Quantifying Aquatic Carbon and Nitrogen Dynamics and Greenhouse Gas Mitigation Potential in Riparian Agroforestry Zones

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.

Abstract

Agricultural intensification in Canada has led to a loss of riparian areas, which has resulted in the degradation of freshwater aquatic ecosystems due to an increasing amount of fertilizer and nutrients being introduced from the upland vegetation. Rehabilitation/restoration of the riparian areas has been shown to minimize these effects. The main objective of my research study is to quantify the carbon (C) and nitrogen (N) dynamics in the aquatic component of the Riparian Agroforestry Systems (RAFS) with varied vegetation located along Washington Creek, Ontario, Canada. The four different treatments studied had the following vegetation types: rehabilitated forest (RH), undisturbed natural forest dominated by deciduous vegetation (UNF-D), herbaceous vegetation (HB), or undisturbed natural forest dominated by coniferous vegetation (UNF-C).

The mean CO_2 concentration (g L^{-1} of CO_2-C) of the stream component of RH, UNF-D, HB, and UNF-C riparian agroforestry systems are 1.25 ± 0.05, 1.25 ± 0.05, 1.28 ± 0.04, and 1.15 ± 0.05, respectively. No significant spatial differences were found in the CO_2 concentrations of the RAFS. The mean CH_4 concentration (μg L^{-1} of CH_4-C) of the stream component of RH, UNF-D, HB, and UNF-C riparian agroforestry systems are 1.81 ± 0.09, 1.36 ± 0.10, 2.51 ± 0.13, and 1.11 ± 0.21, respectively. Amongst the four riparian treatments, UNF-C recorded significantly lower ($p = 0.003$) and HB recorded significantly higher ($p = 0.002$) CH_4 concentration. Stream DOC concentrations were different among the treatments, with UNF-C reporting significantly lower ($p = 0.035$) concentrations as compared to the other treatments. Sediment OC was the highest in the RH treatment, and lowest in the HB treatment.

The mean N_2O concentration (μg L^{-1} of N_2O-N) of the stream component of RH, UNF-D, HB, and UNF-C riparian agroforestry systems are 1.23 ± 0.04, 1.37 ± 0.05, 1.00 ± 0.05, and 3.32 ± 0.30, respectively. Amongst the four riparian treatments, HB recorded significantly lower (p =

0.024) and UNF-C recorded significantly higher ($p = 0.000$) N_2O concentration. Riparian zone averages for TN concentration show that on average UNF-C recorded significantly higher ($p = 0.000$) values compared to the other treatments, where other N species like NH_4^+ and NO_3^- were not significantly different amongst treatments. Mean sediment NH_4^+ concentrations were the highest in the RH treatment, along with stream TN. Stream NO_3^- concentrations were similar among the treatments.

Even though the terrestrial morphology of the RH and UNF-D riparian zone were different, including vegetation type and buffer width, but the aquatic component morphology for parameters like discharge, pH, DO, water temperature were similar. Furthermore, the chemical composition of the water in these riparian streams, that is, the GHG concentrations and other C and N species, were insignificantly different. This finding is the highlight of this study. Despite the differences in the terrestrial component, RH, which is a shorter and younger rehabilitated buffer, is just as effective at improving the water quality as is a 100-year-old and much wider forested buffer UNF-D. Therefore, implementing RH buffers at a BMP could potentially lead to water quality improvement in an agricultural landscape.

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1.0 INTRODUCTION

1.1 Climate Change

Climate is defined as the usual or expected weather of a location; and encompasses the atmospheric, land, and marine conditions of that location (Bush and Lemmen, 2019). Climate Change, therefore, refers to the long-term shift or alteration in a place's usual or expected weather (May, 2017). It is usually a measure of the amount of variability or change in the mean state of a location (Bush and Lemmen, 2019). Climate Change can be used to describe an alteration of the expected temperature patterns or expected precipitation patterns, for example (May, 2017). Currently, this term is often used to define the pattern of global warming that has been observed from the mid-20th century to the present. In most instances today, climate change refers mainly to the change and/or increase in the global average temperature for all the seasons (Lukyanets and Ryazantsev, 2016).

1.1.1 Climate Change and Canada

Like all over the world, Canada has experienced a warming of the climate. The observed increase in the mean temperature of Canada has been double that of the world, and the projections reveal a similar trend (Zhang et al., 2019). Between the years 1948 and 2016, Canada experienced an average temperature increase of 1.7℃. Northern Canada in particular has experienced an increase of about 2.3℃ in temperature (Zhang et al., 2019). More than half of the recorded warming can be attributed to human activity. In addition to an overall increase in temperature, Canada has also experienced extreme temperature changes, including extremely warm temperatures becoming more hot and extremely cold temperatures becoming colder (Zhang et al., 2019).

Similarly, annual and especially winter precipitation has increased in Canada (Zhang et al., 2019). These observations are projected to continue to increase in a similar trend during the 21st century with summer precipitation projected to decrease if high emissions persist (Zhang et al., 2019).

Climate change caused by anthropogenic influences has also increased the likelihood of extreme climate event occurrences in Canada. Although the evidence is medium to low confidence, the 2016 Fort McMurray wildfire and the 2013 southern Alberta flood event due to extreme precipitation are extreme weather events caused by anthropogenic climate change (Zhang et al., 2019). Additionally, over the last three decades, the seasonal snow accumulation and a portion of the year with snow cover have decreased in most parts of Canada (Derksen et al., 2019). The proportion of snow and ice in Canadian marine areas has decreased. This change has been accompanied by an increase in the permafrost temperature by about .01^{o}C per decade for the last 3-4 decades (Derksen et al., 2019). Finally, global warming has caused a shift in the seasonal timing of the peak streamflow since the spring peak streamflow occurs earlier than usual due to early snowmelt (Bonsal et al.,2019). There seems to be no effect yet on the following variables: the surface water levels, like lakes and wetlands; soil moisture and the occurrence of droughts; and groundwater levels. Although future projections show that all of the mentioned could be affected in the near future if high emission scenarios persist (Bonsal et al., 2019).

1.1.2 Causes of Climate Change

Thomas J. Crowley (2000), in his paper titled “Causes of Climate Change Over the Past 1000 Years”, explains how a comparison of climate models shows that much of the warming of the planet observed in the 20th century can be attributed to the anthropogenic increase in the amount of greenhouse gases in the atmosphere. Only a subsidiary part of this warming results from natural variability, which includes factors like the increase in solar irradiance or the reduction in volcanism during the 20th century.

Therefore, the scientific community is divided into two schools of thought regarding the possible causes of climate change. The *first school of thought* is based on the fact that our planet's natural processes are affecting our planet's climate. The natural processes that influence the climate include natural **external** causes like volcanic activity and solar radiation; and **internal** variability in the climate system (New, 2019).

Changes in solar radiation (external natural factor) encompass both: 1. the changes in the solar output, which depends on the intensity of the sunlight, the shape of the earth’s orbit, and the tilt of the earth’s axis; 2. and the changes in the reflectivity (reflection and/or absorbance) of this solar output by the earth’s surface and atmosphere (EPA, 2017). Although volcanic eruptions release carbon di-oxide (CO_2) into the atmosphere, the aerosols released by volcanic eruptions reflect sunlight and hence can have an overall cooling effect on the surface of the planet (EPA, 2017). Over the past 20th century, a reduction in the number of volcanic eruptions, and an increase in the amount of heat due to solar variability, has led to an increase of about 0.15℃ to 0.2℃, which is only one-quarter of the actual increase in temperature (Crowley, 2000). The rest of it can be attributed to the warming effect that the increase in anthropogenic greenhouse gas (GHG) emissions has had on the planet (Crowley, 2000).

Internal variability in the climate system (internal natural factor) refers to the change in air and water. These internal changes can either take place over a decade or longer or can happen over shorter periods of time (Purcell and Hudderston, 2016). Examples include: 1. Longer variation such as Pacific Decadal Variability (PDV) that is dominated by the Pacific Decadal

Oscillation (PDO) and Interdecadal Pacific Oscillation (IPO); 2. Shorter variation such as El Niño (Purcell and Hudderston, 2016).

Although a factor, the influence of natural variables on climate change is minimal. Much of the impact of global climate change can be attributed to anthropogenic or human factors. This leads us to the *second school of thought*. Scientists in this school of thought argue that the main contributor to global climate change is anthropogenic emissions resulting from human activity. These anthropogenic emissions (greenhouse gases, aerosols, and associated precursors) have caused an overall increase in the global temperature by approximately 1℃ (range from 0.8 -1.2 ℃) from pre-industrial temperatures (IPCC, 2018). Greenhouse gas (GHG) emissions (carbon dioxide, methane, nitrous oxide, tropospheric ozone, and water vapour), in particular, are considered the main driving force of this global warming (Lukyanets and Ryazantsev, 2016). Global warming, a consequence of GHG emissions, further has a disastrous impact not only on the ecology of our planet but also has social and economic consequences.

1.1.3 Ecological, Economical, and Social Consequences of Climate Change

Due to its negative consequences, climate change is not just an area of study for natural scientists anymore, but it is also a hot research topic among economists and social scientists. It has become an interdisciplinary problem and therefore requires an interdisciplinary solution (Adams, 2007). The effects of climate change are not the same globally; they are diverse and specific. Geographical location is a big determinant of the type and form of the effect climate change will have (Lukyanets and Ryazantsev, 2016).

Ecological Consequences

As a consequence of Climate Change, changes in the frequency, intensity, and duration of expected climate, and short-term weather extremes can be observed (Bush and Lemmen, 2019).

The abundance and intensity of natural disasters, including droughts, floods, and storms, have increased, with Asia being the most affected continent (Lukyanets and Ryazantsev, 2016). Generalized widespread warming of the planet has resulted in an increase in the atmospheric water vapour content and is causing the decline of snow and ice covers (Bush and Lemmen, 2019). Declining snow and ice covers, along with the expansion of ocean water due to the rise in temperature, have led to the global rise in sea level (Bush and Lemmen, 2019). Temperature increases in near-surface air, lower-atmospheric air, and sea surface have been observed, along with an increase in the heat content of large water bodies (Bush and Lemmen, 2019).

Ecological changes have affected the social and economic sectors as well. In the following two sections, the negative social and ecological consequences of global climate change will briefly be discussed.

Socio-Demographic Consequences

The three main socio-demographic consequences of climate change, existing mostly in developing countries that have been identified are:

- Increased mortality of up to 250,000 deaths per year (WHO, 2016) due to: an increase in the number and intensity of natural disasters because of climate change; an increase in malnutrition as the number of droughts has increased; and an increase in malaria and heat stress occurrences as the temperature of the planet rises (Lukyanets and Ryazantsev, 2016).
- Increased morbidity has increased mortality rates (Lukyanets and Ryazantsev, 2016). In addition, the health of the population is deteriorating as the temperatures increase; higher temperatures can lead to: an increase in ozone concentration; an increase in the abundance of pollen and other air pollutants; an increase in the number of epidemics as

more infections develop due to hot and moist air conditions; lack of clean drinking water due to droughts (Lukyanets and Ryazantsev, 2016).

- Increased mass environmental migration due to climate change (Lukyanets and Ryazantsev, 2016).

Economical Consequences

Although not homogenous throughout the world, reports show that the world's economy is suffering due to climate change. This trend will continue to increase with the increase in the average temperature of the planet (Lukyanets and Ryazantsev, 2016).

The economy of the world, especially that of the developing world, is suffering in two ways. Firstly, the economy suffers due to the reduction of agricultural growth in developing countries that are heavily dependent on the agricultural sector for their GDP (Lukyanets and Ryazantsev, 2016). This economic recession further results in either an increase in the population's death or a reduction in the living standards of the population. Secondly, the economy suffers due to the increasing costs associated with preventing and eliminating the consequences of climate change. For example, a natural disaster like flooding could mean that the population in the affected area needs to be relocated to safer territory, which could get very expensive (Lukyanets and Ryazantsev, 2016).

1.1.4 Climate Change, Sustainability, and Agriculture

Food security, dependence of food security on agriculture, and the impact climate change has on food security were all primary discussion topics in the historic Paris Agreement held in 2015. Food and Agricultural Organization of the United Nations (FAO), in a report that was released in 2016, also acknowledged climate change as the main challenge to present and future food insecurity (FAO, 2016). Lukyanets and Ryazantsev (2016) also recognize the reduction of agricultural growth as one of the negative economic consequences of climate change. Climate change impacts agrarian production in the following ways: an increase in temperature and decrease in freshwater availability affects the productivity of crops and agrobiodiversity; increased likelihood of plant diseases and pest infestation due to the rise in temperature; and an increased likelihood of natural disasters and decreased predictability of weather and climate patterns (FAO, 2016). Overall, the impact of climate change on food security and agriculture is expected to be negative (FAO, 2016). To ensure a plausible and desirable sustainable future, it is essential that sustainable agricultural practices be adapted.

1.2 Sustainability and Sustainable Agriculture

After realizing the extensive environmental degradation caused due to anthropogenic activity, humans have finally resolved to adopt the idea of sustainability as a last resort to save the planet. Although there is no one set definition of sustainability, the following is the definition provided by the Brundtland Commission in 1990: “sustainability is defined as the persistence over an indefinite future of certain necessary and desired characteristics of the socio-political systems and its natural environment” (Robinson et al., 1990).

Sustainable agriculture plays two essential roles in this world:

- For developing countries, their economic and social capacity can be sustained; living standards can be sustained (FAO, 2016).
- For developed countries, it is essential to maintain high water quality; and to reduce the GHG emissions from their agricultural landscape (Raworth, 2012).

1.3 Agroecology and Agroforestry

Agroecology is the area of science that provides a framework to study the complexity of the agricultural ecosystem, known as agroecosystems (Altieri and Nicholls, 2005). *Agroecosystem* can be defined as the interaction of the communities of plants and animals with their chemical and physical environments to produce products like food, fuel, and other products utilized by humans for consumption and processes. The ultimate goal of agroecology is to make agriculture more sustainable. By studying the ecological, social, and economic aspects of the complex agroecosystems, agroecology aims to use this holistic understanding to design diverse agroecosystems that will provide "balanced environments, sustained yields, biologically mediated soil fertility and natural pest regulation, and use low input technology" (Altieri and Nicholls, 2005). One such diversified agroecosystem is the *Agroforestry System.*

Agroforestry involves the integration of trees and shrubs on a farm, along with other enterprises like crops and/or livestock (Beetz, 2002). Agroforestry systems provide various ecological and economic benefits including, and not limited to, the following: an additional source of income; an increase in the productivity of crops and/or livestock on the farm; protect and promote the quality of soil and water; and improve habitat for wildlife (Beetz, 2002). Some examples of such agroforestry systems are alley cropping systems, windbreaks, forest farming, and, most importantly ***<u>riparian buffer systems</u>*** (Beetz, 2002). These systems provide a more sustainable alternative to traditional land use change practices, which usually only involve clear-cutting natural habitats for agricultural practices (Jose, 2009).

A detailed understanding of agroecosystems is required to design and manage sustainable agroecosystems by applying ecological concepts and principles (Altieri and Nicholls, 2005). The field of agroecology is focused on developing alternative practices that will result in agroecosystems that are able to sustain themselves and therefore have minimal dependence on agrochemicals and other energy inputs (Altieri and Nicholls, 2005). Agroecology aims to achieve this goal by studying the ecological, social, and economic aspects of the complex agroecosystems, thereby encompassing a holistic study of all the environmental and human elements (Altieri and Nicholls, 2005).

Shibu Jose (2009), in his paper titled “Agroforestry for ecosystem services and environmental benefits: an overview,” enlists the four major ecosystem services and environmental benefits that agroforestry can provide.

1. Carbon sequestration: this process involves the removal and fixation or storage of carbon from the atmosphere to certain carbon sinks including, and not limited, to oceans, soils, and vegetation. Trees and shrubs in agroforestry systems can not only sequester carbon above-ground biomass but can assist in storing carbon in below-ground sinks.
2. Soil Enrichment: Agroforestry systems are well known to help maintain and improve soil's long-term sustainability and productivity. These systems can help fix nitrogen through the plantation of nitrogen-fixing shrubs and trees in these areas. Additionally, non-nitrogen fixing trees and shrubs can also help improve soil’s chemical, physical and biological properties by recycling and releasing nutrients and by adding aboveground and belowground organic matter to the soils.
3. Biodiversity Conservation: Agroforestry systems, especially in tropical and temperate regions of the world, play an essential role in conserving and enhancing biodiversity. Agroforestry systems not only provide a habitat for these species but also preserves this habitat by preventing soil erosion, for example.

4. Improved Air and Water Quality: Agroforestry vegetation can help improve air quality by filtering out gas, dust particles, and other microbial constituents. These tree and shrub plantations can also help reduce wind chills and wind velocity, remove CO_2 from the air, add more oxygen, reduce noise pollution, limit wind erosion, etc. These plantations also help improve water quality, both surface and ground water, by filtering out the runoff from agricultural fields, for example.

These benefits are not only beneficial for the farmers but are for society in general and can improve the overall health of the planet if implemented rigorously throughout the world.

2.0 LITERATURE REVIEW

2.1 Riparian Agroforestry Buffer Systems

Riparian Agroforestry Systems (RAFS), a type of agroforestry system, are strips of vegetation, trees, and shrubs, planted along streams or rivers that run adjacent to agricultural fields (Beetz, 2002). Since RAFS are transition zones between the upland agricultural vegetation and the water body, stream or river, there is no set boundary to these buffer systems (Hillard and Reedyk, 2014). Planting riparian buffers is a best management practice (BMP) designed to provide the following benefits:

- Riparian buffer systems can help reduce above surface and sub-surface run-off from the upland area to the water body (Beetz, 2002). Runoff, such as excessive nutrients and chemical pesticides from agricultural fields, can be reduced to help maintain and improve water quality (Beetz, 2002). Riparian vegetation can also stabilize the streambank/riverbank through deep roots, thereby reducing soil erosion into the water body (Hillard and Reedyk, 2014). Along with lowering runoff, riparian buffer systems are also very effective at sequestering carbon (Beetz, 2002).
- As a BMP, planting riparian buffer systems can provide an economic incentive to the farmers since these systems can be maintained to provide recreational facilities; biomass production through the plantation of marketable food like nuts; and special forest product plantation (Beetz, 2002).
- Riparian buffer systems can also help improve the aquatic environment by providing shade. The cooler conditions resulting from shaded streams are ideal for desired freshwater species like fish (Beetz, 2002) and not so ideal for algal species that usually require sunlight to grow in abundance (Hillard and Reedyk, 2014). Additionally, the

terrestrial components of the riparian buffer systems provide a habitat for many wildlife species (Beetz, 2002).

As mentioned earlier, effective agroforestry systems can improve air and water quality and play an important role in C sequestering (Jose, 2009). A way to measure how effective a RAFS is at improving the water quality of the aquatic component of the RAFS is to study the Carbon (C) and Nitrogen (N) dynamics of the RAFS.

2.2 Carbon cycling

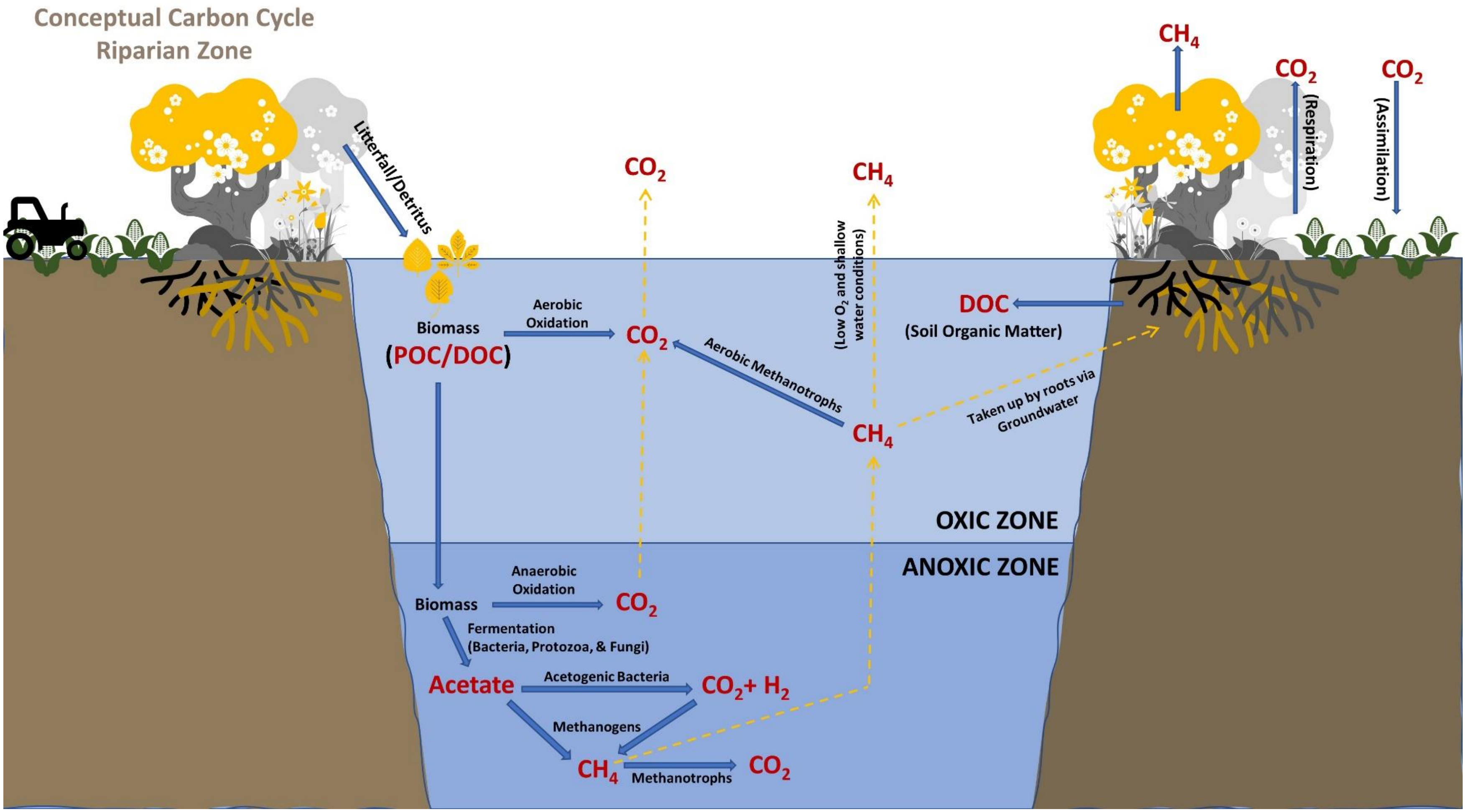

Figure 2.1: Conceptual diagram of the potential C cycling in the aquatic component of a riparian agroforestry system

Adapted from: D’amario and Xenopoulos, 2015; Deirmendjian and Abril, 2018; Hope et al., 1994; Larmola, 2005; Marx et al., 2017; Stanley et al., 2016; Thauer et al., 2008; Zigah et al., 2015

The carbon in headwater streams can significantly influence the overall carbon budget, as 90% of the stream channels of a watershed are headwater streams. Therefore, they play an essential part in the global cycling of carbon (Argerich et al., 2016).

Terrestrial carbon export by headwater streams is crucial in global carbon cycling. Where carbon from the terrestrial environment is introduced to headwater streams through allochthonous, autochthonous, and anthropogenic sources, it is exported via processes like carbon burial and aquatic carbon turnover (Marx et al., 2017). Processes like the mineralization of organic matter to carbon dioxide followed by its outgassing into the atmosphere, is one example of how this is achieved (Marx et al., 2017).

2.2.1 Sources of Carbon

There are three main sources that are responsible for the introduction of carbon into the headwater streams (refer to figure 2.1):

1. Allochthonous sources: the main constituent of this carbon source is terrestrial organic matter, for example: leaf litter from the vegetation growing on the stream's banks (Hope et al., 1994). Plants assimilate CO_2, during photosynthesis, from the atmosphere which enters the stream environment as decomposing litter, dissolved organic carbon leaching from nearby soil, or as CO_2 from groundwater which accumulates as a result of belowground root or microbial respiration (Larmola, 2005).
2. Autochthonous sources: this refers to the in situ biological production and release of carbon into the headwater stream. For example, the release of organic carbon through the decomposition of leaf litter or dead animals because of the microorganismal activity in the stream (Hope et al., 1994). Submerged algae and macrophytes can also photosynthetically or autotrophically fix and/or respire CO_2 (Larmola, 2005).

3. Anthropogenic sources: this category includes the carbon that is introduced, as aboveground and belowground runoff, to the headwater stream due to agricultural, industrial, and domestic activities impacting the headwater stream (Hope et al., 1994).

In headwater streams, carbon exists in two forms: organic carbon (OC) and inorganic carbon (IC). Furthermore, OC exists in two forms in stream water: dissolved organic carbon (DOC) and particulate organic carbon (POC). The distinction between the two is usually determined by using a 0.45-0.50 μm filter. Organic carbon that passes through this filter is considered DOC, and any organic carbon particles that accumulate on the filter are considered POC (Hope et al., 1994).

2.2.2 Particulate Organic Carbon (POC)

POC in headwater streams is inclusive of all the phytoplankton, yeasts, micro-zooplankton, and bacteria present. It also includes other detritus particles, mainly plant litter like leaves and woody debris, and aggregates like eroded soil organic matter and soil (Marx et al.,2017 and Hope et al., 1994). The introduction of POC into the stream body is dependent on: the season, since litter fall is higher in some seasons; the intensity of precipitation and runoff as this would determine how much POC is leaching from soils and sediments; the slope of the watershed; and when applicable, the closeness of wetlands. Most POC loading into stream bodies is the result of a few significant storm events (Jeong et al., 2012). Climate change has caused an increase in the number of storms, and therefore the POC loading into streams has increased (Jeong et al., 2012).

The POC pool is further affected by mechanical abrasion and microbial activity that has the potential of converting POC particles to DOC, hence adding to the DOC pool. Nutrient release from the decomposition of litter fall is an example of this process (Meyer and Tate, 1983). Once in the form of DOC, the organic carbon can be mineralized to CO_2 or other forms of inorganic carbon (D'amario and Xenopoulos, 2015).

2.2.3 Dissolved Organic Carbon (DOC)

Other than decomposition, the primary source of DOC in streams is soil, *especially riparian and organic-rich soils* (Billett et al., 2006). The introduction of carbon into streams through this source of DOC involves a two-step process:

1. The first step involves the production of DOC in the soils. This process is positively correlated to factors including the temperature of the soil, water saturation level of the soil, wet-dry cycle, snowmelt, liming of the soil, and the concentration of organic fertilizer in the soil (Marx et al., 2017). In addition, organic fertilizers promote microbial activity in the soil and positively impact fungal abundance (Kalbitz et al., 2000).
2. The second step involves the release of this DOC from the soil to the stream. The transport or drainage of this DOC to the stream depends on the temperature, land use/ land use change activity, and nutrient inputs to the soil (Marx et al., 2017). Additionally, if the groundwater levels rise or there is abundant rainfall, the moisture in the soil will exceed the critical moisture level. As a result, the DOC in the soil will mobilize (McGlynn and McDonnell, 2003).

As mentioned before, once in the stream, the DOC can be mineralized to either CO_2 and can be released into the atmosphere, or it mineralizes to other forms of inorganic carbon (D'amario and Xenopoulos, 2015).

2.2.4 Inorganic Carbon (IC)

Inorganic Carbon also exists in particulate (PIC) and dissolved (DIC) forms. PIC concentrations in streams and rivers are negligible compared to other forms of carbon. PIC is mostly introduced through rock weathering, and precipitates out easily in carbonate-oversaturated water, thereby decreasing the concentration of DIC as a result (Huang et al., 2012). On the other hand, DIC is the most abundant form of carbon in rivers and streams. DIC can exist in many different forms; it is the sum of CO_2 (CO_2 (aq) + H_2CO_3), HCO_3^-, CO_3^{2-}. The proportional concentration of each of these DIC forms depends mainly on the pH of the water body and, to a lesser extent, on the temperature of the water body (Marx et al., 2017). There are two main sources of dissolved CO_2 input into streams and rivers (refer to figure 2.1):

1. Internal source: this source is comprised of CO_2 released from heterotrophic decomposition and photooxidation of organic matter like algae (Deirmendjian and Abril, 2018).
2. External source: the main source of external DIC loading into streams and rivers is groundwater which is enriched in CO_2 released from plant root/autotrophic and microbial/heterotrophic respiration of organic matter in soils and groundwater (Deirmendjian and Abril, 2018; Hope et al., 2004). Carbonates from weathering of rocks and the introduction of CO_2 through atmospheric exchange, when the dissolved concentration of the gas is below the atmospheric equilibrium, are two other sources that can increase the concentration of dissolved CO_2 in the streams (Hope et al., 2004).

This increase in the amount of CO_2 can cause rock/mineral weathering of carbonates and silicates (Marx et al., 2017). Dissolving carbonates can add more inorganic carbon to the stream/river body, mainly in the form of HCO_3^- (Marx et al., 2017).

2.2.5 CH_4 production

Even though carbon di-oxide (CO_2) is the major by-product of microbial/heterotrophic respiration of organic matter, streams and rivers are often important contributors to methane (CH_4) emissions as well (Stanley et al., 2016). CH_4 is usually a by-product of anoxic rather than oxic respiration (Stanley et al., 2016, refer to figure 2.1). In the water ecosystem, CH_4 is produced mainly in the anoxic sediment environment (Reeburgh and Heggie, 1977). Three types of methanogens produce methane in the aquatic anoxic sediment including: acetoclastic methanogens that use acetate as the electron acceptor; methylotrophic methanogens that use methyl groups as electron acceptors; and hydrogenotrophic methanogens that use H_2 and CO_2 (i.e., CO_2 reduction) to produce methane (Pierangeli et al., 2021). The produced CH_4 can encounter one of the following fates: it can be oxidized anaerobically to CO_2 in the presence of SO_4^{2-} or NO_3^- as the electron acceptors (Thauer et al., 2008; Zigah et al., 2015); it can be oxidized aerobically to CO_2 once in the stream environment in the presence of O_2 as the electron acceptor (Thauer et al., 2008; Zigah et al., 2015); it can be released to the atmosphere once in the stream environment provided that either the oxygen levels are low which reduces CH_4 oxidation (Yeng et al., 2015), and/or the water depth is shallow.

In a stream environment, CH_4 can either be contributed via groundwater (Heilweil et al., 2013; Jones Jr. and Mulholland, 1998), which is also seemingly the main source of CH_4, or it can be produced in the anoxic pockets of the stream sediment (Crawford et al., 2014; Stanley et al., 2016). As mentioned earlier, once this CH_4 makes its way to the stream environment, it can either be oxidized to CO_2 or released into the atmosphere.

2.3 Nitrogen Cycling

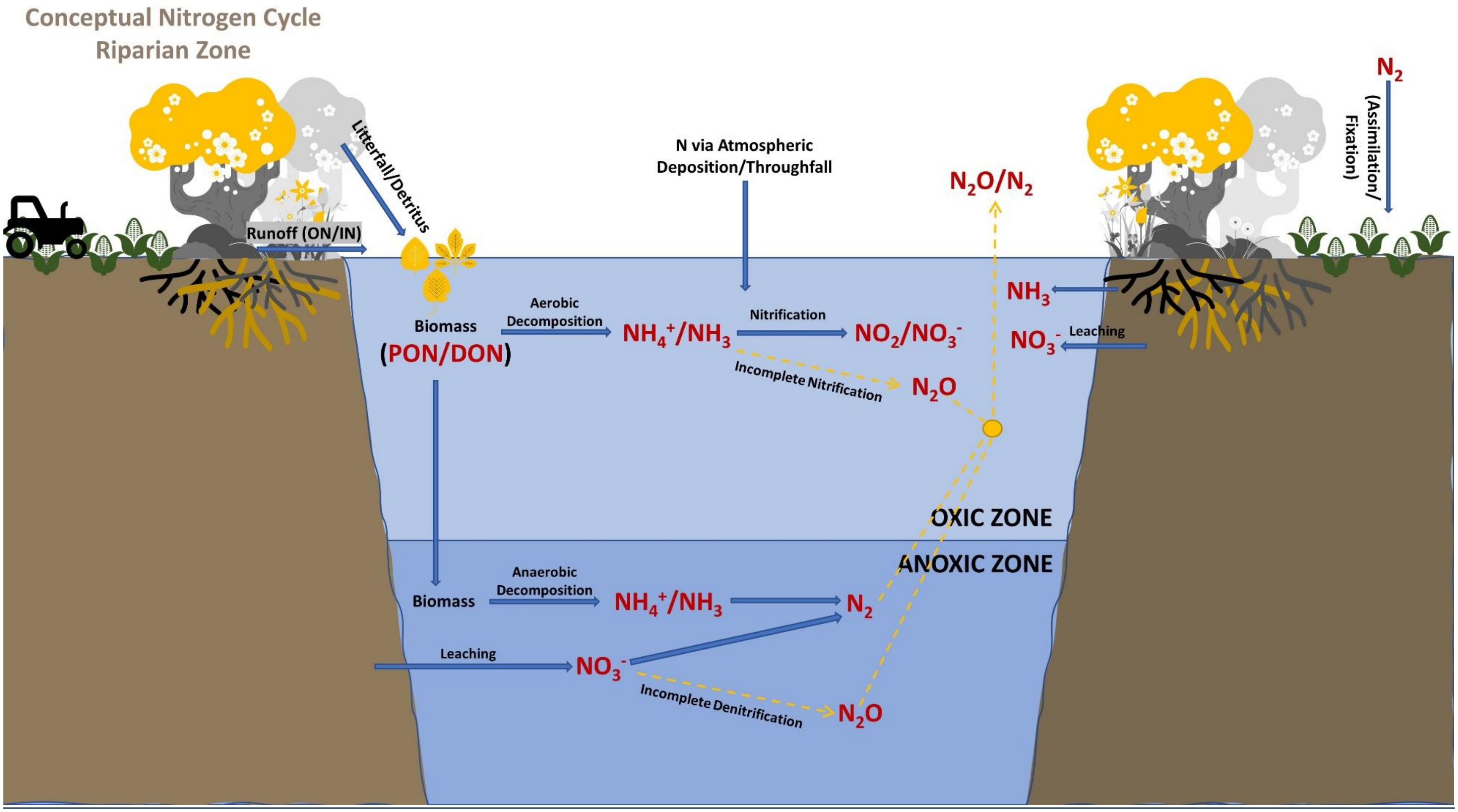

Figure 2.2: Conceptual diagram of the potential N cycling in the aquatic component of a riparian agroforestry system

Adapted from: Duff and Triska, 2000; Fields, 2004; Francis et al., 2007; Mazza et al., 2014; Paerl, 2017; Rassamee et al., 2011; Wall, 2013.

2.3.1 Forms of Nitrogen found in Streams

A water pollutant, and an essential element for plant growth and stream productivity, Nitrogen (N) exists in many different forms in the stream environment (Mazza et al., 2014) including both organic and inorganic forms. The main inorganic forms of N include ammonia, ammonium, nitrate, and nitrite, with nitrate (NO_3^-) being the most dominant form of inorganic N in ground and surface waters (Wall, 2013). Organic N can exist both in particulate (PON) and dissolved (DON) forms and is generally found in amino acids, proteins, and urea, in living and dead organisms and plants, for example (Wall, 2013). The dominant form of N found in soils or water is determined by various factors like the temperature of the soil or the water body, oxygen levels, and bio-chemical conditions (Wall, 2013). Notably, the streams in an agricultural landscape have nitrate as their most dominant form of N, followed by organic N (Wall, 2013).

2.3.2 Input Sources of N in the Streams

There are four main sources of N input in streams, particularly in agricultural landscapes (refer to figure 2.2):

Below-ground Source

1. Groundwater is the belowground source that can introduce nitrogen to surface water bodies. The exchange of nutrients occurs in the hyporheic zone between the groundwater and the stream water. The hyporheic zone is the subsurface area of a stream, where the surface stream water mixes with the shallow layers of groundwater (Mazza et al., 2014). N is introduced into groundwater mainly using two different pathways: nitrate, which is the most mobile form of N, moving vertically through the soil and therefore being leached into the groundwater (Wall, 2013), and via the surface water itself, which can supply nitrate, DON, and DOC to the hyporheic zone (Mazza et al., 2014).

Above-ground Sources

2. Runoff: especially for streams surrounded by agricultural landscape, this runoff water can be N heavy if animal manure or inorganic N-fertilizers are being used on the agricultural fields (Wall, 2013). N fertilizers are a significant source of NO_3^-. Some of this nitrogen will also get attached to the soil particles as ammonium-N and organic-N and will become a part of the runoff resulting from snowmelt and storm events (Wall, 2013).
3. Atmospheric Deposition and Throughfall: during rainfall/precipitation events or through dry deposition, the N in the atmosphere can be introduced to the streams (Wall, 2013).
4. Vegetation: The vegetation growing on the banks of the streams, also known as riparian zones, can assimilate the N from the atmosphere, runoff, or from groundwater. This assimilated N can be released into the streams or into the groundwater and eventually into the stream thereafter (Wall, 2013). Litterfall from vegetation is yet another way riparian vegetation can introduce N and C into the stream environment (Duff and Triska, 2000). The quantity and quality of litterfall will influence the amount and rate of N release through decomposition (Oelbermann and Gordon, 2000).

2.3.3 Organic Nitrogen (ON)

The N introduced into the stream can undergo processing, leading to a change in the state of the N from one form to another. In a stream environment, N can occur in the following forms: as molecular dinitrogen (N_2); as reduced ammonium in organic matter; and as oxides including nitrite (NO_2^-), nitrate (NO_3^-), and nitrous oxide (N_2O) (Duff and Triska, 2000). Nitrogen bonded to carbon is known as organic nitrogen (ON) (Wall, 2013), and can exist in both particulate and dissolved forms. The decomposition of organic nitrogen (fixed nitrogen), introduced through litter fall and throughfall, releases ammonium and ammonia as the end-product in anaerobic and aerobic environments (Duff and Triska, 2000, refer to figure 2.2). Ammonium is then quickly oxidized to nitrite and nitrate by chemolithotrophic nitrifying bacteria. This process is known as nitrification (Duff and Triska, 2000). Once in the form of ammonium or nitrate, this N can be used by algae and other aquatic organisms to grow, resulting in an increase in the particulate organic nitrogen in the stream body (Wall, 2013).

2.3.4 Inorganic Nitrogen (IN)

Most inorganic nitrogen in water is in the dissolved form (DIN). IN is mainly the sum of the following forms of nitrogen: nitrite (NO_2^-), nitrate (NO_3^-), ammonia (NH_3^-), and ammonium (NH_4). These nitrogen species interchange their forms depending on various factors, like dissolved oxygen (DO). In the beginning, the atmospheric nitrogen, which is in the form of N_2 gas, is fixed by terrestrial plants (Fields, 2004) and potentially by nitrogen-fixing photosynthetic cyanobacteria in aquatic environments (Paerl, 2017). The nitrogen fixation process involves the enzymatic conversion of N_2 derived from the atmosphere to $NH_{3,}$ which is then released into the streams either directly by cyanobacteria (Paerl, 2017) or through leaching from soils into groundwater in case of nitrogen fixed by terrestrial plants (Fields, 2004). Nitrogen fixed by terrestrial vegetation also reaches the aquatic environment in the form of litterfall and dead organic matter (Wall, 2013). Microbes then decompose the organic matter to release more ammonium into the stream, both in the oxic stream environment and in the anoxic sediment environment (Duff and Triska, 2000).

As mentioned previously, in the oxic stream environment ammonium is oxidized to nitrite and nitrate by chemolithotrophic nitrifying bacteria. This process is known as nitrification (Duff and Triska, 2000). In the sediment, anaerobic ammonium oxidation converts NH_4^+ to N_2 which is then released into the environment. Additionally, nitrate can undergo denitrification in the anoxic sediment environment and release N_2 as a final product (Duff and Triska, 2000). Nitrous oxide (N_2O) concentrations are a by-product of incomplete nitrification and denitrification processes (Rassamee et al., 2011). That is, N_2O can be produced both in the oxic and in the anoxic environment.

2.4 Coupling of C and N cycle

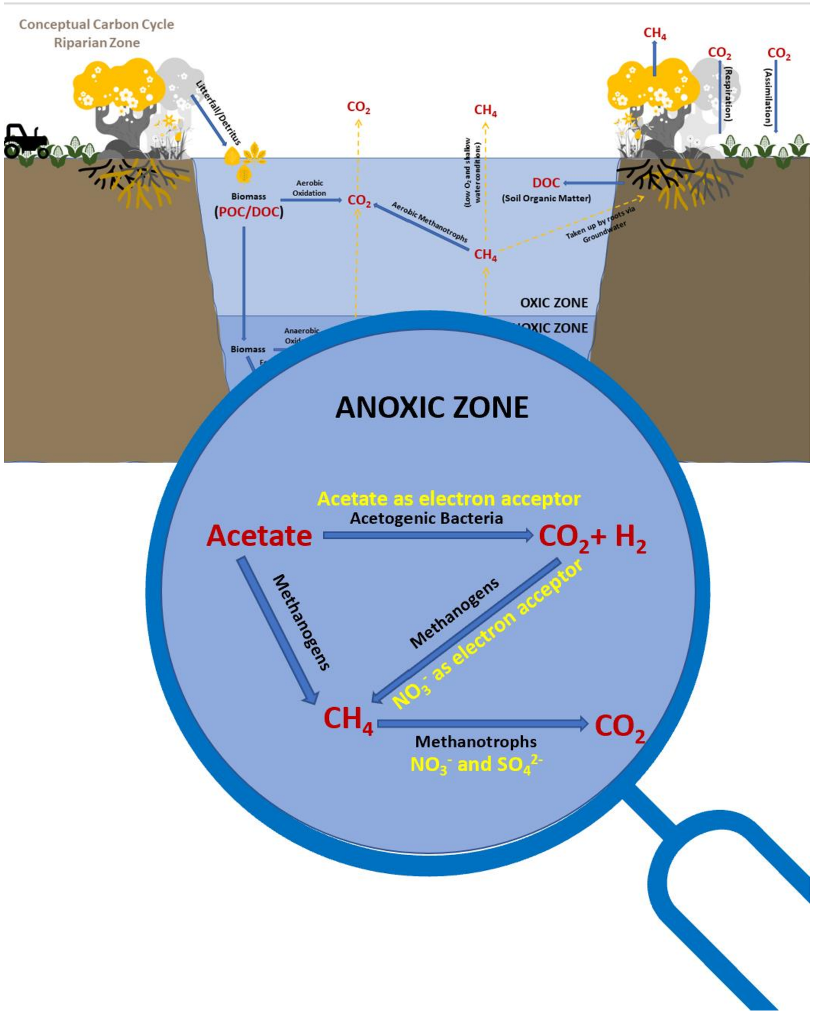

Figure 2.3: Conceptual diagram of the potential C and N cycle coupling process in the aquatic component of a riparian agroforestry system

Adapted from: Chidthaisong and Conrad, 2000; Thauer et al., 2008; Schlesinger and Bernhardt, 2013; Smith and Bohkle, 2019.

At the microbial level, the correlation among the three GHGs (CO_2, CH_4, and N_2O) can be explained by the role of acetate in the denitrification process. The anaerobic processing of organic carbon leads to the formation of acetate and H_2 through fermentation (Schlesinger and Bernhardt, 2013) (refer to figure 2.3). As discussed earlier, three different methanogenesis can occur in the final step, including hydrogenotrophic, acetoclastic, and/or methylotrophic (Pierangeli et al., 2021; refer to section 2.2.5 for details). Acetoclastic methanogens (acetate as e^- acceptor) and hydrogenotrophic methanogens (H_2 and CO_2) are the most common in freshwater systems (Fenchel et al., 2012). Thermodynamically, in the presence of high energy-yielding electron acceptors like SO_4^{2-} and/or NO_3^-, these will be the first ones to be reduced, producing N_2O gas for example (Chidthaisong and Conrad, 2000; Vincent et al., 2021). Therefore this will inhibit acetate as an electron acceptor and consequently reduce methane production through this pathway (Vincent et al., 2021). As a result, the correlation between CH_4 and N_2O production is stronger than the correlation between CO_2 and N_2O production since CH_4 and N_2O production in the anoxic aquatic sediment environment is directly linked (Wang et al., 2019).

On a larger scale, as per Smith and Bohlke (2019), N enrichment can enhance the productivity and growth of algae and other aquatic organisms. This will lead to an increase in the decomposition activity in the stream environment and, therefore, an increase in the available organic carbon and, eventually, CH_4 and CO_2 concentration. N-enriched streams are usually high in NO_3^- concentration which is a good indicator of high N_2O concentration (Smith and Bohkle, 2019). Wall, 2013 also supports this reasoning. However, this positive feedback cycle is only effective until ideal conditions prevail, like the presence of sufficient dissolved oxygen (Hynes, 1960; Dauer et el., 2000).

C and N Dynamics in RAFS and Knowledge Gaps

Riparian zones can be designed to provide multifunctional ecosystem services including: C sequestration to help mitigate climate change (Capon et al. 2013); and improving water quality by reducing C and N inputs into the water body (Fortier et al. 2010). Therefore, the management and restoration of riparian areas can provide long-term fundamental and cost-effective ecosystem services. However, while there is a lot of information regarding the adverse effects of nutrient runoff on water quality (Dodds and Whiles, 2010), empirical data on greenhouse gas (GHG) emissions/dissolved concentrations from riparian zones, particularly the aquatic component, is limited.

3.0 THESIS HYPOTHESIS AND OBJECTIVES

3.1 Agricultural Greenhouse Gases Program (AGGP) objectives

The influence of RBS type (trees or herbaceous), age, and soil texture in relation to carbon (C) sequestration, and reduction of GHG emissions (CO_2, CH_4, and N_2O), in the terrestrial and aquatic components of RBS is not well understood. Therefore, through the AGGP, funded by Agriculture and Agrifood Canada, a series of parallel studies were conducted within the Grand River watershed with the following objectives:

1. To quantify the C and N dynamics of the riparian agroforestry buffer systems (RAFS) and study how these systems influence the greenhouse gas mitigation potential of these riparian systems. As a part of the objective of researching the mechanistic understanding of the GHG emission potential of the agroforestry riparian areas, the following will also be studied: integrations of tress and earthworms; soil microorganisms; nutrient dynamics; and soil structure.

2. Develop GHG mitigation best management practices (BMPs) using results and literature to help benefit Canadian agricultural producers.

3.2 Specific objectives and hypothesis of this study

The *objectives* of this thesis are:

1. To study the greenhouse gas (GHG) mitigation potential of the RAFS and determine which of the following types of RAFS treatments has the highest GHG mitigation potential: rehabilitated forest riparian buffer (RH), undisturbed natural forest riparian buffer dominated by deciduous vegetation (UNF-D), herbaceous vegetation buffer (HB), or undisturbed natural forest riparian buffer dominated by coniferous vegetation (UNF-C).

2. To study the differences in other Carbon (C) dynamics amongst the RAFS treatments and determine which has the highest potential to improve the water quality.
3. To study the differences in other Nitrogen (N) dynamics amongst the RAFS treatments and determine which has the highest potential to improve the water quality.

Hypotheses

H1: There will be a significant difference in the stream chemistry and characteristics among the RAFS treatments (RH, UNF-D and UNF-C, and HB).

H0: There will be no significant difference in the stream chemistry and characteristics among the RAFS treatments (RH, UNF-D and UNF-C, and HB).

H2: There will be significant difference in the Carbon (C) dynamics, using stream dissolved organic carbon (DOC) and sediment organic carbon (OC) concentrations as parameters, among the RAFS treatments (RH, UNF-D and UNF-C, and HB).

H0: There will be no significant difference in the C dynamics, using stream DOC and sediment OC concentrations as parameters, among the RAFS treatments (RH, UNF-D and UNF-C, and HB).

H3: There will be significant difference in the Nitrogen (N) dynamics, using stream and sediment nitrate (NO_3^-), ammonium (NH_4^+), and total nitrogen (TN) concentrations as parameters, among the RAFS treatments (RH, UNF-D and UNF-C, and HB).

H0: There will be significant difference in the N dynamics, using stream and sediment NO_3^-, NH_4^+, and TN concentrations as parameters, among the RAFS treatments (RH, UNF-D and UNF-C, and HB).

H4: There will be a significant difference in the dissolved GHG (CO_2, CH_4, and N_2O) concentrations among the RAFS treatments (RH, UNF-D and UNF-C, and HB).

H0: There will be no significant difference in the dissolved GHG (CO_2, CH_4, and N_2O) concentrations among the RAFS treatments (RH, UNF-D and UNF-C, and HB).

4.0 MATERIALS AND METHODS

4.1 Study site

The study sites are located along the Washington Creek (Lat: 43.30 degrees N and Lon: 80.57 degrees W) located in the Township of Blandford-Blenheim, Oxford County, Southwestern Ontario, Canada. Washington Creek is a first-order stream that feeds into the Nith River and is a part of the Grandriver Watershed. Oxford county has an average elevation, with reference point Roseville (Lat: 43.21-degree N and Lon: 80.28-degree W), of 328 m. The average year-round temperature in the county is around 7℃. Although, like most of Southwestern Ontario, Oxford County experiences temperate climatic conditions, that is, extreme hot and cold temperatures, and its climate is impacted by the Great Lakes that surround the watershed area (Oelbermann et al., 2008). The average precipitation experienced by the area is about 907.5 mm annually (Environment Canada 2019).

Oxford County's landscape is predominantly agricultural; therefore, Washington Creek is a typical agriculturally degraded stream (Oelbermann et al., 2008). The creek is exposed to the erosion of nutrients from the cropped fields and the pastureland that surrounds it, along with much of its bank lacking riparian vegetation (Oelbermann et al., 2008). Previous studies, and as was discovered in this study, the Washington Creek is alkaline, with pH ranging from 7.5 to 8.5 due to the high abundance of calcium in the soils surrounding the stream (Oelbermann et al., 2008). Moreover, the streambed substrate is also made of dolomitic limestone and is coarse in texture with high gravel content (Oelbermann et al., 2008).

Figure 4.1: Aerial image of Washington Creek study site highlighting the RAFS treatments (retrieved from Google Earth Pro).

Much of the land surrounding the Washington Creek is dominated by agricultural landscape, except for the buffered areas surrounding some parts along the creek. Aquatic components of four different riparian type buffers were studied to meet the objectives of this project including: a rehabilitated forest riparian area (RH), restored over 25 years ago; an herbaceous riparian area (HB); and two undisturbed natural forest riparian areas (UNF-C and UNF-D) (refer to Figure 4.1 for site map; refer to table 4.1 for site-specific details).

Table 4.1: The following table represents the details of the four study sites: rehabilitated forest riparian buffer (RH), undisturbed natural forest riparian buffer dominated by deciduous vegetation (UNF-D), herbaceous vegetation buffer (GRS), and undisturbed natural forest riparian buffer dominated by coniferous vegetation (UNF-C).

	RH	UNF-D	HB	UNF-C
Latitude/ Longitude	43°201801.69”N / 80°33’40.27”W	43°201808.46”N / 80°34’19.69”W	43°201823.56”N / 80°34’47.52”W	43°20’12.07”N / 80°36’05.86”W
Altitude	301 m	302 m	305 m	330 m
Terrestrial management practices	Rehabilitated riparian zone dominated by deciduous trees	Undisturbed naturally forested riparian zone dominated by deciduous trees.	Grassed riparian zone	Undisturbed naturally forested riparian zone dominated by coniferous trees.
Dominant terrestrial buffer vegetation	*Alder* spp., *Populus* spp., silver maple (*Acer saccharinum*), multifloral rosevine (*Rosa multiflora*), Russian olive (*Elaegnus angustifolia*), and red-osier dogwood (*Cornus stolonifera)*	American beech (*Fagus grandifolia*), American basswood (*Tilia americana*), American hophornbeam (*Ostrya virginiana*), sugar maple (*Acer saccharum.*) and eastern hemlock (*Tsuga canadensis*)	Bentgrass (*Agrostis app.*), Panicled and purple-stemmed aster (*Symphyotrichum puniceum*)	Eastern White Cedar (*Thuga occidentalis*)
	Tile drained agriculture; maize (2017) - soybean (2018) rotation	Tile drained agriculture; maize (2018) - soybean (2017) rotation	Tile drained agriculture; maize (2018) - soybean (2017) rotation	Tile drained agriculture; maize (2018) - soybean (2017) rotation; At headwaters of Washington Creek
Terrestrial buffer age in 2017 (years)	33	150	60	100
Buffer Width (m)	30	100-130	20	50
Stream width (m)	5.15	5.41	4.40	2.82
Stream depth (m)	0.46	0.15	0.45	0.16
Stream pH	8.38	8.43	8.52	8.19
Stream dissolved organic C (mg C L^{-1})	5.32	5.08	4.83	1.76
Stream dissolved total N (mg N L^{-1})	9.09	9.41	8.98	13.70

4.2 Experimental Design

To quantify the nitrogen (N) and carbon (C) dynamics in the aquatic component of the RAFS, various types of RAFS were studied over a period of 2 years, 2017 and 2018.

Sampling Year 2017

Three different RAFS (also denoted as treatments), located along the same stretch of Washington Creek, were monitored: 1) a rehabilitated forest riparian area (RH), 2) an undisturbed natural forest riparian area dominated by deciduous vegetation (UNF-D), and 3) Herbaceous vegetation (HB) riparian area. The sampling season for the year 2017 ran from June 2017 to October 2017. Sampling for the year of 2017 started late summer on July 13th 2017, with October 31st 2017, being the last sampling date of the season. Water sampling was not conducted during the winter months, for both sampling years 2017 and 2018 due to inaccessibility to the sites. The data from the sampling year 2017 was divided into two seasons for data summarization and analytical purposes:

Summer 2017: July 13th, 2017 – September 14th, 2017

Fall 2017: September 28th, 2017 – October 31st, 2017

Sampling Year 2018

Four different RAFS (also denoted as treatments), located along the same stretch of Washington Creek, were monitored: 1) a rehabilitated forest riparian area (RH), 2) an undisturbed natural forest riparian area dominated by deciduous vegetation (UNF-D), 3) Herbaceous vegetation (HB), and 4) an undisturbed natural forest riparian area dominated by coniferous vegetation (UNF-C). An additional site (UNF-C) was added because UNF-D was flooded due to the high precipitation in April 2018 (www.toronto.weatherstats.ca). The sampling season for the year 2018 ran from 5th April 2018 to 19th October 2018. For the purpose of data summarization and analysis, the data from the sampling year 2018 was divided into the following three seasons:

Spring 2018: April 5th, 2018 – June 6th, 2018

Summer 2018: July 4th, 2018 – September 18th, 2018

Fall 2018: October 3rd, 2018 – October 19th, 2018

For GHG emissions and for chemical and physical characteristics of the aquatic component of RAFS, the sampling was carried out bi-weekly, and three samples were collected from each treatment for each analysis. The sampling was carried out during day light times, between 0900 hours to 1600 hours. Additionally, to reduce variability, sampling of each site was conducted approximately during the same time of the day. The sampling of the sites was always carried out from the most downstream site to the most upstream site to avoid sediment disturbance from impacting the data. For sites RH and HB, water samples and velocity readings were collected halfway through depth of the water column, at approximately 0.2m below the surface of the stream. The stream width at sites UNF-C and UNF-D was shallow, but the depth was enough to completely submerge the sample collection bottles parallel to the flowing stream and the flowmeter for data collection. Sediment sampling was carried out annually. The riparian effect on the reduction of total suspended solids (TSS) and stream sediment, is supported by extensive literature that exists. As per literature, for example, the presence of RAFS reduces the TSS concentration by 50% to 60% (U.S. EPA, 2010). Therefore, it was not deemed necessary to conduct the sediment sampling more than once a year due to the stream sediment's slow-changing characteristics and nutrient dynamics.

Due to the lack of an identical first-order stream in the Grand River Watershed that comprises of RAFS distribution with similar age and composition to Washington Creek, this study was pseudo-replicated. This limits the universality of the results, since the sample size is one, but pseudo-replication allows for the use of data for inferential statistics (Hurlbert, 1984).

4.3 Water Sampling and Analysis

4.3.1 Sample Collection and Storage

Stream adjacent to the respective riparian buffer was sampled bi-weekly, and three samples were collected for the purpose of performing chemical and physical characteristic analysis of the water samples. Water samples were collected in 500 ml Nalgene bottles and were filtered on-site using a 0.45µm syringe filter (Vogt et al., 2015). The samples were placed in a cooler until they were transported back to the Soil Ecosystem Dynamics Laboratory in Waterloo, Ontario, Canada, where they were stored in a cool, at 4 ℃, and dry place until analyzed.

4.3.2 Water Chemical and Physical Characteristics Analysis

The collected samples were used to determine the following chemical characteristics of the stream water: ammonium (NH_4^+), nitrate (NO_3^-), dissolved organic carbon (DOC), and total nitrogen (TN). The samples, stored at 4 ℃, were brought to room temperature before analytical tests were run. To determine the concentration of DOC and TN, the filtered water samples were run on the Shimadzu TOC-L with TN module analyzer (Shimadzu Corp., Kyoto, Japan), which uses combustion catalytic oxidation technology to measure DOC and TN in samples (EPA Method 415.3). NH_4^+ and NO_3^- were measured using colorimetric analysis. NH_4^+ was quantified through the colorimetric detection of the color formation after 1 hour of incubation (Afkhami and Norooz-Asl, 2008). The color formation results from the Berthelot reaction in the solution, where the concentration of NH_4^+ determines the color-changing intensity of the indophenol dye present in the solution (Afkhami and Norooz-Asl, 2008). The ideal detection wavelength for indophenol dye is 650 nm. Following the incubation period, the samples and standards were read on Shimadzu 1800 UV-Vis Spectrophotometer (Shimadzu Corp., Kyoto, Japan) for absorbance values (Afkhami and Norooz-Asl, 2008). The detection limit of this method was 0.015 mg NH_4^+-N L^{-1} (Afkhami and Norooz-Asl, 2008; Shimadzu Corp., Kyoto, Japan). Therefore, the sampling dates with potential NH_4^+ concentration values lower than the detection limit were eliminated from the analysis. Only the sampling dates with concentrations over the detection limit were used to calculate the mean seasonal NH_4^+ concentrations and run other statistical analyses. A similar colorimetric detection method was used to detect the concentration of NO_3^- in the filtered samples. In the case of NO_3^-, Griess reagent was used. Using the Shimadzu 1800 UV-Vis Spectrophotometer (Shimadzu Corp., Kyoto, Japan), the color formation by the Griess reagent was detected at a wavelength of 540 nm following incubation of 12 hours (Miranda et al., 2001).

Several physical characteristics were measured on-site using various lab equipment. YSI meter (Pro Plus Multiparameter Instrument) was used to quantify the following parameters: Air Temperature; Air Pressure; Water Temperature; Water Pressure; Dissolved Oxygen (DO) levels of the stream water; Conductivity of the stream water; pH of the stream water. Additionally, the stream's width and depth were measured using a measuring tape and a meter stick. Finally, the velocity of the stream was measured using the Swoffer Model 3000 Current Velocity Meter-Flowmeter (swoffer.com).

4.3.3 Environmental Parameters

Environmental parameters like Air Temperature and Water Temperature were measured on-site using YSI meter (Pro Plus Multiparameter Instrument).

4.4 Sediment Sampling and Analysis

4.4.1 Sample Collection and Storage

Triplicate sediment samples were collected annually using the Ekman dredge sampler. Sterilized high-density polyethylene (HDPE) or polytetrafluoroethylene (PTFE) containers were used for sample collection (U.S. EPA, 2001). Samples were collected with no headspace and were transported back to the Soil Ecosystem Dynamics Laboratory in Waterloo, Ontario, Canada, in a cooler. The samples were stored at 4 ℃ until analyzed. Unwanted materials, like large particles, trash, etc., were removed manually prior to analysis (U.S. EPA, 2001).

4.4.2 Sediment Chemical and Physical Characteristics

Sediment samples were prepared for chemical analysis by air drying the samples, followed by grinding the samples with mortar and pestle, and then sieving them using a 2 mm sieve. These samples were then analyzed for nitrate (NO_3^-), ammonium (NH_4^+), and pH. For nitrate (NO_3^-) and ammonium (NO_3^-) analysis, 25 ml of 2.0 M KCl was added to 5 g of the air-dried sediment to help extract NO_3^- and NH_4^+ from the sediment. A reciprocating shaker (Heidolpj Unimax 1010 DT) was used to mix the solution for 15 minutes at the rate of 180 rpm. Following this, the solution was filtered using the Whatman 42 filter paper. Colorimetric analysis, identical to the method used for water sample NO_3^- and NH_4^+ analysis, was used to determine the concentration of NO_3^- and NH_4^+ in the extract. Extracts were run on the Shimadzu 1800 UV-Vis Spectrophotometer (Shimadzu Corp., Kyoto, Japan) to determine: NH_4^+concentration through color development following 1 hour of incubation read at 640 nm wavelength (Foster 1995; Afkhami and Norooz-Asl, 2008); and NO_3^- concentration through color development after 12 hours of incubation read at 540 nm wavelength (Miranda et al., 2001).

Total Nitrogen (TN) and Organic Carbon (OC) were measured using the Costech CHNS-O 4010 Elemental Analyzer (Costech Analytical Technologies Inc., Valencia, USA). An excess amount of water was removed from the sediment using a pipette if necessary. Then the sediment was placed in the drying oven at 40 ℃ for 2 days. Once dry, the sediment was sieved using a 2mm sieve. To remove carbonates, 50 ml of 0.5M HCl was added to 2 grams of this sediment subsample, and the mixture was stirred three times over a 24-hour period using a reciprocating shaker (Midwood and Boutton, 1998). Following the shaking with HCl, the sample was rinsed using ultrapure water once every 24 hours for a total of 4 times over the next 4 days. Finally, the sample was then oven-dried for 2 days at 40 ℃ and ground using the ball-mill apparatus (Retsch, Haan, Germany). The ground sample was packed in tin capsules, weighted, and analyzed using the Elemental analyzer to measure OC and TN concentrations (Dyer, 2010). The pH of the sediment samples was measured using the standard 1:1 soil/water suspension (Miller and Kissel, 2010).

4.5 GHG Sampling and Analysis

Three main greenhouse gas (GHG) concentrations were measured from the water samples, including: carbon di-oxide (CO_2); methane (CH_4); and nitrous oxide (N_2O). To measure GHG concentrations, water samples were collected bi-weekly in 500 mL Kartell Graduated Rectangular HDPE Bottle with Cap. Samples were collected with no headspace to avoid interference with the GHG concentrations. Water samples collected for methane (CH_4) and nitrous oxide (N_2O) analysis were preserved using 10 $\mu l/ml$ of 50% $ZnCl_2$ (Zhu-Barker et al., 2015; Ostrom et al., 2016; Verhoeven et al., 2019) (approximately 5.5 ml) on site. Samples collected for carbon dioxide (CO_2) analysis were preserved using 5.5 ml of 1M HCl (Loughrin et al., 2017) on site. Using the dilution equation ($C_1V_1 = C_2V_2$), the approximate volume of 1M HCL required to bring the pH of the aquatic sample at pH value ≤ 2 was calculated. Since bicarbonate abundance is the largest contributor and pool of CO_2 in water bodies (Raymond et al., 2008), it is essential that its contribution is calculated. As a result of acidification, all the carbonate alkalinity sources in the sample are converted to CO_2 for direct measurement; and this step also reduces the interference from non-carbonate alkalinity sources that may be considered possible CO_2 otherwise (Loughrin et al., 2017). Samples were then transported back to the Soil Ecosystem Dynamics Laboratory in Waterloo, Ontario, Canada, where they were stored in a cool, preferably at 4 ℃, and dry place until analyzed for GHG concentrations.

Dissolved gases from the collected samples were analyzed using the gas chromatography method (Rosamand et al., 2012; Bieniada, 2020). The samples were prepared using the following steps. A 60 ml air-tight syringe (Luer-Lock Tip. BD, Franklin Lakes, NJ, USA), was connected to a three-way stopcock valve (2 Female Luers to Male Luer Lock, Nylon Body and Nylon Valve Plug; DWK Life Sciences, Millville, NJ, USA). The stored samples were brought to room temperature. 20 ml of the collected water sample was transferred into the 60 ml syringe. 20 ml of headspace was injected into the syringe containing the water sample. High-purity helium was injected at a flow rate of 30 ml/min. Following this, the syringe was shaken vigorously for 5 minutes by hand to dissolve the greenhouse gases out of the water and into the headspace. This headspace gas was then transferred into an evacuated 10 ml exetainer vial (Labco Ltd., Lampeter, UK), and the GHG concentrations were determined using Agilent 6890 Gas Chromatograph (AgilentTechnologies, Inc., Santa Clara, CA, USA) located in the Wetland Soils and Greenhouse Gas Exchange Lab, University of Waterloo, Waterloo, Ontario.

The concentration of the greenhouse gases was calculated using the following formulas (Bastviken et al., 2008; Bastviken et al., 2010):

<u>Formula</u>

$$C_{sample} = \frac{n_{total}}{V_{sample}}$$

$$n_{total} = n_{headspace} + n_{sample}$$

$$n_{total} = \left[\frac{(P_{pressure} * V_{gas})}{R * T} \right] + \left[P_{pressure} * K_H * V_{sample} \right]$$

<u>Legend</u>

$C_{sample} \left(\frac{mol}{L}\right)$ = concentration of GHG in the water sample

$n_{headspace}(moles)$ = number of moles of GHG in the headspace of the syringe

$n_{sample}(moles)$ = number of moles of GHG in the water sample

$V_{gas}(L)$ = volume of the inert gas (Helium) in the headspace of the syringe

$V_{sample}(L)$ = volume of the water sample in the syringe

$R\left(\frac{L\ atm}{K\ mol}\right)$ = gas constant (value = 0.082056)

$P_{pressure}(atm)$ = GHG partial pressure = $Total\ air\ pressure\ (atm) * \frac{mixing\ ratio\ of\ GHG\ in\ ppm}{10^6}$

$K_H\left(\frac{M}{atm}\right)$ = Henry's Law constant

K_H for CO_2 = 0.03691 $\left(\frac{M}{atm}\right)$ (Sanders et al., 2011)

K_H for N_2O = 0.02705 $\left(\frac{M}{atm}\right)$ (Warneck and Walliams, 2012)

K_H for CH_4 = 0.00151 $\left(\frac{M}{atm}\right)$ (Warneck and Walliams, 2012)

<u>Unit conversion</u>

$$C_{sample}\left(\frac{mol}{L}\right) = C_{sample}\left(\frac{\mu g}{L}\right)$$

Using Molar mass $\left(\frac{g}{mol}\right)$

$$\frac{\mu g}{L} = \frac{mol}{L} * \frac{g}{mol} * \frac{10^6\ \mu g}{g}$$

4.6 Statistical Analysis

To remove outliers in the data set, the Thompson Tau technique was used (Silva et al., 2018). Once the outliers were recognized and removed, Levene's test was run on the data to study the homogeneity of variance (Marques de Sa, 2007). Shapiro-Wilk test for normality (Steel et al., 1997) was also performed on the data. If the data does not fulfill the assumption of normality, the data can be log-transformed and tested again. If the data is still not normal, despite log-transformation, the statistical tests were still performed. When the data set is greater than 30, the central limit theorem justifies violating the normality assumption (Elliott and Woodward, 2007).

One-way analysis of variance (ANOVA) was used to determine if there were statistically significant differences between greenhouse gas concentrations (CO_2, CH_4, and N_2O), water characteristics (temperature, pressure, pH, DO levels, conductivity, discharge) or environmental characteristics (air temperature) among the different treatments within a season or among seasons within a treatment for each of the parameters. For data with non-homogenous variances, Welch test was performed (Tomarken and Serlin, 1986). Where significant differences were present in data (ANOVA or Welch test), Tukey's post hoc test or Games Howell test was performed to determine where exactly the significant difference was present for data with homogenous variance or heterogenous variance, respectively (Hilton and Armstrong, 2006).

Also known as the correlation coefficient, Pearson's correlation measures the degree of linearity between the variables that are being tested (Marques de Sa, 2007). The value of Pearson's correlation (denoted by r) lies between +1 and –1. A value of +1 represents a perfectly positive correlation between the two variables, and a value of –1 represents a perfectly negative correlation (Field, 2009). Consequently, a value of 0 would indicate no correlation between the tested variables (Field, 2009). In this study, Pearson's correlation was used to determine correlations amongst greenhouse gas concentrations (CO_2, CH_4, and N_2O), water characteristics (temperature, pressure, pH, DO levels, conductivity, discharge), and environmental characteristics (air temperature and air pressure). All statistical tests, except the data outlier test, were performed using the SPSS Statistics 25 for Windows (IBM Corp., 2017), with a type I error rate set at $p < 0.05$.

5.0 RESULTS

5.1 Stream Characteristics and Environmental Parameters

5.1.1 Air Temperature

The mean air temperature (in ℃), sample size 144, ranged from 3.67 ± 0.03 to 22.34 ± 0.86. The mean air temperature (in ℃) for RH, UNF-D, HB, and UNF-C sampling treatments were 12.83 ± 0.77, 13.79 ± 0.79, 13.83 ± 0.88, and 13.20 ± 1.02, respectively (refer to table 5.1). The mean seasonal air temperature (in ℃) for the sampling seasons summer 2017, fall 2017, spring 2018, summer 2018, and fall 2018 were 19.72 ± 0.31, 9.81 ± 0.75, 13.07 ± 0.77, 21.18 ± 0.39, and 4.07 ± 0.30, respectively (refer to table 5.2).

No statistically significant differences were found among treatments showing a lack of spatial variability for air temperature. However, a comparison of mean air temperature data, averaged by season, revealed that the mean seasonal air temperatures among seasons were significantly different, showing temporal variability of data. Data followed seasonal trends for both sampling years, 2017 and 2018.

5.1.2 Water Temperature

The mean water temperature (in ℃), sample size 144, ranged from 4.88 ± 0.23 to 18.51 ± 0.37. The mean water temperature (in ℃) for RH, UNF-D, HB, and UNF-C sampling treatments were 11.62 ± 0.66, 11.88 ± 0.52, 11.94 ± 0.59, and 9.94 ± 0.23, respectively (refer to table 5.1). The mean seasonal water temperature (in ℃) for the sampling seasons summer 2017, fall 2017, spring 2018, summer 2018, and fall 2018 were 15.69 ± 0.17, 9.32 ± 0.58, 10.47 ± 0.52, 16.49 ± 0.38, and 6.04 ± 0.29, respectively (refer to table 5.2). Like the air temperature, water temperature showed no spatial variability. Temporal variability, averaged by season, can be explained by general season trends with expected highest temperatures during summer months and lowest during the fall sampling seasons.

5.1.3 Water Pressure

The mean water pressure (mm Hg), sample size 144, ranged from 732.42 ± 0.17 to 740.87 ± 0.03. The mean water pressure (mm Hg) for RH, UNF-D, HB, and UNF-C sampling treatments were 736.56 ± 0.43, 736.12 ± 0.45, 735.94 ± 0.42, and 734.69 ± 0.64, respectively (refer to table 5.1). The mean seasonal water pressure (mm Hg) for the sampling seasons summer 2017, fall 2017, spring 2018, summer 2018, and fall 2018 were 734.74 ± 0.32, 736.53 ± 0.43, 733.64 ± 0.55, 734.86 ± 0.47, and 739.83 ± 0.34, respectively (refer to table 5.2). The statistical analysis depicts no significant spatial or temporal variability in the water pressure data.

5.1.4 pH

The mean water pH (sample size 144) ranged from 8.08 ± 0.02 to 8.70 ± 0.02. The mean pH for RH, UNF-D, HB, and UNF-C sampling treatments were 8.38 ± 0.02, 8.43 ± 0.03, 8.52 ± 0.02, and 8.19 ± 0.02, respectively (refer to table 5.1). The mean seasonal pH for the sampling seasons summer 2017, fall 2017, spring 2018, summer 2018, and fall 2018 were 8.24 ± 0.02, 8.37 ± 0.02, 8.37 ± 0.02, 8.46 ± 0.02, and 8.53 ± 0.05, respectively (refer to table 5.2).

When the mean seasonal pH values recorded throughout the sampling period were statistically compared, a few significant differences were found. Spatial variability in pH values exists among the treatments. pH values in the HB treatment (RH, p = 0.000; UNF-D, p = 0.026; UNF-C, p = 0.000) were significantly higher and that recorded in UNF-C (RH, p = 0.000; UNF-D, p = 0.000; HB, p = 0.000) sampling treatment was significantly lower than the other treatments. For the sampling year 2017, significant temporal variability was recorded between the pH values recorded in Summer 2017 and Fall 2017 (p = 0.007) sampling seasons. For the sampling year 2018, no temporal variability was recorded amongst the pH values.

5.1.5 Dissolved Oxygen (DO)

The mean dissolved oxygen (in mg/L), sample size 144, ranged from 7.62 ± 0.08 to 13.42 ± 0.46. The mean dissolved oxygen (in mg/L) for RH, UNF-D, HB, and UNF-C sampling treatments were 10.27 ± 0.33, 9.88 ± 0.26, 10.93 ± 0.32, and 8.77 ± 0.13, respectively (refer to table 5.1). The mean seasonal dissolved oxygen (in mg/L) for the sampling seasons summer 2017, fall 2017, spring 2018, summer 2018, and fall 2018 were 12.01 ± 0.28, 10.06 ± 0.18, 10.48 ± 0.33, 8.32 ± 0.13, and 10.07 ± 0.29, respectively (refer to table 5.2).

Significant spatial differences in DO data were observed among treatments. The HB sampling treatment has significantly higher DO as compared to UNF-D (p = 0.015) and UNF-C treatment (p = 0.000). Through observation of the seasonal data for the sampling year 2017, it can be concluded that the average of the mean seasonal DO recorded during the Summer 2017 sampling season is significantly higher (p = 0.000) than the DO values recorded in Fall 2017. Finally, the DO values measured during the Summer 2018 sampling season were significantly lower than all the other seasons for the sampling year 2018 (Spring 2018, p = 0.000; and Fall 2018, p = 0.024). No clear temporal trend DO data was observed.

5.1.6 Electric Conductivity

The mean water conductivity (in µS/cm), sample size 144, ranged from 666.38 ± 3.68 to 771.38 ± 3.58. The mean conductivity (in µS/cm) for RH, UNF-D, HB, and UNF-C sampling treatments were 735.08 ± 2.74, 726.60 ± 7.52, 690.43 ± 3.00, and 692.84 ± 1.10, respectively (refer to table 5.1). The mean seasonal conductivity (in µS/cm) for the sampling seasons summer 2017, fall

2017, spring 2018, summer 2018, and fall 2018 were 704.83 ± 3.87, 742.71 ± 4.32, 685.69 ± 7.99, 695.90 ± 2.82, and 742.53 ± 7.05, respectively (refer to table 5.2).

Amongst different treatments, the mean seasonal conductivity of both the HB (RH, p = 0.000; UNF-D, p = 0.000) and the UNF-C (RH, p = 0.000; UNF-D, p = 0.016) sampling treatments were significantly lower than the values recorded at the RH and UNF-D sampling treatments. When looking at the averages of mean seasonal conductivity within different seasons, conductivity recorded during Fall 2017 (p = 0.000 for all seasons) and Fall 2018 (p = 0.000 for all seasons) was significantly higher than all the other seasons in each sampling year. Therefore, a temporal trend of higher Fall conductivity values was observed.

5.1.7 Discharge

The mean water discharge (in m^3/s), sample size 108, ranged from 0.04 ± 0.004 to 0.73 ± 0.06. The mean discharge (in m^3/s) for RH, UNF-D, HB, and UNF-C sampling treatments were 0.35 ± 0.03, 0.35 ± 0.05, 0.49 ± 0.09, and 0.12 ± 0.03, respectively (refer to table 5.1). The mean seasonal discharge (in m^3/s) for the sampling seasons spring 2018, summer 2018, and finally fall 2018 were 0.32 ± 0.03, 0.24 ± 0.04, and 0.43 ± 0.08, respectively (refer to table 5.2). Spatial data revealed that the discharge at the UNF-C sampling treatment was significantly lower than the other three (RH, p = 0.000; HB, p = 0.000; UNF-D, p = 0.000) sampling treatments. There was not enough data to statistically compare the temporal variability in the discharge values.

Table 5.1: Mean aquatic physical and chemical parameters, averaged by treatment, recorded at the Washington Creek, Ontario, Canada, during the sampling year 2017 and 2018 from the aquatic component of the rehabilitated forest riparian buffer (RH), undisturbed natural forest riparian buffer dominated by deciduous vegetation (UNF-D), herbaceous vegetation buffer (HB), and undisturbed natural forest riparian buffer dominated by coniferous vegetation (UNF-C).

Riparian Zones	Air T (ºC)	Water T (ºC)	Water P (mm Hg)	pH	DO (mg/L)	Conductivity (µS/cm)	Discharge (m^3/s)
RH	12.83 (0.77)^{a}	11.62 (0.66)^{a}	736.56 (0.43)^{a}	8.38 (0.02)^{a}	10.27 (0.33)^{ab}	735.08 (2.74)^{a}	0.35 (0.03)^{a}
UNF-D	13.79 (0.79)^{a}	11.88 (0.52)^{a}	736.12 (0.45)^{a}	8.43 (0.03)^{a}	9.88 (0.26)^{ac}	726.60 (7.52)^{a}	0.35 (0.05)^{a}
HB	13.83 (0.88)^{a}	11.94 (0.59)^{a}	735.94 (0.42)^{a}	8.52 (0.02)^{b}	10.93 (0.32)^{b}	690.43 (3.00)^{b}	0.49 (0.09)^{a}
UNF-C	13.20 (1.02)^{a}	9.94 (0.23)^{a}	734.69 (0.64)^{a}	8.19 (0.02)^{c}	8.77 (0.13)^{c}	692.84 (1.10)^{cb}	0.12 (0.03)^{b}

*Significant difference among treatments within the sampling period is represented by $^{abc.}$

**() represent Standard Deviation

Table 5.2: Mean seasonal aquatic physical and chemical parameters, averaged by season, recorded at the Washington Creek, Ontario, Canada, during the sampling year 2017 and 2018 from the aquatic component of the rehabilitated forest riparian buffer (RH undisturbed natural forest riparian buffer dominated by deciduous vegetation (UNF-D), herbaceous vegetation buffer (HB), and undisturbed natural forest riparian buffer dominated by coniferous vegetation (UNF-C).

Seasons	Air T (ºC)	Water T (ºC)	Water P (mmHg)	pH	DO (mg/L)	Conductivity (µS/cm)	Discharge (m^3/s)
Summer 2017	19.72 (0.31)^{A}	15.69 (0.17)^{A}	734.74 (0.32)^{A}	8.24 (0.02)^{A}	12.01 (0.28)^{A}	704.83 (3.87)^{A}	--
Fall 2017	9.81 (0.75)^{B}	9.32 (0.58)^{B}	736.53 (0.43)^{A}	8.37 (0.02)^{B}	10.06 (0.18)^{B}	742.71 (4.32)^{B}	--
Spring 2018	13.07 (0.77)^{C}	10.47 (0.52)^{CB}	733.64 (0.55)^{A}	8.37 (0.02)^{A}	10.48 (0.33)^{A}	685.69 (7.99)^{A}	0.32 (0.03)
Summer 2018	21.18 (0.39)^{DA}	16.49 (0.38)^{DA}	734.86 (0.47)^{A}	8.46 (0.02)^{A}	8.32 (0.13)^{B}	695.90 (2.82)^{A}	0.24 (0.04)
Fall 2018	4.07 (0.30)^{EB}	6.04 (0.29)^{EB}	739.83 (0.34)^{A}	8.53 (0.05)^{A}	10.07 (0.29)^{A}	742.53 (7.05)^{B}	0.43 (0.08)

*Significant difference among seasons within the sampling period is represented by ^{ABC}

**() represent Standard Deviation

5.2 Water Chemistry

5.2.1 Non-Particulate Organic Carbon (DOC)

The mean DOC concentrations (mg C L^{-1}), sample size 156, of RH, UNF-D, HB, and UNF-C riparian agroforestry systems were 8.86 ± 0.56, 9.04 ± 0.63, 9.63 ± 0.67, and 8.71 ± 0.88, respectively (refer to table 5.3), with values ranging from 1.55 ± 0.10 mg C L^{-1} to 12.35 ± 3.17 mg C L^{-1}. Riparian zone averages for DOC concentration shows that on average UNF-C recorded lower values compared to the other treatments; significantly from UNF-D ($p = 0.035$) treatment only. For the sampling year 2017, the DOC concentrations measured in the RH treatment in fall 2017 (12.35 ± 3.17 mg L^{-1}) sampling season were significantly different from that measured in all the other seasons including summer 2017 (5.10 ± 0.48 mg L^{-1}; $p = 0.003$). Similar to RH, the DOC concentration measured during the sampling season fall 2017 (12.03 ± 2.71 mg L^{-1}) at the HB treatment was significantly different from the DOC concentration recorded summer 2017 (3.92 ± 0.87 mg L^{-1}; $p = 0.003$ sampling season. There was no significance difference found amongst seasons within a given treatment for sampling year 2018.

The mean seasonal DOC concentrations (mg C L^{-1}) recorded for Summer 2017 and Fall 2017, Spring 2018, Summer 2018, and Fall 2018 sampling seasons were 4.72 ± 0.44, 11.44 ± 1.60, 2.86 ± 0.30, 2.40 ± 1.06, and 2.98 ± 0.28, respectively (refer to table 5.3). There was no significant difference found among treatments when DOC concentrations for each of the seasons were analyzed separately. The average seasonal values reflect the DOC concentrations measured during fall 2017 sampling season were significantly higher ($p = 0.000$) than all other seasons. Although not significant, year-over-year data suggests that DOC concentrations were higher in the sampling year 2017 versus the sampling year 2018.

Table 5.3: Mean seasonal aquatic Dissolved Organic Carbon (DOC) concentration (mg C L^{-1}) recorded at the Washington Creek, Ontario, Canada, during the sampling year 2017 and 2018 for the aquatic component of the rehabilitated forest riparian buffer (RH), undisturbed natural forest riparian buffer dominated by deciduous vegetation (UNF-D), herbaceous vegetation buffer (HB), and undisturbed natural forest riparian buffer dominated by coniferous vegetation (UNF-C).

		RH	UNF-D	HB	UNF-C	Season ($\bar{x}$)
DOC mg C L^{-1}	**Spring 2017**	--	--	--	--	--
	Summer 2017	5.10 (0.48)^{Aa}	5.14 (0.93)^{Aa}	3.92 (0.87)^{Aa}	--	4.72 (0.44)^{A}
	Fall 2017	12.35 (3.17)^{Ba}	9.94 (2.69)^{Aa}	12.03 (2.71)^{Ba}	--	11.44 (1.60)^{B}
	Spring 2018	3.23 (0.21)^{Aa}	3.79 (0.74)^{Aa}	2.56 (0.57)^{Aa}	1.84 (0.25)^{Aa}	2.86 (0.30)^{A}
	Summer 2018	2.56 (0.16)^{Aa}	3.26 (0.75)^{Aa}	2.24 (0.15)^{Aa}	1.55 (0.10)^{Aa}	2.40 (1.06)^{A}
	Fall 2018	3.38 (0.57)^{Aa}	3.28 (0.55)^{Aa}	3.39 (0.63)^{Aa}	1.88 (0.24)^{Aa}	2.98 (0.28)^{A}
	Riparian Zone ($\bar{x}$)	5.32 (0.83)^{ab}	5.08 (1.27)^{a}	4.83 (0.79)^{ab}	1.76 (0.10)^{b}	

*Significant difference among seasons within a treatment is represented by ^{ABC}; Significant difference among treatments within a season is represented by $^{abc.}$

**() represent Standard Deviation

5.2.2 Total Nitrogen (TN)

The mean TN concentrations (mg N L^{-1}), sample size 156, of RH, UNF-D, HB, and UNF-C riparian agroforestry systems were 9.09 ± 0.22, 9.41 ± 0.27, 8.98 ± 0.15, and 13.70 ± 0.21, respectively (refer to table 5.4), with values ranging from 8.21 ± 0.85 mg N L^{-1} to 14.36 ± 0.32 mg N L^{-1}. Riparian zone averages for DOC concentrations show that on average UNF-C recorded significantly higher ($p = 0.000$) values compared to the other treatments. No other significant differences were found among seasons within treatments.

The mean seasonal TN concentrations (mg N L^{-1}) recorded for summer 2017 and fall 2017, spring 2018, summer 2018, and fall 2018 sampling seasons were 9.61 ± 0.44, 8.56 ± 0.34, 10.27 ± 0.30, 10.87 ± 0.17, and 9.85 ± 0.44, respectively (refer to table 5.4). The average of mean seasonal values shows that the sampling season summer 2018 had significantly different TN concentrations than fall 2017 ($p = 0.000$) and spring 2018 ($p = 0.032$) sampling season. No other significant trend was found among treatments within seasons. Year-over-year data suggests that DOC concentrations were higher (not significant) in the sampling year 2018 versus the sampling year 2017.

Table 5.4: Mean seasonal aquatic Total Nitrogen (N) concentration (mg N L^{-1}) recorded at the Washington Creek, Ontario, Canada, during the sampling year 2017 and 2018 for the aquatic component of the rehabilitated forest riparian buffer (RH), undisturbed natural forest riparian buffer dominated by deciduous vegetation (UNF-D), herbaceous vegetation buffer (HB), and undisturbed natural forest riparian buffer dominated by coniferous vegetation (UNF-C).

		RH	**UNF-D**	**HB**	**UNF-C**	**Season ($\bar{x}$)**
TN mg N L^{-1}	**Spring 2017**	--	--	--	--	--
	Summer 2017	9.39 (0.84)^{Aa}	10.37 (0.89)^{Aa}	9.08 (0.51)^{Aa}	--	9.61 (0.44)^{AB}
	Fall 2017	8.82 (0.57)^{Aa}	8.21 (0.85)^{Aa}	8.63 (0.26)^{Aa}	--	8.56 (0.34)^{A}
	Spring 2018	8.97 (0.21)^{Aa}	9.25 (0.17)^{Aa}	8.77 (0.25)^{Aa}	14.08 (0.05)^{Ab}	10.27 (0.30)^{A}
	Summer 2018	9.57 (0.22)^{Aa}	10.02(0.17)^{Aa}	9.54 (0.15)^{Aa}	14.36 (0.32)^{Ab}	10.87 (0.17)^{B}
	Fall 2018	8.70 (0.40)^{Aa}	9.18 (0.42)^{Aa}	8.87 (0.47)^{Aa}	12.65 (0.32)^{Ab}	9.85 (0.44)^{AB}
	Riparian Zone ($\bar{x}$)	9.09 (0.22)^{a}	9.41 (0.27)^{a}	8.98 (0.15)^{a}	13.70 (0.21)^{b}	

*Significant difference among seasons within a treatment is represented by ^{ABC}; Significant difference among treatments within a season is represented by $^{abc.}$

**() represent Standard Deviation

5.2.3 Ammonium (NH_4^+) Concentrations

The mean NH_4^+ concentrations (mg NH_4^+-N L^{-1}), sample size 204, of RH, UNF-D, HB, and UNF-C riparian agroforestry systems were 0.05 ± 0.006, 0.06 ± 0.006, 0.08 ± 0.013, and 0.09 ± 0.01, respectively (refer to table 5.5), with values ranging from 0.013 ± 0.004 mg NH_4^+-N L^{-1} to 0.264 ± 0.08 mg NH_4^+-N L^{-1}. There were no significant differences among the final average NH_4^+ concentrations of each treatment. With the RH and UNF-D treatment, no significant differences were found amongst the seasonal values recorded. For the HB site, no significant difference was found in the 2017 seasonal data, whereas there was a significant difference between the NH_4^+ concentration measured during fall 2018 (0.264 ± 0.08 mg L^{-1}) versus the concentration measured in spring 2018 (0.019 ± 0.004 mg L^{-1}; $p = 0.00$), and summer 2018 (0.069 ± 0.02 mg L^{-1}; $p = 0.007$) sampling seasons. Furthermore, for the UNF-C treatment the NH_4^+ concentration measured during the fall 2018 (0.229 ± 0.05 mg L^{-1}; $p = 0.003$) sampling season was significantly ($p = 0.025$) different than the values recorded for the summer 2018 (0.028 ± 0.007 mg L^{-1}) sampling season. There were no other significant differences among seasons within treatments.

The mean seasonal NH_4^+ concentrations (mg NH_4^+-N L^{-1}) recorded for summer 2017 and fall 2017, spring 2018, summer 2018, and fall 2018 sampling seasons were 0.04 ± 0.005, 0.01 ± 0.002, 0.02 ± 0.003, 0.05 ± 0.007, and 0.20 ± 0.03, respectively (refer to table 5.5). The seasonal average for fall 2018 ($p=0.000$) sampling season was significantly higher compared to all the other sampling seasons. Year-over-year data suggests that NH_4^+ concentrations were higher (not significant) in the sampling year 2018 versus the sampling year 2017. There were no significant reportable differences for the NH_4^+ concentration measured among treatments within seasons.

Table 5.5: Mean seasonal aquatic Ammonium (NH_4^+) concentration (mg NH_4^+-N L^{-1}) recorded at the Washington Creek, Ontario, Canada, during the sampling year 2017 and 2018 for the aquatic component of the rehabilitated forest riparian buffer (RH), undisturbed natural forest riparian buffer dominated by deciduous vegetation (UNF-D), herbaceous vegetation buffer (HB), and undisturbed natural forest riparian buffer dominated by coniferous vegetation (UNF-C).

		RH	UNF-D	HB	UNF-C	Season ($\bar{x}$)
NH_4^+ (mg NH_4^+-N L^{-1} water)	**Spring 2017**	--	--	--	--	--
	Summer 2017	0.039 (0.009)^{Aa}	0.043 (0.009)^{Aa}	0.038 (0.009)^{Aa}	--	0.04 (0.005)^{A}
	Fall 2017	0.014 (0.004)^{Aa}	0.012 (0.002)^{Aa}	0.013 (0.004)^{Aa}	--	0.01 (0.002)^{A}
	Spring 2018	0.037 (0.008)^{Aa}	0.016 (0.006)^{Aa}	0.019 (0.004)^{Aa}	0.028 (0.03)^{ABa}	0.02 (0.003)^{A}
	Summer 2018	0.032 (0.013)^{Aa}	0.062 (0.012)^{Aa}	0.069 (0.02)^{Aa}	0.028 (0.007)^{Aa}	0.05 (0.007)^{A}
	Fall 2018	0.121 (0.038)^{Aa}	0.185 (0.043)^{Aa}	0.264 (0.08)^{Ba}	0.229 (0.05)^{Ba}	0.20 (0.03)^{B}
	Riparian Zone ($\bar{x}$)	0.05 (0.006)^{a}	0.06 (0.006)^{a}	0.08 (0.013)^{a}	0.09 (0.01)^{a}	

*Significant difference among seasons within a treatment is represented by ^{ABC}; Significant difference among treatments within a season is represented by $^{abc.}$

**() represent Standard Deviation

5.2.4 Nitrate (NO_3^-) Concentrations

The mean NO_3^- concentrations (mg NO_3^--N L^{-1}), sample size 204, of RH, UNF-D, HB, and UNF-C riparian agroforestry systems were 8.86 ± 0.56, 9.04 ± 0.63, 9.63 ± 0.67, and 8.71 ± 0.88, respectively (refer to table 5.6), with values ranging from 4.26 ± 0.23 mg NO_3^- -N L^{-1} to 18.95 ± 1.09 mg NO_3^--N L^{-1}. The riparian zone average did not show any significant differences among treatments for nitrate concentration. For the sampling year 2017, all three treatments (RH, p = 0.00; UNF-D, p = 0.00; HB, p = 0.00) studied showed significantly higher values for NO_3^- concentrations measured in fall 2017 sampling seasons compared to summer 2017 sampling season. For the sampling year 2018, there was no significant difference found among seasons within treatments.

The mean seasonal NO_3^- concentrations (mg NO_3^--N L^{-1}) recorded for summer 2017 and fall 2017, spring 2018, summer 2018, and fall 2018 sampling seasons were 9.86 ± 0.21, 16.69 ± 0.97, 8.76 ± 0.451, 7.29 ± 0.44, and 4.99 ± 0.27, respectively (refer to table 5.6). Individually looking at the data collected for each of the sampling seasons, there were no significant differences among treatments for the NO_3^- concentrations measured during the summer 2017, fall 2017, and spring 2018 sampling seasons. For summer 2018 sampling season, it was observed that the values measured at the UNF-C (9.71 ± 1.02 mg L^{-1}) site were significantly different from all the other treatments including RH (6.30 ± 0.70 mg L^{-1}; p = 0.022), UNF-D (6.65 ± 0.76 mg L^{-1}; p = 0.049), and HB (6.51 ± 0.73 mg L^{-1}; p = 0.036). Finally, the concentrations observed in the UNF-C (6.91 ± 0.43 mg L^{-1}) treatment during the sampling season Fall 2018 (RH, p = 0.00; UNF-D, p = 0.00; HB, p = 0.00) was also significantly different than those measured in all the other treatments. Year-over-year data suggests that NO_3^- concentrations, although not significant, were higher in the sampling year 2017 versus the sampling year 2018.

Table 5.6: Mean seasonal aquatic Nitrate (NO_3^-) concentration (mg NO_3^--N L^{-1}) recorded at the Washington Creek, Ontario, Canada, during the sampling year 2017 and 2018 for the aquatic component of the rehabilitated forest riparian buffer (RH), undisturbed natural forest riparian buffer dominated by deciduous vegetation (UNF-D), herbaceous vegetation buffer (HB), and undisturbed natural forest riparian buffer dominated by coniferous vegetation (UNF-C).

		RH	UNF-D	HB	UNF-C	Season ($\bar{x}$)
NO_3^- (mg NO_3^--N L^{-1} water)	**Spring 2017**	--	--	--	--	--
	Summer 2017	9.98 (0.37)^{Aa}	9.76 (0.30)^{Aa}	9.83 (0.42)^{Aa}	--	9.86 (0.21)^{A}
	Fall 2017	15.29 (1.53)^{Ba}	15.84 (2.16)^{Ba}	18.95 (1.09)^{Ba}	--	16.69 (0.97)^{B}
	Spring 2018	8.40 (0.66)^{Aa}	8.53 (0.76)^{Aa}	8.59 (0.65)^{Aa}	9.53 (0.35)^{Aa}	8.76 (0.451)^{CD}
	Summer 2018	6.30 (0.70)^{Aa}	6.65 (0.76)^{Aa}	6.51 (0.73)^{Aa}	9.71 (1.02)^{Ab}	7.29 (0.44)^{C}
	Fall 2018	4.36 (0.25)^{Aa}	4.26 (0.28)^{Aa}	4.26 (0.23)^{Aa}	6.91 (0.43)^{Ab}	4.99 (0.27)^{D}
	Riparian Zone ($\bar{x}$)	8.86 (0.56)^{a}	9.04 (0.63)^{a}	9.63 (0.67)^{a}	8.71 (0.88)^{a}	

*Significant difference among seasons within a treatment is represented by ^{ABC}; Significant difference among treatments within a season is represented by $^{abc.}$

**() represent Standard Deviation

5.3 Sediment Characteristics and Chemistry

5.3.1 Organic Carbon (OC)

The annual mean organic carbon (OC) in the stream sediment samples ranged from 5.76E-03 ± 7.24E-05 mg/L to 45.87E-03 ± 8.38E-04 mg/L of C. For the sampling year 2017, the sediment OC (in mg C L^{-1}) values measured at the riparian treatments RH, UNF-D, and HB were 19.14E-03 ± 8.41E-04, 5.77E-03 ± 2.75E-04, 5.76E-03 ± 7.24E-05, respectively (refer to table 5.7). For the sampling year 2018, the OC (in mg C L^{-1}) values measured at the riparian treatments RH, UNF-D, HB, and UNF-C were 45.87E-03 ± 8.38E-04, 8.65E-03 ± 1.6E-04, 6.59E-03 ± 4.49E-05, and 14.13E-03 ± 4.47E-04, respectively (refer to table 5.7). Sampling treatment RH (32.51E-03 ± 8.40E-04) had the highest OC concentration in its sediment spatially. Temporally, the sampling year 2018 (18.81E-03 ± 3.74E-04) recorded higher OC concentration in the stream sediment as compared to the results from the 2017 (10.23E-03 ± 3.96E-04) samples.

5.3.2 Total Nitrogen (TN)

Total nitrogen (TN) from the sediment samples collected across different treatments, located along the Washington Creek, ranged from 5.21E-04 ± 1.86E-05 mg/L to 41.83E-04 ± 9.59E-05 mg/L of N. For the sampling year 2017, the TN (in mg N L^{-1}) values measured at the riparian treatments RH, UNF-D, and HB were 21.12E-04 ± 9.15E-05, 6.86E-04 ± 2.32E-05, and 5.74E-04 ± 4.26E-06, respectively (refer to table 5.7). For the sampling year 2018, the TN (in mg N L^{-1}) values measured at the riparian treatments RH, UNF-D, HB, and UNF-C were 41.83E-04 ± 9.59E-05, 6.17E-04 ± 1.30E-05, 5.21E-04 ±1.86E-05, and 9.89E-04 ± 3.17E-05, respectively (refer to table 5.7). On average, the sediment TN (in mg N L^{-1}) concentration for the year 2018 (15.78E-04 ± 3.98E-05) was higher than that of the 2017 (11.24E-04 ± 3.96E-05) sampling year. When looking at the average TN concentrations amongst riparian zones over the sampling period, RH (31.48E-04 ± 9.37E-05) sampling treatment had significantly higher sediment TN concentrations compared to all the other treatments (UNF-D, 6.52E-04 ± 1.81E-05; HB, 5.47E-04 ± 1.14E-05; and UNF-C, 9.89E-04 ± 3.17E-05).

Table 5.7: Mean annual sediment Total Nitrogen (TN) concentration (mg N L^{-1}), Organic Carbon (OC) concentration (mg C L^{-1}), and pH (in units) recorded at the Washington Creek, Ontario, Canada, during the sampling year 2017 and 2018 from the aquatic component of the rehabilitated forest riparian buffer (RH), undisturbed natural forest riparian buffer dominated by deciduous vegetation (UNF-D), herbaceous vegetation buffer (HB), and undisturbed natural forest riparian buffer dominated by coniferous vegetation (UNF-C).

Parameters		**RH**	**UNF-D**	**HB**	**UNF-C**	**Sampling Year**
TN (mg N L^{-1})	2017	21.12E-04 (9.15E-05)	6.86E-04 (2.32E-05)	5.74E-04 (4.26E-06)	--	11.24E-04 (3.96E-05)
	2018	41.83E-04 (9.59E-05)	6.17E-04 (1.30E-05)	5.21E-04 (1.86E-05)	9.89E-04 (3.17E-05)	15.78E-04 (3.98E-05)
	Riparian Zone $(\bar{x})$	31.48E-04 (9.37E-05)	6.52E-04 (1.81E-05)	5.47E-04 (1.14E-05)	9.89E-04 (3.17E-05)	
OC (mg C L^{-1})	2017	19.14E-03 (8.41E-04)	5.77E-03 (2.75E-04)	5.76E-03 (7.24E-05)	--	10.23E-03 (3.96E-04)
	2018	45.87E-03 (8.38E-04)	8.65E-03 (1.6E-04)	6.59E-03 (4.49E-05)	14.13E-03 (4.47E-04)	18.81E-03 (3.74E-04)
	Riparian Zone $(\bar{x})$	32.51E-03 (8.40E-04)	7.21E-03 (2.21E-04)	6.18E-03 (5.86E-05)	14.13E-03 (4.47E-04)	
pH (in units)	2017	8.01 (0.009)	8.03 (0.012)	8.20 (0.021)	--	8.08 (0.014)
	2018	8.32 (0.008)	8.04 (0.010)	8.19 (0.030)	8.04 (0.014)	8.15 (0.014)
	Riparian Zone $(\bar{x})$	8.16 (0.006)	8.03 (0.011)	8.20 (0.025)	8.04 (0.014)	

*() represent Standard Deviation

5.3.3 Ammonium (NH_4^+) Concentrations

The annual mean NH_4^+ concentrations in the aquatic sediment ranged from 1.48 ± 0.078 mg/L to 4.50 ± 0.073 mg/L of NH_4^+-N. For the sampling year 2017, the NH_4^+ concentrations (in mg/L of NH_4^+-N) for RH, UNF-D, and HB riparian treatments were 3.51 ± 0.045, 2.51 ± 0.067, and 1.48 ± 0.073, respectively (refer to table 5.8). NH_4^+ concentrations (in mg/L of NH_4^+-N) for the sampling year 2018 for RH, UNF-D, and HB riparian treatments were 4.50 ± 0.073, 2.80 ± 0.045, 1.50 ± 0.067, and 3.60 ± 0.073, respectively (refer to table 5.8). On average, the NH_4^+ concentration (in mg/L of NH_4^+-N) for year 2018 (3.10 ± 0.065) was higher than that of the 2017 (2.50 ± 0.062) sampling year. When looking at the average NH_4^+ concentrations for riparian zones over the sampling period, RH (4.00 ± 0.059) sampling treatment has the highest average NH_4^+ concentrations compared to all the other treatments (UNF-D, 2.66 ± 0.056; HB, 1.49 ± 0.070; and UNF-C, 3.60 ± 0.073). Results are based on annual data; not enough data was available to conduct statistical analysis.

5.3.4 Nitrate (NO_3^-) Concentrations

The annual mean NO_3^- concentrations in the aquatic sediment ranged from 0.078 ± 0.003 mg/L to 0.127 ± 0.005 mg/L of NO_3^--N. For the sampling year 2017, the NO_3^- concentrations (in mg/L of NO_3^--N) for RH, UNF-D, and HB riparian treatments were 0.078 ± 0.003, 0.116 ± 0.005, and 0.127 ± 0.006, respectively (refer to table 5.8). NO_3^- concentrations (in mg/L of NO_3^--N) for the sampling year 2018 for RH, UNF-D, and HB riparian treatments were 0.127 ± 0.005, 0.078 ± 0.006, 0.116 ± 0.003, and 0.127 ± 0.006, respectively (refer to table 5.8). On average, the NO_3^- concentration (in mg/L of NO_3^--N) for the year 2018 (0.112 ± 0.005) was higher than that of the 2017 (0.107 ± 0.005) sampling year. When looking at the average NO_3^- concentrations for riparian zones over the sampling period, RH (0.127 ± 0.005) and UNF-C (0.127 ± 0.006) sampling treatments have the highest average NO_3^- concentrations compared to the HB (0.116 ±

0.003) and UNF-D (0.078 ± 0.006) sampling treatment. Results are based on annual data; not enough data was available to conduct statistical analysis.

5.3.5 pH

The pH of the sediment collected from different treatments across Washington Creek ranged from 8.01 ± 0.009 to 8.32 ± 0.008. For the sampling year 2017, sediment pH values for the riparian treatments RH, UNF-D, and HB were 8.01 ± 0.009, 8.03 ± 0.012, and 8.20 ± 0.021, respectively (refer to table 5.7). pH values for the sampling year 2018 for the riparian treatments were as following: RH, 8.32 ± 0.008; UNF-D, 8.04 ± 0.010; HB, 8.19 ± 0.030; and UNF-C, 8.04 ± 0.014 (refer to table 5.7). There was insignificant variability in the pH values amongst different treatments and between the two sampling years. On average, the pH of the sediment was higher for the sampling year 2018 (8.15 ± 0.014) than that of the 2017 (8.08 ± 0.014) sampling year. Spatial data of pH values show that UNF-D (8.03 ± 0.014) has the lowest and HB (8.20 ± 0.025) has the highest recorded sediment pH among the treatments.

Table 5.8: Mean annual sediment Ammonium (NH_4^+) concentration (mg NH_4^+-N L^{-1}) and Nitrate (NO_3^-) concentration (mg NO_3^--N L^{-1}) recorded at the Washington Creek, Ontario, Canada, during the sampling year 2017 and 2018 from the aquatic component of the rehabilitated forest riparian buffer (RH), undisturbed natural forest riparian buffer dominated by deciduous vegetation (UNF-D), herbaceous vegetation buffer (HB), and undisturbed natural forest riparian buffer dominated by coniferous vegetation (UNF-C).

Parameters		**RH**	**UNF-D**	**HB**	**UNF-C**	**Sampling Year**
NH_4^+ (mg NH_4^+-N L^{-1} water)	2017	3.51 (0.045)	2.51 (0.067)	1.48 (0.073)	--	2.50 (0.062)
	2018	4.50 (0.073)	2.80 (0.045)	1.50 (0.067)	3.60 (0.073)	3.10 (0.065)
	Riparian Zone ($\bar{x}$)	4.00 (0.059)	2.66 (0.056)	1.49 (0.070)	3.60 (0.073)	
NO_3^- (mg NO_3^--N L^{-1} water)	2017	0.078 (0.003)	0.116 (0.005)	0.127 (0.006)	--	0.107 (0.005)
	2018	0.127 (0.005)	0.078 (0.006)	0.116 (0.003)	0.127 (0.006)	0.112 (0.005)
	Riparian Zone ($\bar{x}$)	0.102 (0.004)	0.097 (0.005)	0.121 (0.004)	0.127 (0.006)	

*() represent Standard Deviation

5.4 GHG Concentrations

5.4.1 CO_2 Concentrations

The mean CO_2 concentration (g L^{-1} of CO_2-C), sample size 185, measured from riparian streams with RH, UNF-D, HB, and UNF-C vegetation were 1.25 ± 0.05, 1.25 ± 0.05, 1.28 ± 0.04, and 1.15 ± 0.05, respectively (refer to table 5.9) with values ranging from 1.13 ± 0.06 g L^{-1} to 1.66 ± 0.03 g L^{-1} of CO_2-C. Amongst the four riparian treatments, although not significant, RH and UNF-D recorded the lowest (1.25 ± 0.05 g L^{-1} of CO_2-C for both) and UNF-C the highest (1.15 ± 0.05 g L^{-1} of CO_2-C) CO_2 concentration. There were no other significant differences among seasons within treatments.

The mean seasonal CO_2 concentration (g L^{-1} of CO_2-C) of the stream component for summer 2017 and fall 2017, spring 2018, summer 2018, and fall 2018 sampling seasons were 1.21 ± 0.06, 1.16 ± 0.08, 1.43 ± 0.05, 1.42 ± 0.03, and 1.22 ± 0.03, respectively (refer to table 5.9 and figure 5.1). Although not significant, amongst the five sampling seasons, fall 2017 recorded the lowest (1.16 ± 0.08 g L^{-1} of CO_2-C; not significant) and spring 2018 the highest (1.43 ± 0.05 g L^{-1} of CO_2-C; not significant) CO_2 concentration. Annual data reflects that CO_2 concentrations were higher for the sampling year 2018 compared to the sampling year 2017. Additionally, the fall season of each sampling year (2017 and 2018) recorded the lowest seasonal CO_2 values, although the difference was not significant. No other distinct seasonal trends were observed. There were no other significant differences found among treatments within seasons.

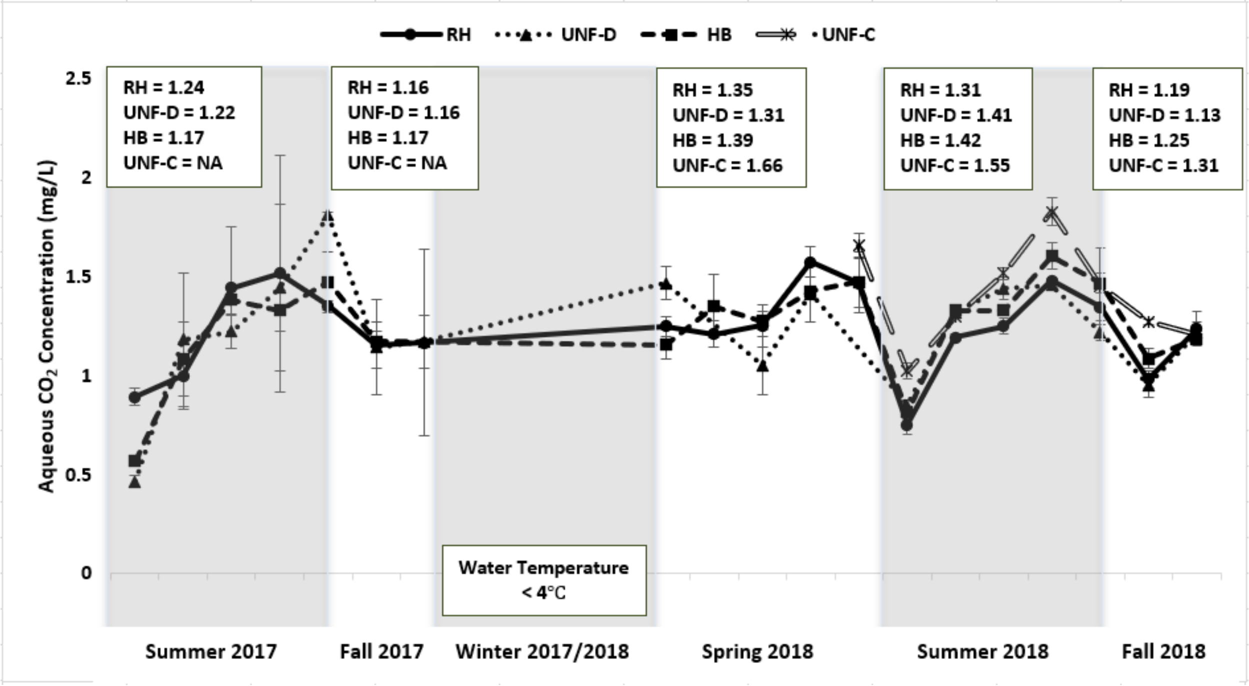

Figure 5.1: Mean seasonal aquatic carbon dioxide (CO_2) concentrations (g CO_2-C L^{-1}) recorded at the Washington Creek, Ontario, Canada, during the sampling year 2017 and 2018 for the aquatic component of the rehabilitated forest riparian buffer (RH), undisturbed natural forest riparian buffer dominated by deciduous vegetation (UNF-D), herbaceous riparian buffer (HB), and undisturbed natural forest riparian buffer dominated by coniferous vegetation (UNF-C).

Table 5.9: Mean seasonal aquatic carbon dioxide (CO_2) concentrations (g CO_2-C L^{-1}) recorded at the Washington Creek, Ontario, Canada, during the sampling year 2017 and 2018 for the aquatic component of the rehabilitated forest riparian buffer (RH), undisturbed natural forest riparian buffer dominated by deciduous vegetation (UNF-D), herbaceous vegetation buffer (HB), and undisturbed natural forest riparian buffer dominated by coniferous vegetation (UNF-C).

		RH	UNF-D	HB	UNF-C	Season ($\bar{x}$)
CO_2-C (g L^{-1})	**Spring 2017**	--	--	--	--	--
	Summer 2017	1.24 (0.11)^{Aa}	1.22 (0.13)^{Aa}	1.17 (0.09)^{Aa}	--	1.21 (0.06)^{A}
	Fall 2017	1.16 (0.14)^{Aa}	1.16 (0.08)^{Aa}	1.17 (0.19)^{Aa}	--	1.16 (0.08)^{AB}
	Spring 2018	1.35 (0.12)^{Aa}	1.31 (0.10)^{Aa}	1.39 (0.04)^{Aa}	1.66 (0.03)^{Aa}	1.43 (0.05)^{AB}
	Summer 2018	1.31 (0.07)^{Aa}	1.41 (0.06)^{Aa}	1.42 (0.07)^{Aa}	1.55 (0.07)^{Aa}	1.42 (0.03)^{B}
	Fall 2018	1.19 (0.06)^{Aa}	1.13 (0.06)^{Aa}	1.25 (0.03)^{Aa}	1.31 (0.02)^{Aa}	1.22 (0.03)^{AB}
	Riparian Zone ($\bar{x}$)	1.25 (0.05)^{a}	1.25 (0.05)^{a}	1.28 (0.04)^{a}	1.51 (0.05)^{a}	

*Significant difference among seasons within a treatment is represented by ^{ABC}; Significant difference among treatments within a season is represented by $^{abc.}$

**() represent Standard Deviation

5.4.2 CH_4 Concentrations

The mean CH_4 concentration (μg L^{-1} of CH_4-C), sample size 185, measured from riparian streams with RH, UNF-D, HB, and UNF-C vegetation were 1.81 ± 0.09, 1.36 ± 0.10, 2.51 ± 0.13, and 1.11 ± 0.21, respectively (refer to table 5.10) with values ranging from 0.81 ± 0.02 μg L^{-1} to 2.66 ± 0.13 μg L^{-1} of CH_4-C. Amongst the four riparian treatments, UNF-C recorded the lowest (1.11 ± 0.21 μg L^{-1} of CH_4-C) CH_4 concentration, significantly lower only than the RH treatment ($p = 0.003$). HB recorded the highest (2.51 ± 0.13 μg L^{-1} of CH_4-C) CH_4 concentration, significantly higher than all other treatments including RH ($p = 0.002$), UNF-D ($p = 0.000$), and UNF-C ($p = 0.000$). There were no other significant differences found among seasons within treatments.

The mean seasonal CH_4 concentration (μg L^{-1} of CH_4-C) of the stream component for summer 2017 and fall 2017, spring 2018, summer 2018, and fall 2018 sampling seasons were 2.05 ± 0.11, 1.99 ± 0.12, 1.72 ± 0.13, 1.68 ± 0.15, and 1.51 ± 0.09, respectively (refer to table 5.10 and figure 5.2). Amongst the five sampling seasons, fall 2018 recorded the lowest (1.51 ± 0.09 μg L^{-1} of CH_4-C) CH_4 concentration; significantly different from only summer 2017 ($p = 0.010$) concentrations. Summer 2017 has the highest (2.05 ± 0.11 μg L^{-1} of CH_4-C) CH_4 concentration; significantly higher from summer 2018 ($p = 0.000$), and fall 2018 ($p = 0.010$) sampling season. Contrary to CO_2 dissolved concentrations in the stream, annual data reflects that CH_4 concentrations were higher for the sampling year 2017 compared to the sampling year 2018. In the sampling season of Summer 2017, the CH_4 concentrations from the UNF-D (1.36 ± 0.14 μg L^{-1}) treatment were significantly lower than the concentrations from RH (2.14 ± 0.19 μg L^{-1}; $p = 0.013$) and HB (2.66 ± 0.13 μg L^{-1}; $p = 0.00$) sampling treatments. Similarly, for the sampling season fall 2017, UNF-D (1.42 ± 0.11 μg L^{-1}) concentrations were significantly lower than the

CH_4 concentrations from the sampling sites RH (2.02 ± 0.14 μg L^{-1}; p = 0.011) and HB (2.55 ± 0.17 μg L^{-1}; p = 0.00). Additionally, for spring 2018 sampling season, CH_4 concentrations from the HB (2.65 ± 0.26 μg L^{-1}) treatment were significantly higher than the other treatment including the RH (1.77 ± 0.11 μg L^{-1}; p = 0.006), UNF-D (1.64 ± 0.04 μg L^{-1}; p = 0.033), and UNF-C (0.81 ± 0.02 μg L^{-1}; p = 0.00) sampling site. Finally, CH_4 concentrations measured during the sampling season of summer 2018 signified that there are significant differences between the concentrations measured from the HB (2.50 ± 0.35 μg L^{-1}) sampling site and the UNF-D (1.36 ± 0.27 μg L^{-1}; p = 0.027) and UNF-C (1.32 ± 0.28 μg L^{-1}; p = 0.012) sampling sites. There were no other significant differences found among treatments within seasons.

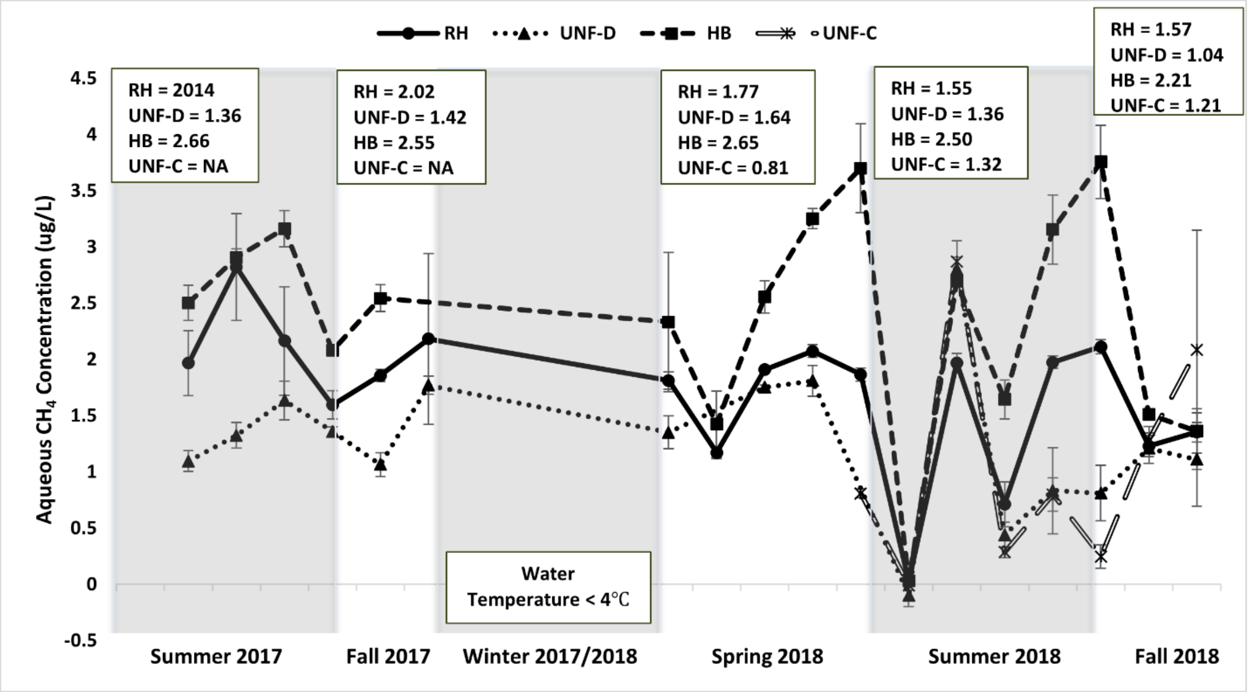

Figure 5.2: Mean seasonal aquatic methane (CH4) concentrations (µg CH4-C L^{-1}) recorded at the Washington Creek, Ontario, Canada, during the sampling year 2017 and 2018 for the aquatic component of the rehabilitated forest riparian buffer (RH), undisturbed natural forest riparian buffer dominated by deciduous vegetation (UNF-D), herbaceous riparian buffer (HB), and undisturbed natural forest riparian buffer dominated by coniferous vegetation (UNF-C).

Table 5.10: Mean seasonal aquatic methane (CH_4) concentrations (µg CH_4-C L^{-1}) recorded at the Washington Creek, Ontario, Canada, during the sampling year 2017 and 2018 for the aquatic component of the rehabilitated forest riparian buffer (RH), undisturbed natural forest riparian buffer dominated by deciduous vegetation (UNF-D), herbaceous vegetation buffer (HB), and undisturbed natural forest riparian buffer dominated by coniferous vegetation (UNF-C).

		RH	UNF-D	HB	UNF-C	Season ($\bar{x}$)
CH_4-C (μg L^{-1})	**Spring 2017**	--	--	--	--	--
	Summer 2017	2.14 (0.19)^{Ab}	1.36 (0.14)^{Aa}	2.66 (0.13)^{Ab}	--	2.05 (0.11)^{A}
	Fall 2017	2.02 (0.14)^{Aa}	1.42 (0.11)^{Ab}	2.55 (0.17)^{Aa}	--	1.99 (0.12)^{ABC}
	Spring 2018	1.77 (0.11)^{Aa}	1.64 (0.04)^{Aa}	2.65 (0.26)^{Ab}	0.81 (0.02)^{Aa}	1.72 (0.13)^{AC}
	Summer 2018	1.55 (0.23)^{Aab}	1.36 (0.27)^{Aa}	2.50 (0.35)^{Ab}	1.32 (0.28)^{Aa}	1.68 (0.15)^{B}
	Fall 2018	1.57 (0.04)^{Aa}	1.04 (0.11)^{Aa}	2.21 (0.06)^{Aa}	1.21 (0.33)^{Aa}	1.51 (0.09)^{C}
	Riparian Zone ($\bar{x}$)	1.81 (0.09)^{a}	1.36 (0.10)^{ac}	2.51 (0.13)^{b}	1.11 (0.21)^{c}	

*Significant difference among seasons within a treatment is represented by ^{ABC}; Significant difference among treatments within a season is represented by $^{abc.}$

**() represent Standard Deviation

5.4.3 N_2O Concentrations

The mean N_2O concentration (μg L^{-1} of N_2O-N), sample size 185, measured from riparian streams with RH, UNF-D, HB, and UNF-C vegetation were 1.23 ± 0.04, 1.37 ± 0.05, 1.00 ± 0.05, and 3.32 ± 0.30, respectively (refer to table 5.11) with values ranging from 0.80 ± 0.02 μg L^{-1} to 3.57 ± 0.04 μg L^{-1} of N_2O-N. Amongst the four riparian treatments, HB recorded the lowest (1.00 ± 0.05 μg L^{-1} of N_2O-N) N_2O concentration; significantly lower than UNF-D ($p = 0.024$), and UNF-C ($p = 0.000$). UNF-C recorded significantly higher (3.32 ± 0.30 μg L^{-1} of N_2O-N; $p = 0.000$ for all treatments) N_2O concentration.

When looking at each of the treatments over the duration of the sampling period, that is, among the different sampling seasons, the following significant differences were measured for N_2O concentrations. Overall, within each treatment, no significant differences were found among seasons in the sampling year 2017; various significant differences were found in the seasonal data collected in the sampling year 2018. The results from the RH treatment denote that the N_2O concentrations measured in the spring 2018 (1.56 ± 0.11 μg L^{-1}) sampling season were significantly higher than the N_2O concentrations measured during the other 2018 sampling seasons ($p = 0.000$ for summer 2018; and $p = 0.049$ for fall 2018) for the same treatment. Furthermore, at the UNF-D site, there was a significant difference ($p = 0.017$) between the N_2O concentration measured during spring 2018 (1.69 ± 0.11 μg L^{-1}) and summer 2018 sampling season (1.40 ± 0.11 μg L^{-1}). There were no other significant among seasons for the sampling year 2018, within treatments, for N_2O concentrations.

Sampling was carried out for a total of five seasons which included two seasons in the sampling year 2017 (summer 2017 and fall 2017), and three seasons in the sampling year 2018 (spring 2018, summer 2018, and fall 2018). The mean seasonal N_2O concentration (μg L^{-1} of N_2O-N) of the stream component for summer 2017 and fall 2017, spring 2018, summer 2018, and fall 2018 sampling seasons were 0.95 ± 0.03, 0.96 ± 0.04, 2.02 ± 0.13, 1.64 ± 0.16, and 1.89 ± 0.12, respectively (refer tot able 5.11 and figure 5.3). Amongst the five sampling seasons, summer 2017 recorded the lowest (0.95 ± 0.03 μg L^{-1} of N_2O-N); significantly lower than spring 2018 (p = 0.000), summer 2018 (p = 0.000), and fall 2018 (p = 0.008). Fall 2018 recorded the highest (1.89 ± 0.12 μg L^{-1} of N_2O-N) N_2O concentration; significantly higher than summer 2017 (p = 0.0008) and fall 2017 (p = 0.029). Annual data reflects that N_2O concentrations were higher for the sampling year 2018 than for 2017.

Foremost, in the sampling season summer 2017, the N_2O concentrations from the HB (0.72 ± 0.03 μg L^{-1}) treatment were significantly (p = 0.000) lower than all the other two treatments including RH (1.06 ± 0.03 μg L^{-1}), and UNF-D (1.08 ± 0.05 μg L^{-1}). For the sampling season fall 2017, all the treatments were significantly (p = 0.000) were significantly different from each other. In the sampling year 2018, for all three sampling seasons, spring 2018, summer 2018 and fall 2018, N_2O concentrations from the UNF-C treatment were significantly (p = 0.000) higher than the other three treatments. Additionally, in the sampling season fall 2018 the N_2O concentrations from the UNF-D (1.60 ± 0.03 μg L^{-1}) treatment were also significantly (p = 0.007) higher than that of the HB (1.25 ± 0.03 μg L^{-1}) treatment. There were no other significant differences among treatments within seasons.

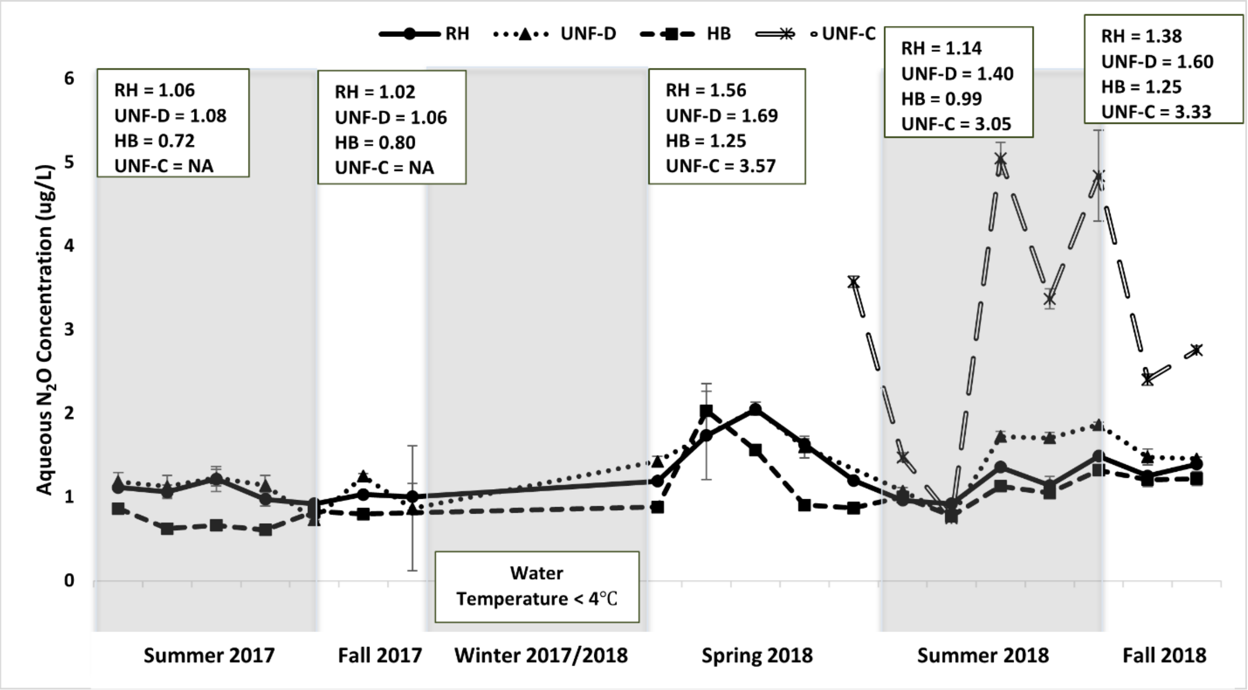

Figure 1.3: Mean seasonal aquatic nitrous oxide (N_2O) concentrations (µg N_2O-N L^{-1}) recorded at the Washington Creek, Ontario, Canada, during sampling year 2017 and 2018 for the aquatic component of the rehabilitated forest riparian buffer (RH), undisturbed natural forest riparian buffer dominated by deciduous vegetation (UNF-D), herbaceous riparian buffer (HB), and undisturbed natural forest riparian buffer dominated by coniferous vegetation (UNF-C).

Table 5.11: Mean seasonal aquatic nitrous oxide (N_2O) concentrations (µg N_2O-N L^{-1}) recorded at the Washington Creek, Ontario, Canada, during sampling year 2017 and 2018 for the aquatic component of the rehabilitated forest riparian buffer (RH), undisturbed natural forest riparian buffer dominated by deciduous vegetation (UNF-D), herbaceous vegetation buffer (HB), and undisturbed natural forest riparian buffer dominated by coniferous vegetation (UNF-C).

		RH	UNF-D	HB	UNF-C	Season ($\bar{x}$)
N_2O-N (μg L^{-1})	**Spring 2017**	--	--	--	--	--
	Summer 2017	1.06 (0.03)^{Aa}	1.08 (0.05)^{Aa}	0.72 (0.03)^{Ab}	--	0.95 (0.03)^{A}
	Fall 2017	1.02 (0.04)^{Aa}	1.06 (0.03)^{Ab}	0.80 (0.02)^{Ac}	--	0.96 (0.04)^{A}
	Spring 2018	1.56 (0.11)^{Ba}	1.69 (0.11)^{Aa}	1.25 (0.15)^{Aa}	3.57 (0.04)^{Ab}	2.02 (0.13)^{BC}
	Summer 2018	1.14 (0.06)^{Aa}	1.40 (0.11)^{Ba}	0.99 (0.05)^{Aa}	3.05 (0.47)^{Ab}	1.64 (0.16)^{ABC}
	Fall 2018	1.38 (0.03)^{Aab}	1.60 (0.03)^{ABa}	1.25 (0.03)^{Ab}	3.33 (0.08)^{Ac}	1.89 (0.12)^{C}
	Riparian Zone ($\bar{x}$)	1.23 (0.04)^{ab}	1.37 (0.05)^{a}	1.00 (0.05)^{b}	3.32 (0.30)^{c}	

*Significant difference among seasons within a treatment is represented by ^{ABC}; Significant difference among treatments within a season is represented by $^{abc.}$

**() represent Standard Deviation

5.4.4 Aquatic GHG concentrations and their CO_2 equivalence

The conversion factor for N_2O and CH_4 concentrations to CO_2 equivalence values are based on the Global Warming Potential (GWP), 100-Year time Horizon, reported in the IPCC's Fifth Assessment Report (AR5), sourced from the Government of Canada website (IPCC, 2014). GWP is a metric that can be used to evaluate the ability of the GHG, compared to CO_2, to trap heat in the atmosphere (IPCC, 2014). Methane (CH_4) is 28 times the GWP, and Nitrous oxide (N_2O) is 265 times the GWP when compared to Carbon dioxide (CO_2) (IPCC, 2014).

Table 5.12: Mean aquatic GHG concentrations, in CO_2 equivalence (g L^{-1}), recorded at Washington Creek, Ontario, Canada, during the sampling year 2017 and 2018 for the aquatic component of the rehabilitated forest riparian buffer (RH), undisturbed natural forest riparian buffer dominated by deciduous vegetation (UNF-D), herbaceous vegetation buffer (HB), and undisturbed natural forest riparian buffer dominated by coniferous vegetation (UNF-C).

		N_2O (CO_2 equivalence)* (g L^{-1})	CO_2 (g L^{-1})	CH_4 (CO_2 equivalence)* (g L^{-1})
Riparian Zones	**RH**	3.27 E^{-4}	1.25	5.07 E^{-5}
	UNF-D	3.63 E^{-4}	1.25	3.81 E^{-5}
	HB	2.65 E^{-4}	1.28	7.03 E^{-5}
	UNF-C	8.80 E^{-4}	1.51	3.11 E^{-5}
Seasons	**Spring 2017**	--	--	--
	Summer 2017	2.52 E^{-4}	1.21	5.75 E^{-5}
	Fall 2017	2.55 E^{-4}	1.16	5.58 E^{-5}
	Spring 2018	5.36 E^{-4}	1.43	4.82 E^{-5}
	Summer 2018	4.35 E^{-4}	1.42	4.70 E^{-5}
	Fall 2018	5.01 E^{-4}	1.22	4.23 E^{-5}

*CO_2 equivalence values are based on the GWPs reported in the Fifth Assessment Report (AR5) by IPCC (IPCC, 2014)

5.5 Correlation Analysis of GHG Concentrations and Stream Characteristics

5.5.1 Correlations by RAFS

Pearson's correlation was used to determine existing correlations between the measured GHG concentrations and water/environmental characteristics recorded in each treatment. Aqueous CO_2 concentration had no significant correlation with any of the water or environmental parameters at the RH and UNF-D sampling treatment (refer to table 5.13). At the HB treatment, CO_2 concentrations are significantly negatively correlated to NO_3^- concentration ($r = -0.375$, $p < 0.01$), DOC concentration ($r = -0.424$, $p < 0.01$), DO ($r = -0.496$, $p < 0.01$), and the depth ($r = -0.299$, $p < 0.05$) of the treatment. There is also a significant positive correlation between the CO_2 concentration and the pH ($r = 0.278$, $p < 0.05$) recorded at the HB treatment. At the UNF-C treatment, CO_2 concentrations are significantly correlated to the DO ($r = 0.522$, $p < 0.05$), and stream width ($r = -0.531$, $p < 0.01$) measurements.

Aqueous CH_4 concentrations recorded in the HB sampling treatment has no significant correlation to any of the water or environmental characteristics (refer to table 5.13). CH_4 concentrations are significantly positively correlated to NO_3^- at the RH ($r = 0.272$, $p < 0.05$) treatment and to DOC at the UNF-D ($r = -0.322$, $p < 0.05$) treatment. Additionally, CH_4 concentrations are negatively correlated to air temperature at the UNF-C ($r = -0.544$, $p < 0.05$) sampling treatment and to pH at the RH ($r = -0.464$, $p < 0.01$) and UNF-D ($r = -0.295$, $p < 0.05$) treatment. At the UNF-D treatment, CH_4 concentrations are significantly positively correlated to the depth ($r = 0.292$, $p < 0.05$), velocity ($r = 0.502$, $p < 0.05$), and discharge ($r = 0.461$, $p < 0.05$) of the stream. Finally, CH_4 concentrations are negatively correlated to the depth at the UNF-C ($r = -0.467$, $p < 0.05$) treatment.

Aquatic N_2O concentrations are significantly negatively correlated to NO_3^- concentrations at all treatments including RH ($r = -0.476$, $p < 0.01$), UNF-D ($r = -0.457$, $p < 0.01$), HB ($r = -0.583$, $p < 0.01$), and UNF-C ($r = -0.599$, $p < 0.01$) (refer to table 5.13). N_2O concentrations are significantly negatively correlated to Air temperature at the RH ($r = -0.344$, $p < 0.05$), and HB ($r = -0.535$, $p < 0.01$) treatments. Additionally, there is also a negative correlation between N_2O concentration and Water temperature at the RH ($r = -0.461$, $p < 0.01$) and HB ($r = -0.559$, $p < 0.01$) sampling site. For pH, it is significantly positively correlated to aquatic N_2O concentration at the RH ($r = 0.332$, $p < 0.05$), UNF-D ($r = 0.434$, $p < 0.01$), and UNF-C ($r = 0.543$, $p < 0.05$) sampling site. At the RH treatment, water characteristics DO ($r = 0.371$, $p < 0.01$) and pH ($r = 0.332$, $p < 0.05$) are also significantly positively correlated to the measured N_2O concentration. Finally, the depth of the stream is significantly positively correlated to the N_2O concentration at the RH ($r = -0.476$, $p < 0.01$), and UNF-D ($r = -0.476$, $p < 0.01$) site.

Table 5.13: Pearson's correlation for all measured variables at the Washington Creek, Ontario, Canada, during the sampling year 2017 and 2018 for aquatic component of the rehabilitated forest riparian buffer (RH), undisturbed natural forest riparian buffer dominated by deciduous vegetation (UNF-D), herbaceous vegetation buffer (HB), and undisturbed natural forest riparian buffer dominated by coniferous vegetation (UNF-C).

Treatment		NO_3^-	NH_4^+	DOC	TN	Air T	Water T	pH	DO	Cond.	Depth	Width	Velocity	Discharge
RH	N_2O	-.476**	-0.101	-0.156	-0.201	-.344*	-.461**	.332*	.371**	-.327*	.510**	0.001	0.197	0.106
	CO_2	0.032	-0.04	-0.105	0.026	0.112	0.093	0.251	-0.214	0.116	-0.091	0.082	-0.217	-0.294
	CH_4	.272*	0.063	0.061	-0.189	0.003	-0.049	-.464**	0.251	0.24	0.077	-0.103	0.015	-0.073
UNF-D	N_2O	-.457**	0.026	-0.287	-0.129	-0.142	-0.265	.434**	-0.061	-0.012	.336*	0.223	-0.226	0.324
	CO_2	0.131	-0.159	0.188	-0.021	-0.086	-0.14	0.287	0.174	.317*	-0.106	-0.244	0.029	-0.091
	CH_4	0.124	-0.065	.322*	0.071	-0.188	-0.188	-.295*	0.209	-0.157	.292*	-0.14	.502*	.461*
HB	N_2O	-.583**	0.154	-0.193	-0.171	-.535**	-.559**	0.114	-0.156	-0.226	-0.187	-0.207	0.186	0.349
	CO_2	-.375**	0.055	-.424**	0.069	0.073	0.034	.278*	-.496**	0.106	-.299*	-0.24	-0.139	-0.208
	CH_4	0.101	-0.121	0.005	-0.033	0.094	0.058	-0.151	-0.135	0.184	0.096	0.043	0.03	-0.061
UNF-C	N_2O	-.599**	-0.069	-0.05	-0.112	0.162	0.005	.543*	0.331	-0.022	-0.103	-0.348	0.261	0.261
	CO_2	-0.401	-0.141	0.09	-0.169	-0.145	0.03	0.082	.522*	-0.311	-0.197	-.531**	0.061	0.06
	CH_4	0.176	-0.055	0.13	-0.192	-.544*	-0.419	-0.199	-0.033	0.079	-.467*	0.337	-0.138	-0.139

****Correlation is significant at the 0.01 level (2-tailed); *Correlation is significant at the 0.05 level (2-tailed)**

5.5.2 Correlations of GHG concentrations over the sampling period

Pearson's correlation was used to determine the correlation among the GHG concentrations, and all the water and environmental characteristics measured during the sampling period. Aquatic *CO_2 concentration* measured in the various RAFS along the Washington Creek had fewer significant correlations to the water and environmental characteristics than N_2O concentration (refer to table 5.14). CO_2 concentrations are significantly positively correlated to TN concentration ($r = 0.196$, $p < 0.05$), and pH ($r = 0.158$, $p < 0.05$); and significantly negatively correlated to DO ($r = -0.232$, $p < 0.01$), depth ($r = -0.181$, $p < 0.05$), width ($r = -0.241$, $p < 0.01$), and discharge of the stream ($r = -0.234$, $p < 0.05$). Aquatic *CH_4 concentrations*, with the least number of correlations, are significantly positively correlated to DOC ($r = 0.179$, $p < 0.05$), DO ($r = 0.230$, $p < 0.01$), and depth ($r = 0.399$, $p < 0.01$) of the stream component of the RAFS. Additionally, measured CH_4 concentrations are significantly negatively correlated to TN concentration ($r = -0.340$, $p < 0.01$), and discharge of the stream ($r = -0.239$, $p < 0.05$).

For the sampling period of 2017 and 2018, it was observed that the aquatic *N_2O concentrations* are significantly positively correlated to CO_2 concentrations ($r = 0.284$, $p < 0.01$), and TN concentrations ($r = 0.562$, $p < 0.01$) measured from the aquatic component of the RAFS. Aquatic N_2O concentrations are also significantly negatively correlated to the following parameters measured at the various treatments along the Washington Creek: CH_4 concentrations ($r = -0.440$, $p < 0.01$), NO_3^- concentrations ($r = -0.276$, $p < 0.01$), DOC ($r = -0.217$, $p < 0.01$), water temperature ($r = -0.287$, $p < 0.01$), DO ($r = -0.210$, $p < 0.01$), depth ($r = -0.384$, $p < 0.01$), width ($r = -0.562$, $p < 0.01$) and the discharge of the stream ($r = -0.230$, $p < 0.05$).

Table 5.14: Pearson's correlation for all measured variables at the Washington Creek, Ontario, Canada, during the sampling year 2017 and 2018 for aquatic component of the rehabilitated forest riparian buffer (RH), undisturbed natural forest riparian buffer dominated by deciduous vegetation (UNF-D), herbaceous vegetation buffer (HB), and undisturbed natural forest riparian buffer dominated by coniferous vegetation (UNF-C).

****Correlation is significant at the 0.01 level (2-tailed); *Correlation is significant at the 0.05 level (2-tailed)**

	N_2O	CO_2	CH_4	NO_3^-	NH_4^+	DOC	TN	Air T	Water T	pH	DO	Cond.	Depth	Width	Velocity	Discharge
N_2O	1															
CO_2	0.284**	1														
CH_4	-0.440**	0.145	1													
NO_3^-	-0.276**	-0.086	0.124	1												
NH_4^+	0.016	-0.018	-0.027	-0.209**	1											
DOC	-0.217**	-0.110	0.179*	0.375**	-0.137	1										
TN	0.562**	0.196*	-0.340**	-0.082	-0.048	-0.116	1									
Air T	-0.028	0.056	-0.111	-0.134	0.100	-0.279**	0.202*	1								
Water T	-0.287**	-0.018	-0.005	-0.120	0.170	-0.232**	-0.073	0.857**	1							
pH	-0.148	0.158*	0.026	-0.200**	0.064	0.026	-0.200*	0.036	0.117	1						
DO	-0.210**	-0.232**	0.230**	0.067	-0.121	0.083	-0.325**	-0.139	-0.231**	-0.164	1					
Cond.	-0.079	0.046	-0.138	0.285**	0.014	0.260**	-0.150	-0.237**	-0.165*	-0.062	-0.112	1				
Depth	-0.384**	-0.181*	0.399**	0.029	-0.061	0.081	-0.400**	-0.190**	-0.112	0.102	0.441**	-0.132	1			
Width	-0.562**	-0.241**	0.074	0.028	-0.112	0.212**	-0.606**	-0.116	0.110	0.154*	0.214**	0.317**	0.141*	1		
Velocity	0.125	-0.077	-0.021	0.005	0.113	0.474**	-0.004	0.131	-0.091	0.123	0.108	-0.020	-0.511**	0.027	1	
Discharge	-0.230*	-0.234*	-0.239*	-0.251**	0.114	0.172	-0.496**	-0.122	-0.135	0.493**	0.554**	-0.237*	0.403**	0.245*	-0.479**	1

6.0 DISCUSSION

Studying the presence and abundance of C and N in the stream body can highlight the influence agriculture has on the water quality of riparian streams. It can also shed light on the impact these streams have on climate change since CO_2, N_2O, and CH_4 are all potent GHGs. Riparian zones are well known to improve the water quality of streams. This study aimed to figure out which RAFS is the most effective at doing the same.

The cycling of nutrients like C and N in riparian streams begins with the effectiveness of the terrestrial component to reduce the input of these nutrients into the streams. Once in the stream, the fate of these nutrients is determined by various factors and influences, like water temperature (Wang et al., 2019). The output, most notably in the form of GHG emissions, delivers evidence of the effectiveness of the streams in sequestering these nutrients. Therefore, the stream nutrient dynamics can be used to study two important aspects of riparian buffer zones: The effectiveness of the terrestrial component of the RAFS to sequester or contain C and N. Lower abundance of nutrients in the stream are evidence of the nutrient mitigation potential of the terrestrial components of the riparian buffers; and the effectiveness of the aquatic component to sequester or contain C and N to reduce the GHG emissions from these streams into the atmosphere. In this discussion section, the measured variables (GHG concentrations; water, environmental, and sediment parameters) in the four RAFS treatments (RH, UNF-D, HB, and UNF-C) will be compared and correlated in an attempt to determine which RAFS is the best management practice (BMP) for agricultural land use in Southern Ontario.

6.1.0 Stream Characteristics

The composition and chemistry of a surface water body depend on several natural and anthropogenic factors that can influence its water quality (Hamid et al., 2020). These factors can cause spatially variation in water quality; however, temporal changes primarily result from daily climatic or long-term seasonal influences (Hamid et al., 2020). The following section focuses on some of the water characteristics that can represent the water quality of the stream body under analysis. As a reference, the following measured water parameters were in the same range as the recorded values in other water bodies, rivers, and streams, in the Grand River watershed for the years 2017 and 2018 (www.grandriver.ca).

6.1.1 Water Temperature

Spatial Variation

There was no significant difference in water temperature among treatments over the entire sampling period, nor within a given season. It was hypothesized that there will be a significant difference in the stream characteristics among the treatments. The hypothesis was hence rejected for the water temperature parameter. A study conducted by Albertson et al., 2018, in Pennsylvania, USA found that riparian streams with grassed (meadow) buffer had the warmest water temperature compared to streams with rehabilitated or forested buffer. The study was conducted only in the summer months (April-July). The riparian zones studied by Albertson et al., 2018 were in the same watershed but were on four different streams. Another year-round study done by Dugdale et al., 2018, in Scotland found that streams with grassland had the warmest summer and coolest winter temperature when compared to streams with semi-natural forest and forested buffer. In Dugdale et al., 2018, the three riparian zones studied were located on three different streams, although they were within a few kilometers of each other.

The four RAFS treatments studied in this research are on the same stream and geographically within a few kilometers of each other. Even though the riparian vegetation differs for each of them, the water temperature remains approximately constant. Water has a high heat capacity; it can absorb a lot of energy before its temperature changes (Meadley and Angell, 2015). Therefore, since the treatments are part of the same stream, it is very likely to record an insignificant shift in water temperature.

Contrary to the findings in the aquatic component of the riparian systems, Baskerville (2020), who observed the terrestrial components of the same riparian sites in 2017 and 2018, found otherwise. Baskerville (2020) found that the HB site had the highest soil temperatures, whereas the UNF sites recorded some of the lowest soil temperatures due to the difference in the exposure of land to direct sunlight.

Temporal Variation

Seasonal variation in air and water temperature is consistent with the expected seasonal changes in weather. Even though the water temperature is highly positively correlated to the air temperature, the seasonal change in water temperature is not as drastic as air temperature because of the high heat capacity of water (Meadley and Angell, 2015). Even though air and water temperature were positively correlated (r = 0.857), the correlation was nonlinear. Morrill et al., 2001, support this finding. They tested 50 streams in 13 countries and found that only a few streams displayed the linear 1:1 relationship. Most streams had a nonlinear positive relationship between air and water temperature.

The summer of 2017 was close to the average observed temperatures, whereas the summer of 2018 was warmer than the average (University of Waterloo, 2017; University of

Waterloo, 2018). The Fall of 2017 was warmer than average fall temperatures, with October temperatures falling between the range that has not been observed since 1971 (University of Waterloo, 2017). Even though the summer of 2018 was warmer than average, the temperatures dropped drastically in mid-October, with November being the coldest on record since 1996 (University of Waterloo, 2018). Increased water temperatures during the warmer months, summer of 2017 and 2018, can also be attributed to the increase in the rate of leaf litter decomposition in low-order streams (Martinez et al., 2014). Increasing decomposition rates can further warm the water bodies as decomposition causes heat release when converting organic C in aerobic and anaerobic environments (Texas A and M Agrilife Extension, 2009). This warming further increases the decomposition rate, hence completing the positive feedback loop. This also explains the significant negative correlation of water temperature to DO; as the microbial activity increases, the available DO in the water body decreases (Hynes, 1960; Dauer et al., 2000).

6.1.2 pH

The physiology of Oxford County, where Washington Creek is located, is characterized by limestone bedrock, with glacial till being the parent soil material (Wicklund and Richards, 1961). When Mallory (1993) measured the pH of the Washington Creek, the findings suggested the pH range to be between 7.5 and 8.5. In 2017 and 2018, the pH measured through this study ranged between 8.08 and 8.70. The alkaline nature of the study site suggests that there is high calcareous content in the soils of the Grand River Watershed.

Spatial Variation

Stream pH recorded at the HB treatment was significantly higher, and that recorded at UNF-C was significantly lower compared to the other treatments. It was hypothesized that there will be significant difference in the stream characteristics among the treatments. The hypothesis was hence accepted for pH. The three main factors that can influence the pH of a freshwater stream include: CO_2, which is the most common influence and is driven by photosynthesis, respiration, and decomposition in the water body (Hakanson, 2005; Hamid et al., 2020); natural influences like carbonates in the water body or the surrounding parent rock/bedrock material, the dissolution of which can be impacted by factors like water temperature (El-Dessouky and Ettouney, 2002); and anthropogenic influences that alter the discharge/runoff or precipitation composition (Hickin, 1995), for example addition of fertilizer to the nearby agricultural land can alkalize the runoff due to the addition of nitrogen ions (Osmond et al., 1995).

In this study, HB site is the only site with aquatic vegetation in its stream component, which are the primary drivers of the significantly high pH and DO measurements recorded at this site. A study conducted by Oliveira et al. (2019) focusing on how land use change affects the dissolved oxygen regimes in stream found that the streams with grassland riparian zones have the highest primary productivity due to abundant nutrients through runoff as compared to forested streams. Oliveira et al., (2019) explains that streams with grassland buffers have high diurnal dissolved oxygen fluctuations which coincides with the light-dark cycle of the macrophytes, hence making it the perfect niche for primary producers to flourish. Similar studies by Finlay (2011) and Bernot et al. (2010) also reported that streams adjacent to agricultural grasslands had higher primary productivity compared to streams adjacent to forested riparian zones. Diurnal photosynthesis can increase the pH of the stream by absorbing the dissolved CO_2 out of the water, whereas respiration and decomposition can decrease pH by releasing CO_2 (Czuba et al, 2011). This increases the dissolved oxygen levels and the pH by several units during the day (Dissmeyer, 2008). At night, plants respire out CO_2 and use O_2 (Dissmeyer, 2008), which increases the CO_2 concentration. This increase in the amount of CO_2 can cause rock/mineral weathering of carbonates and silicates (Marx et al., 2017). Dissolving carbonates can add more inorganic carbon to the stream/river body, mainly in the form of HCO3- (Marx et al., 2017), further increasing the pH.

Moreover, aquatic plants have also evolved the ability to use HCO_3^- due to the restricted gas exchange underwater (Pedersen et al., 2013). The formation/precipitation of calcium carbonate ($CaCO_3$) is a positive feedback loop, where an increase in the pH of the water body increases the precipitation of $CaCO_3$, which will ultimately increase the pH of the water body even more (El-Dessouky & Ettouney, 2002). Calcium carbonate ($CaCO_3$) and other bicarbonates can act as pH buffers to help neutralize the pH by combining with the hydrogen and hydroxyl ions present (McNally & Mehta, 2004). Additionally, an increase in the water temperature also increases the precipitation of $CaCO_3$ (El-Dessouky & Ettouney, 2002). In the present study, the water temperature was not significantly different among the treatments; therefore, water temperature's impact on the stream's pH is limited.

Baseline discharge is influenced by riparian vegetation and groundwater flow (Fitzhugh et al., 1998, Hamid et al., 2020). Therefore, fluctuation in baseline discharge fluctuates the amount of H^+ and Al^{n+} (source: aboveground runoff) (Fitzhugh et al., 1998) and CO_2 (source: groundwater) flowing into the stream (Hamid et al., 2020). This alters the acidity of the stream water. Alternatively, an increase in discharge through rainfall, for example, can dilute the nutrients and increase the pH of the stream body (Wallin et al., 2009; Golderman, 1975). Wallin et al. (2009) studied a 67 km^2 boreal stream network in Sweden, which is predominantly a forested catchment, for spatial and temporal variability in DIC, and one of the conclusions made was that the variability in DIC and CO_2 concentrations are best correlated with discharge. Higher discharge caused dilution in the water bodies, thereby increasing the pH (Wallin et al., 2009). UNF-C had significantly lower discharge and, therefore, significantly lower pH when compared to other treatments. Alternatively, HB treatment had significantly higher discharge and pH. Furthermore, the measured data showed a strong positive correlation between the two variables (discharge and pH).

Temporal variation

Significant for the year 2017 and insignificant for 2018, the recorded pH in the Fall seasons was higher than the other seasons in both sampling years. However, a clear seasonal trend is lacking for pH as a water parameter. This trend follows the discharge trend, which is also significantly higher in the fall seasons (Wallin et al., 2019). Other studies have shown that summer months have the highest pH values due to an increase in photosynthesis and decomposition rates (Kim et al. 2003; Kim and Kim 2006).

6.1.3 Dissolved Oxygen (DO)

Spatial Variation

Stream DO measured at the HB treatment was significantly higher, and that recorded at UNF-C was significantly lower compared to the other treatments. It was hypothesized that there would be a significant difference in the stream characteristics among the treatments. The hypothesis was hence accepted for DO levels in the riparian stream. Peterson (2006), in his study conducted in Dog river watershed in Alabama, found that DO concentrations were higher in non-vegetated streams when compared to streams with forested vegetation. Peterson (2006) attributed this finding to the shallower water depths in the non-vegetated streams. Another study by Wilkinson et al. (2018), conducted in Catalpa Creek in Mississippi, also found that DO concentrations were higher in streams with grassland buffers than those with forested buffer zones. Although the stream with grassland buffer in the Wilkinson et al. (2018) study was deeper in depth than the stream with forested buffer. They attributed their findings to the reaeration process caused by the slope morphology of the stream. In this study, the depth of the stream with a grassland riparian zone (HB site) was deeper than the stream with a forested riparian zone (UNF-C & UNF-D), much like the Wilkinson et al. (2018) study. Although in this present study, there was no abrupt change in slope, which rules out the reaeration explanation. The presence of primary producers in the stream component of the HB site is the most reasonable explanation for the significantly higher DO concentration recorded at the HB site. Oliveira et al. (2019) conducted a study in the temperate region of the Netherlands, where 20 lowland streams with varying riparian zones (natural forests, non-fertilized pastures/extensive grasslands, fertilized pastures/intensive grasslands, and croplands) were sampled for diel dissolved oxygen concentrations. The study found that the streams with grassland vegetation in their riparian zones experienced the highest diel oxygen fluctuation with the highest daytime oxygen concentration compared to all other streams. Oliveira et al. (2019) explain that the streams with grassland riparian zones have the highest primary productivity due to the availability of abundant nutrients through runoff. Similar studies by Finlay (2011) and Bernot et al. (2010) also reported that streams adjacent to agricultural grasslands had higher primary productivity compared to streams adjacent to forested riparian zones. Diurnal photosynthesis can release a large amount of oxygen into the stream (Hamid et al., 2020).

Both photosynthesis and decomposition influence biological oxygen demand, which dictates the DO concentration in streams (Hamid et al., 2020). Dissolved organic matter (DOM) concentration (for example: TN and DOC) can be reflective of the decomposition activity in the stream (Boot and Bunt, 1981). Streams with high DOM have been found to record lower DO (Boot and Bunt, 1981). Significantly lower TN levels were also recorded from the HB treatment, potentially pointing toward low decomposition rates. The lowest levels of DO were recorded in the UNF treatments (UNF-C and UNF-D), although statistically significant for UNF-C only. The thicker terrestrial canopies and presence of higher organic matter UNF terrestrial sites mean that the TN in these treatments is significantly higher. These conditions point towards higher decomposition rates at the UNF treatments and, therefore, lower levels of DO in these treatments.

Temporal Variation

No significant seasonal trends were found in the DO measurements for the years 2017 and 2018. As per literature, as the water temperature increases, dissolved oxygen becomes less soluble; warmer waters require less dissolved oxygen concentration to reach 100% saturation (Wetzel, 2001; Hynes, 1960). Therefore, the DO levels were expected to be lowest during the summer seasons, but no significant trend was recorded.

6.1.4 Water Conductance

Spatial variation

The conductivity of a freshwater stream is its ability to conduct electricity and is dependent on the salinity (that is, ion composition) (Wetzel, 2001) and temperature of the water body (Langland & Cronin, 2003). Freshwater sources have lower ion concentrations than seawater, with bicarbonates, alkali, and earth metal in the highest concentration (Wijgerde, 2012). The high temperature will increase the ions' mobility and, therefore, the water body's conductivity (Courtney & Brodziak, 2010). Additionally, higher discharge or water flow can potentially dilute the ion concentration and thereby decrease water conductivity (Pattillo, 1994).

Water bodies in limestone-dominant geography tend to have high conductivity due to the high concentration of ions. Krawczyk & Ford (2006) explains that the conductivity of uncontaminated carbonate water bodies could range from about 150-1000 µS/cm, and if contaminated with, for example, fertilizer runoff containing high amount of NH_4^+, the values observed can be yet higher. When Wicklund & Richard (1961) studied the aquatic parameters in their study, they found that the conductivity of the Washington Creek water resembled that of an environment with contaminated carbonate soils and limestone bedrock material. In this study, similar findings were observed, and the conductivity ranged from about 600 – 800 µS/cm, indicating the same. A positive correlation was found between the NO_3^- and Conductivity values indicating the contamination of the stream by agricultural runoff.

Spatial variation data shows that HB and UNF-C treatments had significantly lower conductivity when compared to RH and UNF-D sites. It was hypothesized that there would be a significant difference in the stream characteristics among the treatments. The hypothesis was hence accepted for stream conductivity. Although, there was no significant trend found in the spatial conductivity data. When looking at the ionic composition of Washington Creek, both NH_4^+ and NO_3^- concentrations are not significantly different between the different treatments. pH, which can be a good indicator of bicarbonate and hydrogen ions (El-Dessouky & Ettouney, 2002), is significantly higher in HB and lower in UNF-C. Additionally, the water temperature was also not significantly different among treatments. Therefore, none of the variables measured during the study can explain the spatial trend in the stream conductivity data. The spatial variation in the study results cannot be explained and need further investigation.

Temporal variation

Higher temperatures tend to yield higher conductivity measurements in water (Langland & Cronin, 2003) due to the increase in ionic mobility and the solubility of the salts and minerals (Whipple, 2002). Therefore, it was expected that the summer sampling seasons would yield a higher conductivity value. Contrary to the expectation, fall sampling seasons for both sampling year 2017 and 2018 yielded significantly higher conductivity values compared to other sampling seasons in the given sampling year. This increase can perhaps be attributed to the increased aboveground runoff during the fall season due to increased precipitation. Suppose aboveground runoff due to precipitation is the main source of the increase in the stream's discharge. In that case, it is likely that the stream water will be high in fertilizer nutrients (Wall, 2013) and, therefore, conductivity (Krawczyk & Ford, 2006).

6.1.5 Discharge

Spatial variation

UNF-C had significantly lower discharge as compared to the other three treatments (RH, UNF-D, and HB) studied. It was hypothesized that there would be a significant difference in the stream characteristics among the treatments. The hypothesis was hence accepted for discharge. A common assumption in the literature highlights that the discharge of a riparian stream is directly dependent on the vegetation of the terrestrial component of the stream (Bosch and Hewlett, 1982. The reduction in vegetation reduces the amount of water held in soil and increases evaporation due to smaller canopy cover (Bosch and Hewlett, 1982). Grassland riparian zones tend to have a higher baseflow than forested riparian zones since herbaceous vegetation requires less water compared to trees (Lyons et al., 2000). Although not significant, HB treatment had the highest discharge among all the treatments.

Additionally, riparian buffer widths can have an impact on the discharge of the riparian streams. A study was done in 2017 by Larson et al. at the Kings Creek watershed in Kansas, USA compared woody riparian zones, grassland riparian zones, and riparian zones where woody vegetation buffer was removed at different buffer widths to analyze the impact. Larson et al. (2017) found that the woody vegetation removal from riparian zones did not affect the discharge unless the vegetation removal covered at least 20 to 50% of the whole watershed. In this present study, UNF-C and UNF-D both had thickly forested buffers but significantly different discharges. The RH treatment also had forested buffer vegetation, but the buffer width is much smaller compared to UNF-D and UNF-C. The discharge recorded at the RH treatment was similar to that of UNF-D, and significantly higher than UNF-C. Therefore, buffer width does not impact the discharge of the treatments.

Temporal variation

Discharge data in this study was only collected for the sampling year 2018. For reference, the first half of 2017 was the second wettest year on record in the region, with the rest of the year's precipitation falling within the average range (University of Waterloo, 2017). The year 2018 had a wet start, with June and July being drier than average. This was followed by a wetter-than-average October (University of Waterloo, 2018). Even for air temperature, the summer of 2018 was much warmer than average (University of Waterloo, 2018). At Washington Creek, Summer 2018 had the lowest discharge when compared to Spring 2018 and Fall 2018. Drier than usual summer and high evaporation rates can cause the reduction of discharge in the stream body.

6.2 Sediment Analysis

It was hypothesized that there would be a significant difference in the sediment nutrient composition among the treatments. The hypothesis was accepted, and significant differences were found between the different RAFS. Sediment collected at the RH treatment was found to be the most eutrophic compared to UNF-C, UNF-D, and HB treatments. Sediments can alter the water quality of the aquatic component of the riparian zones by affecting the following: higher concentration of silt and clay particles can increase the turbidity and reduce the light penetration; sediments can alter the water temperature and the dissolved oxygen availability in the water body; and can also assist in the transportation of adsorbed pollutants (Vigiak et al., 2016; Chapman et al., 2014; Rickson et al., 2014). Along with the numerous benefits of the terrestrial buffer riparian zones on the aquatic habitat and water quality, vegetation in riparian zones can also have an impact on sediment retention in the riparian streams (Vigiak et al., 2016). The two main processes by which the vegetarian in the terrestrial component of the RAFS can impact the sediment are: by trapping the incoming sediment particles in the runoff; and by stabilizing the morphology of the stream bank through the cohesion provided by the root system of the terrestrial vegetation, which reduces stream bank erosion (Belt et al. 1992; Dillaha and Inamadar 1997). The effectiveness of the ability of the vegetation to trap sediment depends on several riparian buffer factors, including the width and length of the vegetation strip, vegetation height and density, flow rate of the runoff, slope, and roughness of the terrain (Belt et al. 1992; Dillaha and Inamadar 1997).

A review of the effectiveness of vegetative buffers on sediment trapping in agricultural areas is provided by Yuan et al. in their 2009 research review paper. The review paper thoroughly explains how the buffer's width is the most critical factor (Yuan et al., 2009; Gilliam et al., 1997) influencing sediment trapping; and how vegetation type is a secondary factor (Yuan et al., 2009). A study by Wilson (1967) in Arizona reported that riparian buffers are generally more effective at removing larger particles like sand than smaller clay or silt particles. The study specifically looked at grassland buffers and observed that a short buffer of as small as 10 feet was enough to remove larger sand particles from the runoff, whereas a buffer zone of 300-400 feet was needed to remove the clay particles. In Washington Creek, it was observed that treatment with a marrow buffer, e.g., RH and HB, had more finer sediment particles that had runoff from the adjacent terrestrial land when compared to the sediment composition in the UNF-C and UNF-D sites. UNF-C and UNF-D sediment have little to no clay or silt particles present in their sediment. Therefore, the impact of a marrow buffer could clearly be observed. A research paper written by Lyons et al. in 2000 reviewed the implication of forested versus grassy riparian areas, and one of the conclusions made by the paper was that the sediment trapping capacity of both vegetation types was approximately similar. Yuan et al. (2009) also found that sediment trapping efficiency did not vary between grassy or forested riparian vegetation. In this present study, RH, UNF-C, and UNF-D are all considered forested riparian zones, but sediment found at the RH site is heavily eutrophic compared to UNF-C and UNF-D. Therefore, vegetation did not have as significant of an impact as the width of the buffer on sediment retention, as the RH sampling site has one of the least wide buffer strips.

As mentioned previously, an increase in the abundance of silt and clay particles can reduce water quality. Rickson (2014) further explains how smaller size eroded particles are more effective at the adsorption of nutrients and pollutants due to their higher specific surface area and charge density. Therefore, the treatments with a higher proportion of silt and clay particles in their sediment, HB and RH, were expected to record higher concentrations of nutrients and pollutants. Considering the sediment's physical morphology and the buffer's terrestrial characteristics, along with the literature support provided above, it would be fitting to assume that the RH and HB treatments would have the most polluted and highly nutrient-concentrated sediment. The assumption was valid for the RH site but not for HB treatment. The sediment at the RH treatment recorded the highest TN and OC concentration and the highest ammonium concentration. Unexpectedly the HB site recorded the lowest concentration of nutrients for all the C and N variables tested, except for nitrate. The aquatic plants growing at the HB site could be one of the main consumers relying on the sediment for their nutrient uptake, hence lowering the concentration of nutrients in the sediment. The year-over-year data reflected that overall, the nutrient concentration in sediment for all the RAFS treatments was higher in the sampling year 2018 versus the sampling year 2017.

6.3.0 Carbon cycling in the aquatic component of the RAFS

6.3.1 Dissolved Carbon Dioxide Concentration

Spatial Variation (amongst Riparian Zones)

It was hypothesized that there would be a significant difference in the dissolved GHG concentrations among the RAFS treatments. The hypothesis was rejected for dissolved CO_2 concentrations. No significant difference was found in the dissolved CO_2 concentrations amongst the different riparian zones. Streams and rivers tend to be supersaturated with dissolved CO_2 compared to the atmosphere (Smith and Bohlke, 2019; Wallin et al., 2009). The variability in the input and output dynamics of C in different riparian zones contributes to the variability of the dissolved CO_2 concentration amongst the riparian zones. The two primary sources of DIC/CO_2 in a riparian stream environment are: CO_2 released from organic matter decomposition and respiration in terrestrial soils (Billett et al., 2006; Deirmendjian and Abril, 2018) and the stream body; and CO_2 from groundwater (Hamid et al., 2020; Hope et al., 2004). Atmospheric deposition and, more importantly, above-ground runoff/erosion and litterfall can vary depending on the variability of vegetation amongst the different riparian systems (Holeton, 2013). Additionally, carbonates from weathering of the parent rock material can add to the DIC concentrations in the streams (Hope et al., 2004). Literature also provides evidence that CO_2 concentration variability is high in acidic streams compared to neutral streams (Wallin et al., 2009). Since the pH range of Washington Creek falls between 8.08 ± 0.02 to 8.70 ± 0.02, less variability in the CO_2 concentration was expected.

It was expected that a higher concentration of CO_2 would be measured at the HB treatment due to the existence of nutrient cycling between the terrestrial and aquatic components of the riparian zones. Stream DIC/CO_2 concentrations reflect the terrestrial concentrations

(Wallin et al., 2009). Oquist et al., 2009 found a strong correlation between riparian soil DIC and stream DIC. A study by Baskerville (2020) on the terrestrial component of the RAFS on the same treatments recorded consistently higher CO_2 emissions from the HB site due to higher soil temperature and higher root respiration compared to the other treatment. Oelbermann and Raimbault (2015) also conducted a study in the Washington Creek terrestrial riparian zones, although a different site, and found similar results. Hence the HB treatment also has the potential to be a significant source of CO_2 leaching into the stream body compared to the other treatment due to the high CO_2 production and high nutrient leaching potential of grassland riparian zones. High CO_2 leaching also promotes higher rates of mineral weathering (Lu et al., 2014; Wallin et al., 2014). The findings of this study indicated otherwise, and there was no significant difference between the CO_2 concentration among the different treatments. The presence of aquatic plants and, therefore, high diurnal photosynthesis could contribute to the uptake of large amounts of CO_2 from the aquatic environment of the HB site and can have a significant impact. The CO_2 concentration in the HB site does have a very highly significant negative correlation with the DO levels in the HB, providing further evidence that photosynthesis could be the main process impacting the CO_2 concentration by absorbing CO_2 and releasing O_2 into the stream.

Temporal Variation (amongst Seasons)

No significant trend was found in the seasonal variability recorded from the study site. Significant for the sampling year 2018 and insignificant for the year 2017, it was observed that the CO_2 concentrations were lowest in the fall season. As mentioned earlier, respiration and decomposition are one of the main contributors to the CO_2 concentrations in the stream environment (Billett et al., 2006; Deirmendjian and Abril, 2018). As the temperatures start to drop in the fall season, both these processes slow down, and so will the production of CO2.

Additionally, this study also found that the discharge of the streams increased in the fall season; the reduction in CO_2 concentration could simply be the result of dilution (Wallin et al., 2009). The negative correlation between all three dissolved GHG concentrations and discharge further solidifies the evidence for this conclusion.

Dissolved organic carbon (DOC) is the other important carbon component in the carbon cycling system of riparian zones. The DOC was significantly lower in the UNF-C treatment compared to the other treatments. As discussed in the introduction, the two main sources of DOC introduction to the streamwater environment are decomposition (Meyer and Tate, 1983), and the drainage or leaching of DOC produced in the terrestrial component of the riparian zone (Kalbitz et al., 2000; Marx et al., 2017; McGlynn and McDonnell, 2003). In literature, several studies have shown that coniferous forest soils have larger carbon stock and larger carbon sequestration capability than deciduous forest soil (Jandl et al., 2021; Hüblová and Frouz, 2021). Baskerville (2020) also found significantly higher soil organic carbon (SOC) in the undisturbed natural forest (UNF-C and UNF-D) riparian buffer and although insignificant, highest SOC concentrations were measured at the UNF-C site. This therefore further strengthens the argument that the significantly lower DOC in the stream component of UNF-C treatment is the consequences of the higher carbon sequestration potential and lower leaching or drainage of terrestrial organic carbon into the streams.

6.3.2 Dissolved Methane Concentration

Spatial Variation (amongst Riparian Zones)

It was hypothesized that there would be a significant difference in the dissolved GHG concentrations among the RAFS treatments. The hypothesis was accepted for CH_4 concentrations. Dissolved average CH_4 concentrations measured from the HB sampling site were significantly higher, while those from the UNF-C were significantly lower. As mentioned in the introduction, CH_4 can be produced: in the terrestrial component of the riparian zone and introduced into the stream via groundwater (Heilweil et al., 2013; Jones Jr. and Mulholland, 1998), which is seemingly the main source of CH_4; and it can be produced in the anoxic pockets of the stream sediment (Crawford et al., 2014; Stanley et al., 2016). Although not significantly, the HB site had slightly higher average air and water temperature. Methanogens, methane-producing bacteria, are highly sensitive to temperature. They are most effective at warmer temperatures (Huang et al., 2012). Therefore, higher average air and water temperatures could lead to higher methanogenic activity in the stream sediment, but there is a more significant factor at play in this situation. HB was the only sampling site with aquatic plants growing in the stream environment. Aquatic plants release methane through pressurized ventilation of roots which could also contribute to the high CH_4 concentration at the HB site (Joabsson et al., 1999; Milbert et al., 2017).

Moreover, a study conducted in 2009 by Nisbet et al. highlighted that, even though the exact mechanism is not known, there is stress mediated CH_4 released by plants that could be an additional potential source of methane. Ebullition, the release of CH_4 bubbles from the sediment (Bastviken, 2009), was also observed at the HB site. Any disturbance to the sediment seemed to cause the release of large amounts of gas bubbles from the sediment, which could potentially add to the concentration of dissolved gases in the stream. The release of methane bubbles from the sediment was a visual observation.

Additionally, when the terrestrial component of HB was studied, the soil moisture in this sampling site was the lowest compared to the UNF (C and D) and RH sampling sites (Baskerville, 2020). Soil moisture is the most important factor in deciding whether the soil environment is a sink or a source of CH_4. Lower soil moisture makes for an effective methane sink (Baskerville, 2020). This means that the HB site, the warmest and lowest in soil moisture, is the biggest sink of methane gas. This gas can easily leach into the stream through groundwater, thereby increasing the concentration of dissolved CH_4 in the stream environment and therefore cause a significantly greater CH_4 in the HB site.

Temporal Variation (amongst Seasons)

No significant trend was found in the seasonal variability recorded from the study site. Similar to CO_2, significant for the sampling year 2018 and insignificant for the year 2017, it was observed that the CH_4 concentrations were lowest in the fall season. Methanogens are highly sensitive to temperature. They are most effective at warmer temperatures (Huang et al., 2012). Therefore, it was expected that the fall concentrations of CH_4 would be lower than in the other seasons as the temperatures start to drop in the fall season. Alternatively, much like CO_2 concentration, lower CH_4 concentrations in the fall season could result from dilution due to the increased discharge in the streams during these seasons (Wallin et al., 2009).

6.3.3 CH_4 concentration and N limitation

Two studies show the strong association of nitrate concentration with N2O and CH4 emissions in freshwater stream environments. Schade et al. conducted a study in 2016 in three headwater streams in the same watershed to measure gas fluxes in the New Hampshire region of USA, and Smith and Bohlke published a paper in 2019 summarizing their findings from two high nitrate concentrated streams in the midwestern USA that they studied for temporal and spatial GHG emissions. An increase in NO_3^- concentration can reduce CH_4 concentration by suppressing the activity of methanogenesis and increase the N_2O concentration by stimulating the denitrification process (Schade et al., 2016; Smith and Bohlke, 2019). However, the results from this study indicated otherwise. A strong negative correlation was found between the NO_3^- concentration and N_2O concentration, whereas no significant correlation existed between NO_3^- and CH_4 concentration. Hence, although true at the microbial level, other more important factors influence the N_2O and CH_4 production and concentration in this riparian stream.

Literature also states that in the oxic zone, depending on the given high CH_4 abundance, methanotrophs could outcompete nitrifiers/NH_4^+ oxidizers for oxygen (Wang et al., 2019) as oxidizing CH_4 releases more energy. This process would result in the oxidation of CH_4 to CO_2, reducing CH_4 concentration while increasing CO_2 concentration. Although, if NH_4^+ is present in high abundance, if there is high fertilizer runoff, for example, NH_4^+ could inhibit methanotrophs (Jacinthe et al., 2015). In this study, neither of the variables showed a significant correlation to CH_4 concentrations. Despite the lack of direct correlation to NH_4^+ and NO_3^- concentrations, CH_4 did have a significantly negative correlation to TN and N_2O concentrations in the stream, reflecting the negative impact N has on CH_4 concentrations.

6.4.0 Nitrogen cycling in the aquatic component of the RAFS

6.4.1 Nitrous Oxide and Total Nitrogen Concentration

Spatial Variation (amongst Riparian Zones)

It was hypothesized that there would be a significant difference in the dissolved GHG concentrations among the RAFS treatments. The hypothesis was accepted for dissolved N_2O concentrations. Significantly higher aquatic dissolved N_2O concentrations were observed in the undisturbed natural forest dominated by coniferous vegetation (UNF-C). This sampling site also had significantly higher TN; therefore, it can be assumed that the overall input of nitrogen to the streams was highest in UNF-C. This treatment has one of the thickest canopies, one of the main reasons nitrogen input (allochthonous) is high. Oelbermann and Gordon (2000), in their study at the Washington Creek, found that mature riparian zones had higher litterfall than rehabilitated riparian zones, even though the nutrient fluxes were similar.

Both the undisturbed natural forest sites in this study showed higher dissolved N_2O concentrations and higher TN concentrations. These results were significant for UNF-C and insignificant for UNF-D. Higher discharge in UNF-D treatment possibly leads to dilution of nutrients; therefore, the nitrogen concentrations were not significantly higher in UNF-D versus those of UNF-C. The following studies can help shed light on some potential reasons why the undisturbed natural forest vegetation leaches more nitrogen into the stream compared to the RH or HB treatments. Schade et al. (2016), while studying the greenhouse gas fluxes from a variety of riparian streams in New Hampshire, USA, concluded that denser buffer vegetation results in higher litterfall and hence the available organic matter in the stream environment. Soosaar et al. (2011), while studying riparian-dominated forests in agricultural landscapes in Estonia, observed that older riparian buffers tend to lose their buffering capacity over time, leading to a higher leaching of available nutrients. Since UNF treatments (UNF-D and UNF-C) are older compared to RH and HB treatments, it is possible that higher nutrient availability due to abundant litterfall and higher leaching capacity leads to higher nitrogen concentration in streams.

The lowest aquatic N_2O concentration were measured in the HB sampling treatment. The presence of aquatic plants or macrophytes in the HB sampling treatment indicates eutrophication in the stream (O'Hare et al., 2018). In the literature, herbaceous buffers have been shown to have high nitrogen in their terrestrial components (Tufekcioglu et al., 2003). And since herbaceous buffers also have a lower capacity to remove N from runoff (Mayer et al., 2006), this signifies that there is a possibility that a lot of nitrogen is flowing into the stream component of the riparian system. Despite high input, the presence of low dissolved N_2O gas and low TN shows that the aquatic plants are taking up a large concentration of dissolved N. Moreover, the presence of photosynthetic plants indicates the release of large amounts of oxygen from photosynthetic activity by the aquatic fauna in the HB treatment (O'Hare et al., 2018). As per Huang et al., 2015, high amounts of DO can reduce the amount of N_2O produced in the water body as it slows down the process of denitrification, which is the primary source of N_2O production (Smith & Bohlke, 2019).

Temporal Variation (amongst Seasons)

Temporally, the highest aquatic dissolved N_2O concentrations were recorded in Spring 18' sampling season, and the lowest was recorded in the summer sampling seasons (Summer 17' & Summer 18'). However, it should be noted that the TN concentrations were not significantly different amongst seasons. The high Spring 18' concentrations could be attributed to the spring snowmelt event. As mentioned earlier, the snow melt mobilizes the DOC, NH_4^+, and organic N that attaches to the soil particles and becomes part of the aboveground and belowground discharge as the moisture in the soil increases (Marx et al., 2017; Mazza, 2014).

A study published by Webb et al. in 2019 linked the low levels of N_2O concentrations in the summer period to high primary production, which uses the available DIN and introduces O_2 into the water column (Huang et al., 2015), both of which can limit N_2O production via denitrification. Additionally, higher water stratification during summer months, which was not calculated in this study, was recorded as one of the main factors driving low levels of N_2O concentrations in the water columns (Webb et al., 2015). The author further explains that a very limited number of studies have evaluated the temporal/seasonal variation of N_2O concentration in streams, and the ones that have been conducted have had conflicting results (Gao Y et al., 2016; Sovik AK and Klove B, 2007; Xia Y et al., 2013). Another study done by Bruce et al. in 2017 suggested that warmer temperatures fuel higher N_2O production in the stream environment. Still, the emission is also very high because the solubility of N_2O gas decreases with increasing temperature. Therefore, the literature represents conflicting results, but most of these results are based on N_2O emissions and not on dissolved concentrations. Webb et al., 2019 is the only study that looked at the dissolved concentrations.

6.4.2 Ammonium

As described in detail in the introduction, ammonium is formed both in the oxic and anoxic environment as a product of organic nitrogen decomposition. The ammonium (NH_4^+) concentrations were not significantly different among the different RAFS. The NH_4^+ concentrations were very low throughout the Washington Creek, which illustrates that the NH_4^+ formed through the process of decomposition of organic matter or entering the water system through runoff (aboveground & belowground) is being quickly oxidized to other forms of N through the process of nitrification (Duff & Triska, 2000). Partial nitrification releases N_2O, whereas complete nitrification converts ammonium to nitrate (Duff & Triska, 2000). This also explains the negative correlation that was found between nitrate and nitrous oxide concentration.

The temporal variation of the NH_4^+ concentrations shows that the ammonium concentrations were significantly, approximately four times, higher in the Fall 2018 season compared to all the other sampling seasons. NO_3^- during Fall 2018 sampling season dropped drastically in its concentration, approximately four times lower than during the Fall 2017 sampling season. This observation is supported by what we know to be true at the microbial level. Given the optimal conditions, ammonium will be used up quickly to form nitrate and other by-products. This is especially true in surface waters (Wall, 2013) and riparian zone environments (Hefting et al., 2013), where the expected ammonium levels are lower than nitrate. Additionally, the significantly strong negative correlation between the two variables, NH_4^+ and NO_3^- concentrations, further strengthens the evidence.

6.4.3 Nitrate

Although not significantly different among the RAFS, high nitrate (NO_3^-) concentrations were measured from all the treatments which is typical of surface waters and especially streams originating in agricultural landscapes (Wall, 2013). This could indicate a high rate of nitrification in situ and/or high runoff, and leaching of NO_3^- from above ground, that is soil, and below ground, that is groundwater sources.

A few significant differences were observed in the seasonal data collected for nitrate concentrations, but no clear trend in the data was found. The year-over-year data suggested significantly higher NO_3^- concentrations in 2017 than in 2018. This spike in nitrate concentration could be attributed to the use of fertilization in the summer 2017 in the adjacent agricultural landscape during corn plantation. Fertilizer application increases nitrate and ammonium concentration in the soil (Lutes et al., 2019) and, ultimately, in both the aboveground and belowground runoff. The year 2018, highest nitrate concentration was observed in Spring 2018, which can be attributed to the flood event in the Grandriver Watershed. On the contrary, the lowest nitrate concentrations were recorded in the Fall of 2018, when the highest NH4+ concentrations were also observed.

7.0 CONCLUSION

Most of the research on riparian zones focuses on the terrestrial component. A few studies focus on the aquatic component, and yet fewer studies study all three GHG (CO_2, CH_4, and N_2O) concentrations together among treatments differing in riparian vegetation to analyze which treatment has the most significant impact on water quality and GHG concentrations. This research project's broad goal was to bridge that gap in the literature. Reflecting on the results found in this research and others like it, we hope to implement BMPs for Canadian agricultural producers. We hope to influence climate change in the long run positively. The objective of the thesis was to study the GHG mitigation potential of various RAFS treatments (RH, UNF-D, HB, and UNF-C) through measurement of its C and N dynamics and to conclude which RAFS treatment is the most effective at maintaining and/or improving the water quality of the stream.

We hypothesized that there would be a significant difference in the dissolved GHG (CO_2, CH_4, and N_2O) concentrations among the RAFS treatments (RH, UNF-D and UNF-C, and HB). We accepted this hypothesis for CH_4 and N_2O concentrations but rejected it for CO_2 concentrations. The highest N_2O concentration was recorded in the UNF-C treatment and the lowest in the HB treatment. The highest CH_4 concentrations were recorded in the HB treatment, while the UNF-C recorded the lowest CH_4 concentration. CO_2 concentrations were not significantly different amongst the treatments. Furthermore, we hypothesized that other C parameters (stream DOC and sediment OC) would significantly differ among the RAFS treatments (RH, UNF-D and UNF-C, and HB). We accepted our hypothesis and concluded that UNF-C had significantly lower stream DOC, and UNF-C and RH had significantly higher sediment OC as compared to the other treatments. Lastly, we hypothesized that other N parameters (stream and sediment NO_3^-, NH_4^+, and TN) would significantly differ among the

RAFS treatments (RH, UNF-D and UNF-C, and HB). We accepted our hypothesis and concluded that UNF-C had significantly higher stream TN, and UNF-C and RH had significantly higher sediment TN as compared to the other treatments.

Looking at the terrestrial morphology of the riparian treatments, UNF-C and UNF-D were very similar in their characteristics. A closer look at the aquatic morphology and discharge shows that UNF-D and RH were very similar in their morphology. The physical stream characteristics, including discharge, pH, and DO; and their chemical characteristics, including concentrations of GHG were not significantly different. The only significant difference between UNF-D and RH was the morphology and chemical composition of the sediment. Being a shorter buffer width and a newer rehabilitated buffer, the sediment of the RH treatment was much more eutrophic and higher in clay content. Despite the differences, one of the most significant conclusions that can be made from this study is that a rehabilitated forest riparian system can be as effective as a 100-year-old natural forest riparian buffer in improving the water quality of the streams that flow through agricultural landscapes.

8.0 FUTURE RESEARCH

8.1.0 Other confounding factors

The three main confounding factors can be taken into consideration: the tile drainage system that is present in the adjacent agricultural landscape; the effect of in-stream pool-riffle profile and the degree of a stream meandering on the finding of the study; and how the geography of the selected sites can cause variability in the conclusions of the study.

8.1.1 Tile drainage systems

The surface soil at the sampling treatments in this study is characterized as silt loam and clay loam (Baskerville, 2020). Additionally, the agricultural field adjacent to all the sampling treatments practices crop rotation (soy and maize) and uses fertilizer to improve crop yield. All these conditions impact the way water moves from the agricultural field to the nearby surface waters. Several studies conducted in Southern Ontario have analyzed the carbon (C), nitrogen (N), and phosphorus (P) transportation from agricultural land, that has clay loam surface soil, to water bodies through tile drains and surface runoff. A few of these studies and their findings are summarised below.

Tan and Zhang (2011) studied surface runoff and subsurface P losses in free and controlled drainage agricultural fields and concluded that subsurface tile drainage does plan a significant part in soil P losses. Of the total P loss, only 3-5% was lost through surface runoff; the remaining 95-97% was through tile drainage (Tan and Zhang, 2011). Yang Et al. (2022) studied carbon transport from agricultural fields to water bodies in southern Ontario tile drainage systems. This study primarily looked at which vegetation practice contributed to the greatest transport of DIC and DOC and concluded that tile drains were the main mechanism of dissolved carbon loss in agricultural landscapes committed to long-term crop rotation or continuous sod compared to monoculture crop practice (Yang et al., 2022). Additionally, the overall carbon loss in crop rotation was higher than in monoculture crop fields. In clay loam soils, DOC is the main form in which carbon is transported out of the agricultural fields through tile drainage systems (Yang et al., 2022).

Studies done by Duray, along with Woodley (Duray et al., 1996, 2014; Woodley et al., 2018) in Southern Ontario, have focused on nitrate loss in surface runoff and tile drainage systems. One of the studies conducted by Duray et al. (2009) looked at nitrogen losses among unrestricted tile drainage sites, controlled tile drainage, and controlled tile drainage with sub-surface irrigation. Duray et al. (2009) found that controlled drainage systems (with or without subsurface irrigation) are more effective at reducing nitrate losses than unrestricted tile drainage systems. Furthermore, a controlled drainage system with irrigation also increased average crop yields (Duray et al., 2009). Therefore, to understand the impact of tile drains on the stream environment, future endeavors need to focus on defining the type of tile drainage system laid out in the watershed, collecting surface runoff and tile drainage water samples, and comparing these to the values recorded in the stream to investigate the impact of tile drainage systems on the water quality of the riparian streams.

Tile drains can contaminate adjacent groundwater, thereby making tile drainage flow the main source of stream baseflow (Van Stempvoort et al., 2021). This could also be looked at as one of the potential reasons why the RH sampling site had highly eutrophic sediment since this site is closest to the agricultural field among all the treatments, and therefore, the impact of groundwater contamination through tile drains would be the biggest if it were to exist. Therefore, studying levels of groundwater and determining if it is contaminated by tile drainage flow could uncover another variable impacting stream chemistry.

8.1.2 Pool-riffle profile and the degree of a stream meandering

The degree of stream meandering and its pool-riffle profile can influence organic matter retention (Malanson, 1995) and cause variability in sediment depth and nutrient accumulation along the stream (Harrison et al., 2012). A study published in 2012 by Harrison et al. looked at a forested, an urban degraded, and an urban restored steam in Baltimore, MD, USA, to investigate how spatial heterogeneity affects sediment denitrification and other microbial processes such as methanogenesis in streams. They found that forested streams were predominated by organic debris dams, whereas degraded or restored streams most commonly had pool-riffle morphology (Harrison et al., 2012). Additionally, organic debris dams had higher microbial biomass nitrogen (MBN), sediment organic matter (SOM), and moisture content (MC) when compared to pools and riffles. Although not significant but pools, compared to riffles, had higher denitrification potential and organic matter content with a greater possibility of anaerobic conditions (Harrison et al., 2012). No clear trend was found for the process of methanogenesis, but it did exist in all the morphological features, i.e., pools, riffles, and debris dams (Harrison et al., 2012). Another study conducted by Vidon and Serchan (2016) measured the GHG concentrations in the riparian water vs. hyporheic pool vs. hyporheic riffle in a New York mountain stream. They found that in stream pools were a hot spot for CO_2 and CH_4 production, but no clear trend for N_2O concentrations was found.

Therefore, studying the effects of pools, riffles, and meanders and comparing the GHG activity in these different zones could help further our understanding of nutrient dynamics in a stream environment. To reduce the impact of meandering, the sampling sites selected were located on straight patches of the stream. Therefore, there was minimal to no stream meandering within 8-10 meters of the sampling site. As per visual observation, there seemed to be no major pool-riffle profile at the study sites, but this variable was not measured during the study. Considering pools, riffles, and meandering stream morphology as variables in future research endeavors can help either accept or eliminate these variables as confounding factors.

8.1.3 Geography

Lastly, just the geographical distance could ultimately be the defining factor in reasoning out why multiple variables (including discharge, DOC, TN, dissolved CH4, and N2O) for UNF-C had significantly different measurements from the other treatments (UNF-D, RH, and GRS). Treatments HB, UNF-D, and RH were in much closer proximity than UNF-C (refer to figure 4.1). Therefore, creating multiple sampling points between the HB and the UNF-C treatment could potentially provide evidence to either accept or reject geographic location as a confounding factor.

8.2.0 Additional variables to consider

Currently, our major challenge is the lack of full understanding of the nutrient dynamics in different types of RAFS and how this impacts the efficiency and effectiveness of these agroforestry systems. With land use change leaning more towards agriculture and the ever-increasing human population, it is essential that these processes are fully researched and that their GHG mitigation potential and impact on climate change are studied and understood thoroughly. A thorough knowledge of these processes will also help governments implement effective BMPs for Canadian farmers.

To understand the nutrient cycling capacity and capability of RAFS, future research can focus on adding the following variables to the methodology of this research study. GHG emission and emission mitigation potential of a stream is an important variable in understanding the C and N nutrient cycling in RAFS. To understand the full-scale cycling, it is essential to study the input, stream processing, and output of nutrients. Adding the measurement of GHG flux from the stream in future research can help expand the literature. Although the climatic conditions were fairly similar among the different RAFS treatments at Washington sites, due to the close proximity of the study sites, even minor differences in physical stream parameters like oxygen levels and water temperature can impact the GHG emission rates (Huang et al., 2012; Smith and Bohlke, 2019; Wang et al., 2019). These additional measurements can directly reflect the impact that the GHGs produced in the aquatic component of RAFS can have on the environment and therefore, on climate change.

Furthermore, surface water and groundwater systems are two parts of a single interconnected hydrologic system (Naiman et al., 2005). As explained in the introduction, the anoxic zone processing of C and N can considerably impact the in-stream water quality (Deirmendjian and Abril, 2018; Hope et al., 2004; Heilweil et al., 2013; Wall, 2013). To directly measure the magnitude of this impact, it is necessary that groundwater sampling is conducted in future research studies. Lastly, although sediment composition in streams tends to change slowly over time, more frequent sediment sampling can help measure the in-depth impact of soil erosion on water quality and the effectiveness of the riparian buffer in reducing the same.

References

Adair, E. C., D. Binkley, and D. C. Andersen. (2004). Patterns of Nitrogen Accumulation and Cycling in Riparian Floodplain Ecosystems along the Green and Yampa Rivers. Oceologica 139 (1): 108–16.

Adams, B. (2007). Thinking like a human: social science and the two cultures problem. Oryx, 41(3), 275-276.

Afkhami, A., and Norooz-Asl, R. (2008). Micelle-Mediated Extraction and Spectrophotometric Determination of Ammonia in Water Samples utilizing Indophenol Dye Formation. J. Braz. Chem. Soc., 19(8): 1546-1552.

Allan, J.D. (1995). Stream ecology: structure and function of running waters. Chapman and Hall: London.

Altieri, M.A., and Nicholls, C.I. (2005). Agroecology and the Search for a Truly Sustainable Agriculture (1st ed.). Print. United Nations Environmental Programme: Mexico, Mexico. ISBN 968-7913-35-5.

Argerich, A.; Haggerty, R.; Johnson, S.L., et al. 2016. Comprehensive multiyear carbon budget of a temperate headwater stream. *Journal of Geophysical Research: Biogeosciences*. 121: 1306–1315. https://www.fs.usda.gov/treesearch/pubs/56803.

Bastviken, D., Cole, J.J., Pace, M.L., and van de Bogert, M. (2008). The fates of methane from different lake habitats – connecting whole-lake budgets and CH_4 emissions. *J Geophys. Res.*, 113.

Bastviken, D. (2009). CH4. In: Likens GE, ed. Encyclopedia of Inland waters, Vol. 2, Oxford: Elsevier, 783–805.

Bastviken, D., Santoro, A.L., Marotta, H., Pinho, L.Q., Calheiros, D.F., Crill, P., amd Enrich-Prast, A. (2010). Methane Emissions from Pantanal, Soth America, During the Low Water Season: Toward More Comprehensive Sampling. *Environ. Sci. Technol.*, 44: 5450-5455.

Baskerville, M., Reddy, N., Ofusu, E., Thevathasan, N.V., and Oelbermann, M. (2020). Vegetation Type Does not Affect Nitrous Oxide Emissions from Riparian Zones in Agricultural Landscapes. *Environmental Management,* 67:371–383.

Beetz, A. 2002. Agroforestry: An Overview. Horticulture Systems Guide. National Sustainable Agriculture Information Center: Appropriate Technology Transfer for Rural Areas (ATTRA). Fayetteville, AR. http://attra.ncat.org/attra-pub/PDF/agrofor.pdf.

Belt, G. H., Jay O'L. and Troy M. (1992). "Design Of Forest Riparian Buffer Strips For the Protection of Water Quality: Analysis of the Scientific Literature". Idaho Forest, Wildlife, and

Range Policy Analysis Group Report No.8. Retrieved May 17, 2021 from: http://www/uidaho.edu/cfwr/ pag/pagr8.html.

Bernot, M.J., Sobota, D.J., Hall, R.O., Jr, Mulholland, P.J., Dodds, W.K., Webster, J.R., Tank, J.L., Ashkenas, L.R., Cooper, L.W., Dahm, C.N., Gregory, S.V., Grimm, N.B., Hamilton, S.K., Johnson, S.L., McDowell, W.H., Meyer, J.L., Peterson, B., Poole, G.C., Valett, H.M., Arango, C., Beaulieu, J.J., Burgin, A.J., Crenshaw, C., Helton, A.M., Johnson, L., Merriam, J., Neiderlehner, B.R., O'brien, J.M., Potter, J.D., Sheribley, R.W., Thomas, S.M. and Wilson, K. (2010), Inter-regional comparison of land-use effects on stream metabolism. *Freshwater Biology*, 55: 1874-1890. https://doi.org/10.1111/j.1365-2427.2010.02422.x

Bialkowski, S. (2006). Carbon Dioxide and Carbonic Acid. In Chemistry 3650; Environmental Chemistry. Online. Retrieved March 15, 2021, from: http://ion.chem.usu.edu/~sbialkow/Classes/3650/Carbonate/Carbonic%20Acid.html

Bieniada, A. (2020). *Methane cycling in horticultural extracted, restored, and unrestored peatlands in central Alberta, Canada*. PHD Thesis, Environment and Resource Studies. Waterloo: University of Waterloo.

Billett, M. F., C. M. Deacon, S. M. Palmer, J. J. C. Dawson, and D. Hope (2006), Connecting organic carbon in stream water and soils in a peatland catchment, *J. Geophys. Res*., 111, G02010, doi:10.1029/2005JG000065.

Bonsal, B.R., Peters, D.L., Seglenieks, F., Rivera, A., and Berg, A. (2019): Changes in freshwater availability across Canada; Chapter 6 in Canada's Changing Climate Report, (ed.) E. Bush and D.S. Lemmen; Government of Canada, Ottawa, Ontario, p. 261–342.

Bosch J, Hewlett J. 1982. A review of catchment experiments to determine the effect of vegetation changes on water yield and evapotranspiration. J Hydrol 55:3–23.

Brace, L., Bange, H.W., Landt, R., Sanders, T., and Dahnke, K. (2017). High Resolution Measurements of Nitrous Oxide (N_2O) in the Elbe Estuary. *Front. Mar. Sci.*,4:162.

Bush, E. and Lemmen, D.S., editors (2019): *Canada's Changing Climate Report*; Government of Canada, Ottawa, ON. 444 p. Online. Retrieved October 15, 2020, from: https://www.nrcan.gc.ca/sites/www.nrcan.gc.ca/files/energy/Climate-change/pdf/CCCR_FULLREPORT-EN-FINAL.pdf.

Cai, W.-J., Guo, X., Chen, C.-T. A., Dai, M., Zhang, L., Zhai, W., Lohrenz, S. E., Yin, K., Harrison, P. J., and Wang, Y. (2008). A comparative overview of weathering intensity and HCO_3^- flux in the world's major rivers with emphasis on the Changjiang, Huanghe, Zhujiang (Pearl) and Mississippi Rivers. *Continental Shelf Research*, **28**(12), 1538–1549.

Capon SJ, Chambers LE, MacNallly R, Naiman RJ, Davies P, Marshall N, Pittock J, Reid M, Capon T, Douglas M, Catford J, Baldwin DS, Stewardson M, Roberts J, Parsons M, Williams SE (2013) Riparian ecosystems in the 21st century: hotspots for climate change adaptation. *Ecosystems* 16:359–381.

Chapman, J.M., Proulx, C.L., veilleux, M.A.N., Levert, C., Bliss, S., André, M.E., Lapointe, N.W.R. , Cooke, S.J. (2014). Clear as mud: a meta-analysis on the effects of sedimentation on freshwater fish and the effectiveness of sediment-control measures. *Water Res*., 56: 190-202.

Chidthaisong, A. and Conrad, R. (2000).Turnover of glucose and acetate coupled to reduction of nitrate, ferric iron and sulfate and to methanogenesis in anoxic rice field soil, *FEMS Microbiology Ecology,* 31(1):73–86.

Crowley, T. J. (2000). Causes of Climate Change Over the Past 1000 Years. *Science* 289: 270-076.

Courtney, D., and Brodziak, J. (2010). Oceanographic Features in the Vicinity of a North Pacific Swordfish Stock Boundary. Honolulu, HI: NOAA Fisheries, Pacific Islands Fisheries Science Center. Online. Retrieved January 21, 2020 from: http://isc.ac.affrc.go.jp/pdf/BILL/ISC10_BILL_1/BILL_Apr10_FINAL_WP04.pdf

Czuba, J. A., Magirl, C. S., Czuba, C. R., Grossman, E. E., Curran, C. A., Gendaszek, A. S., and Dinicola, R. S. (2011, August). Comparability of Suspended-Sediment Concentration and Total Suspended Solids DataSediment Load from Major Rivers into Puget Sound and its Adjacent Waters. USGS Fact Sheet 2011–3083. Tacoma, WA: U S Geological Survey.

D'amario, S. C., and M. A. Xenopoulos (2015), Linking dissolved carbon dioxide to dissolved organic matter quality in streams, *Biogeochemistry,*126(1–2), 99–114.

Dauer, D.M., Ranasinghe, J.A., Weisberg, S.B. (2000). Relationships between benthic community condition, water quality, sediment quality, nutrient loads, and land use patterns in Chesapeake Bay. *Estuaries* 23(1):80–96.

Deirmendjian, L. and Abril, G. (2018). Carbon dioxide degassing at the groundwater-stream-atmosphere interface: isotopic equilibration and hydrological mass balance in a sandy watershed. *Journal of Hydrology,* 558: 129-143.

Derksen, C., Burgess, D., Duguay, C., Howell, S., Mudryk, L., Smith, S., Thackeray, C. and Kirchmeier-Young, M. (2018): Changes in snow, ice, and permafrost across Canada; Chapter 5 in Canada's Changing Climate Report, (ed.) E. Bush and D.S. Lemmen; Government of Canada, Ottawa, Ontario, p.194–260.

Dillaha, T.A. III and Inamadar, S.P. (1997). "Buffer Zones as Sediment Traps or Sources". In Buffer Zones: Their Processes and Potential in Water Protection, edited by N.E. Haycock, T.P. Burt, K.W.T. Goulding and G. Pinay. Harpenden, Hertfordshire, UK.

Doods, W., Whiles, M. (2010). Freshwater Ecology: concepts and environmental application limnology. Elsevier Inc.: California, USA.

dos Reis Oliveira, P.C., van der Geest, H.G., Kraak, M.H.S., and Verdonschot, P.F.M., (2010). Land use affects lowland stream ecosystems through dissolved oxygen regimes. *Sci Rep* 9, 19685. https://doi.org/10.1038/s41598-019-56046-1

Drury, C.F., Tan, C.S., Gaynor, J.D., Oloya, T.O. and Welacky, T.W. (1996), Influence of Controlled Drainage-Subirrigation on Surface and Tile Drainage Nitrate Loss. *Journal of Environmental Quality*, 25: 317-324.

Drury, C.F., Tan, C.S., Reynolds, W.D., Welacky, T.W., Oloya, T.O. and Gaynor, J.D. (2009), Managing Tile Drainage, Subirrigation, and Nitrogen Fertilization to Enhance Crop Yields and Reduce Nitrate Loss. *J. Environ. Qual*., 38: 1193-1204.

Drury, C.F., Tan, C.S., Welacky, T.W., Reynolds, W.D., Zhang, T.Q. Oloya,T.O. (2014). Reducing nitrate loss in tile drainage water withcover crops and watertable management systems. *J. Environ. Qual*.43: 587–598.

Duff, J.H. and Triska, F.J. (2000). Nitrogen Biogeochemistry and Subsurface Exchange in Streams. In Jones, J.B., and Mulholland, P.J. (Ed.), Streams and Ground Waters (pp. 197-217). Elservier Inc.: San Diego, California.

Dyer, L. (2010). Evaluation of soil chemical and physical characteristics in a complex agroecosystem in the Argentine Pampa. MSc. Thesis, Environment and Resource Studies. Waterloo: University of Waterloo.

El-Dessouky, H.T., and Ettouney, H.M. (2002). Fundamentals of Salt Water Desalination. Elselvier Inc.: Amsterdam, The Netherlands.

Elliot, A. C., and Woodward, W. A. (2007). Statistical analysis quick reference guidebook with SPSS examples (1st Edition ed.). London: Sage Publications.

EPA, (2017). *Causes of Climate Change*. Online. Retrieved on March 7, 2019, from: https://19january2017snapshot.epa.gov/climate-change-science/causes-climate-change_.html#Reflectivity.

FAO (2016). The State of Food and Agriculture: Climate Change, Agriculture and Food Security. Food and Agriculture Organization of the United Nations. Online. Retrieved on November 14, 2019, from: http://www.fao.org/3/i6030e/i6030e.pdf.

Fenchel, T., King, G.M., and Blackburn, T.H. (2012). Chapter 1 - Bacterial Metabolism. In Bacterial Biogeochemistry (Third Edition). *Academic Press*, 1-34. Retrieved from: https://www.sciencedirect.com/science/article/pii/B9780124158368000013.

Field, A. (2009). Discovering statistics using SPSS. London, Great Britain: Sage Publications Ltd.

Fields, S. (2004). Global Nitrogen Cycling out of Control. *Environmental Health Perspectives*, 112(10): A557-A563.

Finlay, J. C., (2011). Stream size and human influences on ecosystem production in river networks. *Ecosphere*, 2(8):art87. doi:10.1890/ES11-00071.1

Fitzhugh, R., Furman, T., Webb, J., Cosby, B., and Driscoll, C. (1999). Longitudinal and Seasonal Patterns of Stream Acidity in a Headwater Catchment on the Appalachian Plateau, West Virginia, U.S.A. *Biogeochemistry, 47*(1), 39-62.

Fondriest Environmental, Inc. "pH of Water." (2013). Fundamentals of Environmental Measurements. Online. Retrieved March 17, 2020 from: < https://www.fondriest.com/environmental-measurements/parameters/water-quality/ph/ >.

Fortier J, Gagnon D, Turax B, Lambert F (2010) Nutrient accumulation and carbon sequestration in 6-year-old hybrid poplars in multiclonal agricultural riparian buffer strips. *Agr Ecosyst Environ* 137:276–287.

Foster, J. C. (1995). Soil Nitrogen. In K. Alef, and P. Nannipieri, Methods in applied soil microbiology and biochemistry. San Diego: Academic Press.

Francis, C., Beman, M., Kuypers, M. (2007). New processes and players in the nitrogen cycle: The microbial ecology of anaerobic and archaeal ammonia oxidation. *The ISME journal,* 1: 19-27. 10.1038/ismej.2007.8.

Gao, Y., Zhang, Z., Liu, X., Yi, N., Zhang, L., Song, W., Wang, Y., Maumdar, A., and Yan, S. (2016). Seasonal and diurnal dynamics of physicochemical parameters and gas production in vertical water column of a eutrophic pond. *Ecol Eng,* 87:313–323.

Gilliam, J.W., D.L. Osmond, and R.O. Evans. 1997. Selected agricultural best management practices to control nitrogen in the Neuse River Basin. North Carolina Agricultural Research Service Technical Bulletin 311. Raleigh, N.C. 58 pages.

Golterman, H.L. (1975) Chemistry. In: Whitton BA (ed) River ecology. University of California Press, Berkeley, pp 39–80.

Hakanson, L. (2005). The relationship between salinity, suspended particulate matter and water clarity in aquatic systems. *Ecological Research*, 21(1): 75-90.

Hamid, A., Bhat, S.U. and Jehangir, A. (2020). Local determinants influencing stream water quality. *Appl Water Sci*, 10:24.

Harrison, M.D., Groffman, P.M., Mayer, P.M., and Kaushal, S.S. (2012). Microbial biomass and activity in geomorphic features in forested and urban restored and degraded streams. *Ecological engineering*. 38(1):1-10.

Hickin, E. J. (Ed.). (1995). River Geomorphology. Chichester: Wiley.

Hilliard, C., and Reedyk, S. (2014). *Riparian Areas Management*. Agriculture and Agri-food Canada.

Hefting, M. M., R. Bobbink, and H. De Caluwe. 2003. Nitrous Oxide Emission and Denitrification in Chronically Nitrate-Loaded Riparian Buffer Zones. *Journal of Environmental Quality* 32: 1194–1203.

Heilweil, V. M., P. L. Grieve, S. A. Hynek, S. L. Brantley, D.K. Solomon, and D. W. Risser. 2015. Stream measurements locate thermogenic methane fluxes in groundwater discharge in an area of shale-gas development. *Environmental Science and Technology*, 49:4057–4065.

Hilton, A., & Armstrong, R.A. (2006). Statnote 6: post-hoc ANOVA tests. Microbiologist, 34-36.

Hope, D., M. F. Billett, and M. S. Cresser (1994), A review of the export of carbon in river water—Fluxes and processes. *Environ. Pollut*., 84(3), 301–324.

Huang, T. H., Y. H. Fu, P. Y. Pan, and C. T. A. Chen (2012), Fluvial carbonfluxes in tropical rivers, *Curr. Opin. Environ. Sustain*.,4(2), 162–169.

Hüblová, L. and Frouz, J. (2021). Contrasting effect of coniferous and broadleaf trees on soil carbon storage during reforestation of forest soils and afforestation of agricultural and post-mining soils. *Journal of Environmental Management*, 290: 112567. 10.1016/j.jenvman.2021.112567

Hurlbert, S.H. (1984). Pseudoreplication and the Design of Ecological Field Experiments. *Ecological Monographs*, 54(2): 187-211.

Hynes, H.B.N (1960). The biology of polluted waters. Liverpool Univ. Press, Liverpool, p 202.

IBM Corp. Released 2017. SPSS Statistics for Windows, Version 25. Armonk, NY: IBM Corp.

IPCC (2014). Climate Change 2014: Synthesis Report (AR5). [R.K. Pachauri and L.A. Meyer (eds.)]. IPCC, Geneva, Switzerland, 151 pp.

IPCC (2018). Global Warming of 1.5°C: An IPCC Special Report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change, sustainable development, and efforts to eradicate poverty [Masson-Delmotte, V., P. Zhai, H.-O. Pörtner, D. Roberts, J. Skea, P.R. Shukla, A. Pirani, W. Moufouma-Okia, C. Péan, R. Pidcock, S. Connors, J.B.R. Matthews, Y. Chen, X. Zhou, M.I. Gomis, E. Lonnoy, T. Maycock, M. Tignor, and T. Waterfield (eds.)]. Online. Retrieved on January 7, 2020, from: https://www.ipcc.ch/site/assets/uploads/sites/2/2019/06/SR15_Full_Report_High_Res.pdf.

Jacinthe, P. A., P. Vidon, K. Fisher, X. Liu, and M. E. Baker. 2015. Soil Methane and Carbon Dioxide Fluxes from Cropland and Riparian Buffers in Different Hydrogeomorphic Settings. Journal of Environment Quality, 44 (4): 1080.

Jandl, R., Ledermann, T., Kindermann, G., and Weiss, P. (2021). Soil Organic Carbon Stocks in Mixed-Deciduous and Coniferous Forests in Austria. *Frontiers in Forests and Global Change*, 4. Retrieved from: https://www.frontiersin.org/articles/10.3389/ffgc.2021.688851.

Jeong, J. J., S. Bartsch, J. H. Fleckenstein, E. Matzner, J. D. Tenhunen, S. D. Lee, S. K. Park, and J. H. Park (2012), Differential storm responses of dissolved and particulate organic carbon in a mountainous headwater stream, investigated by high-frequency, in situ optical measurements. *J. Geophys. Res*.,117, G03013, doi:10.1029/2012JG001999.

Joabsson A, Christensen TR, Wallén B. 1999. Vascular plant controls on CH4 emissions from northern peat forming wetlands. Trends in Ecology and Evolution 14:385–388.

Jones, J. B. Jr, and Mulholland, P. J. (1998). Methane input and evasion in a hardwood forest stream: effects of subsurface flow from shallow and deep pathways. *Limnology and Oceanography* 43:1243–1250.

Jose, S. 2009. Agroforestry for ecosystem services and environmental benefits: An overview. Agro Syst 76:1-10.

Kalbitz, K., S. Solinger, J. H. Park, B. Michalzik, and E. Matzner (2000), Controls on the dynamics of dissolved organic matter in soils: A review, *Soil Sci*., 165(4), 277–304.

Kim, S.J., Ohte, N., Kawasaki, M., Katsuyama, M., Tokuchi, N., and Hobara, S. (2003). Interactive responses of dissolved sulfate and nitrate to disturbance associated with pine wilt disease in a temperate forest. *Soil Sci Plant Nutr*. 49(13):539–550.

Kim, S.J., and Kim, J. (2006). How to evaluate the DOC and POC discharge from forest 15 ecosystem during monsoon? USA PUB Workshop, CUASHI

Krawczyk, W. E. and D. Ford. (2006). Correlating specific conductivity with total hardness in limestone and dolomite karst waters. *Earth Surface Processes and Landforms* 31: 221-234.

Kumar, M.P., and Prabhahar, C. (2012). Physio-chemical parameters of river water: a review. *Int J Pharm Biol Arch*, 3:1304–1312.

Langland, M., & Cronin, T. (Eds.). (2003). A Summary Report of Sediment Processes in Chesapeake Bay and Watershed. In Water-Resources Investigations Report 03-4123. New Cumberland, PA: U S Geological Survey. Retrieved from http://pa.water.usgs.gov/reports/wrir03-4123.pdf

Larmola, T. (2005). Carbon Gas Exchange in the Littoral Zone of Boreal Lakes. Online. Retrieved on January 7th, 2020 from: https://erepo.uef.fi/bitstream/handle/123456789/8551/urn_isbn_952-458-760-2.pdf?sequence=1andisAllowed=y.

Larson, D.M., Dodds, W.K. and Veach, A.M. (2019). Removal of Woody Riparian Vegetation Substantially Altered a Stream Ecosystem in an Otherwise Undisturbed Grassland Watershed. *Ecosystems* **22,** 64–76.

Lindsey, K., Albertson, V.O., and Melinda, D. D. (2018). Impacts of stream riparian buffer land use on water temperature and food availability for fish. *Journal of Freshwater Ecology*, 33:1, 195-210.

Loris, D. and Gwenaël A. (2018). Carbon dioxide degassing at the groundwater-stream-atmosphere interface: isotopic equilibration and hydrological mass balance in a sandy watershed, *Journal of Hydrology*, 558: 129-143.

Loughrin, J.H., Antle, S.W. and Polk, J. (2017). A Gas Chromatographic Method for the Determination of Bicarbonate and Dissolved Gases. *Front. Environ. Sci.* 5:65.

Lu, Y. H., J. E. Bauer, E. A. Canuel, R. M. Chambers, Y. Yamashita, R. Jaffe, and A. Barrett (2014), Effects of land use on sources and ages of inorganic and organic carbon in temperate headwater streams, *Biogeochemistry*, **119**(1–3), 275–292.

Lukyanets, A.S. and Ryazantsev, S.V. (2016). Economic and Socio-Demographic Effects of Global Climate Change. *International Journal of Economics and Financial Issues*, 6 (S8): 268-273.

Lutes K., Oelbermann, M., Thevathasan, N.V., and Gordon, A.M. (2019). Assessing the impact of fertilizer application on net soil-derived emission budgets from a temperate willow short rotation coppice system. *Biomass and Bioenergy,* 120:135-143.

Lyons, J., Thimble, S.W., & Paine, L.K. (2000). Grass Versus Trees: Managing Riparian Areas to Benefit Streams of Central North America. *JAWRA Journal of The American Water Resources Association,* 36:919-930.

Mackie GL (2001) Applied Aquatic Ecosystem Concepts. Kendall/Hunt Publishing, Dubuque IA.

Malanson GP (1995) Riparian landscapes. Cambridge. University Press, New York, NY, p 296.

Mallory, E.C. (1993). Effects of some rehabilitative measures on reaches of two degraded streams draining agricultural areas. MSc. thesis, Department of Environmental Biology, University of Guelph, 142 pp.

Marques de Sa, J.P. (2007). Applied Statistics: Using SPSS, STATISTICA, MATLAB and R (2nd ed.). Heidelberg, NY: Springer.

Martínez, A., Larrañaga, A., Pérez, J., Descals, E., Pozo, J. (2014). Temperature affects leaf litter decomposition in low-order forest streams: field and microcosm approaches, *FEMS Microbiology Ecology*, 8(1): 257–267.

Marx, A., J. Dusek, J. Jankovec, M. Sanda, T. Vogel, R. van Geldern, J. Hartmann, and J. A. C. Barth (2017), A review of CO2 and associated carbon dynamics in headwater streams: A global perspective, *Rev. Geophys*., 55, 560–585, doi:10.1002/2016RG000547.

May, S. (2017). *What is Climate Change*. Online. Retrieved December 10, 2019, from: https://www.nasa.gov/audience/forstudents/k-4/stories/nasa-knows/what-is-climate-change-k4.html.

Mayer, P.M., Reynolds, S.K., McCutchen, M.D., and Canfield, T.J. (2006). Riparian buffer width, vegetative cover, and nitrogen removal effectiveness: A review of current science and regulations. EPA/600/R-05/118. Cincinnati, OH, U.S. Environmental Protection Agency.

Mazza, R.; Wondzell, S.; Zarnetske, J. (2014). The stream subsurface: nitrogen cycling and the cleansing function of hyporheic zones. Science Findings 166. Portland, OR: U.S. Department of Agriculture, Forest Service, Pacific Northwest Research Station. 6 p.

McGlynn, B. L., and J. J. McDonnell (2003), Role of discrete landscape units in controlling catchment dissolved organic carbon dynamics, *Water Resour. Res.*, 39(4), 1090, doi:10.1029/2002WR001525.

McNally, W. H., and Mehta, A. J. (2004, June). Sediment Transport and Deposition in Estuaries (Sample Chapter). In Encyclopedia of Life Support Systesm (EOLSS): Coastal Zones and Estuaries. Retrieved from http://www.eolss.net/sample-chapters/c09/E2-06-01-04.pdf

Meadley, S. L., and Angell, C. (2015). Water and its relatives: The stable, supercooled and particularly the stretched regimes. In F. Bruni, M. A. Ricci, and P. G. Debenedetti (Eds.), *Proceedings of the International School of Physics "Enrico Fermi" - Water: Fundamentals as the Basis for Understanding the Environment and Promoting Technology* (pp. 19-43). (Proceedings of the International School of Physics "Enrico Fermi"; Vol. 187). IOS Press. https://doi.org/10.3254/978-1-61499-507-4-19.

Meyer, J. L., and C. M. Tate (1983), The effects of watershed disturbance on dissolved organic-carbon dynamics of a stream, *Ecology*,64(1),33–44.

Midwood, A.J. and T.W. Boutton. 1998. Soil carbonate decomposition by acid has little effect on δ13C of organic matter. Soil Biol. Biochem. 30:1301-1307.

Milberg, P., Törnqvist, L., Westerberg, L.M., Bastviken, D. (2017). Temporal variations in methane emissions from emergent aquatic macrophytes in two boreonemoral lakes, *AoB PLANTS*, 9 (4): 29. https://doi.org/10.1093/aobpla/plx029

Miller, R.O., and Kissel, D. E. (2010). Comparison of Soil pH Methods on Soils of North America. Soil Sci. Soc. Am. J., 74:310–316.

Miranda, K.M., Espey, M.G., and Wink, D.A. A Rapid, Simple Spectrophotometric Method for Simultaneous Detection of Nitrate and Nitrite. Biology and Chemistry, 5 (1): 62–71.

Morrill, J. C.; Bales, R. C.; Conklin, M. H. (2001). The Relationship Between Air Temperature and Stream Temperature. *American Geophysical Union*, Spring Meeting 2001, abstract id. H42A-09.

Naiman, R. J., H. Decamps, and M. E. McClain. (2005). Riparia: Ecology, Conservation, and Management of Streamside Communities. Elsevier Academic Press, Burlington, MA.

Oelbermann, M. and Gordon, A.M. (2000). Quantity and Quality of Autumnal Litterfall into a Rehabilitated Agricultural Stream. J. Environ. Qual., 29: 603-611.

Oelbermann, M., Gordon, A. M., and Kaushik, N. K. (2008). Biophysical changes resulting from 16 years of riparian forest rehabilitation: An example from the Southern Ontario agricultural landscape. In A. M. Gordon, and S. Jose, Toward agroforestry design: An ecological approach (pp. 13-26). Dordrecht, Netherlands: Springer.

Oelbermann, M., and B. A. Raimbault. 2015. Riparian Land-Use and Rehabilitation : Impact on Organic Matter Input and Soil Respiration. Environmental Management 55: 496–507.

O'Hare, M.T., Baattrup-Pedersen, A., Baumgarte, I., Freeman, A., Gunn, I. D. M., Lázár, A. N., Sinclair, R., Wade, A. J., Bowes, M. J. (2018). Responses of Aquatic Plants to Eutrophication in Rivers: A Revised Conceptual Model. *Front. Plant Sci.,*9:451.

"One-way ANOVA in SPSS Statistics", (2013). Laerd Statistics, Lund Research Ltd. Online. Retrieved December 7, 2018 from: https://statistics.laerd.com/spss-tutorials/one-way-anova-using-spss-statistics.php.

Ostrom, N. E., Gandhi, H., Trubl, G., and Murray, A. E. (2016). Chemodenitrification in the cryoecosystem of Lake Vida, Victoria Valley, Antarctica. Geobiology 14, 575–587.

Oquist, M.G., Wallin, M., Seibert, J., Bishop, K., Laudon, H. (2009). Dissolved inorganic carbon export across the soil/stream interface and its fate in a boreal headwater stream. *Environ. Sci. Technol.,* 43 (19): 7364-7369.

Paerl, H. (2017). The cyanobacterial nitrogen fixation paradox in natural waters. *Research 2017,* 6(F1000 Faculty Rev):244.

Pattillo, C. (1994). Determining the Settling Velocity. In Intro to Biochemical Engineering Term Project. Retrieved from http://www.rpi.edu/dept/chem-eng/Biotech-Environ/SEDIMENT/sedsettle.html

Pedersen, O., Colmer, T.D., Sand-Jensen, K. (2013). Underwater Photosynthesis of Submerged Plants – Recent Advances and Methods. *Frontiers in Plant Science* 4:140. DOI=10.3389/fpls.2013.00140

Pierangeli, G.M.F., Domingues, M.R., Jesus, T.A., Coelho, L.H.G., Hanisch, W.S., Pompêo, M.L.M., Saia, F.T., Gregoracci, G.B., and Benassi, R.F. (2021) Higher Abundance of Sediment Methanogens and Methanotrophs Do Not Predict the Atmospheric Methane and Carbon Dioxide Flows in Eutrophic Tropical Freshwater Reservoirs. *Front. Microbiol.* 12:647921. doi: 10.3389/fmicb.2021.647921

Provin, T.L., and Hossner, L.R. (2018). What Happens to Nitrogen in Soils? Texas AandM Agrilife Extension. Online. Retrieved May 17, 2021 from: https://agrilifeextension.tamu.edu/library/gardening/what-happens-to-nitrogen-in-soils/.

Purcell, A. and Hudderston, N. (2016). Frontiers in Decadal Climate Variability: Proceedings of a Workshop. Washington, DC: National Academies Press. DOI: 10.17226/23552.

Rassamee, V., Sattayatewa, C., Pagilla, K., and Chandran, K. (2011). Effect of oxic and anoxic conditions on nitrous oxide emissions from nitrification and denitrification processes. *Biotechnol Bioeng*., 108(9): 2036-2045.

Raymond, P. A., Oh, N. H., Turner, R. E., and Broussard, W. (2008). Anthropogenically enhanced fluxes of water and carbon from the Mississippi River. *Nature,* 451, 449–452.

Rickson, R.J. (2014). Can control of soil erosion mitigate water pollution by sediments? *Sci. Total Environ*., 468–469: 1187.

Robinson, J., Francis, G., Legge, R. Andamp; Lerner, S. (1990). Defining a sustainable society: values, principles and definitions. Alternatives, 17 (2), 36-46.

Rosamond, M.S., Thuss, S.J., and Schiff, S.L. (2012). Dependence of riverine nitrous oxide emissions on dissolved oxygen levels. Nature Geosci, 5:715-718.

Schade, J.D., Bailio, J. and McDowell, W.H. (2016). Greenhouse gas flux from headwater streams in New Hampshire, USA: Patterns and drivers. *Limnol. Oceanogr*. 61: S165–S174.

Schlesinger, W.H.; Bernhardt, E.S. Biogeochemsitry: An Analysis of Global Change, 3rd ed.; Wiley: New York, NY, USA, 2013.

Seltmen, H.J. (2012). Experimental Design and Analysis. Retrieved December 7, 2018 from: http://www.stat.cmu.edu/~hseltman/309/Book/Book.pdf

Søvik, A.K., and Kløve, B. (2007) Emission of N2O and CH4 from a constructed wetland in southeastern Norway. *Sci Total Environ*, 380:28–37.

Stanley, E.H., Casson, N.J., Christel, S.T., Crawford, J.T., Loken, L.C., Oliver, S.K. (2015). The ecology of methane in streams and rivers: patterns, controls, and global significance. *Ecological Monographs*, 86(2), 146-171.

Steel, G.C., Torrie, J.H., and Dikey, D.A. (1997). Principles and Procedures of Statistics: A Biometrical Approach. McGraw-Hill, New York.

Stephen, J., Dugdale, I.A., Malcolm, K. K,, and David M.H., (2018). Stream temperature under contrasting riparian forest cover: Understanding thermal dynamics and heat exchange processes. *Science of The Total Environment*, 610-611: 1375-1389.

Silva, R.F.B.d.; Batistella, M.; Moran, E.F. (2018). Regional Socioeconomic Changes Affecting Rural Area Livelihoods and Atlantic Forest Transitions. *Land*, 7(4):125. https://doi.org/10.3390/land7040125

Smith, R.L. and Bohlke, J.K. (2019). Methane and nitrous oxide temporal and spatial variability in two midwestern USA streams containing high nitrate concentrations. *Science of the Total Environment*, 685: 574-588.

Soosaar, K., Ü. Mander, M. Maddison, A. Kanal, A. Kull, K. Lõhmus, J. Truu, and J. Augustin. (2011). Dynamics of Gaseous Nitrogen and Carbon Fluxes in Riparian Alder Forests. Ecological Engineering 37 (1): 40–53.

St. Jean, G. (2003). Automated quantitative and isotopic (13C) analysis of dissolved inorganic carbon and dissolved organic carbon in continuous flow using a total organic carbon analyzer. Rapid Communications in Mass Spectrometry, 17: 419-428.

Tan,C.S. and Zhang, T. Q. (2011). Surface runoff and sub-surface drainage phosphorus losses under regular free drainage and controlled drainage with sub-irrigation systems in southern Ontario. *Canadian Journal of Soil Science*. 91(3): 349-359.

Texas A and M Agrilife Extension. 2009. *Don't Bag It – Compost It!! Chapter 1, The Decomposition Process*. College Station, Texas: Aggie Horticulture.

Thauer, R.K., Kaster, A-K., Seedorf, H., Buckel, W., Hedderich, R. (2008). Methanogenic archaea: ecologically relevant differences in energy conservation. *Nat Rev Micro*, 6: 579-591

Tobias, C. and Bohlke, J. (2011). Biological and Geochemical Controls on Diel Dissolved Inorganic Carbon Cycling in a Low-Order Agricultural Stream: Implications for Reach Scales and Beyond. *Chemical Geology*. 283: 18-30.

Tomarken, A.J., & Serlin, R.C. (1986). Comparison of ANOVA alternatives under variance

heterogeneity and specific noncentrality structures. Psychological Bulletin, 99 (1), 90-99.

Tufekcioglu, A., J. W. Raich, T. M. Isenhart, and R. C. Schultz. 2003. Biomass, Carbon and Nitrogen Dynamics of Multi-Species Riuparian Buffers within an Agricultural Watershed in Iowa, USA. Agroforestry Systems 57 (1981): 187–98.

University of Waterloo. *University of Waterloo Weather Station data archives*. Available at (verified 22 March 2021). University of Waterloo, Waterloo, ON, Canada. 2017

University of Waterloo. *University of Waterloo Weather Station data archives*. Available at (verified 22 March 2021). University of Waterloo, Waterloo, ON, Canada. 2018

U.S. EPA. 2001. Methods for collection, storage and Manipulation of sediments for chemical and toxicological analyses: Technical Manual. EPA 823-B-01-002. U.S. Environmental Protection Agency, Office of Water, Washington, DC

U.S. EPA. 2002. Nitrification. U.S. Environmental Protection Agency, Office of Water, Washington, DC

U.S. EPA. 2010. Guidance for Federal land Management in the Chesapeake Bay Watershed. Chapter 5. Riparian Area Management. EPA 841-R-10-002. U.S. Environmental Protection Agency, Office of Water, Washington, DC

Van Stempvoort, D. R., MacKay, D. R., Koehler, G., Collins, P., & Brown, S. J. (2021). Subsurface hydrology of tile-drained headwater catchments: Compatibility of concepts and hydrochemistry. *Hydrological Processes*, 35(9), e14342.

Vidon, P., and Serchan, S. (2016). Impact of Stream Geomorphology on Greenhouse Gas Concentration in a New York Mountain Stream. *Water, air, and soil pollution*. 227(12):1-13.

Wall, D. (2013). Nitrogen in Minnesota Surface Waters. Online. Retrieved February 12, 2020 from: https://www.pca.state.mn.us/sites/default/files/wq-s6-26a.pdf.

Wallin, M., Buffam, I., Oquist, M., Laudon, H., and Bishon, K. (2009). Temporal and spatial variability of dissolved inorganic carbon in a boreal stream network: Concentrations and downstream fluxes. *Journal of Geophysical Research*, 115.

Wallin, M. B., S. Löfgren, M. Erlandsson, and K. Bishop (2014), Representative regional sampling of carbon dioxide and methane concentrations in hemiboreal headwater streams reveal underestimates in less systematic approaches, *Global Biogeochem. Cycles*, 28: 465–479.

Wang, Y., Wang, L., Cheng, J., He, C. and Cheng, H. (2019). Recognizing Crucial Aquatic Factors Influencing Greenhouse Gas Emissions in the Eutrophication Zone of Taihu Lake, China. *Sustainability* 11(5160).

Weiss, R.F., Price, B.A. (1980). Nitrous oxide solubility in water and seawater. *Marine Chemistry*, 8(4): 347-359.

Wetzel, R. G. (2001). Limnology: Lake and River Ecosystems (3rd ed.). San Diego, CA: Academic Press.

Whipple, K. (2002). Factors Influencing Hydraulic Roughness. In Surface Processes and Landforms. Retrieved from http://ocw.mit.edu/courses/earth-atmospheric-and-planetary-sciences/12-163-surface-processes-and-landscape-evolution-fall-2004/labs/roughnes_handout.pdf

Wicklund, R.E. and Richards, N.R. (1961). The soil survey of Oxford County. Report No. 28 of the Ont. Soil Survey. Research Branch, Canada, Dept. of Agriculture and the Ont. Agricultural College, ON, Canada, 63 pp.

Wijgerde, T., Jurriaans, S., Hoofd, M., Verreth, J.A.J, Osinga, R. (2012) Oxygen and Heterotrophy Affect Calcification of the Scleractinian Coral *Galaxea fascicularis*. PLoS ONE 7(12): e52702. https://doi.org/10.1371/journal.pone.0052702

Wilkinson, H. M., Spiller, B., Forbes, N., Ortega-Achury, S., and Ramirez Avila, J. J. (2018). The Effects of Forested Riparian Zones on Stream Conditions. 318-326. 10.1061/9780784481424.033.

Wilson, L.G. 1967. Sediment removal from flood water by grass filtration. Transactions of the American Society of Agricultural Engineers 10:35-37.

Woodley, A.L., Drury, C.F., Reynolds, W.D., Tan, C.S., Yang, X.M., and Oloya, T.O. (2018). Long-term cropping effects on partitioning of water flow and nitrate loss between surface runoff and tile drainage. *J. Environ. Qual*. 47: 820–829.

Verhoevan, E., Barthel, M., Yu, L., Celi, L., Said-Pullicino, D., Sleutel, S., Lewicka- Szczebak, D., Siz, J., and Decock, C. (2019). Early season N2O emissions under variable water management in rice systems: source-partitioning emissions using isotope ratios along a depth profile. *Biogeosciences,* 16: 383-408.

Verhoeven, J.T.A., Arheimer, B., Yin, C., Hefting, M.M. (2006) Regional and global concerns over wetlands and water quality. Trends Ecol Evol 21:96–103.

Vigiak, O., Malagó, A., Bouraoui, F., Grizzetti, B., Weissteiner, C.J., Pastori, M. (2016). Impact of current riparian land on sediment retention in the Danube River Basin. *Sustainability of Water Quality and Ecology*, 8:30-49.

Vincent, S.G.T., Jennerjahn, T., Ramasamy, K. (2021). Chapter 3 - Environmental variables and factors regulating microbial structure and functions. In Microbial Communities in Coastal Sediments. *Elsevier*, 79-117. Retrieved from: https://www.sciencedirect.com/science/article/pii/B9780128151655000030.

Vogt, E., Barban, C.F., Dragosits, U., Durand, P., Sutton, M.A., Theobald, M.R., Rees, R.M., McDonald, C., Murray, S., and Billett, M.F. (2015). Catchment land use effects and concentrations of organic and inorganic nitrogen in streams. Agr. Ecosyst. Environt., 199:320-332.

Xia, Y., Li, Y., Ti, C., Li, X., Zhao, Y., and Yan, X. (2013) Is indirect N2O emission a significant contributor to the agricultural greenhouse gas budget? A case study of a rice paddy-dominated agricultural watershed in eastern China. *Atmos Environ*, 77:943–950.

Yang, X., Drury, C., Reynolds, D, and Reeb, M.A. (2022). Carbon Loss in Tile Drainage and Surface Runoff from a Clay Loam Soil after a Half Century of Continuous and Rotational Cropping. *Canadian Journal of Soil Science*. 102:10.

Yuan, Y., Bingner, R.L. and Locke, M.A. (2009), A Review of effectiveness of vegetative buffers on sediment trapping in agricultural areas. *Ecohydrol*., 2: 321-336.

Zhang, X., Flato, G., Kirchmeier-Young, M., Vincent, L., Wan, H., Wang, X., Rong, R., Fyfe, J., Li, G., Kharin, V.V. (2019). Changes in Temperature and Precipitation Across Canada; Chapter 4 in Bush, E. and Lemmen, D.S. (Eds.) Canada’s Changing Climate Report. Government of Canada, Ottawa, Ontario, pp 112-193.

Zhu-Barker, X., Cavazos, A. R., Ostrom, N. E., Horwath, W. R., and Glass, J. B. (2015). The importance of abiotic reactions for nitrous oxide production. Biogeochemistry 126, 251–267.

Zigah, P.K., Oswalk, K., Brand, A., Dinkel, C., Wehrli, B., and Schubert C.J. (2015). Methane oxidation pathways and associated methanotrophic communities in the water column of a tropical lake. *Limnol. Oceanogr*. 60, 2015, 553–572.