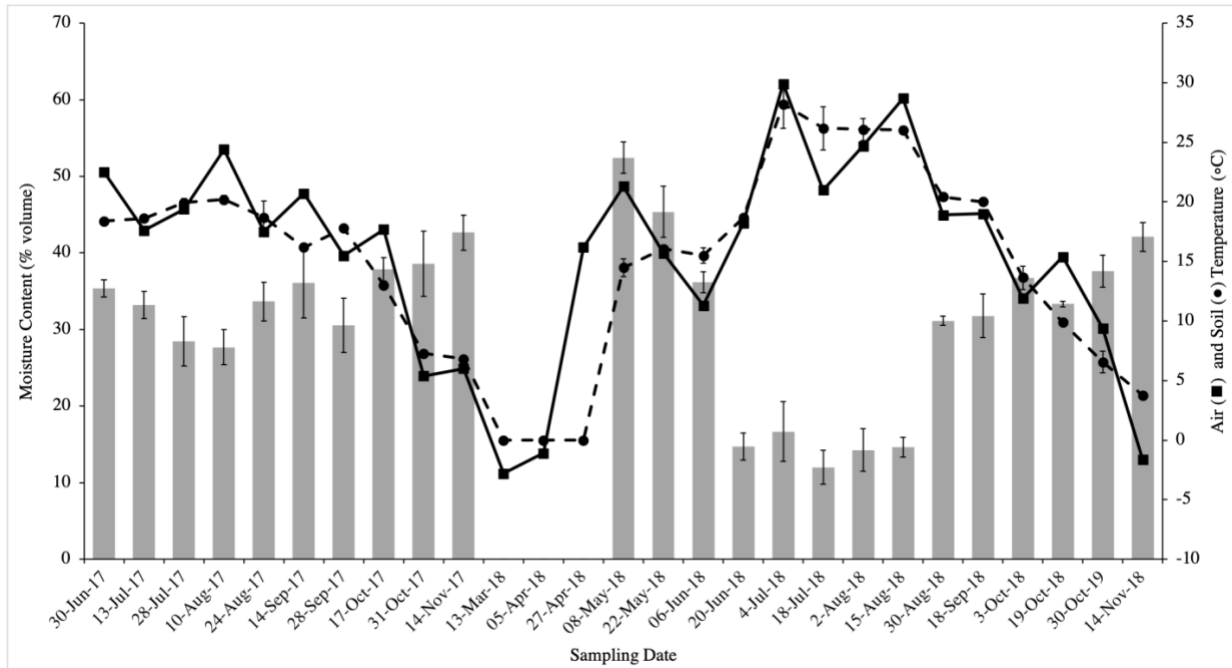


Figure 4.1b. Mean ambient air temperature, soil temperature and soil moisture for the grassed buffer (GRS) found along Washington Creek in southern Ontario, Canada for all sampling dates from June 30th, 2017 to November 14th, 2018.

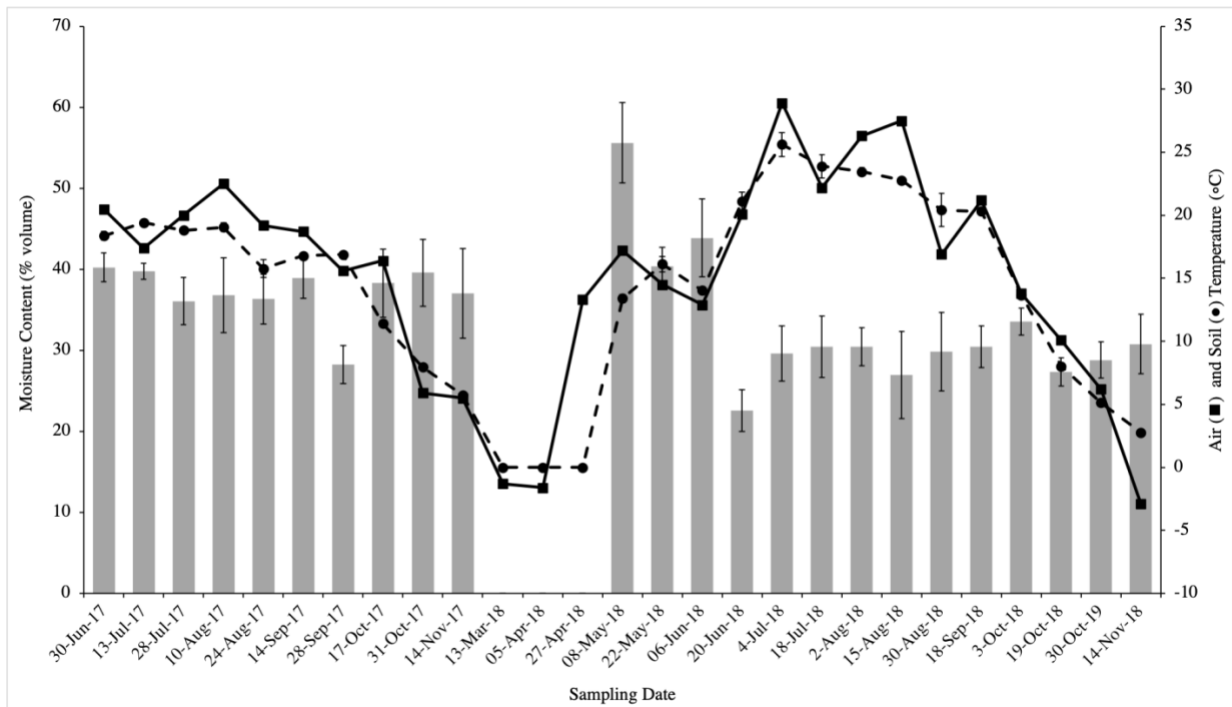


Figure 4.1c. Mean ambient air temperature, soil temperature and soil moisture for the rehabilitated forest buffer (RH) found along Washington Creek in southern Ontario, Canada for all sampling dates from June 30th, 2017 to November 14th, 2018.

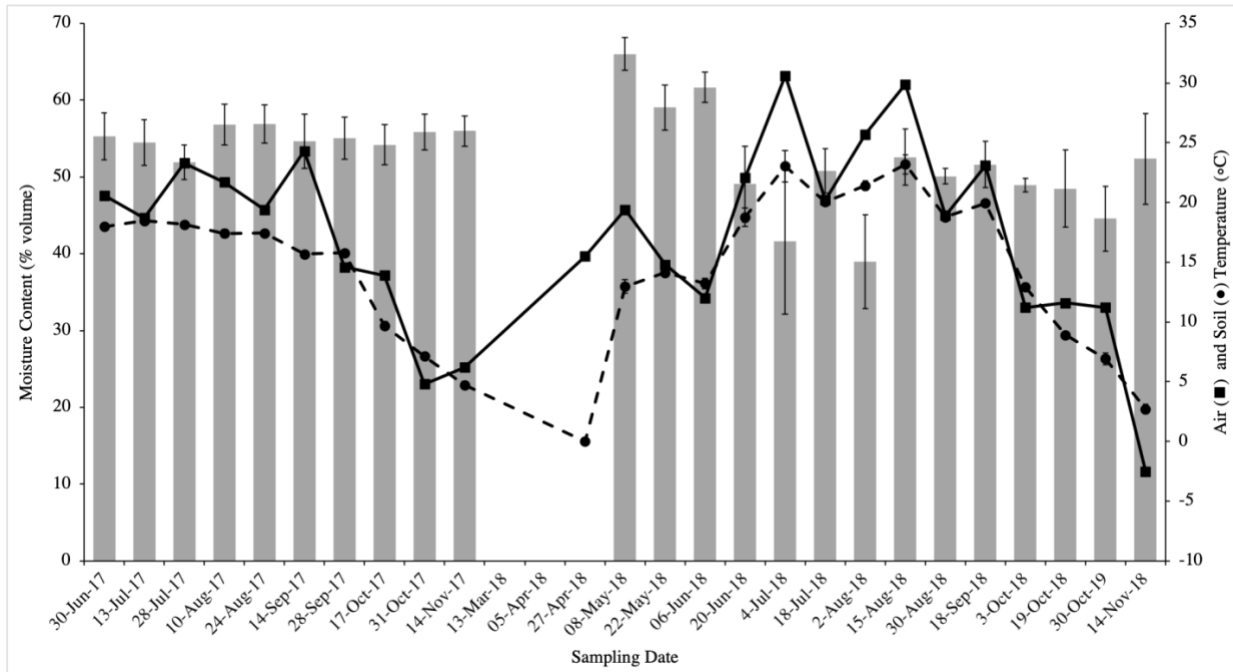


Figure 4.1d. Mean ambient air temperature, soil temperature and soil moisture for the undisturbed natural forest A (UNFA) found along Washington Creek in southern Ontario, Canada for all sampling dates from June 30th, 2017 to November 14th, 2018.

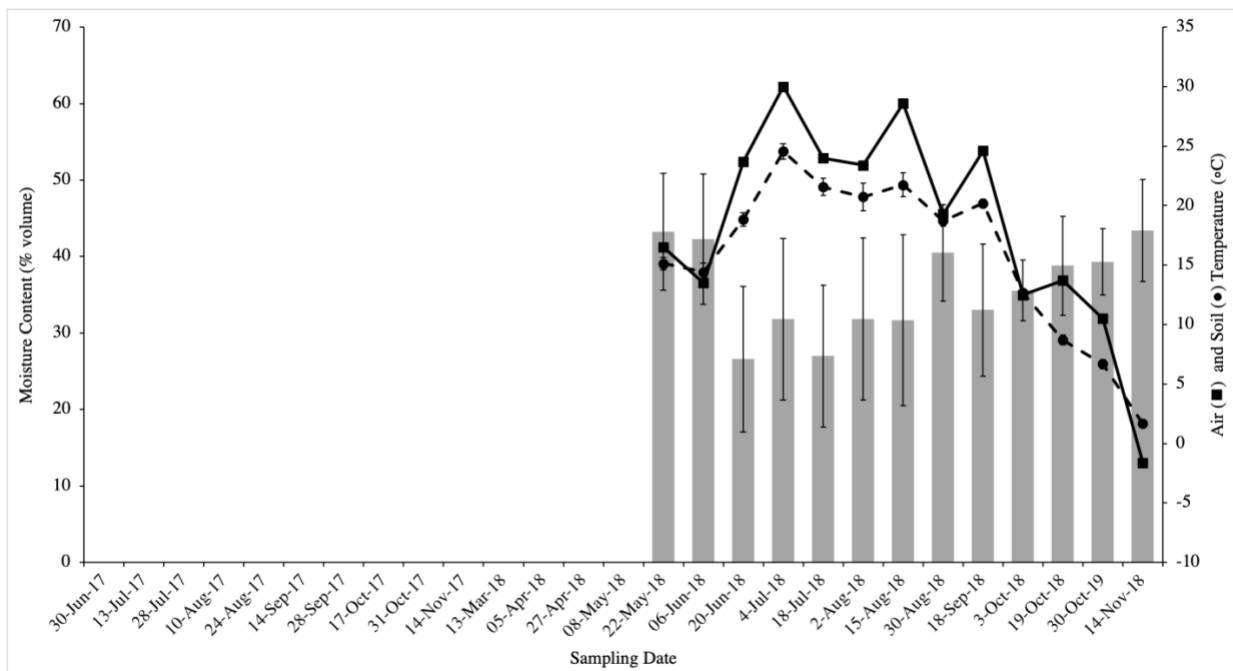


Figure 4.1e. Mean ambient air temperature, soil temperature and soil moisture for the undisturbed natural forest B (UNFB) found along Washington Creek in southern Ontario, Canada for all sampling dates from June 30th, 2017 to November 14th, 2018.

Table 4.1. Mean seasonal soil temperature (°C) and soil moisture (% volume) for the agricultural field (AGR), grassed buffer (GRS), rehabilitated forest buffer (RH), undisturbed natural forest A (UNFA), and undisturbed natural forest B (UNFB) found along Washington Creek, southern Ontario, Canada during 2017-2018.

	Land-Use	2017			2018		
		Spring	Summer	Autumn	Spring	Summer	Autumn
Soil Temperature (°C)	AGR	---	21.43 (0.80) ^{Aa}	9.99 (1.02) ^{Ab}	16.64 (1.55) ^{Aa}	24.29 (0.90) ^{Ab}	10.71 (0.98) ^{Aa}
	GRS	---	18.67 (0.81) ^{ABa}	11.22 (0.99) ^{Ab}	15.34 (1.27) ^{Aa}	24.26 (0.90) ^{Ab*}	10.78 (0.98) ^{Aa}
	RH	---	18.04 (0.81) ^{Ba}	10.49 (0.99) ^{Ab}	14.53 (1.27) ^{Aa}	22.88 (0.90) ^{Ab*}	9.99 (0.98) ^{Aa}
	UNFA	---	17.52 (0.81) ^{Ba}	9.33 (0.99) ^{Ab}	13.44 (1.14) ^{Aa}	20.88 (0.90) ^{Ab}	10.29 (0.98) ^{Aa}
	UNFB	---	---	---	14.76 (1.55) ^{Aa}	21.03 (0.90) ^{Ab}	9.99 (0.98) ^{Aa}
Soil Moisture (% volume)	AGR	---	25.61 (2.23) ^{Aa}	28.87 (2.36) ^{Aa}	35.05 (3.95) ^{Aa}	16.73 (3.40) ^{Ab*}	22.71 (3.46) ^{Ab}
	GRS	---	32.42 (2.22) ^{ABa}	37.41 (2.34) ^{Ab}	44.66 (4.05) ^{ABa}	17.25 (3.79) ^{ACb*}	36.32 (3.85) ^{ABa}
	RH	---	38.33 (2.22) ^{Ba}	35.79 (2.34) ^{Aa}	46.63 (4.05) ^{ABa}	28.31 (3.79) ^{ABCb*}	30.18 (3.85) ^{ABa}
	UNFA	---	55.00 (2.22) ^{Ca}	55.26 (2.34) ^{Ba}	62.23 (4.05) ^{Ba}	47.18 (3.79) ^{Bb*}	49.18 (3.85) ^{Bb}
	UNFB	---	---	---	42.79 (3.51) ^{ABa}	31.81 (3.40) ^{BCa*}	38.26 (3.46) ^{Ba}

*Significant differences among land uses within year and season are represented by ^{ABC}. Significant differences among seasons within year and land-use are represented by ^{abc}. A * indicates a significant difference within land-use and within season from 2017 to 2018.

The mean seasonal soil moisture (% volume) in 2017 across all land-use types ranged from 25.61 ± 2.23 to 55.26 ± 2.34 (Table 4.1). In summer 2017, the UNFA site ($55.00 \pm 2.22\%$) had significantly (AGR, $p=0.0001$; GRS, $p=0.0001$; RH, 0.0020) higher soil moisture than the AGR, GRS and RH sites (25.61 ± 2.23 , 32.42 ± 2.22 , and $38.33 \pm 2.22\%$). Additionally, the RH site had significantly ($p=0.0193$) higher soil moisture than the AGR site. For the within land-use seasonal variation, only the GRS site had significant differences, where the soil moisture was significantly ($p=0.0500$) higher in autumn 2017 ($37.41 \pm 2.34\%$) compared to summer 2017 ($32.42 \pm 2.22\%$). For the 2018 sampling year, mean seasonal soil moisture (% volume) across all land-use types ranged from 16.73 ± 3.40 to 62.23 ± 4.05 (Table 4.1). In the spring 2018 season, the UNFA site ($62.23 \pm 4.05\%$) had significantly ($p=0.0026$) higher soil moisture than the AGR site ($35.05 \pm 3.95\%$). There were no other significant differences among land-use types within spring 2018. For summer 2018, the UNFA site ($47.18 \pm 3.79\%$) had significantly (AGR, $p=0.0004$; GRS, $p=0.0014$) higher soil moisture than the AGR and GRS sites (16.73 ± 3.40 and $17.25 \pm 3.79\%$). Further, the UNFB site ($31.81 \pm 3.40\%$) also had significantly ($p=0.0350$) higher soil moisture than the AGR site, but no other significant differences from the other land-use types. In autumn 2018, the UNFA ($49.18 \pm 3.85\%$) and UNFB ($38.26 \pm 3.46\%$) sites were both significantly (UNFA, $p=0.0024$; UNFB, $p=0.0312$) higher than the AGR site ($22.71 \pm 3.46\%$), with no other significant differences among land-use types. For the within land-use, seasonal changes in soil moisture for the 2018 sampling year, most land use types experienced significant seasonal changes except for the UNFB site. The AGR site had significantly higher soil moisture in spring 2018 compared to both summer and autumn 2018 (summer, $p<0.0001$; autumn, $p=0.0031$). The GRS site had significantly ($p<0.0001$) higher mean soil moisture in the spring and fall 2018 seasons compared to the

summer 2018 season, with both differences having a p-value of <0.0001. For both the RH and UNFA sites, the spring 2018 season was significantly higher than both summer and autumn 2018. These significant differences all had a p-value of <0.0001, except at the UNFA site between the spring and fall 2018 seasons (p=0.0001). For the within land-use, within season annual variation, all land use types excluding the UNFB site had significantly (AGR, p=0.0016; GRS, p=<0.0001; RH, p=<0.0001; UNFA, p=0.0084) higher soil moisture in summer 2018 than summer 2017. There were no other significant differences in annual variation for soil moisture.

4.1.2 Inorganic Nitrogen

In the 2017 sampling year, mean seasonal NH_4^+ concentration in the soil ($\text{mg NH}_4^+\text{-N kg}^{-1}$ dry soil) across all land-use types ranged from 1.93 ± 0.89 to 9.92 ± 0.86 (Table 4.2). For summer 2017, there were no significant differences among land-use types. For the fall 2017 season, the UNFA site ($9.92 \pm 0.86 \text{ mg NH}_4^+\text{-N kg}^{-1}$ dry soil) was significantly higher than the AGR, GRS and RH sites (1.93 ± 0.89 , 3.24 ± 0.86 and $2.30 \pm 0.86 \text{ mg NH}_4^+\text{-N kg}^{-1}$ dry soil), with all significant differences having a p-value of <0.0001. For the within land-use seasonal variation, only the UNFA had significant seasonal changes with autumn 2017 having a significantly (p=0.0002) higher NH_4^+ concentration than summer 2017 ($4.78 \pm 0.70 \text{ mg NH}_4^+\text{-N kg}^{-1}$ dry soil). In the 2018 sampling year, mean seasonal NH_4^+ concentrations ($\text{mg NH}_4^+\text{-N kg}^{-1}$ dry soil) across all land-use types ranged from 2.31 ± 1.82 to 15.19 ± 2.23 . For spring, summer and autumn 2018, there were no significant differences among land-use types for mean NH_4^+ concentration. However, there were within land-use seasonal changes for the 2018 sampling year. The AGR site in spring 2018 ($13.73 \pm 2.58 \text{ mg NH}_4^+\text{-N kg}^{-1}$ dry soil) was significantly (p=0.0268) higher than summer 2018 ($2.31 \pm 1.82 \text{ mg NH}_4^+\text{-N kg}^{-1}$ dry soil). The RH site in

spring 2018 (14.40 ± 2.23 mg $\text{NH}_4^+\text{-N}$ kg^{-1} dry soil) has a significantly (summer, $p=0.101$; autumn, $p=0.0226$) higher mean NH_4^+ concentration than summer and autumn 2018 (3.17 ± 1.82 and 3.29 ± 2.05 mg NH_4^+ kg^{-1} dry soil). The UNFA followed the same trend as the RH site for seasonal variation, and had a significantly (summer, $p=0.0085$; autumn, $p=0.0417$) higher spring 2018 (15.19 ± 2.23 mg $\text{NH}_4^+\text{-N}$ kg^{-1} dry soil) season NH_4^+ concentration to that of summer and autumn 2018 (3.83 ± 1.82 and 4.65 ± 2.05 mg $\text{NH}_4^+\text{-N}$ kg^{-1} dry soil). There were no other significant within land-use seasonal differences. There were also no within land-use, within season annual significant differences for NH_4^+ concentration in the soil.

In the 2017 sampling year, the mean seasonal NO_3^- concentration in the soil (mg $\text{NO}_3^-\text{-N}$ kg^{-1} dry soil) across all land-use types ranged from 13.34 ± 6.66 to 64.83 ± 6.72 (Table 4.2). For summer 2017, the AGR site (64.83 ± 6.72 mg NO_3^- kg^{-1} dry soil) had a significantly (GRS, $p=0.0015$, RH, $p=0.0028$; UNFA, $p=0.0009$) higher mean NO_3^- concentration than the GRS, RH and UNFA sites (15.64 ± 6.66 , 18.61 ± 6.66 and 13.34 ± 6.66 mg $\text{NO}_3^-\text{-N}$ kg^{-1} dry soil). For autumn 2017, there were no significant differences among the land-use types. For within land-use seasonal differences, the AGR site had significantly ($p<0.0001$) higher mean NO_3^- concentrations in summer 2017 compared to autumn 2017 (19.78 ± 7.41 mg $\text{NO}_3^-\text{-N}$ kg^{-1} dry soil) season. In the 2018 sampling year, the mean seasonal NO_3^- concentration (mg $\text{NO}_3^-\text{-N}$ kg^{-1} dry soil) across all land use types ranged from 2.19 ± 2.49 to 26.03 ± 3.83 . In spring 2018, the UNFB site (26.03 ± 3.83 mg $\text{NO}_3^-\text{-N}$ kg^{-1} dry soil) had a significantly ($p=0.0488$) higher seasonal NO_3^- concentration than the AGR site (9.04 ± 3.13 mg $\text{NO}_3^-\text{-N}$ kg^{-1} dry soil). There were no significant differences among the land-use types in summer 2018. In autumn 2018, the GRS site (15.59 ± 2.43 mg $\text{NO}_3^-\text{-N}$ kg^{-1} dry soil) had a significantly ($p=0.0154$) higher mean seasonal NO_3^- concentration than the UNFA site (2.19 ± 2.49 mg $\text{NO}_3^-\text{-N}$ kg^{-1} dry soil). Only the UNFB

site had significant differences among seasons for mean seasonal NO_3^- concentration in the 2018 sampling year. Summer 2018 was significantly (summer, $p=0.0266$; autumn, $p=0.0002$) higher than both spring and autumn 2018 (9.99 ± 2.22 and 3.58 ± 2.49 mg NO_3^- -N kg^{-1} dry soil). There were no within land-use, within season annual significant differences for NO_3^- concentration in the soil.

Table 4.2 Mean seasonal NH₄⁺ and NO₃⁻ concentration (mg kg⁻¹ soil) for the agricultural field (AGR), grassed buffer (GRS), rehabilitated forest buffer (RH), undisturbed natural forest A (UNFA), and undisturbed natural forest B (UNFB) found along Washington Creek, southern Ontario, Canada during 2017-2018.

	Land-Use	2017			2018		
		Spring	Summer	Autumn	Spring	Summer	Autumn
NH₄⁺ (mg NH₄⁺-N kg⁻¹ soil)	AGR	---	4.45 (0.72) ^{Aa}	1.93 (0.89) ^{Aa}	13.73 (2.58) ^{Aa}	2.31 (1.82) ^{Ab}	2.76 (2.00) ^{Ab}
	GRS	---	5.46 (0.70) ^{Aa}	3.24 (0.86) ^{Aa}	11.24 (2.23) ^{Aa}	2.77 (1.82) ^{Aa}	6.75 (1.99) ^{Aa}
	RH	---	3.43 (0.70) ^{Aa}	2.30 (0.86) ^{Aa}	14.40 (2.23) ^{Aa}	3.17 (1.82) ^{Ab}	3.29 (2.05) ^{Ab}
	UNFA	---	4.78 (0.70) ^{Aa}	9.92 (0.86) ^{Bb}	15.19 (2.23) ^{Aa}	3.83 (1.82) ^{Ab}	4.65 (2.05) ^{Ab}
	UNFB	---	---	---	9.02 (3.15) ^{Aa}	10.79 (1.82) ^{Aa}	5.63 (2.05) ^{Aa}
NO₃⁻ (mg NO₃⁻-N kg⁻¹ soil)	AGR	---	64.83 (6.72) ^{Aa}	19.78 (7.41) ^{Ab}	9.04 (3.13) ^{Aa}	9.29 (2.22) ^{Aa}	4.14 (2.43) ^{ABa}
	GRS	---	15.64 (6.66) ^{Ba}	27.75 (7.29) ^{Aa}	16.70 (2.71) ^{ABa}	16.08 (2.21) ^{Aa}	15.59 (2.43) ^{Ba}
	RH	---	18.61 (6.66) ^{Ba}	18.61 (7.29) ^{Aa}	15.81 (2.71) ^{ABa}	12.42 (2.21) ^{Aa}	4.72 (2.49) ^{ABa}
	UNFA	---	13.34 (6.66) ^{Ba}	17.06 (7.29) ^{Aa}	10.12 (2.71) ^{ABa}	10.58 (2.21) ^{Aa}	2.19 (2.49) ^{Aa}
	UNFB	---	---	---	26.03 (3.83) ^{Ba}	9.99 (2.22) ^{Ab}	3.58 (2.49) ^{ABa}

*Significant differences among land uses within year and season are represented by ^{ABC}. Significant differences among seasons within year and land-use are represented by ^{abc}. A * indicates a significant difference within land-use and within season from 2017 to 2018.

4.1.3 Soil Organic Carbon (SOC)

The mean concentration of SOC (g kg^{-1}) for the AGR, GRS, RH, UNFA, and UNFB sites was 21.87 ± 4.68 , 43.08 ± 4.68 , 40.44 ± 4.68 , 68.75 ± 4.68 , and 76.54 ± 4.68 , respectively. The UNFA site was significantly (AGR, $p < 0.0001$; GRS, $p = 0.0115$; RH, $p = 0.0053$) higher than the AGR, GRS and RH sites. The UNFB site was also significantly (AGR, $p < 0.0001$; GRS, $p = 0.0012$; RH, $p = 0.0006$) higher than the AGR, GRS and RH sites. The GRS site was significantly ($p = 0.0411$) higher than the AGR site. The RH and GRS sites were not significantly different from each other, as well as the UNFA and UNFB sites.

4.1.4 Photosynthetic Photon Flux Density (PPFD)

Throughout the sampling period, the PPFD ($\mu\text{Mol m}^{-2} \text{s}^{-1}$) ranged from 3 ± 0 to 1985.67 ± 1.84 . For the 2017 sampling year, the mean annual PPFD for the AGR, GRS, RH, and UNFA sites were 313.86 ± 95.65 , 618.52 ± 93.01 , 125.46 ± 93.01 , and 49.6 ± 93.01 , respectively. The GRS site had a significantly (RH, $p = 0.0095$; UNFA, $p = 0.0012$) higher mean PPFD than the RH and UNFA sites. There were no other significant differences for the 2017 sampling year. For the 2018 sampling year, the mean annual PPFD ($\mu\text{Mol m}^{-2} \text{s}^{-1}$) for the AGR, GRS, RH, UNFA and UNFB sites were 609.08 ± 58.0 , 622.04 ± 57.68 , 290.79 ± 55.59 , 185.51 ± 56.62 , and 20.94 ± 60.25 , respectively. The AGR site had a significantly (RH, $p = 0.0161$; UNFA, $p = 0.0007$; UNFB, $p < 0.0001$) higher mean PPFD than the RH, UNFA, and UNFB sites. The GRS site also had a significantly (RH, $p = 0.0107$; UNFA, $p = 0.0004$; UNFB, $p < 0.0001$) higher PPFD than the RH, UNFA, and UNFB sites. There were no significant within land-use differences in mean annual PPFD between 2017 and 2018 for each land-use type.

3.2 Soil Greenhouse Gas Emissions

3.2.1 Nitrous Oxide

Throughout the entire sampling period, N₂O emissions ($\mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$) ranged from -6.39 ± 20.94 to 119.38 ± 33.63 across all land-use types (Figure 4.2). In the 2017 sampling year, the mean seasonal N₂O emissions ($\mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$) ranged from 5.3 ± 17.0 to 63.58 ± 15.7 (Table 4.3). There were no significant differences among land-uses for both summer and autumn 2017. There were also no significant differences between seasons within land-use type. In the 2018 sampling year, the mean seasonal N₂O emissions ($\mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$) ranged from 0.07 ± 4.96 to 20.68 ± 5.08 . This year yielded a similar result as the 2017 sampling year, as there were no significant differences among seasons or land-use types.

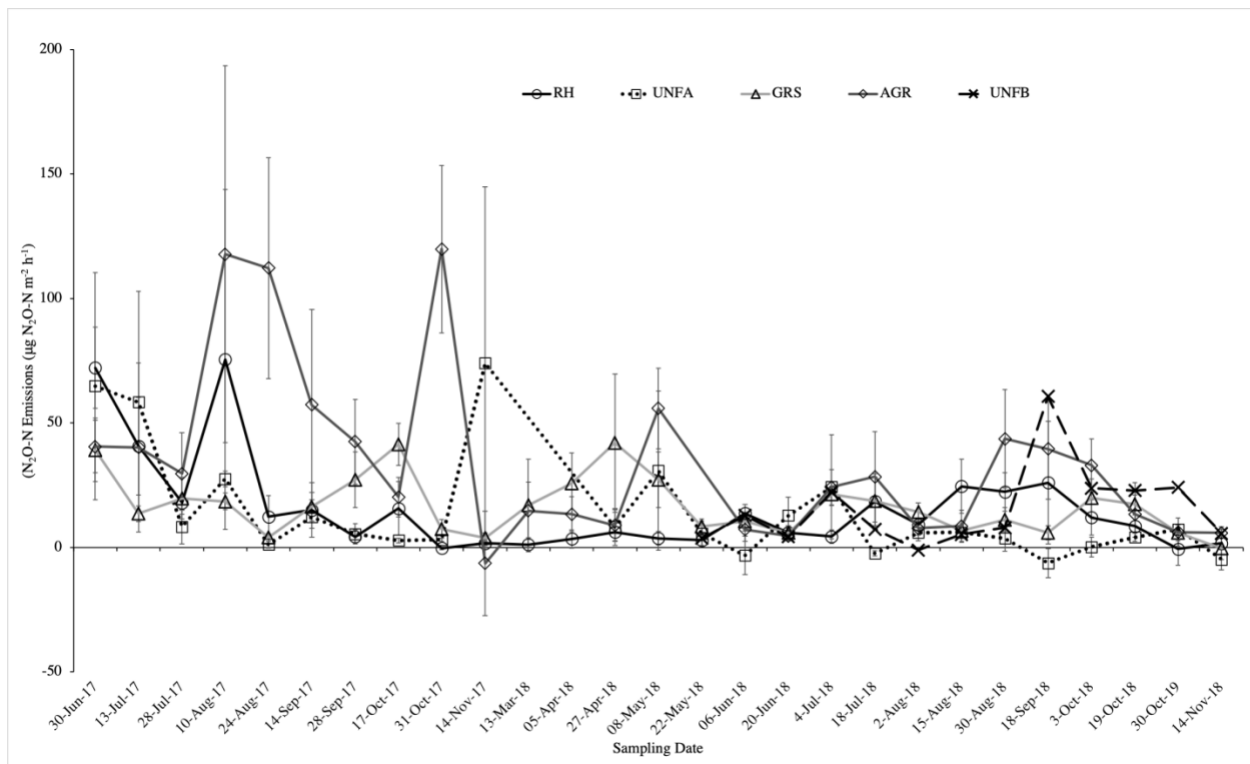


Figure 4.2. Mean soil N₂O emissions ($\mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$) for each sampling date at the agricultural field (AGR), grassed buffer (GRS), rehabilitated forest buffer (RH), undisturbed natural forest A (UNFA), and undisturbed natural forest B (UNFB) found along Washington Creek in southern Ontario, Canada for the full sampling period (June 30th, 2017 to November 14th, 2018).

Table 4.3. Mean seasonal soil N₂O emissions ($\mu\text{g N}_2\text{O-N m}^{-2} \text{h}^{-1}$) for the agricultural field (AGR), grassed buffer (GRS), rehabilitated forest buffer (RH), undisturbed natural forest A (UNFA), and undisturbed natural forest B (UNFB) found along Washington Creek, southern Ontario, Canada during 2017-2018.

	Land-Use	2017			2018		
		Spring	Summer	Autumn	Spring	Summer	Autumn
N ₂ O-N ($\mu\text{g m}^{-2} \text{h}^{-1}$)	AGR	---	63.58 (15.7) ^{Aa}	43.47 (17.29) ^{Aa}	20.17 (4.97) ^{Aa}	19.68 (4.62) ^{Aa*}	20.68 (5.08) ^{Aa}
	GRS	---	18.55 (15.57) ^{Aa}	19.94 (17.0) ^{Aa}	22.32 (4.78) ^{Aa}	13.03 (4.61) ^{Aa}	9.73 (4.96) ^{Aa}
	RH	---	41.05 (15.7) ^{Aa}	5.30 (17.0) ^{Aa}	5.13 (4.61) ^{Aa}	14.12 (4.61) ^{Aa}	9.54 (4.96) ^{Aa}
	UNFA	---	28.50 (15.7) ^{Aa}	21.33 (17.0) ^{Aa}	10.34 (5.45) ^{Aa}	8.39 (4.61) ^{Aa}	0.07 (4.96) ^{Aa}
	UNFB	---	---	---	8.21 (7.27) ^{Aa}	7.45 (4.62) ^{Aa}	16.22 (5.21) ^{Aa}

*Significant differences among land uses within year and season are represented by ^{ABC}. Significant differences among seasons within year and land-use are represented by ^{abc}. A * indicates a significant difference within land-use and within season from 2017 to 2018.

3.2.2 Carbon Dioxide

Throughout the entire sampling period, mean CO₂ emissions (mg CO₂-C m⁻² h⁻¹) ranged from -15.48 ± 15.14 to 625.34 ± 49.30 across all land-use types (Figure 4.3). In the 2017 sampling year, the mean seasonal CO₂ (mg CO₂-C m⁻² h⁻¹) emissions ranged from 60.26 ± 54.63 to 316.90 ± 53.8 (Table 4.4). For summer 2017, mean CO₂ emissions did not differ significantly among land-use types. For autumn 2017, the GRS site (316.90 ± 53.8 mg CO₂-C m⁻² h⁻¹) experienced significantly ($p=0.0492$) higher mean CO₂ emissions than the AGR site (60.26 ± 54.63). There was no significant seasonal effect within land-use type. In the 2018 sampling year, mean seasonal CO₂ (mg CO₂-C m⁻² h⁻¹) emissions ranged from 45.15 ± 43.10 to 417.66 ± 40.66 . There were no significant differences among the land-use types in spring and autumn 2018. In summer 2018, the AGR, UNFA, and UNFB (150.05 ± 40.31 , 170.34 ± 40.66 , and 129.06 ± 40.31 mg CO₂-C m⁻² h⁻¹) sites had significantly (AGR, $p=0.0032$; UNFA, $p=0.0101$; UNFB, $p=0.0011$) lower mean seasonal emissions than the GRS site (417.66 ± 40.66 mg CO₂-C m⁻² h⁻¹). Only the GRS site experienced significant changes in mean emissions between seasons, for summer 2018 had significantly ($p<0.0001$) higher CO₂ emissions than spring and autumn 2018 (153.73 ± 41.65 and 190.88 ± 42.76 mg CO₂-C m⁻² h⁻¹). There was no significant effect of year on the within land-use and within season mean for CO₂ emissions.

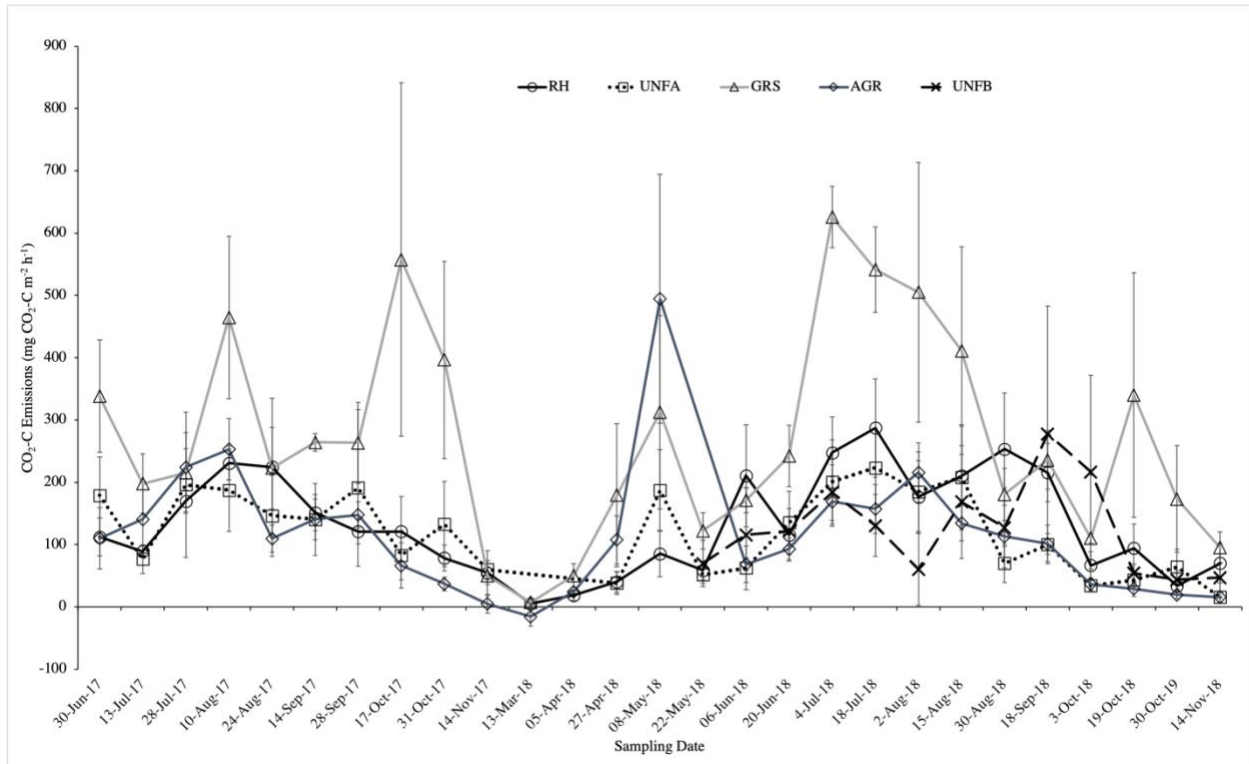


Figure 4.3. Mean soil CO₂ emissions (mg CO₂-C m⁻² h⁻¹) for each sampling date at the agricultural field (AGR), grassed buffer (GRS), rehabilitated forest buffer (RH), undisturbed natural forest A (UNFA), and undisturbed natural forest B (UNFB) found along Washington Creek in southern Ontario, Canada for the full sampling period (June 30th, 2017 to November 14th, 2018).

Table 4.4. Mean seasonal soil CO₂ emissions (mg CO₂-C m⁻² h⁻¹) for the agricultural field (AGR), grassed buffer (GRS), rehabilitated forest buffer (RH), undisturbed natural forest A (UNFA), and undisturbed natural forest B (UNFB) found along Washington Creek, southern Ontario, Canada during 2017-2018.

	Land-Use	2017			2018		
		Spring	Summer	Autumn	Spring	Summer	Autumn
CO ₂ -C (mg m ⁻² h ⁻¹)	AGR	---	160.34 (50.19) ^{Aa}	60.26 (54.63) ^{Aa}	138.84 (42.43) ^{Aa}	150.05 (40.31) ^{Aa}	45.15 (43.10) ^{Aa}
	GRS	---	288.55 (50.19) ^{Aa}	316.90 (53.8) ^{Ba}	153.73 (41.65) ^{Aa}	417.66 (40.66) ^{Ba}	190.88 (42.76) ^{Aa}
	RH	---	163.13 (49.8) ^{Aa}	93.82 (53.8) ^{ABa}	69.88 (40.66) ^{Aa}	215.10 (40.66) ^{ABa}	96.05 (42.76) ^{Aa}
	UNFA	---	154.34 (49.8) ^{Aa}	116.70 (53.8) ^{ABa}	84.86 (45.73) ^{Aa}	170.34 (40.66) ^{Aa}	51.54 (42.76) ^{Aa}
	UNFB	---	---	---	92.55 (54.93) ^{Aa}	129.06 (40.31) ^{Aa}	117.85 (43.11) ^{Aa}

*Significant differences among land uses within year and season are represented by ^{ABC}. Significant differences among seasons within year and land-use are represented by ^{abc}. A * indicates a significant difference within land-use and within season from 2017 to 2018.

3.2.3 Methane

Throughout the entire sampling period, mean soil CH₄ ($\mu\text{g CH}_4\text{-C m}^{-2} \text{ h}^{-1}$) emissions ranged from -558.43 ± 395.46 to 3050.88 ± 1593.26 across all land-use types (Figure 4.4). The mean seasonal CH₄ ($\mu\text{g CH}_4\text{-C m}^{-2} \text{ h}^{-1}$) emissions in the 2017 sampling year ranged from -59.16 ± 164.71 to 1272.05 ± 201.72 (Table 4.5). In summer 2017, the UNFA site ($760.97 \pm 164.71 \mu\text{g CH}_4\text{-C m}^{-2} \text{ h}^{-1}$) had significantly (AGR, $p=0.0444$, GRS, $p=0.0258$) higher mean CH₄ emissions than the AGR and GRS sites (-13.14 ± 168.34 and $-59.16 \pm 164.71 \mu\text{g CH}_4\text{-C m}^{-2} \text{ h}^{-1}$). Autumn 2017 followed a similar trend, with the UNFA site ($1272.05 \pm 201.72 \mu\text{g CH}_4\text{-C m}^{-2} \text{ h}^{-1}$) having significantly (AGR, $p=0.001$; GRS, $p=0.0005$; RH, $p=0.0008$) higher mean emissions than the AGR, GRS, and RH sites (-11.11 ± 208.5 , -44.46 ± 201.72 , and $-12.37 \pm 201.72 \mu\text{g CH}_4\text{-C m}^{-2} \text{ h}^{-1}$). The mean seasonal CH₄ ($\mu\text{g CH}_4\text{-C m}^{-2} \text{ h}^{-1}$) emissions in the 2018 sampling year ranged from -137.75 ± 152.06 to 1232.62 ± 167.68 . Land-use type did not significantly influence mean seasonal CH₄ emissions, except for spring 2018. The UNFA site ($1232.62 \pm 167.68 \mu\text{g CH}_4\text{-C m}^{-2} \text{ h}^{-1}$) was significantly (AGR, $p=0.0001$, GRS, $p=0.0004$; RH, $p=0.0002$; UNFB, $p=0.0008$) higher than the AGR, GRS, RH, and UNFB sites (-120.46 ± 155.95 , -6.20 ± 156.75 , -61.43 ± 152.06 , and $29.06 \pm 191.12 \mu\text{g CH}_4\text{-C m}^{-2} \text{ h}^{-1}$). Season did not significantly influence within land-use mean CH₄ emissions, excluding the UNFA site. Spring 2018 had significantly ($p<0.0001$) higher mean emissions than summer and autumn 2018 (408.23 ± 152.06 and $314.0 \pm 166.13 \mu\text{g CH}_4\text{-C m}^{-2} \text{ h}^{-1}$).

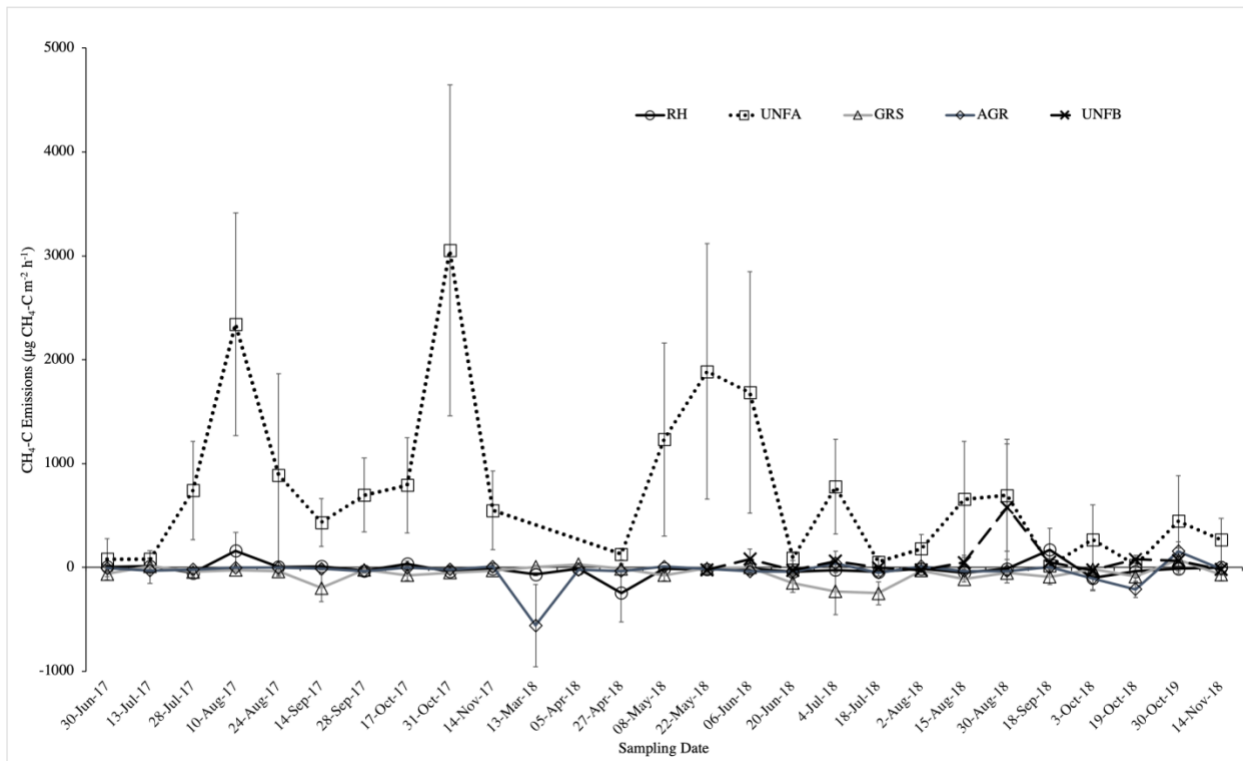


Figure 4.4. Mean soil CH₄ emissions (µg CH₄-C m⁻² h⁻¹) for each sampling date at the agricultural field (AGR), grassed buffer (GRS), rehabilitated forest buffer (RH), undisturbed natural forest A (UNFA), and undisturbed natural forest B (UNFB) found along Washington Creek in southern Ontario, Canada for the full sampling period (June 30th, 2017 to November 14th, 2018).

Table 4.5. Mean seasonal soil CH₄ emissions ($\mu\text{g CH}_4\text{-C m}^{-2} \text{ h}^{-1}$) for the agricultural field (AGR), grassed buffer (GRS), rehabilitated forest buffer (RH), undisturbed natural forest A (UNFA), and undisturbed natural forest B (UNFB) found along Washington Creek, southern Ontario, Canada during 2017-2018.

	Land-Use	2017			2018		
		Spring	Summer	Autumn	Spring	Summer	Autumn
CH₄-C ($\mu\text{g m}^{-2} \text{ h}^{-1}$)	AGR	---	-13.14 (168.34) ^{Aa}	-11.11 (208.5) ^{Aa}	-120.46 (155.95) ^{Aa}	-8.87 (149.41) ^{Aa}	-39.50 (158.05) ^{Aa}
	GRS	---	-59.16 (164.71) ^{Aa}	-44.46 (201.72) ^{Aa}	-6.20 (156.75) ^{Aa}	-137.75 (152.06) ^{Aa}	-38.80 (158.50) ^{Aa}
	RH	---	22.86 (164.71) ^{ABa}	-12.37 (201.72) ^{Aa}	-61.43 (152.06) ^{Aa}	-30.87 (152.06) ^{Aa}	3.28 (158.50) ^{Aa}
	UNFA	---	760.97 (164.71) ^{Ba}	1272.05 (201.72) ^{Ba}	1232.62 (167.68) ^{Ba}	408.23 (152.06) ^{Ab}	314.0 (166.13) ^{Ab}
	UNFB	---	---	---	29.06 (191.12) ^{Aa}	78.26 (150.95) ^{Aa}	33.44 (160.71) ^{Aa}

*Significant differences among land uses within year and season are represented by ^{ABC}. Significant differences among seasons within year and land-use are represented by ^{abc}. A * indicates a significant difference within land-use and within season from 2017 to 2018.

4.3 Correlational Analysis of Greenhouse Gas Emissions and Environmental Characteristics

4.3.1 Land Use Correlations

Spearman rank correlations were used for each land-use type to determine significant relationships between the GHG emissions, and soil and environmental characteristics (Table 4.6). N₂O emissions were significantly positively correlated to air temperature at the GRS ($r_s=0.284$, $p=0.0032$) and RH ($r_s=0.343$, $p=0.0003$) sites. Soil temperature was also significantly positively correlated to N₂O-N emissions at the GRS ($r_s=0.204$, $p=0.0461$) and RH ($r_s=0.299$, $p=0.0033$) sites. At the AGR ($r_s=0.334$, $p=0.0011$) site, NO₃⁻ concentration had a significant positive correlation with N₂O emissions. There was a significantly negative correlation between N₂O-N emissions and SOC at the UNFA ($r_s=-0.517$, $p=0.0487$) site. Finally, N₂O-N emissions were significantly negatively correlated to PPF_D at the RH ($r_s=-0.284$, $p=0.0128$) site.

For CO₂ land-use correlations, air temperature had a significant positive correlation at the AGR ($r_s=0.743$, $p<0.0001$), GRS ($r=0.599$, $p<0.0001$), RH ($r=0.618$, $p<0.0001$), UNFA ($r_s=0.457$, $p<0.0001$), and UNFB ($r_s=0.39$, $p=0.0047$) sites. An identical trend was observed with soil temperature, as it was also significantly positively correlated at the AGR ($r_s=0.630$, $p<0.0001$), GRS ($r_s=0.488$, $p<0.0001$), RH ($r_s=0.503$, $p<0.0001$), UNFA ($r_s=0.397$, $p<0.0001$), and UNFB ($r_s=0.436$, $p=0.0014$) sites. Soil moisture had a significant negative correlation with CO₂ emissions at the AGR ($r_s=-0.286$, $p=0.0066$), GRS ($r_s=-0.478$, $p<0.0001$), and UNFB ($r_s=-0.612$, $p<0.0001$) sites. Additionally, the NO₃⁻ concentration had a significant positive correlation to CO₂-C at the UNFA ($r_s=0.219$, $p=0.0295$) site. SOC was also positively related to CO₂-C emissions at the GRS ($r_s=0.696$, $p=0.0039$) site. Finally, CO₂ emissions were significantly negatively correlated to PPF_D at the RH ($r_s=-0.436$, $p<0.0001$) site.

For CH₄ emissions, air temperature had a positive correlation at the GRS site ($r_s=-0.318$, $p=0.0009$). Soil moisture had a significant positive correlation with CH₄ emissions at the RH ($r_s=0.247$, $p=0.0151$), UNFA ($r_s=0.321$, $p=0.0017$), and UNFB ($r_s=0.552$, $p<0.0001$) sites. Finally, NH₄⁺ concentration was positively correlated to CH₄ at the GRS ($r_s=0.231$, $p=0.0213$) site.

Table 4.6. Spearman product-moment correlation r_s -values for environmental characteristics and greenhouse gas (GHG) emissions for the agricultural field (AGR), grassed buffer (GRS), rehabilitated forest buffer (RH), undisturbed natural forest A (UNFA), and undisturbed natural forest B (UNFB) found along Washington Creek in southern Ontario, Canada during 2017-2018.

Land-Use	GHG	Air Temperature	Soil Temperature	Soil Moisture	NH ₄ ⁺	NO ₃ ⁻	SOC	PPFD
AGR	N ₂ O	0.191	0.097	0.193	0.179	0.334**	0.139	-0.010
	CO ₂	0.743**	0.630**	-0.286**	0.175	0.143	0.382	-0.218
	CH ₄	0.177	0.017	0.096	-0.038	0.056	0.243	0.122
GRS	N ₂ O	0.284**	0.204*	-0.029	0.093	-0.011	0.207	0.206
	CO ₂	0.599**	0.488**	-0.478**	-0.171	-0.083	0.696**	0.173
	CH ₄	-0.318**	-0.187	0.276**	0.231*	0.095	-0.486	-0.155
RH	N ₂ O	0.343**	0.299**	0.074	0.076	0.007	-0.189	-0.284*
	CO ₂	0.618**	0.503**	-0.092	-0.047	0.154	-0.468	-0.436**
	CH ₄	0.002	-0.149	0.247*	0.080	0.019	-0.257	0.045
UNFA	N ₂ O	0.165	0.002	0.113	0.011	0.062	-0.517*	0.139
	CO ₂	0.457**	0.397**	0.003	-0.007	0.219*	-0.096	0.058
	CH ₄	-0.054	-0.167	0.321**	0.191	0.166	-0.379	0.114
UNFB	N ₂ O	-0.048	-0.070	0.092	0.181	0.208	0.251	0.160
	CO ₂	0.39**	0.436**	-0.612**	0.065	0.009	0.143	-0.037
	CH ₄	0.106	-0.023	0.552**	0.213	0.169	-0.096	-0.177

*R-values followed by a * or ** are significant at $p < 0.05$ and $p < 0.01$, respectively.

3.3.2 Annual Correlations of All Variables

Spearman rank correlations were also used on all variables measured to determine if there were significant relationships between soil characteristics or environmental characteristics and GHG emissions (Table 4.7). N₂O emissions were significantly positively correlated with CO₂ ($r_s=0.325$, $p<0.0001$), air temperature ($r_s=0.178$, $p=0.0001$), soil temperature ($r_s=0.184$, $p=0.0001$), NO₃⁻ concentration ($r_s=0.168$, $p=0.0004$), and PPFD ($r_s=0.217$, $p<0.0001$). Additionally, N₂O emissions had a negative correlation with soil moisture ($r_s=-0.150$, $p=0.002$). The CO₂ emissions had a significant positive correlation with air temperature ($r_s=0.532$, $p<0.0001$), soil temperature ($r_s=0.462$, $p<0.0001$), and NO₃⁻ concentration ($r_s=0.183$, $p=0.0001$). There were significant negative correlations between CO₂ emissions and CH₄ emissions ($r_s=-0.113$, $p=0.0152$), as well as soil moisture ($r_s=-0.250$, $p<0.0001$). CH₄ emissions had significant positive correlations with soil moisture ($r_s=0.425$, $p<0.0001$), and NH₄⁺ concentration ($r_s=0.150$, $p=0.0016$). There were significant negative correlations with soil temperature ($r_s=-0.111$, $p=0.0227$) and PPFD ($r_s=-0.182$, $p=0.0009$). Air temperature had a significant positive correlation with soil temperature ($r_s=0.867$, $p<0.0001$). There were significant negative correlations between air temperature and soil moisture ($r_s=-0.196$, $p<0.0001$), NH₄⁺ concentration ($r_s=-0.142$, $p=0.0028$), and PPFD ($r_s=-0.110$, $p=0.0421$). Soil temperature also had significant negative correlations with soil moisture ($r_s=-0.401$, $p<0.0001$), and NH₄⁺ concentration ($r_s=-0.103$, $p=0.0337$). Soil moisture had a significant positive correlation with ammonium concentration ($r_s=0.312$, $p<0.0001$), and a significant negative correlation with PPFD ($r_s=-0.212$, $p=0.0001$). NH₄⁺ concentration had a significant positive correlation with NO₃⁻ concentration ($r_s=0.212$, $p<0.0001$). Finally, NO₃⁻ had a significant positive correlation with

PPFD ($r_s=0.107$, $p=0.0497$), and SOC had a significant negative correlation with PPFD ($r_s=-0.302$, $p=0.0289$).

Table 4.7. Spearman product-moment correlation r_s -values for all measured variables for the agricultural field (AGR), grassed buffer (GRS), rehabilitated forest buffer (RH), undisturbed natural forest A (UNFA), and undisturbed natural forest B (UNFB) found along Washington Creek in southern Ontario, Canada during 2017-2018.

	N₂O	CO₂	CH₄	Air Temperature	Soil Temperature	Soil Moisture	NH₄⁺	NO₃⁻	SOC	PPFD
N₂O	1									
CO₂	0.325**	1								
CH₄	0.008	-0.113*	1							
Air Temperature	0.178**	0.532**	0.017	1						
Soil Temperature	0.184**	0.462**	-0.111*	0.867**	1					
Soil Moisture	-0.150**	-0.250**	0.425**	-0.196**	-0.401**	1				
NH₄⁺	0.049	0.026	0.150**	-0.142**	-0.103**	0.312**	1			
NO₃⁻	0.168**	0.183**	-0.038	-0.017	0.058	0.048	0.212**	1		
SOC	-0.143	-0.068	-0.048	0.221	0.160	0.101	-0.115	-0.011	1	
PPFD	0.217**	0.106	-0.182**	-0.110*	-0.083	-0.212**	0.035	0.107*	-0.302*	1

*R-values followed by a * or ** are significant at $p < 0.05$ and $p < 0.01$, respectively.

4.3.3 Regression Analysis of Greenhouse Gas Emissions, and Soil and Environmental Predictors

A stepwise regression analysis was run on linear models for each GHG with varying combinations of soil and environmental predictors to determine the best model (Table 4.8). Models were selected based on the lowest Akaike Information Criteria (AIC) and Bayesian Information Criteria (BIC). Due to the AIC and BIC preferentially selecting more complicated models, models that contained all measured predictors were not selected despite having the lowest AIC and BIC. For N₂O emissions, the best model to estimate emissions contained the predictors soil temperature, NO₃⁻ concentration, and SOC (AIC, 648.7461; BIC, 434.3878). The best individual predictor was NO₃⁻ concentration (AIC, 4402.832; BIC, 3155.207). The best model to predict CO₂ emissions contained soil temperature and SOC (AIC, 749.8156; BIC, 973.2984). The best individual predictor was air temperature (AIC, 4737.827; BIC, 6071.787). For CH₄ emissions, the best model contained the predictors soil moisture, NO₃⁻ concentration, SOC, and PPFD (AIC, 877.5101; BIC, 722.9009). The most influential individual predictor on CH₄ emissions was soil moisture (AIC, 6713.298; BIC, 5515.65).

Table 4.8. Stepwise regression analysis on linear models for each greenhouse gas (GHG) using combinations of air temperature (Air temp.), soil temperature (Soil temp.), soil moisture (MC), ammonium (NH₄⁺), nitrate (NO₃⁻), soil organic carbon (SOC) and photosynthetic photon flux density (PPFD) to determine the best model based on the R², adjusted R², Akaike Information Criteria (AIC) and Bayesian Information Criteria (BIC).

GHG	Model Predictors	R ²	Adjusted R ²	AIC	BIC
N₂O	NO ₃ ⁻	0.0291	0.0268	4402.832	3155.207
	Soil temp., SOC	0.0695	0.0437	649.0862	434.9205
	Soil temp., NO₃⁻, SOC	0.0981	0.06	648.7461	434.3878
	Soil temp., MC, NO ₃ ⁻ , SOC	0.1066	0.0556	650.0323	435.395
	Air temp., Soil temp., MC, NO ₃ ⁻ , SOC	0.1101	0.0456	651.7404	436.7968
	Air temp., Soil temp., MC, NO ₃ ⁻ , NH ₄ ⁺ , SOC	0.1108	0.0323	653.6822	438.4072
CO₂	Air temp.	0.1408	0.139	4737.827	6071.787
	Soil temp., SOC	0.2176	0.1958	749.8156	973.2984
	Soil temp., NO ₃ ⁻ , SOC	0.2375	0.2053	749.6354	975.6815
	Soil temp., MC, NO ₃ ⁻ , SOC	0.2462	0.2031	750.4856	979.1345
	Soil temp., MC, NO ₃ ⁻ , NH ₄ ⁺ , SOC	0.2519	0.1977	751.6256	982.8796
	Air temp., Soil temp., MC, NO ₃ ⁻ , NH ₄ ⁺ , SOC	0.2521	0.1861	753.2574	987.1809
CH₄	MC,	0.1524	0.1504	6713.298	5515.65
	MC, SOC	0.1962	0.1739	1179.662	968.4011
	MC, NO ₃ ⁻ , SOC	0.202	0.1683	1181.121	970.5065
	MC, NO₃⁻, SOC, PPF	0.2059	0.1424	877.5101	722.9009
	Air temp., MC, NO ₃ ⁻ , SOC, PPF	0.217	0.1371	878.7365	724.6168
	Air temp., MC, NO ₃ ⁻ , NH ₄ ⁺ , SOC, PPF	0.2182	0.1205	880.6493	726.8909

*Lines in **bold** represent the combination of variables that best predicted the GHG

5. Discussion

5.1 Soil and Environmental Characteristics

5.1.1 Soil Temperature, Moisture Content, and PPF

Over the entire sampling period, the AGR and GRS sites had consistently higher mean soil temperatures than all the other land use types. This was expected as a larger proportion of the soil is exposed to direct sunlight due to the lack of tree cover (Jurik and Van 2004; Teasdale and Mohler 1993), which was reflected in the greater PPF observed at these sites. Additionally, under forest canopies there is increased shading and evaporative cooling (Correll 2005). The increased shading was also reflected in the PPF for each of the forested sites. This relationship is explained further by the significant ($p < 0.05$) negative correlation observed between air temperature and PPF (Table 4.7). The GRS site having higher soil temperature than the RH and UNFA sites were consistent with Oelbermann and Raimbault (2015), who used the same study sites in 2010. Soil temperature for all land-use types increased in the 2018 sampling year, which was expected as the summer and autumn were much warmer than the previous year and corresponded to the significant ($p < 0.01$) positive correlation found between air and soil temperature. However, this was somewhat unexpected in the AGR site as the crop changed from corn in 2017 to soybean in 2018, and the average PPF quantified dropped considerably during the peak growing season from 2017 to 2018. Jurik and Van (2004) also observed this pattern, and found that soybean significantly limited the amount of light reaching the soil surface and improved microclimate. Additionally, Thapa et al. (2016) found that row-planting corn significantly increased canopy temperature, which could explain why the AGR site in 2017 had significantly higher soil temperature than the RH and UNFA sites, but this significance was not

observed in 2018 under a soybean crop. The RH site had higher soil temperatures than the UNFA site, which was consistent with De Carlo et al. (2019), who observed the same sites in 2016. This was due to differences in stand age among sites, as Schwendenmann (2000) also found this pattern in 25-year-old and 125-year-old riparian boreal forest communities. Further, the differences in canopy cover and understory vegetation may have also contributed to variation among forested sites (Polglase et al. 2003). Rambo and North (2009) found that a taller canopy, which is characteristic of the UNFA site, is associated with a cooler understory.

There was decreased light penetration at both the UNFA and UNFB sites, but Ritter et al. (2005) found that the rapid succession in new forests keeps soil temperatures similar to that of a mature natural forest. This explains why the soil temperatures were still very similar at the RH and UNFA/B sites. The UNFA site was characteristic of waterlogged soils, and coupled with slow decomposition of organic matter also led to lower soil temperatures (Rayment and Jarvis 2000). Oelbermann and Raimbault (2015) found that there was increased litterfall and soil organic matter (SOM) at the UNFA site compared to the RH site, and along with the saturated conditions at the UNFA site, this would explain the lower soil temperatures. The lack of waterlogged conditions at the RH and UNFB sites also explains why they have consistently higher soil temperatures than the UNFA site, as they had similar soil moisture contents despite differences in SOM. All land-uses experienced significantly higher soil temperatures in the summer compared to both spring and fall. James et al. (2003) observed this same trend between a riparian grassland, shrubland and forest in Saskatchewan, Canada. This is likely due to the higher ambient air temperatures, as well as increased PPFD (Smith et al. 2003; Jurik and Van 2004).

The UNFA site had significantly higher soil moisture than all other sites throughout the majority of the entire sampling period, with near or at saturated conditions. This was consistent

with both Oelbermann and Raimbault (2015) and De Carlo et al. (2019), who observed this trend at the UNFA site in 2010 and 2016, respectively. The UNFA was observed to have a higher water table creating saturated conditions, which is typical of riparian forests (Audet et al. 2014). Higher water tables likely also explains the wet conditions at the RH and UNFB sites, as they are also riparian forests. Schwendenmann (2000) also found that a mature riparian boreal forest had a higher soil moisture than a newly established forests after clear-cutting. However, the UNFB site is also considered a mature forest, and exhibited similar soil moisture contents to the RH site. There were higher amounts of SOC observed at the UNFA and UNFB sites, which explains the higher soil moisture as well (Schwendenmann 2000; De Carlo et al. 2019).

The RH site and GRS site had similar soil moistures, which was consistent with the results found in Oelbermann and Raimbault (2015). Although not significant, the RH site had consistently higher soil moisture than the GRS site in all seasons excluding the fall. This is contrary to the results of James et al. (2003), who found that a grassland had higher soil moisture (depth of 10-cm) than a riparian forest in the spring and fall. All sites experienced their lowest soil moistures in the summer months, and is likely a result of the negative relationship between air and soil temperature and soil moisture in temperate climates, as seen from the annual correlations (Table 4.7) (Smith et al. 2003; Redding et al. 2011). This describes why there were lower soil moisture contents for all sites in 2018 than 2017, when average daily ambient temperatures were higher. Additionally, riparian areas are characteristic of frequent flood events, with them most frequently occurring in the spring and autumn (Jacinthe 2015). This also explains why soil moisture contents were higher for all land-uses during the spring of 2018, when there was a significant flood event within the Grand River watershed.

4.1.2 Inorganic Nitrogen

There was very little variation in NH_4^+ concentration among land-use types, with no clear trend throughout the entire sampling period (Table 4.2). The only significant difference occurred in the fall of 2017, where the UNFA site has significantly higher than all other land use types observed. This observation was consistent with Oelbermann and Raimbault (2015) and De Carlo et al. (2019), who worked at the same site in 2010 and 2016, respectively. Lake et al. (2013) and Adair et al. (2004) found that older riparian forests contained higher amounts of inorganic nitrogen than younger forests, which explains why the UNFA site was significantly higher than the RH site. Hefting et al. (2003) found higher amounts of NH_4^+ in the topsoil in European riparian forests where the water table was high. The waterlogged conditions of the soil at the UNFA site likely caused the NH_4^+ to be higher than the other land uses during fall 2017. This relationship is also reflected in the significant positive correlation seen between NH_4^+ and soil moisture in this study (Figure 4.7). Araya et al. (2013) found that in riparian grasslands, increases in water-filled pore space facilitated higher availability of plant available nitrogen. This explains the drop in average seasonal NH_4^+ in the summer of 2018, as soil moisture decreased within all land-use types.

There was a negative correlation between NH_4^+ and air and soil temperature, suggesting that the drop in NH_4^+ in the summer months when the high air temperatures reduced soil moisture (Smith et al. 2003; Redding et al. 2011). There was little variation between the summer and autumn, but in spring 2018 there was a significantly higher concentration of NH_4^+ in all land-use types. Owen et al. (2003) found that the lowest NH_4^+ concentrations were in the summer, with a significant drop from the spring, which is consistent with what is seen at all land-use types. This high concentration in the spring is likely due to the soil freeze-thaw cycles

prevalent during this time, which have been proven to increase ammonification and nitrification, and a result of significant build-up of inorganic N during the winter months (Urakawa et al. 2014). Ye et al. (2015) also observed this trend in a riparian forest and grassland. However, Ye et al. (2015) attributed the pattern to increased plant uptake of N and N leaching, as well as altered microbial activity in the presence of lower moisture regimes.

Soil NO_3^- was considerably higher compared to NH_4^+ in all land-use types, which is typical of riparian zones and agricultural fields (Hefting et al. 2003; Drury et al. 2008). The highest concentration of NO_3^- was seen in the summer of 2017 at the AGR site, and was significantly higher than all other land use types. This is likely due to the fertilization treatments involved in producing corn, as it was considerably higher than the following year when soybean was grown. Drury et al. (2008) also observed this trend when comparing corn, soybean, and winter wheat monocultures, and saw the highest NO_3^- under the corn rotation, which decreased significantly once the corn reached maturity. The RH site had similar NO_3^- concentrations to the other land use types (excluding AGR), despite being characteristic of receiving high amounts of available N from the adjacent AGR site (Table 4.2). However, these results are contrary to what was found in Oelbermann and Raimbault (2015) and De Carlo et al. (2019), as they observed that the RH site had lower NO_3^- than both the UNFA and GRS sites. Typically, the older the forest age the higher the available N (Adair et al. 2004).

However, Soosaar et al. (2011) observed that the buffering capacity of riparian zones diminishes over time, which could explain the discrepancies between the RH and the UNFA/B sites. Adair et al. (2004) also observed some instances when a younger riparian forest had higher available N when compared to a mature riparian forest, which they attributed to the lack of scouring floods and a high water table that supported continual plant and microbial growth

throughout the growing season. Gift et al. (2010) observed restored riparian forests compared to natural forests in an urban setting, and found that the restored forests had higher NO_3^- than the natural forests. Higher NO_3^- at the RH site may also be due to NO_3^- -contaminated groundwater originating from the adjacent AGR site, which is drawn up by capillary action (Audet et al. 2014). This is more likely in areas where the water table is near the soil surface. Surface runoff from the neighbouring AGR site likely contributed to NO_3^- concentrations at the RH site (Kim et al., 2009), but the moderate concentrations are likely a result of the tile drainage present at the AGR site allowing the NO_3^- to bypass the buffer through subsurface flows (Jaynes and Isenhardt, 2014). The location of the study plots at the UNFA and UNFB were over 50 m away from the neighbouring agricultural field, so it is likely that surface runoff and leaching were not impact NO_3^- concentration at these sites.

The GRS site had consistently (excluding the summer of 2017) the highest soil NO_3^- concentrations throughout the entire sampling period. This was contrary to what was found by Hefting et al. (2003), who saw higher levels of NO_3^- in a forested riparian buffer compared to a grassland buffer. They attributed this to dilution of N-rich groundwater by deeper seepage water, but at the GRS site the soil surface is far above the water table. The high NO_3^- within the GRS site likely can be attributed to the density of grasses resulting in high amounts of input from dead plant matter and dead roots (Kim et al. 2009). Tufekcioglu et al. (2003) also saw high amounts of N in a grassed buffer compared to an agricultural land and a forested buffer. This was due to the high concentration of roots near the soil surface, increasing susceptibility to desiccation and subsequent decomposition. This could explain why the GRS site had high NO_3^- , as it has visually observed from taking soil samples that there was a high density of roots within the first 10-cm of soil. Additionally, there can be a high turnover of roots in the first 0-10 cm of soil in grasslands

after rainfall events, where there is substantial root growth followed by significant die-off once the soil dries out (Hayes and Seastedt 2008).

The NO_3^- levels at all land use types showed very little seasonal variation, excluding the AGR site in 2017, and in the fall of 2018. As previously discussed, the high level of NO_3^- in the summer of 2017 was attributed to the fertilization treatment under the corn rotation (Drury et al. 2008). The lack of overall seasonal variation is consistent with Vidon and Hill (2004), who found no effect of season on NO_3^- concentration or filtration in seven different riparian buffers located in southern Ontario. This is somewhat reflected in the overall correlations, as NO_3^- was not significantly correlated to air temperature, soil temperature, and soil moisture, which vary the most seasonally (Smith et al. 2003). In the fall of 2018, there was a significant drop in NO_3^- at all land-use types. This is expected as there is evidence for increased plant uptake of nitrate in the fall months for all land-use types observed (Dhondt et al. 2004; Drury et al. 2008; Pinay et al. 2006).

4.1.3 Soil Organic Carbon

The highest soil organic carbon concentration was observed at the undisturbed natural forests (UNFA and UNFB). This is consistent to what was seen in De Carlo et al. (2019) and Oelberman and Raimbault (2015), who observed the same sites and observed that the UNFA site contained at least double the concentration of SOC than the RH site. Both studies saw similar concentrations of SOC at the RH site to this study, but observed $\sim 20 \text{ g kg}^{-1}$ higher SOC at the UNFA site than in this study. These differences are likely a result of the spatial heterogeneity of SOC in forest soils (Hale et al. 2013), as well as the heterogeneity in sample collection compared to De Carlo et al. (2019) and Oelbermann and Raimbault (2015). The high SOC at the UNFA

and UNFB sites in this study are likely a result of stand age (De Carlo et al. 2019; Oelbermann and Raimbault 2015; Corre et al. 1999). Corre et al. (1999) looked at riparian forest stands of differing age and found that forests greater than 60 years had higher SOC than those under 30 years. Further, Bush (2008) observed riparian forests that used to be under agriculture of differing ages, and also found in naturally succeeding riparian forests the older stands had increased SOC. Hale et al. (2013) also observed riparian forests and found differences in SOC between sites was a result of differing nutrient inputs, rates of nutrient cycling, and differing patterns of vegetation.

The GRS site had a similar SOC to that of the RH site. This is also contrary to the results of Oelbermann and Raimbault (2015), who saw that a grassed buffer also located on Washington Creek had double the SOC than the same RH site observed in this study, and was more similar to that of the UNFA site. Oelbermann and Raimbault (2015) attribute this difference to higher biomass inputs in the grassed buffer. However, Tufekcioglu et al. (2001) suggest that lower SOC in a grassed buffer, despite high availability of soil organic matter, is a result of poor substrate quality and therefore decreased C cycling (i.e. slower decomposition). However, a more likely reason for the differences in SOC between the grassed buffer in Oelbermann and Raimbault (2015) and GRS site in this study is a result of the former being used by livestock only 5 years prior of the study before being fenced off. The manure from the livestock in this area would have contributed greater input of organic matter, increasing SOC at the grassed buffer in Oelbermann and Raimbault (2015) (Maillard and Angers 2014). Bush (2008) also found that the addition of woody vegetation to a riparian grassland increased SOC by altering the soil physical and chemical properties, and that adjacent woody areas had higher SOC than adjacent herbaceous areas. However, this increase in SOC in the woody areas was not significantly different, as was

seen in this study. Corre et al. (1999) also observed the SOC from riparian forests and cool-season grass buffers, and also found no significant difference between the two types of vegetation.

The lowest SOC was seen at the AGR site, which was expected. The field is managed under conventional practices, and therefore a significant amount of SOC is likely lost to rapid turnover after the soil is disturbed, and there are little additions of C to the soil due to the removal of crop residues (West and Marland 2002; Tufekcioglu et al. 2001).

4.2 Greenhouse Gas Emissions

4.2.1 Nitrous Oxide

The highest N₂O emissions were observed at the AGR site, and were considerably higher in 2017 compared to 2018 (Table 4.3). This annual change is likely due to corn being planted in the first sampling year, and soybean in the second. Drury et al. (2008) saw significantly higher N₂O emissions under a corn rotation compared to soybean and winter wheat rotations in southern Ontario (Drury et al., 2008). Furthermore, emissions were approximately 2.8 times higher under corn than the soybean rotation (Drury et al., 2008). They attributed this difference to the fertilization of the corn field, particularly in conjunction with rainfall events, which is why their peak emissions were seen in early June (Drury et al., 2008). This is consistent with this study, as the seasonal N₂O emissions during the corn year (when soil NO₃⁻ was highest) were approximately 2-3 times higher than the in the soybean year. This was consistent with the land-use correlations and model, at NO₃⁻ significantly (p<0.01) positively correlated the N₂O emissions (Table 4.7), and was the single biggest predictor of N₂O emissions (Table 4.8), likely fueling denitrification at the AGR site. Ozlu and Kumar (2018) also evaluated N₂O emissions

from corn and soybean monocultures on a temporal scale, and found that N fertilizer and manure were the predominant factor influencing emissions in an agricultural setting. Additionally, when inorganic N is not limiting, there has been recorded exponential relationships between N₂O and temperature and water-filled pore-space (WFPS) (Smith et al. 2003).

Kim et al. (2009) found that agricultural fields were significantly more susceptible to freeze-thaw cycles than riparian buffers, and saw a 70-fold increase in emissions in the spring months. However, this was not observed in this study, and there was no seasonal change between the spring and summer months. This may be due to the change in type of crop produced in 2018, as the spring season was not captured in 2017 when corn was planted, and Kim et al. (2009) observed this trend under a corn monoculture. Davis et al. (2019) also observed this result when comparing a corn crop to saturated and unsaturated riparian buffers. Further, there were higher temperatures recorded in the AGR site in 2018, when there was considerably lower soil moisture. This may have also attributed to the N₂O emissions, but due to the high emissions in the summer of 2017 and lack of correlation to soil temperature at the AGR site, N fertilizer is likely the most important influencing factor.

The RH site was expected to have high N₂O emissions due to nutrient loading from the adjacent AGR site, but this was not the case. This is consistent with what was observed in De Carlo et al. (2019), who worked at the same site in 2016. Hefting (2003) observed considerably higher N₂O emissions in a forested riparian buffer compared to a grassed buffer, but the forested buffer they observed had received substantial amounts of N-rich runoff. As previously discussed, the RH site did not have higher NO₃⁻ levels than the other buffer sites, which is likely limiting N₂O emissions. Audet et al. (2014) found similar results to this study when looking at riparian wetlands located in agriculturally-dominated catchments, with frequently negative emissions

within the buffers (i.e. N₂O uptake). Audet et al. (2014) had difficulty determining why emissions were low, considering they saw high amount of nitrate-contaminated groundwater within the buffer, and the only positive correlation was with groundwater ammonium concentration. Audet et al. (2014) suggested that when the buffers were relatively undisturbed, the conditions are right for complete denitrification, therefore limiting N₂O emissions. Further, the soil within the RH site was not wet enough to create a favourable environment for N₂O emissions, as Schaufler et al. (2010) estimates highest emissions occur at 50-60% WFPS. Jacinthe et al. (2012) also observed no relationship between nitrate removal and N₂O emissions in both grassed and forested riparian buffers. They also suggested a link between flood events and higher N₂O emissions, but this was not seen in this study after the significant flood event in the spring of 2018 (Jacinthe et al., 2012). Kim et al. (2009) observed the N₂O emissions from a cool-season grassed buffer, a forested buffer, and an agriculture (corn) field in central Iowa, and found that the emissions from the agricultural field were significantly higher than from the buffers. However, the buffers in their study received far more inorganic N inputs, so the magnitude of their emissions is far greater than in this study. Though Kim et al. (2009) mention that on a watershed scale, the emissions from the riparian buffers studied are negligible in comparison to agricultural lands. Kim et al. (2009) also found a significant correlation between soil temperature and moisture and N₂O emissions for all sites, with the biggest impact on the agricultural field. The microclimate controls of the riparian buffer may also be limiting N₂O emissions by keeping the soil cooler, as it has been found the optimal temperature for N₂O production is 20°C (Muñoz-Leoz et al. 2011; Kim et al. 2009; Smith et al. 2003).

This relationship is seen further in the land-use correlations, as air and soil temperature were significantly ($p < 0.01$) positively correlated to N₂O emissions, indicating that when

temperature rose in the RH site, N₂O emissions subsequently rose as well (Table 4.6). Soil temperature was also a variable that best predicted N₂O emissions (Table 4.8). Dhondt et al. (2004) found that riparian buffers in Belgium had higher N₂O emissions than this study, but they were still modest in comparison to Hefting et al. (2003). This suggested that higher nitrate loading into the buffer may have led to higher N₂O emissions in Hefting et al. (2003) (Muñoz-Leoz et al. 2011; Dhondt et al. 2004; Audet et al. 2014; Hefting et al. 2003). Dhondt et al. (2004) also recorded little seasonal variation, which is consistent with this study. Audet et al. (2013) evaluated riparian wetlands and when undisturbed observed similar emissions compared to this study. They observed a correlation between SOC stock and N₂O emissions, but this was not observed in this study at the RH site. However, SOC was included in the model that best predicted N₂O emissions (Table 4.8), indicating it may still be influencing emissions. Audet et al. (2013) also saw that denitrification was the main pathway for N₂O release from the wetlands. It is possible that N₂O release via denitrification has been overestimated for riparian buffers (Audet et al. 2013; Jacinthe et al. 2012). Overall, the most likely reason for the modest N₂O emissions in the RH site are due to the lack of significant NO₃⁻ loading.

The low N₂O emissions at the UNFA and UNFB site was consistent with Jacinthe et al. (2012) who compared emissions at young and mature forest buffers, and saw no significant differences despite the common notion that older forest have higher N₂O emissions. Jacinthe et al. (2012) also saw a weak link between seasonal variation and N₂O emissions, suggesting that the forest annual growth cycle has little impact on N₂O emissions. Further, Davis et al. (2019) found that saturated forested riparian buffers had similar N₂O emissions of that of unsaturated buffers, despite the belief that more moisture could enhance N₂O emissions (Schaufler et al. 2010; Eickenscheidt et al. 2014). Eickenscheidt et al. (2014) also found that saturated soil

conditions had no real impact on N₂O emissions despite NO₃⁻ availability, and this was likely because the high water content led to complete denitrification (i.e. release of N₂ gas) and limited nitrification reducing NO₃⁻ availability. This is consistent with Hopfensperger et al. (2009), who found that in saturated riparian forest soils that nitrification leading to N₂O release was limited, and that the high soil moisture may have limited full N₂O reduction. As NO₃⁻ was typically low in the forested sites with persistent wet conditions, this likely led to the modest N₂O emissions in the UNFA and UNFB sites.

There were very little differences seen between the RH and the GRS sites in N₂O emissions. This is consistent with the current literature, for Jacinthe et al. (2012) also observed no real effect of grassed or woody vegetation on N₂O emissions in riparian buffers. Jacinthe et al. (2012) suggested that the soil conditions (i.e. soil moisture and temperature) have greater influence on emissions than the vegetative community in buffers, and the soil conditions were very similar at the GRS and RH sites. As previously mentioned, soil temperature heavily influences N₂O emissions (Muñoz-Leoz et al. 2011; Kim et al. 2009). Given the similar soil temperatures at the RH and GRS sites, this was likely a factor limiting N₂O emissions from the GRS site. This relationship is also reflected in the land-use correlations, as air and soil temperature were significantly positively correlated to N₂O emissions at the GRS site as well. Kim et al. (2009) also observed so significant differences in N₂O emissions between grassed and forested riparian buffers, again suggesting that this is not a significant influencing factor. The moderate N₂O emissions at the GRS site are most likely a result of soil moisture being too low to create favourable conditions for denitrification and subsequent N₂O release (Schaufler et al. 2010; Jacinthe et al. 2012).

4.2.2 Carbon Dioxide

The GRS site had consistently and often significantly higher CO₂ emissions than all the other land use types (Table 4.4). This is very consistent with the current literature (Shrestha et al. 2009; Bailey et al. 2009; Schaufler et al. 2010; Gritsch et al. 2015; Oelbermann and Raimbault 2015). Bailey et al. (2009) looked at an agricultural field (corn-soybean rotation), an agroforestry buffer and a grassed buffer, and found that regardless of soil moisture or N content the grassed buffer had the highest CO₂ emissions. The range of emissions seen in this study at the GRS site (0.18 to 15.01 g CO₂-C m⁻² day⁻¹) were quite similar to what was observed by Bailey et al. (2009) (1.78 to 17.58 CO₂-C m⁻² day⁻¹). There is a strong positive correlation between soil temperature and soil moisture, and CO₂ emissions, as was seen in this study at the GRS site (Table 4.7) (Bailey et al. 2009; Gritsch et al. 2015; Smith et al. 2003). These factors significantly controlled CO₂ emissions in Bailey et al. (2009), as well as in Shrestha et al. (2009) who observed GHG emissions from forest, grassland, pasture and agricultural soils. Shrestha et al. (2009) saw their highest emissions from the grassland and agricultural soils, and attributed this to soil temperature and root respiration. Root respiration is most likely why the CO₂ emissions were so high at the GRS site due to the dense root mat, continual input of biomass by plants and roots, and high microbial decomposition (Shrestha et al. 2009; Bailey et al. 2009; Smith et al. 2003; Schaufler et al. 2010). This relationship is seen in the strong (p<0.01) positive correlation to SOC at the GRS site. Further, Schaufler et al. (2010) found that microbial activity leading to CO₂ emissions was stimulated in grassland soils due to the high inputs of C and N from plant biomass, leading to rapid turnover. Both soil temperature and SOC were the components of the model that best predicted CO₂ emissions. Therefore, the high soil temperatures and sustained soil moisture, coupled with high availability of plant matter, likely allowed for high microbial

turnover and subsequently higher CO₂ emissions at the GRS site, as seen in Schaufler et al. (2010).

Although riparian buffers are considered to be a potential hot spot of GHG emissions, this trend was not seen at the RH site in this study for CO₂ emissions. There was no clear trend, as the RH site alternated from having the lowest seasonal CO₂ emissions to the second highest next to the GRS site, particularly in the summer seasons. There has been frequent comparisons of emissions from riparian buffers and adjacent agricultural fields in the literature, such as the work by Jacinthe et al. (2015). Jacinthe et al. (2015) saw significantly higher CO₂ emissions in the riparian buffer compared to the agricultural field, and attributed this to higher quantity and quality of C inputs and regulation of soil temperature. The emissions were similar at the RH and AGR sites, but higher CO₂ emissions seen at the RH site may be the combination of soil microclimate regulation (lower temperatures maintaining soil moisture) and C inputs (Table 4.4). Tufekcioglu et al. (2001) also compared grassed and forested buffers to agricultural fields, and also found higher CO₂ emissions in the buffers than in the agricultural field. Tufekcioglu et al. (2001) attributed these differences to higher soil respiration in the buffers, and soil temperature and moisture strongly controlled seasonal variation. Bailey et al. (2009) also compared GHG emissions from an agroforestry buffer in relation to an agricultural field (corn), and found significantly higher emissions from the agroforestry buffer. They considered the optimum level of WFPS for CO₂ emissions at 60-80% (consistent with Gritsch et al. 2015; Schjøning et al. 2014). This is likely the reason for the modest emissions at the RH site, and explains the low emissions experienced at the AGR site. Soosaar et al. (2011) observed two alder-dominated riparian forests of different age classes and moisture regimes. Their study found lower average flux in CO₂ emissions (42 and 45 g CO₂-C m⁻² hr⁻¹) than in this study (131.27 g CO₂-C m⁻² hr⁻¹)

(Soosaar et al. 2011). Soosaar et al. (2011) also found a significant positive correlation between air temperature and lower water table depth with CO₂ flux. A similar correlation was seen in this study at the RH site, as air and soil temperature significantly positively correlated to CO₂ emissions, and soil moisture was negatively correlated. Therefore, lower soil temperatures at the RH site (particularly in relation to the GRS and AGR sites) likely limited CO₂ emissions, despite high soil C availability and consistent soil moisture content. This explains the higher flux in emissions in the summer months, when soil temperatures were at their highest for the RH site, as well as the drop in CO₂ emissions for all sites in the fall.

The UNFA and UNFB sites had frequently low to moderate CO₂ emissions in comparison to the other land-use types, and were usually similar to or slightly below the RH site. This is somewhat unexpected, due to the high SOC at both sites, particularly in contrast to the other land-use types. Vidon et al. (2015) found similar results, as they saw no significant differences between a mature buffer and a restored buffer. Slightly higher organic carbon at the mature site resulted in slightly higher CO₂ emissions, but again this difference was not statistically significant. This may indicate that the SOC found in the mature forested sites is more recalcitrant, leading to more sequestered C, as mature forests often have more stable forms of C in the soil (Chen and Shrestha 2012). Hopfensperger et al. (2009) also evaluated riparian wetland forests to measure their GHG potential, and saw similar average CO₂ emissions (0.01 to 0.10 g CO₂-C m⁻² hr⁻¹) as seen in this study (0.02 to 0.22 g CO₂-C m⁻² hr⁻¹). Hopfensperger et al. (2009) reported a positive correlation between understory plant cover and CO₂ emissions, leading to enhanced root and microbial activity in the soil. This likely explains why the RH site was slightly higher than the UNFA and UNFB sites, as the RH site has a denser understory community (De Carlo et al., 2019). The type of C in the soil may also have caused the slightly

higher emissions at the RH site, as younger forest often contain C that is more labile (Chen and Shrestha 2012).

Bailey et al. (2009) compared mature riparian forest to young riparian forest, and saw that in the young forest there higher temperatures that could lead to increased soil respiration. They also noted that the grassed and young forested buffer received more nutrients to fuel biological activity. However, the most likely cause of the modest CO₂ emissions from the UNFA/B sites are due to low soil temperatures experienced at both sites due to dense canopy cover, as well as the high soil moisture at the UNFA site limiting root and heterotrophic respiration due to lack of oxygenated soil (Gritsch et al. 2015; Hopfensperger et al. 2009; Smith et al. 2003; Bailey et al. 2009; Mander et al. 2015). This relationship was clear from the land-use correlations, where air and soil temperature were significantly positively correlated to CO₂ emissions at both the UNFA and UNFB sites, and was negatively correlated to soil moisture at the UNFB site.

The AGR site also did not have a clear trend in CO₂ emissions, and was frequently similar to that of the forested sites. There were no differences in emissions from the 2017 sampling year to the 2018 sampling year, when the crop changed from corn to soybean. This was consistent with Tufekcioglu et al. (2001) found no differences in CO₂ emissions under corn compared to soybean, as seen in this study. Additionally, Tufekcioglu et al. (2001) found that low C inputs, high soil temperature and low soil moisture were limiting CO₂ emissions in agricultural fields. Amadi et al. (2016) also found that low C inputs in agricultural fields limits CO₂ production, specifically in comparison to agroforestry shelterbelts (including riparian buffers). This was consistent with this study, as the AGR site had the lowest SOC compared to the other land use types.

Further, Jacinthe et al. (2015) found that higher soil temperatures in an agricultural field limited soil moisture, and there reduced microbial activity resulting in CO₂ emissions. This is consistent with Gritsch et al. (2015), that found that the moisture sensitivity of CO₂ emissions increased with increasing temperature, meaning moisture became a more important predictor as temperatures rose. Although this study saw significant positive correlation between CO₂ emissions and soil temperature at the AGR site, there was a significant negative correlation with soil moisture, suggesting if the soil moisture was too high (i.e. oversaturated) at the AGR site (such as in the spring), it could limit CO₂-producing microbial communities. However, the higher temperatures, lower soil moisture and limited C availability at the AGR site likely kept the CO₂ emissions low compared to the other land use types.

4.2.3 Methane

Negative CH₄ emissions represented that the land-use was acting as a sink for CH₄. The only land-use that consistently acted as a source of CH₄ was the UNFA site, while all other sites typically acted as a sink (Table 4.5). The high soil moisture created an anaerobic environment suitable for methanogenesis, which drove the emissions at the UNFA site (Aronson et al. 2012). Aronson et al. (2012) observed two riparian pine forests, one upland well-drained forest and one lowland poorly-drained forest. Aronson et al. (2012) also found that the poorly-drained site had higher CH₄ emissions and this was driven by the long-term drainage differences, noting that soil moisture had the strongest correlation with CH₄ emissions, as seen at most land-uses in this study (Table 4.6). However, Aronson et al. (2012) did note that the higher emissions were strongly influenced by the N by relieving that N limitation for the methanotrops, and this created a mosaic

pattern of emissions in the lowland site. This was consistent with this study, as NO_3^- concentration was included in the model that best predicted CH_4 emissions (Table 4.8).

Sun et al. (2013) also looked at CH_4 emissions from a northern marsh in China, and saw that plant community also contributed significantly to spatial variation in emissions. This would explain why the UNFB site, despite higher moisture than the RH, GRS, and AGR sites, did not have as high CH_4 emissions as the UNFA site. The UNFB site was predominantly Eastern white cedar, while the UNFA site was predominantly deciduous species and Eastern skunk cabbage,; and high levels of deciduous litterfall has been linked with decreased oxygenation of the soil contributing to CH_4 release (Smith et al. 2003). Macdonald et al. (1998) found that temperature had significant influence on CH_4 emissions on northern Scottish wetlands, and as temperature increased the CH_4 release rose exponentially. Temperature was likely not the most influencing factor in this study, as all forested sites had similar soil temperatures, but only the UNFA acted as a CH_4 source. There were also no correlations to air or soil temperature at any of the sites (excluding the GRS), and temperature was not included in the model that best predicted CH_4 emissions. Hopfensperger et al. (2009) did not observe a correlation between soil moisture and CH_4 emissions, but did acknowledge that water table depth influences the redox potential that could increase CH_4 release. This was contrary to what was seen in this study, as soil moisture was significantly positively correlated to CH_4 emissions at all sites except the AGR site. Water table depth was not measured in this study, but from visual examination the water table was likely high as water was being drawn up into the GHG chambers. This also explains the high emissions seen in the UNFA site, and also explain the lower magnitude of emissions from the UNFB site.

As previously mentioned, the AGR, GRS, and RH sites predominantly acted as a CH₄ sinks throughout the sampling period. However, the RH site did act intermittently as a source. This was somewhat expected, as the soil moisture was maintained at a moderate level (22.55 to 55.6% soil volume) for the majority of the sampling season, but there were never prolonged instances of complete soil saturation. Teiter and Mander (2005) looked at a riparian alder forest and a constructed wetland in northeastern Estonia, and found that the riparian alder forest consistently acted as a CH₄ source with average hourly emissions ranging from 14 to 144 $\mu\text{g m}^{-2} \text{hr}^{-1}$, which is much lower than what was observed in this study. However, the riparian forest contained wet, dry and edge microsites, and the wet sites were the only areas contributing to the high CH₄ emissions. Mander et al. (2015) found no effect of age on CH₄ emissions from riparian alder forests, and noted that the most influencing factor was water table depth. Further, Audet et al. (2013) observed restored riparian wetlands compared to natural wetlands, and found that there were high emissions of CH₄ from the restored wetlands. However, this occurred in the first few months after restoration after a major soil disturbance, as well as prolonged flooding, which was likely what led to higher emissions. Jacinthe (2015) evaluated the effect of flooding on young riparian forests in Indiana, USA and found that the riparian forests had a greater potential to act as a CH₄ sink, but increased flood frequency could change this. This will become increasingly important for riparian zones as climate change continues, as extreme flooding events are expected to increase (IPCC 2014). However, Jacinthe (2015) noted that even when the soils were near saturation after a flood event, there was still little CH₄ release and temperature may have been a limiting factor after early spring floods. This explains why the lowest seasonal CH₄ emissions in the RH site were in the spring, when despite high soil moisture the soil temperature was still very low. Further, the higher average seasonal emissions in the summer of 2017 may

also be a consequence of higher soil temperature, coupled with high soil moisture. Although there were no significant correlations found in this study between soil temperature and CH₄ emissions at the RH site, PPF_D was included in the model that best predicted CH₄ emissions and it has a strong influence on soil temperature (Jurik and Van 2004; Teasdale and Mohler 1993; Correll 2005).

Additionally, Jacinthe et al. (2015) noted that hydromorphology will greatly impact CH₄ emissions in grassed and forested riparian buffers. They observed higher emissions than in this study, but the forested riparian area was on a topographical depression and this accounted for 78% of the CH₄ emissions. Topography was not determined in this study, but from visually assessing the RH site and the moderate soil moisture, it was likely not contributing to enhanced CH₄ production. Tile drainage present at the RH site may also be impacting the potential for CH₄ release, as it would limit the possibility for long-term flooding (Jacinthe et al. 2015). However, water table depth and a lack of persistent saturated conditions is likely what is limiting the CH₄ emissions at the RH site, creating the discrepancy with the UNFA site (Smith et al. 2003; Teiter and Mander 2005; Mander et al. 2015; Audet et al. 2013; Jacinthe 2015).

The GRS and AGR sites almost never acted as a source, and on a seasonal level were considerable sinks of CH₄. This was expected, as soil temperatures were high at these two sites, limiting sustained soil moisture (Smith et al. 2003; Dijkstra et al. 2011; Redding et al. 2011). This relationship was observed at the GRS site where there was a significant ($p < 0.01$) negative correlation between CH₄ emissions and air temperature, which subsequently impacted soil temperature. Jacinthe (2015) determined GHG emissions from grass-dominated riparian buffers under variable flooding, and also found that the buffers acted as a CH₄ sink. Jacinthe (2015)

found that even if CH₄ was being produced at depth closer to the water table where there are anaerobic conditions, when it reached the soil it was consumed by biological oxidation.

Jacinthe (2015) also found a strong positive correlation with soil moisture, as with this study, and that was likely the most limiting factor at the GRS site. Kim et al. (2010) also evaluated CH₄ emissions from a cropland, and forested and grassed riparian buffers in central Iowa, and found that all the land-uses acted as CH₄ sinks. Kim et al. (2010) wanted to see if the soil being previously cropped in the buffers impacted emissions, and found there was no relationship. Kim et al. (2010) also attributed the low CH₄ emissions to the lack of persistent saturated soil conditions. Jacinthe et al. (2015) observed CH₄ emissions from a cropland and grassed riparian buffer, and found that the cropland acted as a CH₄ source while the grassed buffer acted as a CH₄ sink. In the grassed buffer, they attributed this to tile drainage limiting soil moisture. This explains the low CH₄ emissions seen at the GRS site in this study, as the neighbouring agricultural field is tile drained. Although Jacinthe et al. (2015) observed the cropland to be a net source of CH₄, they attributed this to some croplands acting as weak CH₄ sinks due to frequent physical disturbance of the soil from ploughing and N fertilizers inhibiting CH₄ production, because NH₄⁺ inhibits methanotrophs. Further, Kim et al. (2010) attributed the low CH₄ emissions in the cropland to high bulk density, low SOC and increased light intensity limiting soil moisture. This was also supported by Amadi et al. (2016), who quantified GHG emissions from croplands, and found that factors that influence gas diffusivity (bulk density, soil texture and soil moisture) were the most important influences on CH₄ emissions, regardless of the high soil temperatures experienced in croplands. Therefore, these soil factors, along with the AGR site being conventionally managed, likely explain why CH₄ emissions were low at the AGR site.

Conclusion

There is a growing interest in how to mitigate climate change as global temperatures continue to rise (Masson-Delmotte et al. 2018). The agricultural sector contributes significantly to global annual GHG emissions (10-12%) and accounts for 6% of Canada's overall GHG emissions (AAFC 2019). Consequently, management of this sector is essential in meeting targets set out in the Paris Accord (Jones and Sands 2013; Smith et al. 2009). Agricultural intensification has also led to the degradation of neighbouring water courses through sediment loading, streambank erosion, and pollution by agricultural chemicals (Yates et al. 2007; Zhang et al. 2017). The use of forested riparian buffers can reduce this impact of agriculture on streams, and also contribute to on-farm carbon sequestration (Lovell and Sullivan 2006; Gregory et al. 1991). Unfortunately, the close proximity of these buffers to both agriculture and water courses create the ideal conditions for GHG production, resulting in riparian buffers as a potential hot spot for GHG emissions (Bradley et al. 2011). However, there have been few recent studies comparing GHG emissions on a temporal scale across multiple temperate riparian land-uses (Kim et al. 2009; Bailey et al. 2009; Kim et al. 2010; Jacinthe et al. 2012; Audet et al. 2013; Audet et al. 2014; Jacinthe 2015; Jacinthe et al. 2014).

This study found that the highest N₂O emissions in the AGR site, though this relationship with the other land-use types was not significant. The GRS site had the highest CO₂ emissions, and was significantly higher than the other land-use types. The UNFA site had the highest CH₄ emissions, and was significantly higher than the other sites. Seasonality had very little impact on GHG emissions at each of the land-use types, with few significant differences among seasons. Although the N₂O emissions were higher on average at the AGR site, there was very little variation among the other land-uses. N₂O emissions at the AGR site were mostly

influenced by the addition of N-based fertilizers, while variation in N₂O emissions at the other land-uses was likely influenced by differences in soil temperature and moisture. The high CO₂ emissions observed at the GRS site are likely a result of the high availability of plant matter and high root respiration, as well as moderate soil temperature and moisture. CO₂ emissions were limited at other sites either as a result of a soil moisture outside of the optimal range for the microbial communities (too high or too low), or were limited by low soil temperatures, particularly in the forested land-uses. Only the UNFA was a source of CH₄, while all other land-uses were a CH₄ sink. This is a direct result of the saturated soil conditions at the UNFA site, allowing for anaerobic conditions that fueled methanogenesis.

Correlation analyses reiterated the abovementioned relationships between GHGs and soil characteristics at the land-use level. NO₃⁻ concentration was strongly correlated to N₂O emissions at the AGR site, showing the relationship between fertilizer application and N₂O emissions. At the other land-uses, there were few correlations. This reiterates the lack of variation among the other land-use types. CO₂ emissions were strongly correlated to soil and/or air temperature at most land-use types, showing the strong influence it has on the microbial community responsible for CO₂ emissions. Further, there was a negative correlation between CO₂ emissions and soil moisture at most sites. Under increasing soil moisture regimes, oxygen becomes limiting, reducing CO₂ emissions. Comparatively, soil moisture was significantly positively correlated to CH₄ emissions at most sites. As soil moisture increases, oxygen becomes limiting creating an anaerobic environment, favouring the production of CH₄. These correlations were further supported using stepwise regression models, that were used to find the soil and environmental characteristics that best predicted emissions for each GHG. N₂O emissions were best predicted from soil temperature, NO₃⁻ and SOC. CO₂ emissions were best predicted by soil

temperature and SOC. Finally, CH₄ emissions were best predicted by soil moisture, NO₃⁻, SOC, and PPF. These model predictors frequently echoed the characteristics that significantly correlated to GHG emissions at each land-use type.

The results highlight that soil microclimate more significantly influenced GHG emissions than soil chemical characteristics (NO₃⁻, NH₄⁺, SOC). There are other important environmental factors that influence emissions that were not measured in this study, such as water table depth, topography, and the effect of tile drainage. Additionally, the management of the agricultural field adjacent to the buffer likely has a large influence on the soil characteristics, such as NO₃⁻ concentration. Therefore, the interpretation of the results of this study are limited by the few environmental factors that were measured. Since only few studies have taken place in temperate climates, particularly Canada, there needs to be more long-term research that evaluates how forested riparian buffers contribute to GHG emissions in different landscapes. However, this study demonstrated that the RH site had similar or lower emissions compared to the other land-use types, indicating that forested riparian buffers may not significantly contribute to climate change. This is significant, as it shows there may be no ecological disservices as a result of implementing forested riparian buffers, and they could be suggested as a best management practice (BMP) for farmers. Further, these results show that forested riparian buffers may actually have a reduced the climate change impact when compared to the most commonly used riparian land-use, especially grassed buffers. The additional ecological services (streambank stabilization, enhanced nutrient filtration, etc.) by adding trees to buffers, coupled with their reduced impact on GHG emissions, demonstrate why forested riparian buffers are a BMP over traditional grassed buffers.

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