A field-scale study of controlled tile drainage and a pond-wetland to attenuate nutrients from agricultural overland runoff and subsurface drainage on a farmer-operated seed farm in Saint-Isidore, ON

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A thesis submitted to the University of Ottawa under the supervision of Dr. Christopher Kinsley and Dr. Robert Delatolla in partial fulfillment of the requirements for the degree of Master of Applied Sciences in Environmental Engineering

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Table of Contents

List of Tables

List of Figures

Phosphorus

Appendix

List of Commonly Used Abbreviations

Abbreviation	Full Form
ANOVA	Analysis of Variance
BOD_5	Five-day Biological Oxygen Demand
BMP	Beneficial or Best Management Practice
CDS	Control Drainage Structure
COD	Chemical Oxygen Demand
CTD	Controlled Tile Drainage
DNA	Deoxyribonucleic acid
DO	Dissolved Oxygen
DRP	Dissolved Reactive Phosphorus
ET	Evapotranspiration
DS	Drainage Structures
FDS	Free Drainage Structures
FWSW	Free Water Surface Wetland
GLWQA	Great Lakes Water Quality Agreement
GS	Growing Season
GS-D	Dry Period of the Growing Season
GS-W	Wet Period of the Growing Season
HAB	Harmful Algal Blooms
IJC	International Joint Commission
LEWMS	Lake Erie Wastewater Management Study
MOE	Ontario Ministry of Environment
MGD	Million gallons per day
NGS	Non-growing season
NH_3	Unionized ammonia
NH_4	Ammonium
NO_3^-	Nitrate
NO_3^--N	Nitrate as N
NPS	Non-point Sources
NPK	Nitrogen, Phosphorus, Potassium (ratio in fertilizer)
OMAFRA	Ontario Ministry of Agriculture, Food and Rural Affairs
o-PO_4	Orthophosphate
pH	logarithmic scale of the concentration of hydrogen ions
PS	Point Source
PO_4^{3-}	Phosphate
PP	Particulate phosphorus
PWQO	Provincial Water Quality Objectives
RNA	Ribosomal Nucleic Acid
SRP	Soluble Organic Phosphorus
SS	Suspended Solids
TN	Total Nitrogen
TP	Total Phosphorus
TSS	Total Suspended Solids
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey

Abstract

Agricultural runoff and drainage are significant contributors to the deterioration of water quality in receiving water bodies. Ponds and constructed wetlands are proven treatment systems that can remove nutrients and reduce peak flow. A combined controlled drainage structure (CDS), free drainage structure (FDS) and pond-wetland system was installed on a 64-acre seed farm in St. Isidore, Ontario as a flood mitigation and nutrient attenuation measure. The effectiveness of the combined use of controlling drainage and a pond-wetland system to attenuate flow, solids and nutrients was studied during the growing season (GS) and non-growing season (NGS) of 2017. The GS was subdivided into wet (GS-W) and dry (GS-D) periods.

The mean daily precipitation was 3.95±8.86 mm d^{-1} and the mean daily flow at the drainage structures was greater ($p>0.05$) at the CDS (1.05±1.59 mm d^{-1}) than the FDS (0.58±0.93 mm d^{-1}) during the GS-W and significantly lower between the CDS (0.13±0.21 mm d^{-1}) and the FDS (0.21±0.13 mm d^{-1}) during the GS-D ($p\leq0.05$). In the NGS, all DS were free flowing. In comparison to the GS, however, flow was reduced at the CDS (0.41±0.64 mm d^{-1}) in comparison to the FDS (0.56±0.81 mm d^{-1}). Reductions in turbidity (81%), and concentrations of TSS (40%), NH_4^+-N (19%), NO_3^--N (43%), soluble reactive phosphorus or SRP (78%) were observed during the GS-D. Mean daily mass flux reductions of TSS (53%), NH_4^+-N (54%), NO_3^--N (46%) and SRP (82%) were observed in the dry period of the growing season between the CDS and the FDS.

Composite flow data over the study period indicate that on average, the pond-wetland inflow was reduced by 17% compared to the pond-wetland outflow. Reductions in turbidity (52%), and concentrations of TSS (55%), TP (21%) and NH_4^+-N (27%) were observed between the pond inlet

and outlet for the study period. The combined flow and nutrient attenuation contributed to effective mass removal of nutrients daily and seasonally. On average, the pond-wetland system reduced mean mass flux of TSS (33%), TP (43%), TN (41%), NH_4^+-N (61%). The pond-wetland attenuated NO_3-N (48%) and SRP (27%) mass in the GS-W and released both nutrients in the GS-D and NGS suggesting an effect of seasonality for nitrate and SRP attenuation in small pond-wetland systems. These results show that a combined controlled drainage and pond-wetland system can be a beneficial tool to reduce flow as well as reduce the impact of nutrient migration from farmlands with a low economic footprint, especially in the context of particulate-bound nutrients.

Preface

I would like to thank my supervisor, Dr. Christopher Kinsley, P. Eng, for his mentorship, perseverance, and guidance. I appreciate the dedication and time you have put into this piece of writing and into me as a writer and communicator. I am grateful to Dr. Robert Delatolla, P. Eng, Benoit Lebeau, P. Eng., (OMAFRA) and Dr. Anna Crolla, P. Eng., (OMAFRA) for their direction. The contributions of the Ontario Ministry of Agriculture, Food and Rural Affairs to equipment and fieldwork and the Bercier Seed Cleaning Company for the use of their facilities are greatly appreciated. I am very thankful to Marc Bercier for the provision of equipment, good company and a helping hand when needed.

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1. Introduction

Eutrophication is the nutrient enrichment of a water body. In nature, this process occurs over centuries, however, the anthropogenic scene has caused its acceleration in recent years. Anthropogenic eutrophication of lakes and rivers is caused by the influx of phosphorus (P) and nitrogen (N) which subsequently depletes water quality for essential and recreational use. Point sources of nutrient input were historically controlled at the source; however, the identification and mitigation of nutrient pollution from nonpoint sources remains a challenge. Agriculture is a major contributor of nonpoint nutrient pollution through subsurface, surface, and overland flow. Controlled tile drainage systems, ponds, wetlands, cover crops, reduced or no tillage are examples of beneficial management practices that can be used alone or as a combined system to target nutrient migration from agricultural fields.

The sources of pollution can either be traced back to a point source (PS) or nonpoint sources (NPS) from diffuse locations. PS, such as wastewater treatment plants, combined sewer overflows and industrial effluent sources, are considered easy to treat. NPS, which are heterogenous mixtures of sediment, bacteria, organic matter, pesticides, toxins, and nutrients, are largely subdivided into two subcategories: rural and urban sources (Phosphorus Reduction Task Force (PRTF), 2012). Unlike PS, NPS presents a challenge for quantification and regulation due to its variable interactions with precipitation, geography and soil stratigraphy (Carpenter et al., 1998). Agricultural runoff, the major NPS of nutrient pollution in many watersheds, routes contaminants to receiving waters such as freshwater lakes and streams.

As population density increases with globalization, anthropogenic discharge of N and P into freshwaters can cause the proliferation of microorganisms, including algae, and consequently shift ecosystems. Algal proliferation in freshwater systems depletes and deprives oxygen from fish and other plant life. In addition to sediment-bound P loss through surface flow, subdrainage flow has been shown to contribute to the nutrient enrichment of freshwater systems.

The recurrence of eutrophication has led provincial and federal governments to enact mitigation measures, including binational agreements, for nutrient enrichment in North America. A binational wastewater treatment plant effluent target of 1 mg P L^{-1} was implemented between the United States of America and Canada in the 1980s to address the eutrophication of the Great Lakes. However, re-eutrophication events in the early 2000s drew attention to the role of soluble or reactive phosphorus species in nutrient enrichment, especially in the context of agricultural practices. The Ontario Provincial Water Quality Objectives (PWQO) have set an acceptable criterion for ammonia (20 µg NH_3-N L^{-1}); but no such objective exists for nitrate (PWQO, 1994). The Canadian Water Quality Guidelines for the Protection of Aquatic Life have acceptable criteria for ammonia (0.019 mg NH_3-N L^{-1}) and nitrate (3 mg NO_3^--N L^{-1}) in freshwater, and no guideline exists for the phosphorus (CCME, 2004, 2010, 2012). Additionally, the Ontario Drinking Water Quality Standards requires a maximum concentration of 10 mg NO_3^--N L^{-1} (Ontario, 2002). Interim objectives have been set for TP at 20 µg L^{-1} to prevent nuisance concentrations in lakes; 30 µg L^{-1} to prevent excessive plant growth in rivers and streams and 10 µg L^{-1} to prevent aesthetic deterioration as well as for lakes naturally below this value (PWQO, 1994). A binational agreement by the International Joint Commission

(IJC) recommended a 40% reduction of total phosphorus (TP) and dissolved reactive phosphorus (DRP) loading to the Western and Central Basins of Lake Erie by 2025 (Fussell et al., 2017). To address these concerns, a combination of methods including the improvement of soil testing methods, application of fertilizer based on crop-demand and water management systems to reduce nutrient loss are recommended by the IJC.

Nutrient loss has been historically considered a surface flow problem; however, a plurality of studies has shown that subsurface drainage is also a major contributor to nutrient loss from farms. It is therefore important to understand the mechanisms through which beneficial management practices impact nitrogen and phosphorus transport, speciation and uptake. This thesis will examine the effectiveness of controlling drainage to attenuate nutrients from subsurface drainage and pond/wetland system to attenuate nutrients from surface flow runoff and drainage. This study is a collaborative effort of the Ontario Ministry of Agriculture, Food and Rural Affairs, the University of Ottawa and the Bercier Farm to mitigate surface and subsurface flow of nutrients into the South Nation River.

1.1. **Objectives**

The aim of this study is to evaluate two beneficial management systems namely pond-wetlands and controlled drainage systems to regulate the flow and nutrient loading at various sites in this system. The specific objectives are listed as below:

- Evaluate the effectiveness of controlled tile drainage to control tile flow and attenuate dissolved nutrients and solids;
- Evaluate the effectiveness of a pond-wetland system to control effluent flow from farm fields and attenuate particulate and dissolved nutrients;
- Identify a correlation between phosphorus and nitrogen levels compared to other water quality parameters, if possible;
- Identify a correlation between nutrient concentrations and precipitation, if possible;
- Identify a correlation between precipitation and flow, if possible.

1.2. Thesis Organization

Chapter 1 is an introduction to the topic of nutrient pollution from agricultural sources with emphasis on phosphorus due to recent eutrophication events in the Great Lakes. The objectives of this study are detailed in this chapter. In Chapter 2, current literature is reviewed and the removal of phosphorus, nitrogen and solids using drainage water management, ponds and free water surface wetlands are discussed. The research methodology is provided in Chapter 3. In Chapter 4, the findings of the study are presented and discussed. This chapter presents an understanding of the flow conditions, and results of the solids and nutrient monitoring program, as well as mass flux of each analyte. The behaviour of two controlled drainage structures for 24 hours following stop log removal and the effect of drainage water management on yield, soil nutrient content and crop density are presented. The last chapter is a conclusion which presents the findings of this research.

1.3. Contribution of Authors

The contribution of the various authors is described as below:

K. R. Mathew: Conducted the literature review, field sampling, laboratory analyses, data acquisition and analysis. K. R. Mathew wrote this thesis.

C. Kinsley: Supervised and developed the experimental protocols, analyzed results and revised this thesis.

R. Delatolla: Supervised and developed the experimental protocols, analyzed results and revised this thesis.

2. Literature Review

The purpose of this literature review is to present a global understanding of the challenges and pressures facing agricultural production, address the adverse environmental consequences of current agricultural practices that are in place to produce high yield and efficiency and discuss the use of low-cost, passive nutrient treatment technologies for nutrient management in drainage and surface runoff. In particular, the necessity and benefits of fertilizer application to agriculture and the effect of overfertilization on receiving waters, the interaction of nutrients with soil, sediment, surface and groundwater, runoff and water bodies will be considered. The use of agricultural beneficial management practices (BMPs) in combination with three parallel passive treatment technologies for phosphorus and nitrogen attenuation will be described: controlled tile drainage water management, ponds, and constructed wetlands.

2.1. Nutrient Transport to Receiving Water from Fertilizer in Canada, North America and Worldwide

The reported values of applied fertilizer that is ultimately lost to the environment as runoff are highly variable. Erisman et al. (2008) estimated that half or more of the applied fertilizer is lost as runoff or to the atmosphere, while Bindraban et al. (2015) estimated that up to 20-80% of nutrients in fertilizers are lost to the environment or accumulate in soil in a non-bioavailable form. A review of nitrate leaching mechanisms by Meisinger and Delgado showed that nitrate leaching losses varied between 0% to 60% of the applied nitrogen and that nitrate losses would range from 10% to 30% of N added in fertilizer and/or manure from common grain-production systems (Meisinger & Delgado, 2002). Fertilizer loss is dependent on many external factors, which selectively impact certain nutrient forms (particulate or dissolved) over others. The

Millenium Ecosystem Assessment attributed the variability of nitrogen fertilizer loss to the effectiveness with which fertilizer application is managed (Howarth & Ramakrishna. K., 2005). Masarik et al. (2014) researched the leaching of nitrate-N from various agricultural tillage practices on a continuous corn agroecosystem: the use of a chisel-plow or no-tillage was compared against a nearby prairie restoration natural system over an eight-year span. The researchers reported that nitrate leaching was lowest in the control method (prairie restoration) and highest with no tillage. Nutrient leaching is dependent on many factors including fertilizer management, fertilizer type, crop type, crop rooting depth, irrigation system, climate, precipitation volume, soil type, site hydrology and hydrogeology (Almasri, 2007; Balderacchi et al., 2013; Robinson, 2015). Matching the application of fertilizer to match the needs of the crop minimizes the amount of nitrogen lost to the environment as runoff.

The time or season of fertilizer application impacts nutrient leaching. The application of fertilizer in the autumn following crop harvest is likely to be lost to runoff or leaching as a result of snowmelt compared to application in the spring of the following year. Smith and Cassel (2015) estimated the leaching depth for various nitrogen application times and found that a November application would likely leach to 1.5 metres (m) by April 1 of the following year and that a May 1 application would remain within 30 cm of the soil surface. This study recommended the application of fertilizer in the spring as opposed to the fall to minimize nutrient leaching. Similarly, Sanchez and Blackmer (1988) reported that between 50 to 64% of fall-applied N was lost from the upper 1.5 m of soil due to processes other than plant uptake. Nitrogen loss is not limited to nitrogen leaching; nitrogen can be lost to the atmosphere as nitrous oxide or nitrogen gas. In a recent study, Xia et al. (2018) reported that streams and rivers convert approximately 50% of the input nitrogen to nitrogen gas in transit. A study by Beaulieu et al. (2011) estimated that 0.68 Tg N per year in streams and rivers was converted into nitrous oxide using a global river network model, accounting for approximately 10% of total nitrous oxide emissions. Fertilizer be lost to the environment as drainage, runoff or to the atmosphere.

Fertilizer type impacts fertilizer loss. A comparison of organic fertilizers and inorganic fertilizers shows that the application of organic fertilizers (specifically municipal solid waste compost) improves soil porosity, water retention, soil aggregation, sorption capacity, organic matter content and bioavailability of macronutrients (Sharma et al., 2018). Treating soil with vermicompost increased water availability and reduced water tension, leading to significant soil detachment and loss, leaching and water runoff and leaching of ammonia and nitrate, thereby reducing soil erosion (Doan et al., 2015). The organic content of applied fertilizer shows variable effects on nutrient leaching.

2.2. Environmental and Health Effects of Excess Nutrient Loading to Surface and Groundwater

Agricultural practices have adapted to the increasing demand for food crop through agricultural intensification and optimization of nutrient and water use efficiency to match the supply with greater crop yield. Agricultural intensification is an umbrella term that describes the increased use of inorganic and organic fertilizer and the incorporation of beneficial management practices (BMPs) to meet the increasing demand for a larger output and variety of crops (Canning & Stillwell, 2018). However, intensified use of fertilizers can result in intensified mass loading of leached nutrients to surface and groundwaters, which can significantly deteriorate natural systems. Unused fertilizer accumulates in rivers and lakes through runoff and drainage. Waters impacted by agricultural intensification require a large volume of water or other chemicals to either dilute the concentration of the contaminant (eg. nitrate) or to neutralize and precipitate the contaminant.

Nutrients that are applied improperly or in excess have an environmental cost and significantly alter the natural biogeochemical cycles of nitrogen and phosphorus. In soil, nitrogen is often found in bound organic forms and/or as labile inorganic nitrate. Phosphorus is also found in organic and inorganic forms. Nitrate leaching and phosphate loss from runoff can cause algal proliferation, excess plant growth and downstream eutrophication in receiving rivers, streams and lakes. The release of nitrous oxide from soil is another potential deleterious effect of fertilizer use (Davidson, 2009). The effects of fertilizer use are highly variable by climate and location. For example, the overuse of fertilizer in North America, Western Europe, China and India has been identified as the cause of environmental pollution, whereas the underuse of fertilizer in Africa, Eurasia and parts of Latin America have resulted in soil mining (Bindraban et al., 2015). Therefore, fertilizer use must be adapted to climate and geographical location based on the composition of naturally prevalent elements in the soil.

2.3. **Eutrophication and Its Impacts on Human and Environmental Health**

Farms can incur losses as a result of unforeseeable and uncontrollable forces, including but not limited to drought, frost, natural disasters and invasive species. Fertilizer application is a controllable variable that is beneficial to crop quality and yield. The application of fertilizer to suit the exact needs of the soil and crop through soil quality testing can be expensive, labour-intensive and bureaucratic. As a result of these factors compounded with the relative inexpensiveness of fertilizer, fertilizer is habitually applied in excess of nutrient demands to increase crop yield.

However, the overapplication of fertilizer saturates the soil and surplus nutrients accumulate in surface waters through runoff and drainage. The inflow of a nutrient into a given ecosystem will impact the ecosystem that the nutrient supports. For example, a phosphorus flux can cause a shift in populations favoring P-limited autotrophs. In a hypothetical scenario where the growth of a species is limited by the environmental availability of P, then an increase in environmental P concentrations will cause a population growth for that species. This is likely the case in most freshwater systems where organismal growth is P-limited. Nitrogen has been generally identified as the primary limiting nutrient of eutrophication in coastal ecosystems, whereas freshwater systems are limited by phosphorus availability (Carpenter et al., 1998; WEF, 2011). Predictably, P has been the major identified contributor to eutrophication in freshwater systems since the 1970s and 1980s (Le Moal et al., 2019). However, the surplus of other nutrients to freshwater systems can create similar outcomes. N-loading into freshwaters in the Great Lakes caused the proliferation of zebra mussels, which subsequently promoted algal blooms (*Microcystis aeuroginosa)* in the Bay of Quinte in Lake Ontario. Raikow et al. (2004) linked this correlation with a low total phosphorus (TP) concentration (<25 mg L^{-1}). Harmful algal blooms (HABs) affect the taste and odour of the water, create hypoxic zones that kill aquatic life, reduce biodiversity and stress drinking water and tourism industries (Carpenter et al., 1998). Cyanobacterial or blue-green algal blooms release water-soluble toxins called microcystins that are hepatoxic to humans, dogs, and livestock (A. Martin & Cooke, 1994). Algal blooms prevent the diffusion of oxygen into the water and create hypoxic zones in water. While subsurface drainage reduces surface runoff and sediment-bound contaminant migration through sediment retention, it increases nitrogen losses. Subsurface drainage has been identified as one of the major causes of algal blooms and hypoxic zones in the US Midwest (Jacobs & Gilliam, 1985). The Gulf of Mexico Hypoxia Zone is the second largest dead zone on the planet, draining over 50% of agricultural land in the U.S., spanning over 26, 000 km^2 (Canning & Stillwell, 2018). Agricultural drainage waters with high concentrations of nitrate have been identified as the primary source contributing to the periodic hypoxia of the Gulf of Mexico (Scavia et al., 2003). In addition to phosphorus and nitrogen, silica and iron have also been shown to stimulate algal growth (Moon & Carrick, 2007; North et al., 2007).

Eutrophication is a scientific term for the natural process in which organic materials accumulate or are produced increasingly with time in an aquatic system to the point of saturation. For example, when a system is saturated with nutrient fertilizer or sunlight, this system allows for the growth of excessive plant and algal growth (Chislock & Doster, 2013). The Lake Erie Partnership (2019) and the International Great Lakes Water Quality Agreement (2012) are notable examples of agreements that identify nutrient loading from point and nonpoint sources as primary contributors to deteriorating water quality (Maguire et al., 2018). Anthropogenic eutrophication is the increased production in organic materials in an aquatic system directly as a result of anthropogenic inputs of phosphorus and nitrogen (Le Moal et al., 2019). The difference between the two is the time scale: anthropogenic eutrophication can occur within a timespan of hours, days, months, or years; whereas natural eutrophication occurs over a geological time scale which can span thousands or millions of years. The role of nutrient enrichment in eutrophication is complex. The causes of eutrophication in lakes and reservoirs, streams and rivers, and estuaries and coastal waters differ seasonally and interannually (Correll, 1998). While intensified farming and fertilizer use increase nutrient inputs into aquatic systems, artificial water reservoirs and dam construction alter the microbial distribution, sedimentation properties and hydraulic conditions of these systems and their ability to retain nutrients (Xia et al., 2018).

Unionized ammonia (NH_3) is toxic to aquatic organisms at low concentrations. NH_3 depletes dissolved oxygen readily; unionized ammonia oxidation into nitrate can consume 4.3 g of oxygen per gram of ammonia. Nitrates are detrimental to human health in drinking water supplies, especially in immune-compromised people and are known to cause methemoglobinemia (blue-baby syndrome) and gastrointestinal cancers (Canning & Stillwell, 2018). Nitrates are also harmful to aquatic health. Excess nitrates fertilize aquatic plants, especially algae. The overgrowth of plant material may form mats that deplete dissolved oxygen levels in the water and indirectly causes fish kills.

2.4. **Regulatory Framework**

During the initial repetitive eutrophication events of the Great Lakes in the 1970s, point source pollution was initially identified as the major contributor to eutrophication in North America. In 1972, the Lake Erie Wastewater Management Study (LEWMS) linked the HABs to increased total phosphorus (TP) loadings by determining relative inputs of PS pollution (wastewater treatment plant effluent) versus NPS pollution (runoff) (Strickland et al., 2010). In the 1980s, the binational Great Lakes Water Quality Agreement (GLWQA) was enacted enforcing wastewater treatment plants discharging more than 1 million gallons per day (MGD) to meet the effluent TP concentration target of 1 mg L^{-1} to achieve the TP target load of 11 000 metric tonnes per year (MTY) into Lake Erie (Strickland et al., 2010). In order to quantify the contribution of TP from NPS, the International Joint Commission (IJC) subtracted the PS contribution from the total watershed P export. This approach over-estimated the P contribution of PS and underestimated the P contribution of NPS. However, the IJC was successful in reducing the TP export into Lake Erie **(Figure 1.1)** through urban wastewater management, control of phosphates in detergents, as well as the promotion of no-till or reduced tillage (RT) practices to decrease P loss through runoff. Tillage is the practice of overturning soil to recycle nutrients, and as such, no-till refers to omitting tillage, and reduced tillage refers to a reduction of tillage.

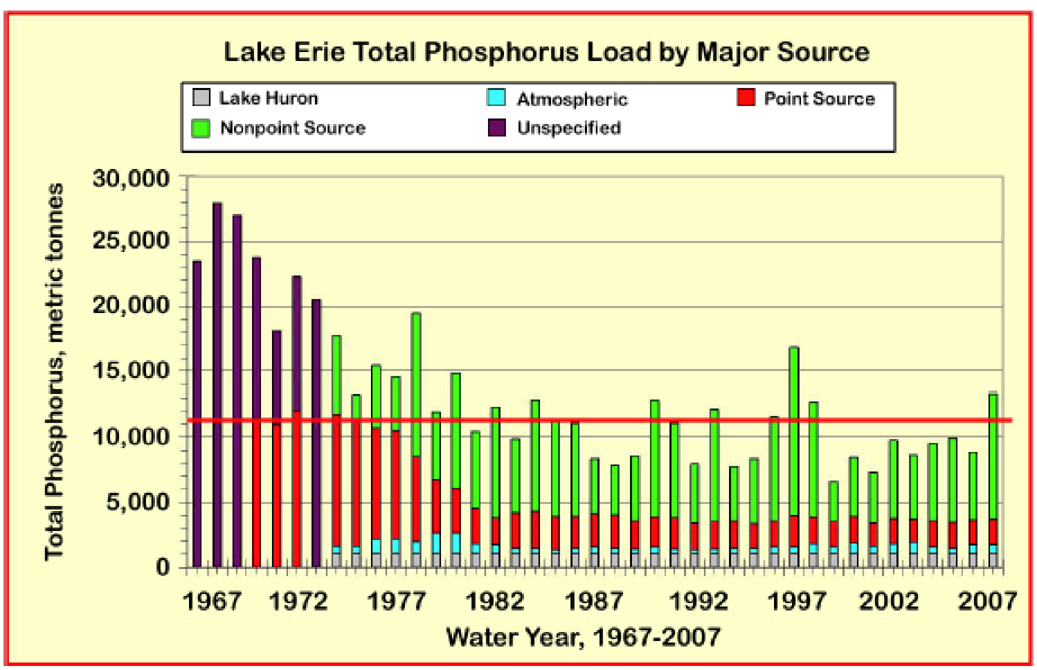

Figure 1.1: Reduction in Annual Loading of Total Phosphorus to Lake Erie, 1967-2007 (Strickland et al., 2010)

In **Figure 1.1**, the red line indicates the target of 11 000 MT P loading into Lake Erie enforced in 1988. NPS TP was identified as the dominant source of P loading into Lake Erie since these regulations were implemented and a significant contributor of freshwater eutrophication globally (King et al., 2015). Lake Erie, in particular, has experienced re-eutrophication by *Mycrosystis aeruginosa* in the western basin in 2003 (Phosphorus Reduction Task Force (PRTF), 2012), a cyanobacterial bloom (*Lyngbya wollei)* in Maumee Bay in 2006, and more recently, filamentous *Cladophora* blooms in 2012 (Strickland et al., 2010). TP concentrations were relatively constant and below the target of 11 000 MTY of TP after 2003 **(Figure 1.1).** A combination of interacting factors including P-cycling due to invasive species of zebra mussels, climate change, changing land management practices have been cited as the cause of the re-eutrophication events (C. (University of W. Van Esbroeck, 2015). These factors have resulted in elevated levels of dissolved or soluble reactive phosphorus (DRP/ SRP) which are highly bioavailable forms of phosphorus. Therefore, recent re-eutrophication events have been linked to reactive phosphorus loads into Lake Erie.

2.5. **Agricultural Production, Fertilization and Nutrient Losses**

Crops, like all living things, need nutrients to grow. A nutrient is a molecule or compound that is essential to the growth of living organisms. In the context of organismal growth, carbon (C), nitrogen (N) and phosphorus (P) are the most important nutrients. C, N and P are the building blocks of nucleic acids (DNA or RNA), which are composed of carbonaceous sugars (containing C) and nitrogenous bases (containing N) that are connected to each other through a type of phosphorus linkage called the phosphodiester bond (containing P). On a cellular level, organismal growth, reproduction, and repair are synonymous with cellular replication, that is to say, the replication of nucleic acids. When an organism grows, reproduces, or repairs itself, C, N, and P are needed to replicate DNA and RNA.

In addition to this foundational role, nutrients have an impact on many other biological cycles. Nitrogen is a critical component of amino acids (defined as such, due to the 'amino' or C-N bond), which when linked together are assimilated into proteins. Proteins are integral for energy storage in organisms. In the same vein, energy conversion is mediated by a component called adenosine triphosphate (ATP) that is, as the name suggests, composed of phosphorus in the form of phosphate ions and specifically three phosphate ions. ATP can undergo hydrolysis to form ADP (adenosine diphosphate, containing two phosphate ions), while releasing electrons. Similarly, ADP can revert to ATP and consume electrons. The incorporation or hydrolysis of phosphate ions into ADP or ATP determines organismal metabolic activity at the cellular level.

Nutrients are subclassified as micronutrients or macronutrients; a greater concentration of macronutrients is required for growth in comparison to micronutrients. The table below describes the general concentrations of nutrients required for plant growth.

Table 2.1: Typical Concentrations (mg kg^{-1}) Required for Plant Growth (Epstein, 1965) Mineral Metabolism. Plant Biochemistry (J.Bonner and J.E. Varner, eds.). Academic Press, London. pp. 438-466. Retrieved from https://soils.wisc.edu/facstaff/barak/soilscience326/macronut.htm).

Macronutrients		
Element	Symbol	Concentration (mg kg^{-1} or ppm)
Nitrogen	N	15, 000
Potassium	K	10, 000
Calcium	Ca	5, 000
Magnesium	Mg	2, 000
Phosphorus	P	2, 000
Sulfur	S	1, 000
Micronutrients		
Element	Symbol	Concentration (mg kg^{-1})
Chlorine	Cl	100
Iron	Fe	100
Boron	B	20
Manganese	Mn	50
Zinc	Zn	20
Copper	Cu	6
Molybdenum	Mo	0.1
Nickel	Ni	0.1

Nitrogen (N), potassium (K), calcium (Ca), magnesium (Mg), phosphorus (P) and sulphur (S) are macronutrients; whereas chlorine (Cl), iron (Fe), boron (B), manganese (Mn), zinc (Zn), copper (Cu), molybdenum (Mb) and nickel (Ni) are micronutrients. Both macronutrients and micronutrients are essential for plant growth (Dawson & Hilton, 2011). The natural abundance of these different elements varies and the biological availability of certain key nutrients (eg. P) limits the growth and over-reproduction of any one particular species in ecosystems. For example, carbon, hydrogen and oxygen are universally abundant. While inert nitrogen gas is abundant, bioavailable nitrogen or reactive N, is in limiting supply. Xia et al. (2018) estimated that less than two percent (2 %) of all total nitrogen is bioavailable to living organisms.

Potassium and sulfur are neither in limiting supply and the processing of neither potassium nor sulfur is considered energy-intensive. However, the production of ammonia for agricultural use is energy-intensive due to the requirement of methane-derived hydrogen and phosphorus is a natural resource with limiting supply due to the depletion of total available phosphate rock reserves. Therefore, while the plant growth nutrient requirements for potassium and sulfur can be met easily, the nutrient requirements for ammonia and phosphorus are more challenging due to the labour, cost, and energy intensity of making the latter two elements available.

The concentration of land-applied nutrient should supplement the pre-existing nutrient concentration in native soil and is dependent on the crop type, soil chemistry, and the growth stage of the crop. If a nutrient that is land applied is naturally abundant in native soil, it is unlikely to have an impact on yield. The application of unbalanced compositions of fertilizers on poor soils in African countries has been shown to have limited impact on crop yield. 2.8 Mt of N and 96 Kt of P are used in Africa, resulting in increases of 150 and 16% in crop yield, respectively (Bindraban et al., 2015). The addition of phosphorus to P-rich soils did not provide the desired increase in yield.

The type of crop that is being planted is critical – for example, blueberries require between 150-500 ppm of magnesium compared to the 20-200 ppm that is required for apples (OMAFRA, 2021). Some soils are more acidic than others and so may require the addition of lime. For example, lime is applied heavily in eastern Canada and less so in western Canada because the soil is naturally less acidic to the west of Quebec (Dorff & Beaulieu, 2011). The type of soil plays a role. Clay or silty loams retain water and are less prone to nutrient leaching. In Ontario, where clay is predominant in the overburden, granular fertilizers are often used (OMAFRA, 2018).

Another factor is the timing of fertilizer application. Fertilizer that is applied in the fall is more prone to leaching than fertilizer applied in the spring.

Nutrient needs are highest during periods of growth and reproduction. In the framework of commercial agriculture and specifically the growth of crops on farmlands, it is important to maintain the necessary nutrient ratios and also ensure the availability of these nutrients for bio-assimilation. As plants grow, they uptake these nutrients from the soil into their tissues and therefore deplete the soil. This is why fertilizer, biosolids, or manure are applied onto croplands in order to sustainably replenish the nutrient content of the soil and increase agricultural productivity. A study of winter wheat yields since 1850 showed that yield increased relative to control by about 800% with the combined use of cultivars, pesticides, weedicides, fertilizers or manure (Johnston, 1997; Johnston & Poulton, 1992; Rothamsted, 2006). Similarly, an increase of yield of 400% for wheat and 1000% for corn in the U.S., 300-400% for spring cereals in Denmark, 150%-300% for wheat in U.S. have been observed with the increases in nutrient input (Boman et al., 1996; Paul, Paustian, Elliott, Cole, Buyanovsky, et al., 2019; Paul, Paustian, Elliott, Cole, Juma, et al., 2019).

Phosphorus use has been steadily on the rise to meet the increasing demands for food, feed, fibre and fuel. The increased usage has increased the amount of P exported from agricultural fields, making agriculture an important contributor of NPS pollution into surface waters (Zhang et al., 2017). Agricultural non-point sources include runoff from fertilizer, manure and biosolids, milking parlour wastewater, or seepage for silage piles (Gottschall et al., 2006). More fertilizer P is applied to land than is taken up by crops. Excess P accumulates in soil or is transported via overland flow or runoff. Carpenter et al. (1998) studied this phenomenon between 1950-1995 and observed that of the 600 x 10^6 Mg P of that was land-applied globally, approximately 250 x 10^6 Mg P were harvested. Of this last fraction, ~50 x 10^6 Mg P was reapplied as manure. A net ~400 x 10^6 Mg P were unaccounted for either in the soil or in water as a result of erosion during this period (Brown et al., 2014; Carpenter et al., 1998; Food and Agriculture Organization, n.d.).

Historically, surface runoff was considered to be the primary mechanism of sediment-bound P loss from farm fields. The impact of subsurface drainage on P-loading into surface waters from agricultural sources was considered minimal and therefore reduced and no tillage practices were recommended to reduce surface erosion (Lam et al., 2016). However, changing tillage practices have been associated with increased SRP and TP loading into Lake Erie. The adoption of reduced and no tillage practices have been shown to increase the SRP and TP loss in surface flow and subsurface drain effluent (Lam et al., 2016). While erosion control is important, there is also a need to improve tillage methods that take P speciation to dissolved or soluble species into consideration.

A second contributing factor is the application of fertilizer in the fall season that is subject to loss as a result of erosion during fall precipitation and subsequent spring thaw or snowmelt after winter. A study of seasonal phosphorus export in cold climates by Van Esbroeck et al. (C. Van Esbroeck et al., 2016) reported that 83-97% of annual combined runoff occurred during the NGS (October-April). The likelihood of erosion and drainage of particulate and soluble nutrients is linked to the texture, structure and organic matter content of the soil. Extreme precipitation events of increasing intensity and frequency also increase P-erosion.

2.6. **Classifications and Composition of Fertilizer**

In the current climate of concern over the downstream effects of using inorganic fertilizer, it is important to address the benefits and limitations of organic fertilizers and consider alternative fertilizer management systems. As discussed above, inorganic fertilizer is synthetic and organic fertilizer consists of natural sources of nutrients including manure, compost, crop residues, pig and cow slurry, etc. There is considerable evidence that the use of organic fertilizers increases the organic matter in soil and therefore, the improves the physicochemical and biological properties of soil (Edmeades et al., 2008). Given the benefits of using organic fertilizers and the wide use of organic fertilizers until the mid 1700s; it is important to understand why inorganic fertilizer use is prevalent today.

The existing agricultural practices of the time were inadequate to meet the needs of this an unprecedented population growth during the industrial revolution (c. 1700s). Organic fertilizers were no longer sufficient to sustain agricultural production as naturally available phosphorus and nitrogen were depleting irreversibly. The two processes that aided the agricultural revolution were, first, the commercial manufacturing of phosphatic fertilizer in the 1840s which alleviated the severe P deficiency and subsequently, the Haber Bosch process for the manufacture of anhydrous ammonia (NH_3) in 1909 to alleviate the limited supply of reactive N (Dawson & Hilton, 2011). As a result of these revolutions, one of the major biogeochemical effects of industrialization was the increase in the amount of total available nitrogen and phosphorus in the biosphere (Hessen, 2013).

Comparison of Organic vs. Inorganic Fertilizers

Inorganic fertilizers contain urea that is synthesized using the Haber-Bosch process and contains easily reactive N. Nutrients in organic fertilizers are often bound in a compound and are less reactive than in inorganic fertilizers. The nutrient composition of manure is dependent on many factors, including the type of livestock. Inorganic fertilizers are mass produced at various distinct N-P-K ratios, in high concentrations and the type of fertilizer that is purchased can be matched to the type of crop, or stage of crop growth as needed. The nutrients in inorganic fertilizer are more labile and are prone to be lost from the land in surface runoff. The reactivity of these nutrient species changes the pH of soil causing acidification or basification and therefore, alters the soil microbiome. On the other hand, as the nutrients are more tightly-bound to other organic compounds in organic fertilizers, they are slowly released into the soil over time with decomposition and provide a more balanced supply of nutrients compared to the more labile nutrients in inorganic fertilizer. Compared to inorganic fertilizers, the nutrient content of organic fertilizers is considerably lower. Unlike inorganic fertilizer that is synthesized chemically containing a specified nutrient ratio and mass-produced, the nutrient content in organic fertilizer is more variable (Doan et al., 2015). Organic fertilizers also contain micronutrients, whereas synthetic fertilizers usually only contain macronutrients. Manure improves soil structure, thereby reducing the likelihood of soil erosion and runoff.

2.7. A comparison of organic vs. inorganic fertilizer

Han et al. (2016) investigated the effect of treating yellow poplar seedlings (two years old) with organic manure, inorganic (NPK) fertilizer and a mix of organic manure and inorganic fertilizer on seedling growth and nutrient accumulation in soil as well as plant tissue. The authors reported that following organic manure application, soil pH and the concentrations of N, available P, exchangeable K, Ca and Mg increased. Organic manure application resulted in the basification of soil and the soil retained the applied nutrients. The soil pH and the concentration of exchangeable Ca decreased following the application of inorganic fertilizer, while the concentration of available P and exchangeable K increased. There was no effect of inorganic fertilizer on soil concentrations of N or Mg. Inorganic fertilizer application caused the acidification of soil and had an overall variable and inconclusive impact on nutrient concentration in the soil. Seedling height, root collar diameter (21 and 29%) and mean dry weight of stems and leaves increased (72 and 123%) with both methods of fertilization, with inorganic fertilizer showing a higher efficiency. The authors attributed the decrease in soil pH as a result of inorganic fertilizer application to the potential leaching of basic cations (Ca^{2+}, K^+ and Mg^{2+}) from the soil and reduce the buffering capacity of soil (Van Miegroet & Cole, 1984). Another explanation for the soil acidification is the primary conversion of urea in the inorganic fertilizer into ammonium ion for plant uptake, which causes the release of hydrogen ions into the soil.

2.8. **N, P Use in the Fertilizer Production**

Despite the industrial revolution that began in the mid 1700s, most farming in the United States still occurred on small family farms that relied heavily on organic fertilizers. The shift from small-scale farming to the commercial farming of the 1950s created the prevalence of fertilizer use in the form of nitrogen, phosphate and potash[1], that we know today (USEPA, 2018). The production of nitrogen increased from a total of 5 kT N in 1850 to 85 700 kT N in 2000 (Dawson

[1] Potash is the common name for potassium oxides including potassium chloride, potassium sulfate and potassium nitrate (US EPA, 2018).

& Hilton, 2011). With respect to phosphorus, it is estimated that 158 Mt/year was being mined by 2009. The United States of America Geological Survey estimated that there are approximately 16 000 Mt of phosphate reserves, whereas the International Fertilizer Development Center (IFDC) estimated that there are 60 000 Mt of phosphate rock product in reserve comprising usable or marketable reserves of phosphate rock and 290 000 Mt of ore potential which includes resources as unprocessed rock of varying quality.

2.9. **Agricultural Reliance on Inorganic Fertilizer**

Inorganic fertilizer use comprises a significant portion of total agricultural production. Smil (1999) estimated that 40% of the world's dietary protein supply in the mid-1990s originated in the Haber-Bosch process synthesis of ammonia. Erisman et al. (2008) estimated that 48% of the world's protein supply originated from inorganic fertilizer N. Inorganic fertilizer use varies by region in not only the concentration used, but also the type of fertilizer that is used. According to the 2011 Census of Agriculture, synthetic fertilizers were applied on 24.9 million hectares of land in 2010, comprising a total of less than 100 000 farms in Canada, of which 84.5% were in the Prairie Provinces. Inorganic fertilizer use is highest in the 'Breadbasket' of Canada, which consists of the provinces of Saskatchewan, Alberta, and Manitoba. The addition of lime is highest in Quebec, Ontario and decreases steadily towards the western provinces as acidity rates in soil decrease westward.

Fertilizer use is highly dependent on market volatility. Total commercial fertilizer use was 24 million tonnes in 1981 due to global grain demand according to the USEPA (2018). The same USEPA Report on the Environment states that fertilizer use declined until 1983 and increased until 2004, after which fertilizer use has experienced volatility that has been reflected in its market price. Acreage used for fertilization has mirrored the fertilizer use patterns, from 51.8 nutrient kg ha^{-1} y^{-1} in 1960 to a peak of 163.6 kg ha^{-1} y^{-1} in 2004 and has experienced volatility since. Nitrogen and potassium use have both increased since the 1960s, at differing rates. It is estimated that nitrogen use increased from 19.0 kg ha^{-1} y^{-1} in 1960 to 93.7 kg ha^{-1} y^{-1} in 2013, while phosphorus and potash use was estimated to be 28 kg ha^{-1} y^{-1} in the 1960s to 40 kg ha^{-1} y^{-1} in 2014. Nitrogen accounted for 57% of total fertilizer use, phosphate 20% and potash 23%, respectively in 2014 (USEPA, 2018). Overall, it is estimated that the production of the four major crops of the U.S., soybean, corn, wheat, and cotton, used 15.4 MTY of fertilizer between 2015-2016. The pattern of increasing fertilizer use with crop demand is expected to continue in the future. It is anticipated that global crop demand will increase by 100 to 110% between 2005 to 2050 (Tilman et al., 2011). It is projected that consumption of nitrogen fertilizers will increase to 80-180 million tonnes (MT) in 2050 compared to the 105 MT in 2010 and that the consumption of phosphate would increase from 40 Mt in 2015 to 35-70 MT in 2050 (Bindraban et al., 2015).

2.10. **An Overview of Nutrient Status in Groundwater**

Groundwater has been identified as an NPS of nutrients into the Great Lakes (Barton et al., 2013) and is important especially in municipalities that use groundwater as a source for drinking water. A 2010 study by the United States Geological Survey (USGS) reported that the nitrate concentration in 64% of surface water and shallow groundwater monitoring wells in the United States were above recommended levels between 1990 and 2006 (Dubrovsky et al., 2010). Warner and Arnold (2010) prepared a report for the USGS that reported that 58% of shallow aquifers in agricultural areas exceeded background nitrate concentrations (1 mg L^{-1}). A similar survey was conducted at 144 farms in Ontario through the installation of multilevel monitoring wells to test for nitrate near drinking water wells (Rudolph et al., 1998). Concentrations of nitrate exceeded the provincial drinking water standard during the winter and summer sampling sessions at 23% of the sites. Another survey by Rudolph et al. (1998) of 1298 drinking wells in Ontario showed that 14% of the drinking wells exceeded the drinking water quality standard of 10 mg L^{-1} NO_3-N. The Canadian federal regulations, Ontario Drinking Water Quality Standard and the USEPA Drinking Water Standard require NO_3^- concentrations to be below 10 mg L^{-1} NO_3^--N in drinking water and the Canadian Guideline for the Protection of Aquatic Life is set at 2.95 mg L^{-1} NO_3^--N (CCME, 1999; MOE, 2003; USEPA, 2002). The concentration of N and P in groundwater is variable and largely dependent on a combination of factors including land use, hydrogeology, and geochemistry, that are specific to each property. There is no regulatory environmental guideline for P in Canada. Critical thresholds as high as 0.1 mg L^{-1} PO_4^{3-}-P have been reported to cause algal growth (Robinson, 2015), while concentrations as low as 0.01 mg P L^{-1} have been reported to cause algal growth (Zhang et al., 2017). The USEPA (2000) conducted ecological threshold studies on biological responses to SRP which demonstrated that concentrations less than 0.047 mg P L^{-1} prevented nuisance algal growth and preserved water quality for recreational use in freshwater, whereas concentrations less than 0.015 mg P L^{-1} ensured the maximum periphyton biomass remained below 100 mg m^{-2}.

2.11. **Nitrogen Transformation and Transport from Agricultural Fields**

Nitrogen is the most abundant element in the atmosphere and is found in its organic or inorganic forms between the valence states of -3 (in NH_3) to +5 (NO_3^-). Nitrate is the most thermodynamically stable inorganic form of nitrogen, accounting for more than eighty percent

(80%) of dissolved inorganic nitrogen in rivers (Xia et al., 2018). The anthropogenic discharge of nitrogen renders it abundant in freshwater ecosystems; however, is in limiting supply in marine environments. Therefore, marine ecosystems tend to be limited by nitrogen. The biological conversion of nitrogen into its different forms has been outlined below in **Figure 2.1**.

2.11.1. General Transformations (Ammonification, Nitrification, Denitrification)

The nitrogen cycle describes the microbially-mediated reduction and oxidation of nitrogen into various species **(Figure 2.1)**. Nitrogen-fixing bacteria convert atmospheric nitrogen into a form that is bio-available through nitrogen fixation. This organic form of nitrogen is converted to ammonia through bacterial degradation in a process called ammonification by ammonifying bacteria. Anhydrous ammonia is converted to nitrate through an aerobic microbial process called nitrification. This process increases the acidity of the soil. Nitrate undergoes denitrification or annamox and is converted to nitrogen gas, effectively completing the nitrogen cycle. Interfaces between suspended particles and water and riparian zones are hotspots for microbial activity, including interactions with sulfur, iron and manganese (Xia et al., 2018). Riparian zones are interfaces between groundwater and surface waters, where groundwater interacts heavily with biota and soil. Hill (1996) estimated that nitrate removal in 20 riparian zones in Ontario ranged from 65-100% and that of the total number of zones studies, 14 of these zones removed nitrate by more than 90% through denitrification and bio-assimilation. Some nitrogen transformations are favoured under certain conditions such as denitrification under anoxic conditions, whereas others exist in a background equilibrium such as ammonification and denitrification.

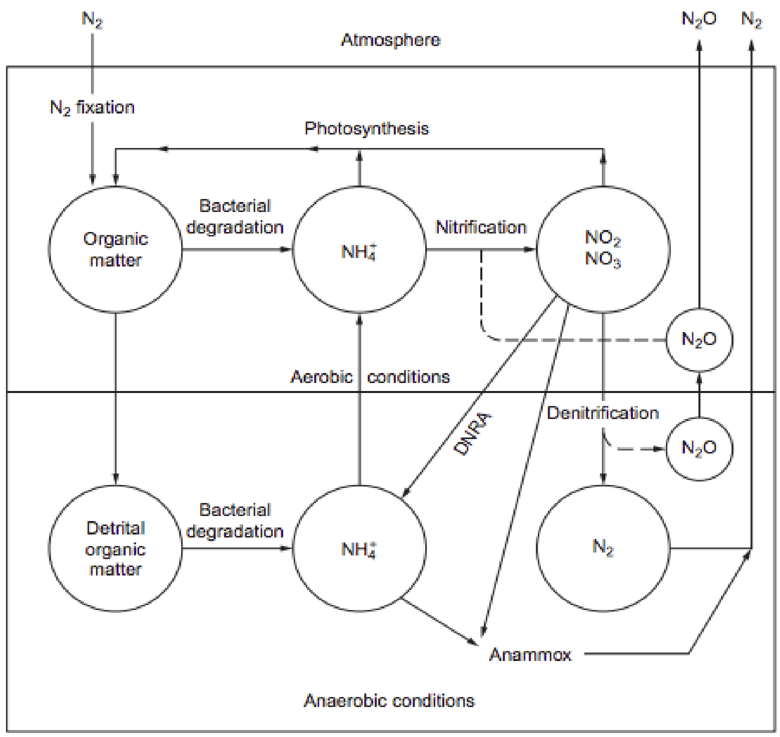

Figure 2.1: Microbial Mediation of the Nitrogen Cycle (DNRA = Dissimilatory Nitrate Reduction to Ammonium) (Schlesinger, W.H., and Bernhardt, 2013)

Ammonification is the conversion of organic nitrogen into ammonia by (facultative) heterotrophs under both aerobic and anaerobic conditions. Ammonification occurs in conjunction with bio-assimilation. Nitrification is the biologically mediated two-step conversion of ammonium (NH_4^+) into nitrate (NO_3^-) through intermediary nitrite (NO_2^-) (Eq. 1) metabolism primarily by ammonia oxidizing bacteria (AOB) such as *Nitrosomonas* and *Nitrospira* (Kadlec & Wallace, 1996). Recent studies have shown that archaea are also involved in the first rate-limiting step of nitritation (Xia et al., 2018). Denitrification is the conversion of nitrate (NO_3^-) into atmosphere nitrogen (N_2) by *Bacillus, Enterobacter and Pseudomonas* (Eq. 2). Nitrification followed by denitrification is an effective permanent pathway to reduce the total soluble nitrogen content in the aqueous phase.

$$NH_4 + 2O_2 \leftrightharpoons 2\,H^+ + H_2O + NO_3^- \;(Eq.1)$$

$$5C_2H_4O_2 + 8NO_3^- \leftrightharpoons 10CO_2 + 6H_2O + 8OH^- + 4N_2 \;(Eq.2)$$

Nitrate can also be microbially reduced to nitrite and subsequently: 1) reduced to ammonia through dissimilatory nitrate reduction to ammonium (DNRA); 2) reduced to either nitrogen gas or nitrous oxide through denitrification, or 3) reduced to nitrogen gas through annamox (Xia et al., 2018). Nitrite reduction can be linked to fermentation or chemolithoautotrophic sulfide oxidation and iron oxidation. The processes of denitrification and anammox usually occur following the transport of water from overland into groundwater, predominantly in the pore spaces of soil. Denitrification is the primary mechanism in which nitrogen fertilizer is lost and results in decreased efficiency (Knowles, 1982). Denitrification can also result in the production of nitrous oxide, a greenhouse gas that contributes to the depletion of the ozone layer.

2.11.2. Drainage

Following the application of fertilizer to agricultural soil, nutrients lost from soil or plant residues will interact with precipitation and subsequently the soil porewater space and groundwater through subsurface drainage or with surface water through overland flow or erosion. The solubility of the species is an important consideration when considering their mobility in runoff or drainage. The implementation of drainage ditches, deepening existing water ways, subsurface tile drainage, ponds, and wetlands are commonly used drainage practices.

Drainage ditches or subsurface tile drainage on farm fields removes excess water that would otherwise result in crop root rot and therefore greatly improving crop yield. Previous studies have shown that while agricultural drainage reduces surface runoff, sediment loss, and particulate or sediment-bound nutrient loss (Baker et al., 1975), drainage increases labile nitrogen loss (Gilliam et al., 2015). Rates of tile drainage nitrate export have been linked to the rate of fertilizer application, tile drainage spacing and depth and intensity of precipitation (Blann et al., 2009; Cordeiro et al., 2014). Higher intensity precipitation years have been associated with higher nitrate loss. Cordeiro et al. (2014) attributed this effect to the loss or flushing of nitrate that had accumulated in the soil profile with high intensity precipitation through the tile drains. It is difficult to compare studies on nutrient export in tile drainage due to sensitivity of nutrient loss to episodic precipitation, seasonal bioaccumulation, effect of snowmelt, soil capacity or saturation, hydrologic factors, among other variables.

2.11.3. Groundwater Interaction

The species of nitrogen that are found in groundwater are similar to those found in surface water, or wetlands. These forms of N include nitrate (NO_3^-), ammonium (NH_4^+), nitrite (NO_2^-), soluble organic N, N associated with sediment as exchangeable ammonium or organic N (Robinson, 2015). The processes of mineralization, nitrification, denitrification, annamox, and bio assimilation are still at play. Nitrate is the most common nitrogen species in groundwater. Nitrate is extremely mobile and does not bind to sediment. Therefore, groundwater can act as a pathway of transport for nitrate into surface waters, especially in aquifers with coarse-grained sediments containing few electron donors (Ranalli & Macalady, 2010; Robinson, 2015). Groundwater is usually anoxic, and the presence of electron donors (eg. organic matter, ferrous iron, or sulfide), provides a suitable condition for denitrification. Ammonia in groundwater is less abundant than nitrate and is more adherent to sediment via cation exchange or adsorption (Robinson, 2015). In 2010, Dubrovsky et al. (2010) conducted a survey of wells across the U.S.

for the USGS NWQA Program and discovered that ammonia levels in groundwater are typically below background levels (0.1 mg L^{-1} NH_4-N).

2.11.4. Surface Water Interaction

When the soil is saturated, accumulating precipitation cannot drain through soil macropores and results in surface runoff. Surface runoff occurs in drained systems when precipitation exceeds the capacity of the subsurface system ('hortonian overland flow') or falls at a rate greater than the infiltration capacity of the soil ('saturated overland flow'). This surface runoff eventually meets with a surface water body.

Oxygen and nitrate diffuse into pond sediment primarily through the water column. Ammonia can be delivered to surface water from groundwater through sediment erosion and from the ground via surface runoff (Balderacchi et al., 2013). The rate of substrate diffusion into the sediment is highly variable and dependent on hydraulic head gradient, roughness, porosity, and connectivity of the sediment (Xia et al., 2018). The sediment-water interface has a high oxygen gradient that drives chemical interactions through molecular diffusion. Nitrification occurs within the upper oxic layer of sediment that typically spans several centimetres (cm). Anoxic processes such as denitrification and annamox occur in the anoxic subsurface sediment. Coupled nitrification-denitrification occurs under low nitrate concentrations in the overlying water. High rates of denitrification have been correlated with high levels of nitrate in the overlying water. The nitrification rate in water systems containing suspended particles was found to be 2.5 times higher than without suspesended particles in a study by Xia et al. (2018).

2.11.5. Regulatory Framework

The Canadian Water Quality Guidelines for the Protection of Aquatic Life have acceptable criteria for ammonia (0.019 mg NH_3-N L^{-1}) and nitrate (3 mg NO_3^--N L^{-1}) in freshwater (CCME, 2010, 2012). The Ontario Provincial Water Quality Objectives (PWQO) have set an acceptable criterion for ammonia (0.02 mg NH_3-N L^{-1}); and no such objective exists for nitrate (PWQO, 1994).

2.12. Phosphorus Transformation and Transport from Agricultural Fields

Phosphorus is a macronutrient and trace element organic metal that is used in agriculture and in the production of detergents. Most phosphorus species are bound to oxygen (PO_4^{3-}) with a valence of +5. The type of prevalent ion is dependent on pH. In well-buffered seawater systems (pH ~ 8.2), HPO_4^{2-} is the dominant form of P; whereas $H_2PO_4^-$ is the dominant species in freshwaters where pH is more variable, but lower (WEF, 2011). A parallel trend is seen with soil, where HPO_4^{2-} is more prevalent in cultivated soils with high pH (Holtan, H.; Kamp-Nielsen & Stuanes, 1988).

In the aqueous phase, phosphorus interconverts between particulate, soluble and sedimented forms. Phosphorus is predominantly naturally derived in small quantities from the weathering of calcium phosphorus rocks (apatite) in the continental crust. It is transported into the hydrological cycle through rivers. With the exception of watersheds near volcanic activity, atmospheric deposition is not a primary method of transport for P (Correll, 1998).

Phosphorus is up taken by living organisms for cellular processes. The cellular demand for phosphorus is greater than its supply through weathering of phosphate rocks. Following transport by rivers into seas, marine systems are considered to be a large pool of P with an overall mean residence time of 25 000 years (Schlesinger, W.H., and Bernhardt, 2013). Therefore, the limited total availability of phosphorus establishes P as a non-renewable resource and most internal cycling of phosphorus is biologically mediated through senescence and uptake. Terrestrial vegetation contains approximately 0.5 x 10^{15} g P, while soils contain approximately 46 x10^{15} g P, of which, approximately 13.8 x 10^{15} g P is labile (Schlesinger, W.H., and Bernhardt, 2013).

Phosphorus is an essential nutrient for agricultural crops. It is applied to agricultural land to maintain soil fertility. Some soil phosphorus is lost to the environment through surface runoff or leaching following significant rain events and snowmelt, especially during the non growing season (NGS). In receiving waters that are P-limited, as is often the case for lakes, streams and rivers, the addition of P-rich agricultural runoff and drainage stimulates microbial growth. Phosphorus mining has depleted the naturally existing levels of phosphorus. This counterintuitive phenomenon of simultaneous phosphorus scarcity for mining as well as overabundance to the point of environmental degradation has been termed the 'phosphorus paradox' (Leinweber et al., 2017). The implementation and improvement of systems that capture and recycle P addresses both ends of this paradox. The subsequent sections will follow the path P takes from farm-fields to receiving waters.

2.12.1. General Transformations

Phosphorus in Soil

The P content of soil is variable from 200 – 5000 mg/kg, with a mean of 600 mg/kg (Strickland et al., 2010). Topsoil contains between 100-3000 mg P kg^{-1} and P removal was observed to be highest when P is lost from the soil as harvested grain (C. Van Esbroeck et al., 2016). Sources of P can be natural or anthropogenic. On average over eleven years, Mallarino et al. (2018), stated that the average 10.67 mt ha^{-1} corn harvest removed 30 kg P ha^{-1} y^{-1} from the system. Natural sources include primary and secondary minerals, or plant residues which release P through dissolution, decomposition, and mineralization. Fitzgerald et al. (2015) showed that phosphorus concentration in groundwater between 0.8-4 mg L^{-1} PO_4-P was linked to desorption from sediments or organic matter mineralization. Soil P could also come from fertilizer, manure/biosolids, runoff or leachate. Soil P either exists in solid state, or in solution. The inorganic phosphates that are dissolved in soil solution can be taken up by plants and this concentration is less than 1% of the TP content of the soil (Brady & Weil, 2004; Strickland et al., 2010). Solid state P can be organic or inorganic; of which the inorganic phosphates are bio-available to varying degrees.

Phosphorus can interconvert between the soil solution and solid state through sorption/desorption and precipitation/dissolution. Orthophosphates from the soil solution can be taken up by plants or leached into surface water through tile flow. P can interconvert between P in soil solution and organic phosphorus through immobilization-mineralization.

Sorption/Desorption

Sorption refers to the removal of phosphate in solution to a solid state due to either reversible physical sorption, or partly or completely irreversible chemisorption (Holtan, H.; Kamp-Nielsen & Stuanes, 1988). Chemisorption can include adsorption both through surface ligand exchange and incorporation into clay. Soil solution P sorbs to Iron (Fe) and Aluminum oxides, clay minerals, calcium carbonate, magnesium carbonate and humic compounds (C. Van Esbroeck et al., 2016). Soil pH determines the type of ligand binding. At low pH, orthophosphate binding is favoured to the positively charged metal ions. Phosphate can sorb onto metals through ligand exchange with aquo-, hydroxo, or ol- groups, in that order of reactivity (Holtan, H.; Kamp-Nielsen & Stuanes, 1988; Stuanes, 1982). The type of soil and the concentration of P in solution are also important factors in sorption. Clay soils contain more binding sites than sandy soils, improving phosphate binding. Phosphate replaces water molecules at the broken edges of clay lattices in low P concentration and exchanges with hydroxyl groups or displaces structural silicate in high P concentration. Phosphate can replace water molecules, bicarbonate ions and hydroxyl ions in a monolayer on calcite surface under low concentration. Humus can sorb P in association with Fe^{2+}, Al^{3+} and Ca^{2+} ions. A positive correlation exists between phosphate sorption and clay content and could be attributed to the presence of Fe and aluminum on clay surfaces (Holtan, H.; Kamp-Nielsen & Stuanes, 1988). A negative correlation exists between sorption and pH. Phosphate sorption decreases with decreasing redox potential due to conversion of Fe^{3+} to Fe^{2+}. Organic matter has been seen to sorb phosphate and block phosphate binding also. These processes are reversible and solid P can enter the soil solution pool through desorption. Desorption may be favoured if the phosphate ion concentration in soil solution is decreased (LeChatelier's principle), or if there is competition for ligand binding sites with another anion.

Precipitation/Dissolution

Precipitation describes the process of removing two or more components in solution to create a new solid-state product. Phosphate precipitates with metal cations such as Calcium (Ca), Iron (Fe) and Aluminum. Phosphate can sorb to calcite prior to forming calcium phosphates and then hydroxyapatite. Aluminum and Fe precipitates are favoured in acidic soils. This process can be reversed through dissolution and is favoured when sufficient sinks for P and Ca exist.

Mobilization/Mineralization

The interconversion of organic and inorganic P is through immobilization and mineralization. Plants and micro-organisms uptake inorganic P either as inorganic orthophosphate, or convert it to organic P. Inorganic P comprises 15-50% of total P in agricultural soils (C. Van Esbroeck et al., 2016). On the other hand, inorganic P from post-harvest crop residues is rapidly sorbed by the soil. Organic P from crop decay is converted to inorganic P through the microbial process of mineralization.

Phosphorus Speciation in Water

Phosphorus enters the aquatic phosphorus cycle naturally through organismal decay and waste, weathering of P-containing rocks and dissolved minerals, atmospheric deposition (dust) and tributary inputs. Atmospheric deposition inputs of up to 50 kg P $(km^2\ yr)^{-1}$ and 770 kg N $(km^2\ yr)^{-1}$ have been reported in the Great Lakes Basin by Winter et al. (2007). Anthropogenic P inputs include industrial and municipal effluents, detergents, fertilizer, runoff, agricultural activities and soil erosion (Strickland et al., 2010; Walker Jr & Kadlec, 2011). DRP in sewage and fertilizers is highly bioavailable.

In aquatic systems, P exists in pentavalent forms as orthophosphate, pyrophosphate, longer-chain polyphosphates, organic phosphate esters/phosphodiesters and organic phosphonates (Correll, 1998). P can be classified as soluble or particulate, which can be divided further into organic or inorganic. Each of these categories are a complex mixture of the pentavalent forms.

Phosphorus is classified by its ability to respond to colorimetric tests. Phosphates that respond to colorimetric tests without undergoing acid digestion or hydrolysis are terms reactive phosphates. TP includes soluble reactive phosphorus (SRP), particulate phosphorus (PP) and dissolved organic phosphorus. These species are likely to interconvert. Dissolved reactive phosphorus (DRP) is bio-available for uptake by microorganisms including bacteria, algae and plants. A subset of DRP known as orthophosphates are inorganic DRP (HPO_4^{3-} and $H_2PO_3^{2-}$) which can interact electrostatically with polar chemicals (Strickland et al., 2010).

Particulate organic phosphorus is incorporated into organisms and particulate inorganic phosphorus is attached to particles. Particulate phosphorus is likely to settle to the base of aquatic systems, however, is prone to resuspension and conversion to reactive phosphates under appropriate conditions. Lakebed P can be resuspended following heavy precipitation events. While oxygenated base waters in oligotrophic systems promote settling of particulate P, anoxic base waters in eutrophic systems promote resuspension and diffusion of sediment P (Correll, 1998).

This dynamic phenomenon of interconversion between particulate and dissolved states of P has been called the phosphate buffer mechanism. Particulate P can be slowly or rapidly equilibrating. Rapid reactions occur at the particulate surface and slow reaction involves solid-state diffusion within particulates. If a stream inputs suspended sediments into a receiving water, the suspended P re-equilibrates with receiving water's dissolved P.

Phosphorus Speciation in Sediments

Sediments in lakes and ponds act as phosphorus sinks containing particulate phosphorus or dissolve phosphorus that is sorbed onto surface sediment. The sources include organic matter produced along the shoreline, or transported by tributaries, soil erosion, biota, detritus, precipitated humic substances and excretory products.

Overland Flow

Phosphorus in overland flow can be soluble or particulate. Soil erosion preferentially removes finer soil particles which contain higher P concentrations. P from post-harvest crop residues, unused fertilizer, manure and biosolids end up in agricultural runoff. Phosphorus loss has been shown to be greater in surface runoff in the form of DRP or SRP from desorption of reactive soil P and from crop residues. Precipitation is constant throughout the year in temperate weather, however runoff peaks following snowmelt in March. While tile drainage contributes greater water volume, surface flow contributes the greatest nutrients with the snowmelt runoff being the largest contributor of annual P loss in the form of particulate and dissolved P (Harrigan, 2016).

2.12.2. Drainage and Subsurface P Transport

P can either percolate through the soil by matrix flow or through preferential flow. Matrix flow is the even, slow movement of water through the soil, whereas preferential flow occurs when water bypasses a drier soil matrix quickly due to its pressure (Jarvis, 2020; C. Van Esbroeck et al., 2016). The soil surface is connected to the tile drains through preferential flow paths, which can be in the form of cracks or biopores. When the matrix soil suction exceeds the tensile strength of the soil during natural dessication, cracks and fissures appear. P-loss is increased in medium and coarse-textured soils compared to soils containing clay. Biopores are a result of biological root or earthworm activity, while structural cracks occur as a result of the shrinking and swelling of clays. Preferential flowpaths are a significant mechanism of P movement from surface to subsurface tile drainage. Another factor is the P sorption capacity of a soil, with finer-textured soils having a greater capacity to sorb P. Other contributing factors include redox potential of the soil as a function of water table height and drainage depth and spacing. P concentrations were shown to be higher in shallow drains, however deeper tile systems had greater discharge (King et al., 2015).

Inorganic organophosphate forms stable minerals through ionic binding to cations in clay sediments (Robinson, 2015). Plants uptake inorganic phosphate and convert it to organic phosphate, which when consumed by other living beings, is excreted back into the soil and accumulates as organic P in sediments. Alternatively, the unused organic P from bio-assimilation also cycles back into the landscape as a result of plant senescence. Tillage has been shown to reduce P-transport by disrupting movement through macropores (King et al., 2015).

Additionally, King et al. concluded that P application rate, source, placement, timing and soil test concentration are greater contributors of subsurface P than the type of cropping system.

2.12.3. Groundwater Interaction

Inorganic soluble phosphate, orthophosphate (PO_4^{3-}), is the most common form of P in waters. Groundwater interaction with phosphorus is generally considered negligible because orthophosphate reacts with cations in sediments to form stable minerals or are bio-assimilated by plants and converted to organic phosphate (Robinson, 2015). A survey of groundwater quality across the U.S. by the USGS NWQA Program found that orthophosphate concentrations in groundwater were below background concentrations of 0.03 mg L^{-1} PO_4-P (Dubrovsky et al., 2010). Contradicting studies have shown that increasing orthophosphate mobility is linked to increasing pH, organic content and metal oxide content in anoxic aquifers (Carlyle & Hill, 2001; Domagalski & Johnson, 2011). Phosphate mobility in groundwater is high when sediments are saturated with phosphate (for example, due to excessive fertilizer loading). In the Great Lakes Basin, concentrations of up to 6 mg L^{-1} PO_4^{3-}-P and 1.5 mg L^{-1} PO_4^{3-}-P have been reported (Robertson et al., 2016). Orthophosphate migration into groundwater is enhanced in areas containing unsaturated fractured bedrock and shallow water table, or in areas containing coarse sediment composed of sand or gravel. A study of five agricultural watersheds across the U.S. that drained water from fertilizer-applied farms showed high spatial variability of phosphate concentrations in groundwater, where median concentration ranged from 0.25 mg L^{-1} PO_4^{3-}-P to 0.01 mg L^{-1} $PO_4^{3—}$P (Domagalski & Johnson, 2011). Other sources of nutrients into groundwater include septic systems and greenhouses.

2.12.4. Surface Water Interaction

Particulate phosphorus enters surface waters through sediment or surface erosion. Phosphorus accumulates in sediment; subsequently, sediment erosion and surface runoff load phosphorus into surface waters (Pärn et al., 2012). However, the concentration of P varies within the same system or lake. A lake undergoes thermal stratification into three main layers in the summer: the epilimnion (warmer upper layer); the metalimnion (intermediary layer) and the hypolimnion (cool base layer) (Strickland et al., 2010). These layers do not mix and often show distinctive nutrient depletion patterns; for example, oxygen is often depleted in the hypolimnion. During the summer months, P is taken up by algae and upon their decomposition, the base layers of the lake are enriched with P. Anoxic or anaerobic conditions affect the redox potential of the sediment-to-phosphorus bond and iron undergoes reduction from the ferric state to the ferrous form under conditions of low or no oxygen. In the Fall, temperatures drop and stratification ends. The layers are miscible, and the entire lake becomes P-enriched.

Groundwater can flow into surface waters such as lakes either near the shoreline, or offshore, or as baseflow through streams and rivers that discharge into lakes (Robinson, 2015). The contribution of nutrients from groundwater to surface water is considered negligible. Kornelsen and Coulibaly (2014) estimated that groundwater contributed between 5-25% of total water inflow in the Great Lakes. Groundwater contributes nutrients to tributaries when surface water flow is low and mostly maintained by groundwater discharge. 31-68% of warm season total N loads and 7-32% of warm seasonal total P loads to receiving water resulted from baseflow groundwater to surface water in six watersheds of Minnesota.

TP is most often used to demarcate the nutrient status of a water body as DRP is more challenging to characterize due its easily reactive nature. On average, the TP concentration of a lake varies from 10-80 μg L^{-1}; the TP concentration of an ultra-oligotrophic lake may be as low as 1 μg L^{-1}, while hyper-eutrophic lakes may have TP concentrations of 200 μg L^{-1} (Strickland et al., 2010). TP levels in the South Nation River exceed provincial water quality standards of 30 μg L^{-1}, with average concentrations ranging from 40-150 μg L^{-1} in the river and maximal values of 250 μg L^{-1} in the tributaries (Gottschall et al., 2006).

2.12.5. Regulatory Framework

The regulatory framework for phosphorus is loosely defined and follows a guideline approach as opposed to a target approach. In the 1980s, the binational Great Lakes Water Quality Agreement (GLWQA) required wastewater treatment plants discharging more than 1 million gallons per day (MGD) to meet the effluent TP concentration target of 1 mg L^{-1}. There is no defined criterion for phosphorus by the Canadian Water Quality Guidelines for the Protection of Aquatic Life. Interim objectives have been set for TP at 20 μg L^{-1} to prevent nuisance concentrations in lakes; 30 μg L^{-1} to prevent excessive plant growth in rivers and streams and 10 μg L^{-1} to prevent aesthetic deterioration as well as for lakes naturally below this value (PWQO, 1994). A binational agreement by the International Joint Commission (IJC) recommended a 40% reduction of TP and DRP loading to the Western and Central Basins of Lake Erie by 2025 (Fussell et al., 2017). There is no regulated criterion under either the CCME or PWQO for SRP. Ecological threshold studies on biological responses to SRP have shown that concentrations less than 47 μg L^{-1} prevented nuisance algal growth and preserved water quality for recreational use in freshwater, whereas concentrations less than 15 µg L^{-1} ensured the maximum periphyton biomass remained below 100 mg m^{-2} (USEPA, 2000).

2.13. Beneficial Management Practices

Beneficial management practices (BMPs) describe an integrative approach to address diffuse and non-localized nutrient pollution sources and soil and water conservation on farms without a reduction in yield or productivity. BMPs can vary from tillage practices to the appropriate ratio and rate of fertilizer application, the implementation of cover crops and nutrient attenuation through subsurface drainage, wetlands, ponds or other biofilters.

Other examples of BMPs include soil testing to determine nutrient deficiencies, plant tissue analysis and visual deficiency symptoms to assess soil fertility and crop nutrition complemented by the selection of an appropriate fertilizer. Testing the nutrient content of soil is an effective way to determine what type of fertilizer to use to complement plant growth and reduce nutrient runoff.

2.13.1. Agronomic Practices: Tillage Practices, Crop Rotation, Cover crops

The types of agronomic practices on a field can impact nutrient export from farm fields. The effect of tillage practices, crop rotation and cover crops have been described below.

Tillage

Conservation practices such as no-till and reduced tillage have been encouraged since the 1970s and these have led to reduced soil erosion and associated nutrient loads. Tillage refers to the preparation of an agricultural field for growing crops. Conservation tillage (also known as reduced tillage) is the practice of allowing organic residue from crops to remain on the field to varying degrees. These practices improve soil health by reducing soil disturbance and preserving crop residues (King et al., 2015). No-till cropping results in soils with improved macropore development and increased organic matter. However, with reduced tillage, nutrients can pool near the surface and may enter discharge waters through runoff. Contradictory research also indicates that periodic tillage is likely to break through preferential flowpaths and allow for nutrient cycling throughout the root zone. These above two practices reduce the potential loss of sediment-bound particulate P in runoff that can contribute to NPS pollution. However, soluble reactive species of P and N are increasingly acknowledged for their detrimental impact on aquatic ecosystems due to their bioavailability and tillage management alone has not been shown to affect the mitigation of soluble nutrient export.

Cover Crops

In countries where seasonality plays a role in farming, crops are grown for the summer and fields are fallow during the months following harvest. Crop rotation and the planting of nitrogen-fixing plants (eg. soybean) are a method of nutrient replenishment in soil. Cover crops can protect the soil during these periods from soil erosion, temperature swings (The Lexicon, 2017) and enhance evapotranspiration of soil water (Dabney et al., 2001). Cover crops can reduce surface runoff and nutrient concentrations in both runoff as well as tile drainage. A four-year study by Zhang et al. (2017) found that cover crop reduced surface runoff flow volume by 32% irrespective of drainage water management. In the same study, cover crops were found to reduce flow-weighted mean (FWM) particulate P (PP) concentrations by 26% and TP by 12% in surface runoff and FWM PP concentrations by 21% and TP by 17% in free tile drainage. Cover crops were reported to reduce nitrate export by 84% in surface runoff (Sharpley et al., 1991) and 62% in tile drainage (Constantin et al., 2010). Cover crops allow for the biological uptake of excess nutrients in the soil, which would be otherwise lost to runoff during erosion events.

i. Water Management: surface and subsurface drainage, buffer strips, ponds and wetlands

Nutrient export can be managed on farms by managing the water: the surface water can be kept on the land with the use of ponds, wetlands, and buffered with the use of buffer strips; subsurface drainage can be used to drain the surface water and controlled for use during dry periods.

2.13.2. Tile Drainage

In Eastern Canada (including Ontario, Quebec and the Maritimes), agriculture is predominantly sustained on drained wetlands (that formed due to poorly draining, glacially-derived soils) with the aid of surface ditches and subsurface drainage (King et al., 2015). Tile drains are a system of perforated subsurface pipe systems that allow excess water to drain from subsurface soil for final discharge into a receiving water body. In North America, the first tile drains made of clay, concrete or wood were installed in late 1800's in midwestern United States to drain areas on the field where surface water collected in shallow ponds (King et al., 2015). Since its initial introduction, tile drainage continues to be extensively applied and has evolved to incorporate plastic tiling that drains entire fields, with reduced inter-drain spacing. Tile drains are generally perforated plastic pipes installed between 0.6-1.2 m below ground surface and spaced between 10-100 m apart, effectively lowering the water table and allowing sustained root development (Stone Environmental, 2016).

Tile drainage improves water infiltration into soil, soil aeration, bearing strength, temperature and nitrate production; reduces runoff; increases water storage; and promotes germination, deeper root growth and therefore yielding more crops in a longer GS (Harrigan, 2016; King et al., 2015). Subsurface drainage allows water to percolate through preferential flowpaths, allowing the infiltration water directly into deep groundwater and reducing the potential for upward movement of groundwater towards the root zone for crop use (Ayars et al., 2006). Drainage also provides greater control to the farmer, reduces crop losses and affords the farmer more choice in types of crops to cultivate. An estimated 8 million hectares of land are drained in Canada (King et al., 2015). In Ontario, an estimated 63% of non-pasture, agricultural land is drained (C. Van Esbroeck et al., 2016; Wang et al., 2012).

Tile drainage has been shown to increase the total water outflow from agricultural fields. Tile drainage increases the total water yield of the watershed between 10-25% as a result of precipitation, compared to stored, evaporated or transpired (King et al., 2015). In 2007, Macrae et al. estimated that 42% of an annual watershed discharge in Ontario was from tile flow. Tile drainage was shown to contribute 87-90% of the annual water export compared to 10-22% from surface runoff in a study by Van Esbroeck et al. (2016). Land drained with tile drains showed 10% greater total discharge than lands that were naturally drained (Blann et al., 2009; C. Van Esbroeck et al., 2016). Evans et al. (1993) reported that artificial drainage typically increased the total annual outflow from agricultural fields by less than 20% in North Carolina, in comparison with natural, undrained conditions.

Subsurface drainage has been shown to reduce peak flow by dispersing excess water in the soil profile over a longer time. Blann et al. (2009) reported that tile drainage reduced overland flow by 60%. Gilliam and Skaggs (1986) demonstrated a two- to three- fold reduction of peak runoff in subsurface-drained watersheds. As the water table is lowered in subsurface drainage, there is more accessible soil pore space for the water to drain through, effectively reducing surface runoff. However, these patterns are dependent on soil conditions. Downstream peak flow and the rate of tile drainage are increased in soils that are already permeable. Macropore flow and increased connectivity of surface land to drainage are often attributed as the causes of increased peak flow and rate of tile drainage.

Subsurface drainage is linked to high N losses in the form of nitrate due to the leaching of nutrients from the soil profile. Beauchemin et al. (2003)demonstrated the transport of P from soil to surface waters through subsurface drainage waters in Quebec. The reduction in overland flow has shown parallel reductions in TP export by 30-36% (McDowell et al., 2003). Christen et al. (2001) reported that most drainage systems drained more water than was applied through irrigation in Australia. To minimize NPS pollution from agriculture, other forms of conservation and management practices such as planting cover crops, reduced tillage and establishing riparian buffers have been developed.

2.13.3. Riparian Buffers

Riparian buffers and vegetated constructed wetlands provide pathways of biological uptake that can mitigate excess orthophosphates and nitrates. In addition to uptake, shoreline buffers are effective as they reduce nutrient flow to surface waters and have been shown to reduce P transport to streams by 50-85% (Carpenter et al., 1998; Correll, 1998; Hill, 1996; Lowrance et al., 1985; Osborne & Kovacic, 1993).

Due to the natural filtration capacity of soil, subsurface nutrient loss was not conventionally considered as a source of non-point pollution. However, recent findings indicate the existence of preferential flow pathways in soil for highly concentrated water that contributes to P transport. Sims et al. (1998) concluded that subsurface P transport was significant in soils containing high P concentrations (King et al., 2015). Another important consideration for runoff is the type of soil. Ulen et al. (2007) found that areas with clay soil have large transports of P to surface water. Clay soils are under-drained as clay is cohesive, compact and contains fewer pore spaces for nutrient drainage and therefore clay does not bind nutrients effectively and contributes to nutrient transport to surface water.

2.13.4. Controlled Tile Drainage (Drainage Water Management)

Drainage is necessary in many parts of the world to facilitate agricultural production. For example, 25% of the total agricultural production in Canada and the United States requires drainage to reduce subsidence (Shady, 1981). While drainage reduces the introduction of sediment-based nutrients to surface waters, increased water drainage has been linked to elevated nutrient loss (Tan & Zhang, 2011; Zhang et al., 2017) in soluble forms such as nitrate (Baker et al., 1975; Ikenberry et al., 2014; Randall et al., 1997). Drainage water management (DWM), interchangeably synonymous to controlled tile drainage (CTD) or controlled drainage (CD) in literature, is the management of water discharged from surface and subsurface drainage systems in an agricultural context (BRDFN, 2018). Drainage water management helps reduce nutrients including phosphorus and nitrogen farm field output by controlling the volume of discharged water. Such systems elevate the water table by controlling flow from the outlet so that water is accessible to root systems during periods when drainage is not needed. To reduce nutrient loss, existing tile drainage systems can be retrofitted by installing a riser or stop log on the tile outlet to manage the water table and crop sub-irrigation[2].

Controlled drainage structures are a type of drainage water management system that contain stop logs that can control the water table elevation in the field (**Figure 2.2**). Therefore, excess water is drained during periods of heavy precipitation and maintained in the tile drains during dry conditions. Unlike other passive technologies which require a maturation time (eg. wetlands or vegetative buffers), an advantage of using drainage water management is its immediate net effect on environmental quality through flow retention (Sunohara et al., 2016).

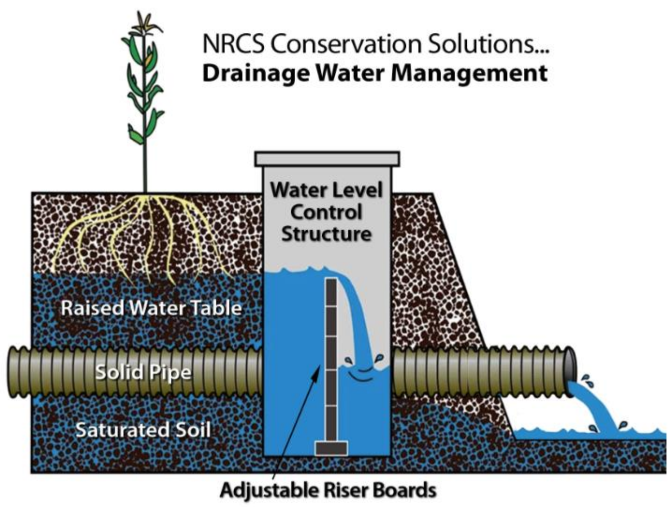

Figure 2.2: Schematic Diagram of a Controlled Drainage System (BRDFN, 2018)

Controlled drainage structures are especially useful in dry climates as the stop logs can be used to maintain a reservoir of water from wet periods for crop use during dry periods. Controlled drainage structures can also be used for sub-irrigation by pumping water to meet the desired water level.

[2] Sub-irrigation is a method of irrigating plants by delivering water directly to the root zone.

Water Table Effect and Crop Growth

Controlled drainage systems (CDS) allow for the control of the water table, especially in areas where the ground water is shallow. CDS have been seen to be most effective on flat topography where one drainage structure can be used to control the rate, time of drainage and the water table across a large drainage area from one single outlet (Strock et al., 2015). During high precipitation events, shallow groundwater will rise and rot the crop. Controlled drainage systems can be opened during periods of high precipitation to drain the land during the wet season, but also retained during the dry season to sub-irrigate crops. Conceptual flow paths for free drainage and CD is shown below in **Figure 2.3**.

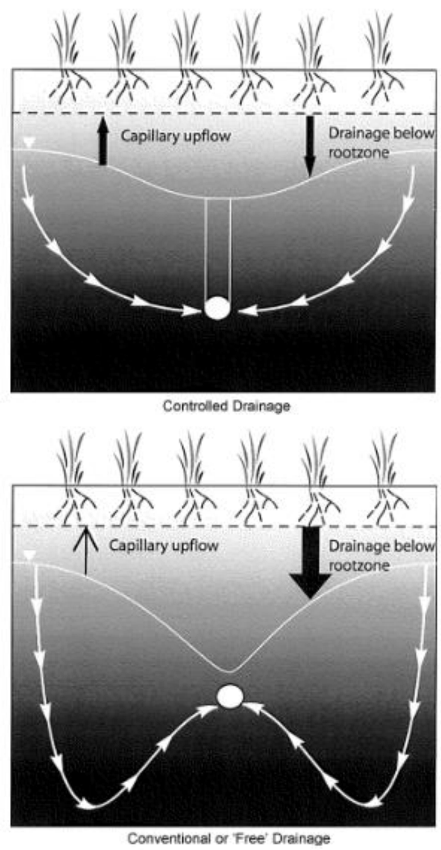

Figure 2.3: Conceptual Flow Paths in Controlled Versus Free Drainage Systems (Ayars et al., 2006).

In the free drainage scenarios shown in **Figure 2.3**, water from precipitation percolates through the soil at varying depths below the root zone, either maintaining the existing water table or lowering it. Deep percolation of irrigation water results in increased drainage flow and nutrient loss. Controlled drainage has been shown to reduce drainage outflow from irrigation in published literature. In comparison to free drainage which drained 5% of the total irrigation volume, Hornbuckle et al. (2005) showed that drainage volume represented 0.5% of irrigation water volume with controlled drainage. In the controlled drainage scenario shown above, the water table is maintained at a depth closer to the root zone, increasing the likelihood of capillary upflow.

Outflow Reduction

Controlling the water table has been seen to have a variable effect on total drainage outflow depending on the use and the volume of precipitation. In a literature review, Evans et al. (1993) reported that CDS could reduce total outflow by 30% compared to FDS when operated year-round. Lalonde et al. (1996) demonstrated that CD reduced drain flow by 58.7% and 65.3% by controlling the water table at 0.25 and 0.50 m above the water table, respectively in 1992. The study was replicated in 1993 and the reductions were 40.9% and 95% for the same riser depths. Gunn et al. (2015) compared case studies in poorly drained soils in Ohio and found the median daily subsurface drainage volumes were 40-100% lower from the zone with drainage water management compared to free drainage. Cordeiro et al. (2014) reported 39% reduction in tile drainflow compared to free drainage in tile flow from corn fields in Manitoba.

The amount of received precipitation changes the volume and behaviour of tile drain outflow. Evans et al. (1993) reported that during dry years, controlled drainage can eliminate outflow and during wet years, there may not be any difference between controlled and free drainage. Flow reduction with drainage control in the GS was only 15% compared to conventional subsurface drainage according to Evans et al. (1993). Additionally, peak storm event outflows was reduced during dry periods and had little or increased peak flow during wet periods. This reduction of drainflow has been demonstrated to reduce nitrate N concentration and annual P loads by various authors.

A few considerations must be accounted for when comparing the results achieved by research studies of drainage water management. Some studies compare conventional drainage to DWM on field-scale, replicated plots. Other studies pair DWM and conventional drainage on farmer-operated fields that span across large topographically heterogenous sites. Variables such as the length of the growing season, the period during which the water table is managed, the number of years or growing seasons observed, soil type, soil stratigraphy, field topography, cropping systems and climate are often different between similar types of studies.

Nitrogen

The reduction of nitrogen as nitrate in drainage water due to controlling the water table with drainage water management is well established in literature. Gilliam et al. (1977) reported that nitrogen losses were reduced by 40 to 50% using controlled drainage through the winter in North Carolina for a corn-wheat-soybean rotation.

A cold climate study conducted in Ontario showed that the depth of tile drainage can impact total nitrogen reduction through a total reduction in tile drain outflow. A water management field study by Lalonde et al. (1996) reported nitrate concentration decreased by 75.9% and

68.9% by controlling the water table 0.25 m and 0.50 m above the drain level in 1992. The study was replicated in 1993 and nitrate concentration was reduced by 62.3% and 95.7% by controlling the water table at 0.25 m and 0.5 m above the drain level, respectively. Madramootoo et al. (1993) demonstrated that soil nitrate concentration decreased, and soybean yield increased when the water table was controlled between 0.60 and 0.80 m below the soil surface. Drury et al. (2001) demonstrated that CDS reduced total discharge by 26% and total nitrate loss in tile discharge by 55% compared to free drainage during a continuous corn cycle and total discharge by 38% and total nitrate loss by 66% in a soybean-corn rotation. Tan et al. (2011) determined that nitrate loss was reduced by 14% using controlled drainage on a conventional tillage site and by 25.5% on a site with no tillage in Southwestern Ontario.

A drainage water management study conducted by Sunohara et al. (2016) on agricultural fields used to grow dairy-feed related corn, soybean and mixed forage crop rotations in an experimental watershed of eastern Ontario compared the effect of paired field systems of controlled and uncontrolled tile drainage for nine growing seasons (May to October). Approximately 170 kg N ha^{-1} and 50 kg P ha^{-1} of fertilizer were applied for corn and 10 kg N ha^{-1} and 60 kg P ha^{-1} were applied for soybean to a predominantly Bainsville silt loam. Ammonia concentrations were found to be similar between the CTD (0.05±0.12 mgL^{-1} NH_4^+-N) and the UCTD (0.06±0.29 mgL^{-1} NH_4^+-N). Reductions of 58% and 51% in ammonium and nitrate fluxes in Southeastern Ontario were reported as a result of controlling the water table. One major mechanism for nitrate loss reduction is through the effect of DWM on hydrology and therefore on nitrogen mobility in soil. Increased evapotranspiration can result in increased nitrogen uptake by plants. When the water table is raised, the base of the soil profile may be saturated

and anaerobic. Raising the water table promotes denitrification as the soil is maintained in saturated anaerobic conditions (Gilliam & Skaggs, 1986). This promotes the reduction of nitrate to atmospheric nitrogen gas and therefore, reduces nitrate output in drainage water.
A 6-year corn-soybean study conducted on eight 0.1 ha field plots (slope 0.5-1%) of an experimental farm in Woodslee, Ontario on Brookston clay loam soil by Drury et al. (2014) showed that flow-weighted mean nitrate concentration was reduced by 15-33% and cumulative nitrate loss was reduced between 38-39% relative to the uncontrolled drainage.

A field-scale evaluation of denitrification bioreactors in combination with controlled drainage during a three-year crop rotation on a dairy farm in Quebec, Canada achieved 55% reduction in drainage water, and reductions of 72% (TN concentration), 99% (NO_3^--N concentration) and 99% (NO_3^--N load).

Phosphorus

As seen with ammonia and nitrate reduction, drainage water management has been shown to reduce phosphorus flux due to the reduction of outflow but has been shown to have little effect on concentration. Sunohara et al. (2016) reported slightly lower concentrations of DRP in drainage water from CTD and reductions of 66% and 66% in TP and DRP respectively in drainage water fluxes in Southeastern Ontario as a result of controlling the water table. Similarly, Evans et al. (1993) reported that the reduction of outflow achieved by controlling drainage was able to reduce phosphorus between 30-50%.

The effectiveness of CDS is a function of climate, soil and field management practices. A five-year study compared the effectiveness of CDS and FDS in attenuating DRP, PP and dissolve unreactive P (DURP) in surface runoff as well as tile drainage. This study found that the flow-weight means of DRP, DURP, PP and TP were higher in surface runoff and lower in tile drainage water with CDS (Tan & Zhang, 2011). The authors found that of the total loss of phosphorus in the field, in the FD systems 3-5% occurred in surface runoff and 95-97% occurred in the tile effluent; in comparison, in the CD systems, P loss in surface runoff accounted for 29-35%, whereas 65-71% of total P loss occurred in the tile effluent. Therefore, the cumulative mass load of phosphorus in tile drainage was reduced due to CD, but the cumulative mass load of phosphorus in the surface runoff was increased. Ford et al. (2015) theorized that decreasing soil permeability and increasing evapotranspiration as a result of CD may increase P loads in surface runoff.

Some studies indicate that CTD reduces P losses in tile drainage for dissolved species of phosphorus. Cordeiro et al. (2014) reported 69% reductions in PO_4-P load compared to free drainage in tile flow from corn fields in Manitoba. During the GS, PO_4-P export was 0.6 kg/ha with conventional drainage compared to 0.08 kg/ha with CD. Williams et al. (2015) demonstrated a reduction of dissolved P loads by 40-68% with CD ranging between 0.05-0.51 kg/ha.

CD has shown to decrease TP concentrations in drainage effluent but increase the concentration of SRP or DRP. CDS systems provide reducing conditions by elevating the water table which promotes the dissolution of TP into SRP or DRP. In 2011, Tan and Zhang found that compared to free drainage, controlled tile drainage contained elevated flow-weighted mean DRP concentrations by 30% but reduced particulate phosphorus losses by 15% and of TP by

12%. Similar trends were reported by Sanchez Valero et al. (2007) who reported a 178% increase in SRP concentration in controlled versus free tile drainage. The P losses occurred during the NGS and the authors reported reduced P loss in in CD during the GS-D.

The Effect on Crop Yield

The effect of DWM on crop yield is less conclusive, as the combined effect is dependent on the weather conditions encountered. DWM is able to retain water from the wet period in the subsurface drains, which can be used to supply roots in subsequent dry periods. However, if the growing season is unusually wet, then DWM is not required and if the growing season is unusually dry, there may be insufficient water to retain in the drains. Crézé and Madramootoo (2019) demonstrated that controlled drainage and subsurface irrigation can increase crop yields during dry periods of the GS. Skaggs et al. (2012) concluded that the use of DWM when a wet period is following by a moderately long dry period during the growing season would be optimal for crop yield. Previous studies that have measured the effects of drainage water management in Ontario have shown no effect on soybean yield (Tan et al., 1999) or corn yield (Drury et al., 2009). Skaggs et al. (2012) reviewed ten studies on the effectiveness of DWN on crop yields and reported that DWN resulted in yield increases in some cases and not others. A 6-year corn-soybean study conducted on eight 0.1 ha field plots (slope 0.5-1%) of an experimental farm in Woodslee, Ontario on Brookston clay loam soil by Drury et al. (2014) demonstrated that controlled tile drainage-subirrigation did not significantly impact annual soybean yields.

2.13.5. Engineered Ponds: Attenuation Ponds

Engineered ponds are an alternative treatment system that can be considered as designed reactors that have been constructed through excavation and compaction to store and treat water or wastewater (Oswald, 1995). Ponds can be classified as dry or wet detention basins. A wet detention basin is engineered to contain a permanent reservoir of water and contain an outlet to slowly release water over time.

Stormwater ponds or retention ponds are the most common type of engineered pond used for urban stormwater runoff and flood mitigation. Stormwater retention ponds improve water quality through particulate sedimentation and retaining the water before outflow and therefore diluting the contaminant of concern. Engineered ponds are able to remove nutrients, pathogens and particulates through various hydrogeochemical pathways described in the figure below to varying effectiveness and seasonal conditions (Beckingham et al., 2019). Mechanisms that contribute to nutrient and solids removal are similar to those described previously and are similar to those that occur in a lake and include physical processes (sedimentation), chemical processes (precipitation, adsorption) and biological uptake and transformation (Harper & Baker, 2007). Attenuation ponds are designed to store rainwater and are often found following a drainage system. Attenuating ponds can be designed so as to slowly release the water over following a flood event to reduce risk of groundwater infiltration and release to surface waters. The water that is released is a mix of rainwater and the permanent pool. Dredging of the sediment in the pond is required to maintain optimal removal efficiency.

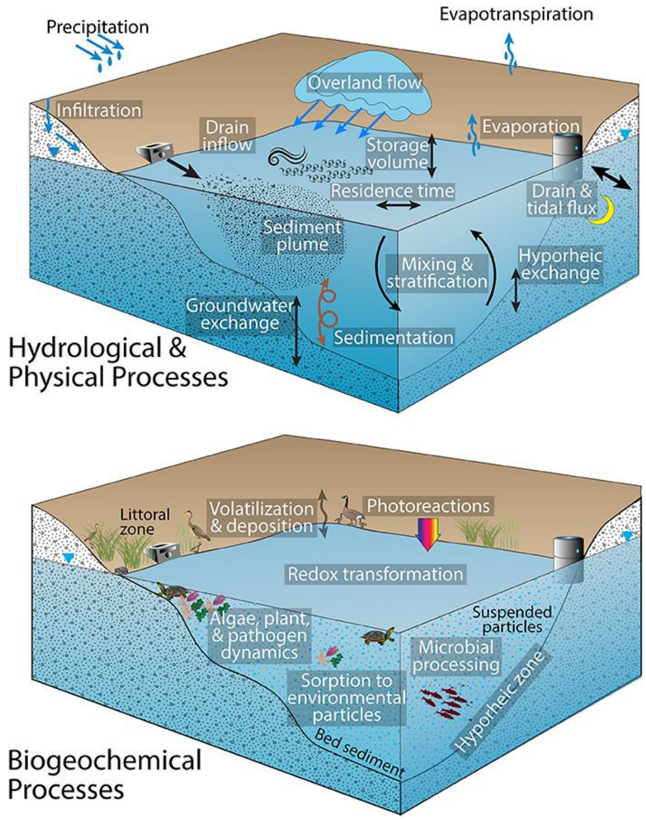

Figure 2.4: Overview of Physical, Hydrological and Biogeochemical Processes in Ponds (Beckingham et al., 2019)

Parameters that contribute to peak flow include proximity to impervious surfaces (Roodsari & Chandler, 2017) watershed slope and drainage density (Meierdiercks et al., 2017). The existing research has predominantly focused on constructed stormwater ponds and so, there is little research that pertains directly to runoff attenuation ponds in an agricultural context.

Effect on Flood Mitigation

Stormwater ponds are designed to reduce peak volume and flow during storm events (Moore et al., 2017). There is a variable range for the published effectiveness of retention ponds. Retention ponds are able to reduce peak volume between 0-20% and attenuate peak flow between 0-60% (Lawrence et al., 1996). The flood mitigation capacity of a pond is dependent on the type of weather that the pond is subjected to. For example, a tornado-prone or hurricane-prone pond is likely to be more at risk of flooding nearby properties.

Removal of Contaminants of Concern

Published literature shows a large range of reported removal efficiencies for nutrients. Lawrence et al. (1996) reported that retention ponds/wetlands were able to remove solids with an efficiency between 60-80%, phosphorus (40-80%) and nitrogen (20-40%). The USEPA (2002) reported that detention ponds can remove between 49-80% of TSS, 20-52% of TP and -3 to 64% of DRP. Harper and Baker (2007) conducted a review of wet retention ponds and reported removal efficiencies for ortho-phosphorous (39-94%), TP (39-93%), TSS (55-94%) and TN (12-63%). In this study, it was evident that a longer retention time resulted in improved removal efficiency. The authors average the removal efficiencies across ten studies based on a 14-day residence time to provide a mean removal efficiency of 37% for TN, 79% for SRP, 69% for TP and 77% TSS. However, it is important to note that this comparison between ponds did not account for differences in design type, soil characteristics or other environmental conditions including the location of the pond. Sanchez Valero et al. (2007) reported that stormwater detention ponds removed between 65-80% of TSS, 35-45% of TN and 50-70% TP. Retrofitting a stormwater pond by introducing a baffle can increase the retention time and therefore the removal of solids and nutrients. A 2014 study of a retrofitted stormwater detention pond for a small residential catch basin reported an improved removal efficiency from 39 to 90% for TSS and 10 to 84% for ammonia.

Nutrients in stormwater ponds have also been described as infiltrating the groundwater by various authors. Bunker (2004) reported that ammonium and nitrate were migrating from the stormwater pond into the groundwater and vice-versa. Shukla et al. (2017) reported that dry detention ponds were able to produce high P removal efficiencies due to the formation of a groundwater plume and not nutrient removal. Memon et al. (2017) reported that TSS concentrations likely exhibit a first flush pattern, in that TSS concentrations peak following a peak flow event. Ponds have been shown to display episodic or seasonal behaviour in nutrient release and attenuation. Bennion and Smith (2000) studied the variability in water chemistry of 31 shallow, artificial ponds in southeast England and concluded that while TP showed no seasonal pattern, SRP and NO_3-N concentrations showed a decrease in the spring, low levels during the summer and the highest levels during the winter.

2.13.6. Constructed Wetlands

A countermeasure to eutrophication is the construction and restoration of wetlands. Constructed wetlands (CWs) have been historically used for tertiary treatment of municipal wastewater, but they are gaining popularity as an alternative wastewater treatment technology. CWs are a low-cost, land-intensive, energy-effective technology that have been proven to treat wastewaters for organic matter, suspended solids, pathogens and nutrients. CWs have been used to remove nitrogen from domestic wastewaters, industrial wastewaters, leachate and polluted surface water.

A wetland is an area of land that is wet during part or all of the year, often a transitional zone between uplands and aquatic or flooded systems (Kadlec & Wallace, 2008). Wetlands can be primarily characterized by water salinity and plant form and secondarily by hydrology, soil, climate and plant community. Wetlands are unique, biologically active habitats that can transform contaminants into harmless by-products. Wetlands can be designed to maximize these transformational abilities and improve water quality. A constructed wetland (CW) differs from a natural wetland in one other significant way: the original landform. CWs can be built in nearly any location and are often built for habitat creation, water quality management, flood control and aquaculture. When water or wastewater flows through a CW before discharge, the water is able to undergo complex physiochemical and biological mechanisms that can reduce nutrient concentrations. Wetlands can treat wastewaters from municipal, industrial and agricultural sources, rural and urban stormwaters as well as polluted surface waters.

Constructed wetlands can be divided into three categories: free water surface wetlands, horizontal subsurface wetlands and vertical subsurface wetlands. Free water surface wetlands (FWSW) have areas of open water with floating and emergent vegetation. Of the three subtypes, FWSW most resemble natural wetlands and are the subject of discussion in this chapter. The primary characteristic that distinguishes the different types of wetlands is the direction and location of wastewater flow, as well as the type of planted vegetation. Wastewater flows above-ground through emergent macrophytes in FWSW, while the wastewater flows below ground through a porous substrate in subsurface flow wetlands (SSFW). FWSW can have one or many cells in series or parallel to one another and have been used as nutrient sinks downstream of cattle exercise yards (Gottschall et al., 2006). The incorporation of submerged vegetation along with the substrate provides a greater surface area for chemical interactions that facilitate nutrient removal in SSFW compared to FWSW. While subsurface flow wetlands are more efficient and less land-intensive than FWSW, they are more likely to clog due to the incorporation of porous media. Therefore, SSFW are more expensive operationally as well as for construction and long-term maintenance.

Effect on Flood Mitigation

In temperate climates, high flow and low biological activity in the fall and spring create an environment that promotes nutrient loss from arable fields (Kynkäänniemi et al., 2013). In wetlands, the predominant mechanism of nutrient removal is soil accretion. This is to say that the majority of the removed nutrients are stored in the soil, however biomass, microorganisms, litter and sediment also play a role.

As full-scale constructed wetlands are generally very dissimilar spatially and temporally, it is challenging to accurately predict and form generalized conclusions about their effects on water quality improvement. However, wetland nutrient removal displays seasonality. Some studies have shown that there is enhanced removal during the spring in northern climates where seasonal effects are seen in the winter with lower removal rates (Bishay & Kadlec, 2005). As temperature fluctuations occur daily, temperature alone should not be used as a sole indicator of season. Another factor that compounds uniqueness is the presence of ice cover and snow melt in colder climates.

On the one hand, nutrient removal can be considered temperature-sensitive when dependent on microbial activity or absorptive capacity. The removal of nitrogen through microbial activity and phosphorus through sorption to soil is temperature-sensitive as enzymatic activity and the sorptive capacity changes with temperature. However, nutrient removal that is dependent on the growth cycle of plants, which though seasonal, is not temperature-sensitive. As mentioned previously, the soil will reach its sorption capacity over time. In particular, the zone near the inlet is likely to reach saturation first. In systems where the C:N ratio is below 10 under oxic conditions and below 25 under anoxic conditions, ammonia is more likely to be released than retained (Xia et al., 2018). Due to the seasonal dependence of bio assimilation, there is a potential for particulate ammonia to become resuspended in such systems following senescence. Over time, nitrogen removal is expected to increase with the establishment of vegetation and the build-up of carbon as a source of denitrification; whereas phosphorus removal is expected to decrease with time as the sorptive capacity of the soil is maximized (Kadlec & Wallace, 1996). The applicability of this data to Canadian winter conditions has not been evaluated.

FWS wetlands contain emergent and submerged aquatic vegetation (EAV), (SAV), floating mats (FM), floating aquatic plants (FAP) and algal systems. EAV and SAV are the most common in wetlands. A newly constructed wetland (CW) or an existing wetland that is introduced to wastewater may experience an adaptation period, where the system adapts to high nutrient conditions and water depths. In the latter case, such a system may display a high level of removal before stabilization until the sorption and uptake mechanisms are saturated. Biomass removal has been largely concluded to be ineffective.

Vegetation reduces turbulence and encourages particle settling and facilitates chemical and bacterial processes (Gottschall et al., 2006). Brix showed in 1997 that nutrient uptake by plants was only significant when nutrient levels were low and have been shown to account for 3-47%

of nitrogen removal and 3-60% of phosphorus removal (Gottschall et al., 2006; Greenway & Woolley, 2001; A. Martin & Cooke, 1994; Tanner, 1996).

Nitrogen

The nitrogen-removal capacity of constructed wetlands from non-point sources is well-documented in literature. The predominant species of nitrogen in constructed wetlands are ionized ammonia (NH_4^+) and nitrate (NO_3^-). Ionized ammonium and nitrate are readily bioavailable for uptake by plants. Nitrogen removal is largely dependent on microbial activity in the rhizomes of the biota and occurs primarily through nitrification/denitrification, assimilation by biota and accretion in sediment. Peat formation through the accumulation of organic matter is another sink of nitrogen. Peat contains 3% nitrogen in natural wetlands (Kadlec & Wallace, 1996). In CWS, this percentage and rate of peat formation is higher.

Nitrogen removal efficiency is critically linked to water loading and as such, flood events can cause temporal export of N. Another factor critical to the net removal of nitrogen is the residence time. A short residence time can cause resuspension of nitrogen instead of removal. The role of plant cover in nitrogen removal is subject to debate. Authors have found that accumulating plant material significantly contributed towards decrease in nitrogen removal with time and on the other hand, contradicting studies have found that harvesting wetland vegetation did not significantly impact nitrogen removal. An 18-ha constructed wetland in southeast Sweden was exporting nitrogen as a result of wetland plant decomposition. Thorén et al. (2004) concluded that nitrogen export was correlated with the release of organic and inorganic nitrogen from the senesced submerged plant community.

FWSW are usually designed as shallow ponds to promote denitrification, which provides long-term nitrogen removal. Therefore, nitrogen removal is largely depended on microbial processes. Restored wetlands in Spain that treated runoff were found to reduce nitrate by 98% and ammonia by 33 to 95% under low nutrient loading conditions (Comín et al., 1997; Gottschall et al., 2006).

Phosphorus

Wetlands can provide both short-term and long-term storage of phosphorus through biological, chemical and physical processes (Bishay & Kadlec, 2005). Introducing nutrient-rich influent into a wetland is likely to impact the molar Redfield ratio of C:N:P = 106:16:1 that is required for a stable ecosystem. Phosphorus in a wetland can be dissolved in water, a solid mineral as part of the soil structure, or solid organic in biomass. HPO_4^{2-} is the predominant form of phosphate in wetlands and is bioavailable.

Phosphorus removal in wetlands occurs through sorption, sedimentation, precipitation and biota cycling (Reddy et al., 1999). Uptake by biota and soil sorption are temporary forms of nutrient removal within a wetland. Sorption is impacted by factors such as flow rate, flow path, water and soil chemistry, pH and the oxidation-reduction potential. The sorption capacity of the soil is limited but increases when the soil contains a high proportion of mineral cations. Uptake by macrophytes is considered to be short-term and temporary as their decay reintroduces the nutrient back into the system. Dissolved phosphorus in the water column may be abiotically co-precipitated with metal cations such as calcium, iron and aluminum. Particulate phosphorus can be accreted into sediment through sedimentation and can also incorporate organic matter through soil building. Soil accretion occurs following the saturation of sorption and biotic uptake and while it occurs at a lower rate than the latter two processes, is more sustainable. Soil accretion accounts for the long-term and permanent P storage within the system. FWSW wetlands have a low areal efficiency for phosphorus removal compared with nitrogen and biological oxygen demand (BOD), indicating that P is often the controlling design factor (Kadlec & Wallace, 1996). Phosphorus concentrations decrease asymptotically with wetland area and is well-described by the k, P, C* model. While unable to account for pulse-driven runoff sequences, it can incorporate the addition of labile P within the wetland ecosystem. The first-order model was determined to be ineffective for small gravity-fed inflow CWs (Braskerud, 2002).

Wetlands that treat NPS runoff vary in the removal efficiency due to differences in season, precipitation, location, hydraulic and nutrient loading. For P, sedimentation is the primary long-term mechanism of removal (Kadlec & Wallace, 1996). The same wetland may act as a P sink and a P source depending on nutrient saturation in soil. A small constructed free water surface (FWS) wetland in Sweden that captured phosphorus from agricultural tile drainage water acted as a net P sink annually, with a specific mean retention of 69 kg TP, 17 kg DP and 30 t TSS ha^{-1} yr^{-1}, which corresponded to a relative retention of 36% TP, 9% DP and 36% TSS. This wetland was able to reduce P loss by 0.22 kg TP ha^{-1} yr^{-1} (Kynkäänniemi et al., 2013). In a study of four FWS constructed wetlands in Norway, Braskerud (2002) achieved TP reduction of 20-44% under high hydraulic loading conditions (0.7-1.8 m/d).

2.14. **Conclusion**

Conventional wastewater treatment technologies are costly, energy-intensive and impractical for nutrient management in agricultural settings. Alternative wastewater treatment technologies often have a lower capital and operational cost and require minimal maintenance. A pond-wetland system may provide a practical alternative to reduce nutrient concentrations from non-point sources, especially in rural locations where land is more available. Drainage water management is a feasible upgrade to existing tile drainage systems to reduce nutrient loss due to drainage. There is a possibility that the successful control of one form of the nutrient worsens the loss of another form of the same nutrient.

The objective of this literature review was to outline key research findings and present an overview of nutrient management, specifically phosphorus cycling and capture in agriculture using constructed pond-wetlands and CDS. Phosphorus concentrations are stochastic in nature and are dependent on many external variables including soil characteristics, precipitation events, drainage type and existing management practices. The integration of multiple practices for phosphorus loss attenuation is the most effective way to increase efficiency. This may include the addition of riparian buffers, drainage water management, cover crop, as well as pond-wetland systems. There are large gaps between the needs of effective watershed-scale P-management and actions and decisions at the individual farm-scale.

3. Materials and Methods

Study Location

This field study was conducted at the Agribert grain farm in Saint Isidore, Ontario, which is located in Eastern Ontario, Canada approximately 80 km east of Ottawa. The study site is within the Lower South Nation River sub-watershed of the South Nation River **(Figure 3.1A)**. The South Nation River is 175 km and spans from Brockville to Plantagenet, where it flows into the Ottawa River, a tributary of the St. Lawrence River. The Bercier pond-wetland system is a part of the Scotch Creek catchment area **(Figure 3.1B)** within the St-Lawrence drainage basin, which drains an area of approximately 3,810 km^2.

The grain farm is owed and operated by Marc Bercier to produce cash crops including corn, soybean and wheat which are rotated on a yearly basis. The farm contains an approximate 89 hectares of cultivated areas, of which an approximate 33 hectares, or approximately 37% is expected to flow into the pond-wetland. The fields are mainly flat in silty loams and are drained into tile drains. Controlled and free drainage structures were installed at the outlets of these tile drains to capture drainage waters. A drainage ditch installed at the outlet of the controlled drainage structures transported the drainage waters. An estimated additional 20 hectares of off-Site fields are drained east of Caledonia Road and captured within the drainage ditch. The drainage ditch captures drainage waters and overland flow to finally flow into a pond-wetland system **(Figure 3.1C)**.

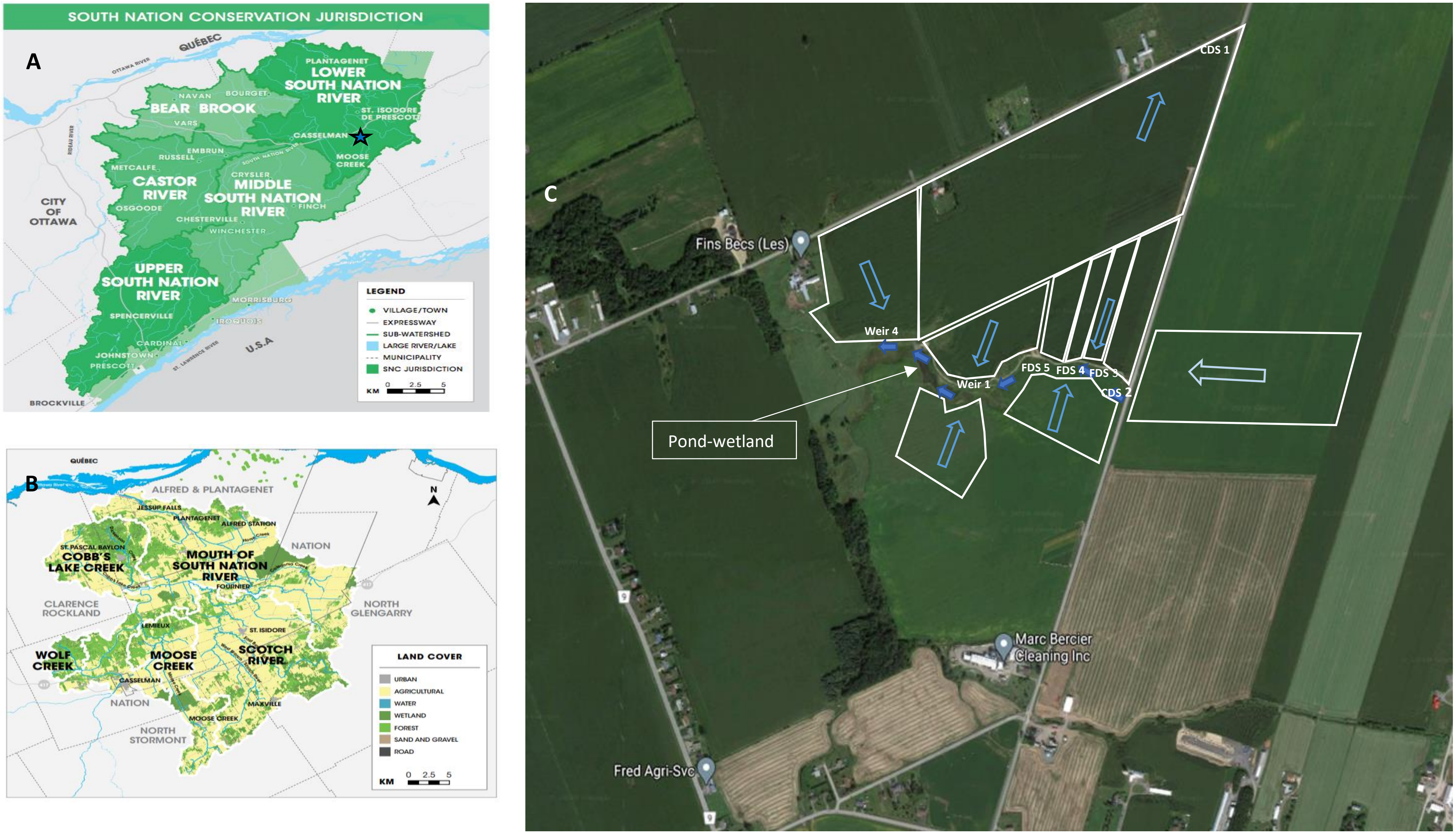

Figure 3.1: Location of Field Study: A) Location of Saint Isidore of Prescott within the Lower South Nation Conservation Authority (SNCA, 2014) B) Location of Saint Isidore within the Scotch River Catch Basin Area (SNCA, 2018) C) Aerial Image of the Bercier Farm and Schematic Diagram Indicating Drainage and Overland Flow Direction.

Field Site Drainage

The farm subsurface drainage systems consist of 4-inch (0.1 m) diameter tile drains that were installed at a spacing of 12 m and depth of 3 feet (0.91 m) below ground surface (bgs) to drain approximately 80% of the cropland. Drainage systems (DS) were installed at six tile outlets with triangular weirs to monitor the tile drain flow. Two controlled drainage structures (CDS) were implemented with stop logs to manage the water table and paired with four free drainage structures (FDS). Drainage waters from CDS 1 were received in a drainage ditch to the north of the property. Tile drainage outflow from the remaining north fields was received by CDS 2 and FDS 3-5 before release into a drainage ditch that traversed the field centrally and monitored at the pond-wetland inlet monitoring station equipped with a triangular weir, Weir 1. Tile drainage outflow from the south fields drained into FDS 6 and directly into the pond-wetland. In total, an estimated 54 hectares (ha) of tile drainage drain into the pond-wetland. A monitoring station, Weir 4, was equipped with a rectangular weir at the final outlet of the pond-wetland. The location and schematic of the drainage flow is shown below in **Figure 3.1**. The site was equipped with a weather station to collect meteorological data, water level loggers to measure flow over the weirs at the DS, the pond inlet and the pond outlet and automated ISCO water samplers to collect samples. In this study, composite samples were taken from the drainage structures (DS) and two pond monitoring locations (weirs) on a daily basis. Grab samples were taken from these locations on a bi-weekly basis.

The study is comprised of one year (2017) of data pertaining to a growing season (GS: June 14 to September 27) that was subdivided into a wet period (GS-W: June 14 – July 31) and a dry period (GS-D: August 1 – September 27), followed by a non-growing season (NGS: September

28 – November 14) on a farmer-operated field located on a seed farm in Saint Isidore, Ontario, Canada. The stop logs were removed from the controlled drainage structures on September 27, 2017, marking the distinction between the GS and the NGS. The division of the GS into wet and dry periods allows for the comparison of the flow response of the CDS in late summer to that of FDS and also compare the effect of controlling the water table at the same drainage structures between the GS and the NGS, especially with respect to nutrient and solids transport. The study period for the mass flux begins on June 14, 2017 due to a two-week delay in the set-up of water level loggers.

The 30-year normal annual precipitation (1981-2010) was 920 mm, and the average daily temperature was 6.6°C (Environment and Climate Change Canada, 2020). A corn-soybean-wheat rotation was in place for the cultivation of cash crops. Soybean was grown in the north fields (DS 1-5); corn was grown on the south fields (FDS 6). Soybean was cultivated with minimum tillage and no fertilizer application. Soybean was harvested between September 29 and 30, 2017. Fertilizer was applied at 15.47 kg N ha^{-1} as ammonium nitrate, 75.79 kg P_2O_5 ha^{-1} and 63.42 kg K_2O ha^{-1} on the north fields on September 29, 2017 in preparation for the planting of a cover crop, Princeton winter wheat, on September 30, 2017. Pre-existing tile drains (0.1-m diameter) were reportedly at depths approximately 1 m bgs at 12-m intervals (Bercier, 2016).

3.1. **Controlled Drainage**

Five drainage structures (the mean of CDS 1 and CDS 2 and the mean of FDS 3, FDS 4 and FDS 5) were paired together to compare the effect of drainage water management on drainage outflow, nutrient concentrations and flux. Soybean was grown on a silty loam with minimum tillage in the fields draining into DS 1-5 and therefore, the soil type and cropping practices were not varied for DS 1-5. FDS 6 was unpaired and monitored tile outflow from a corn field (south field). Tile depth, spacing and pipe diameter were reportedly common across the study area. Pre-existing tile drains (0.1-m diameter) were reported at depths approximately 1 m bgs at 12-m intervals (Bercier, 2016). The north field was reportedly divided into five plots with isolated tile drainage systems that drained out of five outlet points into drainage ditches. The existing tile drainage systems were retrofitted with water level control structures at the drainage outlets to monitor tile flow. Individual plot areas varied between 2.85 to 7.45 ha (**Table 3.1)**.

Table 3.1: Crop and Drainage Plot Area by Drainage Structure (DS) and Pond (Inlet/ Weir 1 and Outlet/ Weir 4)

Drainage structures were controlled (CDS) at CDS 1 and CDS 2, and free (FDS) at FDS 3,4 and 5. A weir (Weir 1) was installed at the pond-wetland inlet and at the outlet (Weir 4).

Description	Crop	Location	Areas (ha)[1]	Breakdown of Drainage Area
Controlled Drainage Structures	Soybean	CDS 1	7.45	Same as overall area
		CDS 2	4.00	
Free Drainage Structures		FDS 3	4.75	
		FDS 4	6.50	
		FDS 5	3.35	
	Corn	FDS 6	2.85	
Pond Inlet and Outlet	All	Weir 1	42.98	The sum of DS areas 2-5: 18.6 ha Additional area of farmland east of Caledonia Road: 20.23 ha Area south of central drainage ditch: 4.05 ha
		Weir 4	53.24	Weir 1: 42.98 ha Additional area of farmland draining into Weir 4 from north: 7.5 ha FDS 6: 2.85 ha

Notes: [1] Drainage areas were estimated from original drainage maps provided by Marc Bercier (c. 2018).

The drainage map in **Figure 3.2** shows the direction and allocation of tile drainage per drainage structure. Field 27 drained into CDS 1-2 and FDS 3-5; and field 23401 drained into FDS 6. Field 275 and 23401 contributed to Weir 1 flow. Fields 23401, 400 and 402 contributed to drainage at Weir 4.

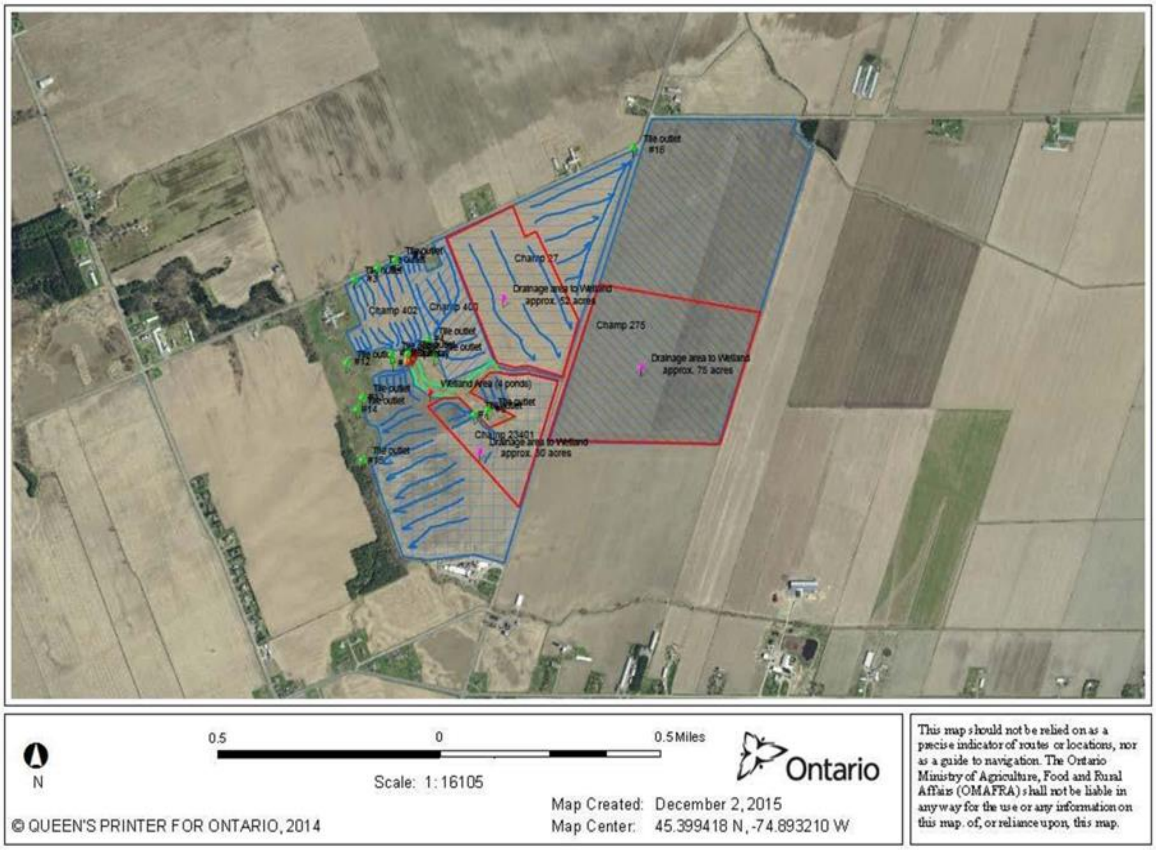

Figure 3.2: Drainage Systems Impacting the Bercier Pond-Wetland, Saint Isidore, ON.
This figure was used with permission from the Ontario Ministry of Agriculture and Rural Affairs.

The height of all six drainage structures was measured to be 2.42 m below the top of the drainage structure. Stop logs were set at 0.66 m and 0.76 m above the drainage structure floor (m adsf) at CDS 1 and CDS 2 respectively to control the water table above its native level. Weir structures were installed at 0.22 m adsf at FDS 4 and 0.05 m adsf at FDS 3, 5 and 6. A partial stop log was installed at FDS 4 to prevent stream backflow from the central drainage ditch into FDS 4. All DS were fitted with a triangular V-notch weir (approximate angle of 22.5°) at the top log. The dimensions of all weirs installed at the drainage structures and pond monitoring locations are shown below in **Table 3.2.**

Table 3.2: Weir Dimensions, Type and Angle by Monitoring Location

Location	Height to Base of Weir in GS[1] (m adsf)	Height to Top of Weir in GS[1] (m adsf)	Weir Type	Weir Angle (°)	Height to Top of Rectangular Weir in NGS (m)	Weir Width (m)	CDS Width (m)
CDS 1	0.658	0.790			0.178	0.314	0.335
CDS 2	0.763	0.918			0.306		
FDS 3	0.047	0.179	Triangular V-notch	22.5			
FDS 4	0.226	0.356			-	0.162	0.197
FDS 5	0.047	0.179					
FDS 6	0.047	0.179					
Weir 1	-	-	Triangular V-notch	90	-	-	-
Weir 4	-	-	Rectangular	180	10 L 12 R	59.4 L 91.8 R	

Notes:
GS — Growing Season
NGS — Non-growing Season
m adsf — metres above drainage structure floor
[1] — Stop logs were removed prior to the non-growing season at monitoring locations, CDS 1 and CDS 2.

Drainage was not controlled in the non-growing season as stop logs were removed on September 27, 2017. Other local studies have demonstrated that the employment of controlled drainage during the non-growing season (corresponding to winter months) have correlated with a shorter growing season as a result of reduced drainage, soil frost, ice lensing, enhanced surface runoff and surface erosion (Sunohara et al., 2016) in Southeastern Ontario. The effect of winter conditions on drainage was not monitored after November 2, 2017 during this study.

Bercier Pond-Wetland System Design and Characteristics

The Bercier pond-wetland system (45°23’N, 74°54'W) is a constructed pond-wetland system located on the Marc Bercier seed farm in Saint Isidore, ON. It is a small, constructed pond-wetland with a surface area of approximately 4,000 m^2 (0.99 acres) that was constructed by Ducks Unlimited and captures flow from 54 ha of tile drainage. Aquatic vegetation was introduced naturally or replanted after construction. The pond-wetland system was divided into five sub-ponds so as to coordinate sampling and characterize the nutrients consistently. A gravel spillway was built at the Pond 4 outlet to control base flow out of the pond and to allow excess wetland to discharge following large precipitation events. A monitoring station was located at the inlet of the pond (Weir 1) and at the outlet of the pond (Weir 4) as shown in **Figure 3.3** below.

Figure 3.3: Left: Pond Inlet (Weir 1) and Right: Pond Outlet (Weir 4).
These photographs were used with permission from Olatian Edu (2017 Water Budget Balance for Wetland in Bercier Farm).

The topography is generally flat (slopes <1%) and drainage ditches are present to the north, east and west boundaries of the property. The overburden soil is expected to be silty sand to silty clay from glacially-derived till of the Russell and Prescott Sand Plains and the bedrock is expected to be Carlsbad formation consisting of interbedded dark grey shale in fossiliferous calcareous siltstone and silty bioclastic limestone from the Ordovician age (Armstrong & Dodge, 2007). The soil in the pond-wetland system is predominantly clay. The surrounding soil is classified as hydrologic soil type group D, which has a high potential for runoff and slow infiltration when thoroughly wetted (AGR-CAN, 1998).

3.2. **Flow Measurement**

3.2.1. Automated Measurements of Water Height

A barometric (Hobo Onset U20) level logger was installed at all sampling locations to calculate continuous head measurements at the weir every 15 minutes. The loggers were placed at the base of each DS and affixed to a pole upstream of each weir. An additional logger was pole-mounted at Weir 1 to record atmospheric pressure and temperature. The difference in pressure recorded by the water logger and the atmospheric logger was used to calculate water head at the weirs. The water height per 15-minute interval (m^3 s^{-1}) was averaged daily and converted to average water height per day (m^3 d^{-1}) and normalized by the drainage area of each monitoring location.

At the monitoring locations Weirs 1 and 4, water head was defined as flow over the base of the weir. Similarly, the base of the DS was used as the reference elevation to calculate the water table level in the field. A 22.5° V-notch weir was installed at DS 1-6. Flow through the weir was calculated using the triangular weir equation and flow above the weir was calculated using the equation for flow over a suppressed rectangular weir. A 90° V-notch weir was installed at Weir 1 and 180° rectangular weir was installed at Weir 4. Manual measurements of height of water above each weir at the pond inlet and outlet were performed during each field visit approximately once every 2- 3 weeks using a ruler during the 2017 GS.

3.2.2. Flow Calculation

Flow calculation was conducted depending on the height of water over the weir. If the water height was below the base of the V-notch weir, then Equation 1 was used to calculate flow.

Equation 1: $Q = 0$

If the water height was higher than base of the V-notch weir, but lower than or equal to the total height of the V-notch weir, then Equation 2 for the calculation of flow through a triangular weir was used (USDI, 1974).

Equation 2: $Q = \frac{8}{15} C_e \sqrt{2g} \tan\left(\frac{\theta}{2}\right) h_e^{\frac{5}{2}}$

where C_e is the discharge constant, g is the gravitational constant, θ is the weir angle in radians and h_e is the effective height. The calculations for the above constants and values used for each monitoring location are shown in the **Appendix**. The equation for the calculation of flow over a contracted rectangular weir at Weirs 1 and 4, where weir length is less than channel width, Equation 3, was used for the calculation of flow over a rectangular weir was used.

Equation 3: $Q = \frac{2}{3} C_D \sqrt{2g} B H^{\frac{3}{2}} + Q_a$

When water flowed over the top of a DS weir, the weir was assumed to behave as a suppressed rectangular weir[c] and therefore, Equation 4, for the calculation of flow through a rectangular weir was used.

Equation 4: $Q = 1.84 B H^{\frac{3}{2}} + Q_a$

[c] A suppressed rectangular weir is a weir where the weir length is equal to the channel length and in which end contractions are suppressed or not present.

The calculations for the above constants and values used for each monitoring location are shown in **Appendix**. The calculated flow was normalized by the drainage area per sampling location. Data gaps were estimated using correlations between flow at various sampling locations, with the exception of a data gap in the NGS at FDS 6 that was not estimated due to a technical malfunction.

The flow at Weir 4 was calculated from the difference between the sum of the average daily flow at FDS 6, Weir 1, and the precipitation over the pond surface area and the net evaporation of the pond. FDS 6 flow has not been presented in this thesis.

Evaporation

Evaporation of the pond was calculated using the Penman formula for the evaporation from a lake (Linacre, 1977; Statcan, 2017):

$$E_o = \frac{\frac{700T_m}{100-A}+15(T-T_d)}{(80-T)} \text{ (mm d}^{-1}\text{)}$$

Where E_o, evaporation rate, was calculated from T_m = T+0.006h, h is the elevation (meters), T is the mean temperature, A is the latitude (degrees), and T_d is the mean dew point where $(T-T_d)=0.0023h+0.37T+0.63R+0.35R_{ann}-10.9°C$.

Soil Samples

Soil samples were collected from plots draining into drainage structures (DS) prior to planting and post-harvest for N and P analysis at depths of 6 inches and 12 inches bgs.

Automated Monitoring

An automated water sampler (ISCO Model 6700 and Model 3700, Teledyne Isco) was installed at each of the 11 sites: CDS 1-6, Weirs 1-4 and the Spillway. Pump tubing was installed at the height of the V-notch weir and configured to sample in flow conditions. A subsample of 50 mL was taken every 6 hours in order to collect a daily composite sample of 200 mL consisting of four subsamples. The samples were contained in 250 mL plastic bottles and stored at the site for a period of two to three weeks before transportation to the laboratory for analysis in coolers packed with ice. Samples were refrigerated before laboratory analysis.

Grab Sampling

Grab samples were taken from the weirs directly and using a handheld sampler from drainage structures during field visits. Grab samples were analyzed on-site for dissolved oxygen, pH, electrical conductivity and temperature.

3.3. **Analytical Methods**

All grab samples were analyzed for turbidity, total suspended solids (TSS), total phosphorus (TP), total chemical oxygen demand (TCOD), total nitrogen (TN), soluble reactive phosphorus (SRP), ammonia (NH_4^+-N) and nitrate (NO_3^--N). Composite DS samples were analyzed for turbidity, TSS, NH_4^+-N, NO_3^--N and SRP. Composite samples collected from the pond monitoring locations were analyzed for turbidity, TSS, TP, NH_4^+-N, NO_3^--N and SRP. The analyses as conducted per site are clarified in **Table 3.3** below.

Table 3.3: Sample Analysis Plan Organized by Monitoring Location and Classification

Analysis	Grab Samples	Composite Samples from Pond Monitoring Locations	Composite Samples from CDS
Turbidity	X	X	X
TSS	X	X	X
TP	X	X	
TN	X		
TCOD	X	X	
SRP	X	X	X
Ammonia	X	X	X
Nitrate	X	X	X

3.3.1. Laboratory Analyses

The determination of TP, NH_4^+-N, NO_3^--N and SRP required the use of a cuvette that was rinsed with distilled water in between samples for each of the analyses. The cuvette was rinsed with the sample as a pre-condition for the ammonia and nitrate tests. All cuvettes and HACH vials were wiped with a delicate task wipe before placement in the HACH DR 6000 spectrophotometer. A standard curve for the determination of concentration is provided in **Appendix** for all parameters.

Turbidity

The turbidity of each sample was measured using a turbidimeter (HACH, Model 2100 AN, Loveland, CO) with a repeatability of ±1% of 0.01 NTU.

Total Suspended Solids

Total suspended solids (TSS) were measured using USEPA standard methods (USEPA, 1979). A 1.5-µm filter was weighed in a weighing pan before filtration of 100 mL of each sample, filtration, heating and desiccation to determine the mass of the TSS. A filtration apparatus, powered by a Marathon Electric 110-115V ¼ HP vacuum pump (ThermoFisher Scientific, Waltham, MA), was used to filter the sample. This filtrate was subsequently used to quantify the concentration of soluble NH_4^+-N, NO_3^--N and SRP.

Total Chemical Oxygen Demand and Total Nitrogen

Total chemical oxygen demand (TCOD) and Total Nitrogen (TN) were measured using HACH "Test N Tube^{TM} (TNT) Vials" 8000 LR (3-150 mg L^{-1})[d] and 10071 LR (0.5-25.0 mg N L^{-1}) respectively to determine the TCOD and TN concentration of undiluted, unfiltered samples. The vials were prepared with 2 mL of sample and placed in a pre-heated digital reactor block (HACH Company, Model DRB200, Loveland, CO), cooled and analyzed colorimetrically using a UV-VIS spectrophotometer (HACH Company, Model DR6000, Loveland, CO) stored program 430 COD LR and 350 N Total LR TNT respectively. Each set of thirteen samples was digested and analyzed with a blank containing distilled water and a standard of known concentration.

Total Phosphorus

Total Phosphorus (TP) concentration was determined using a modified HACH TNT Method 8190 (LR 0.06-3.50 mg PO_4^{3-} L^{-1}). 5 mL of each unfiltered sample and 0.1 g of the Potassium Persulfate Powder Pillow for Phosphonate was added to a HACH Total Phosphorus TNT Vial and inverted 10 times before placing in a pre-heated HACH DRB200 digester at 150°C for 30 minutes. The vials were removed shortly after and cooled to room temperature. 2 mL of 1.54 NaOH standard solution was added to each vial. The sample was transferred to a 50-mm cuvette. The cuvette containing the sample was zeroed in a HACH DR6000 spectrophotometer at the optical wavelength of 880 nm. The sample was transferred back to the HACH TNT Phosphorus LR vial and 0.32 g of PhosVer3 Powder Pillow was added to the vial. The vial was

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[d] This method is adapted from USEPA approved standard method for wastewater analysis of COD (Standard Method 5220 D).

shaken for 20 seconds and returned back to the cuvette. The sample was colorimetrically read after 2 minutes.

Soluble Reactive Phosphate

Soluble Reactive Phosphate (SRP) concentration was determined using a modified HACH TNT Vial Method 8048 (LR 0.06-5.00 mg L^{-1} PO_4^{3-}). 5 mL of filtered sample were added to a HACH TNT Reactive Phosphorus Vial. The sample was transferred to a 50-mm cuvette. The samples were analyzed colorimetrically using a UV-VIS spectrophotometer (HACH Company, Model DR6000, Loveland, CO) at an optical wavelength of 880 nm. The sample was transferred to the HACH TNT Phosphorus LR vial and 0.32 g of PhosVer3 Powder Pillow were added to the vial. The vial was shaken for 20 seconds and the sample was transferred to the 50-mm cuvette. The sample was colorimetrically read after 2 minutes.

Soluble Ammonium/ Ammonia and Nitrate

The concentration of soluble ammonium and nitrate were measured according to Standard Methods (“4500-NH_3 NITROGEN (AMMONIA),” 2018; “4500-NO3 NITROGEN (NITRATE),” 2018). The samples were analyzed colorimetrically using a UV-VIS spectrophotometer (HACH Company, Model DR6000, Loveland, CO).

3.4. **Calculation of Mass Flux and Mass Removal Efficiency of Pond**

Mass Flux

Daily flux was calculated by multiplying the average daily flow (Q_i) with the daily parameter concentration (C_i) at each sampling location, which was subsequently normalized by the drainage area (A).

$$\textbf{Equation 4}: Z_i = C_i \times Q_i \times A^{-1}$$

Percent Change (%)

The percentage change was calculated using Equation 5.

$$\textbf{Equation 5}: 100 \times \frac{(C_i \times Q_i) - (C_o \times Q_o)}{C_i \times Q_i}$$

where C_i is the average pond inflow concentration or the concentration at the FDS (mgL^{-1}), Q_i is the average pond inflow or the daily flow at the FDS (m^3d^{-1}), C_o is the average pond outflow concentration or the concentration at the CDS (mgL^{-1}), Q_o is the average pond outflow or the daily flow at the CDS (m^3d^{-1}) during the study period.

3.5. **Statistical Analyses**

The data for concentration and mass loadings were analyzed using ANOVA to determine the effect of the GS on controlled drainage, as well as the effect of controlled drainage on nutrient concentration and mass attenuation. A paired T-test for two statistical means (μ) was used to determine statistical difference between data sets if $p < 0.05$. The data set was analyzed for outliers where an outlier was defined as a variable $x_i = \mu + 3s$[e]. A correlational analysis was performed to determine the presence of a positive or negative correlation between analytes per sample set. The strength of a correlation was defined such that a weak correlation was $0.1<R<0.30$, a moderate correlation was $0.30 \leq R<0.70$ and a strong correlation was $R \geq 0.70$. The range of the moderate correlation is defined as such to accommodate environmental variability. Correlations where $0.10 \leq R$ were not considered. Analytes were compared within

[e] S is defined as one standard deviation from the mean.

data sets; i.e., analytes in the grab data set were correlated with each other and analytes in the composite data set were correlated with each other.

3.6. **Evapotranspiration Calculation**

Evapotranspiration was calculated using the soil water balance method (OMAFRA, 2008). The used crop factors are shown in the **Appendix**.

4. Results

4.1. Meteorological Conditions

Ottawa received a cumulative precipitation of 1349 mm in 2017, which exceeded the 30-year normal average of 920 mm between 1981-2010 (Environment and Climate Change Canada, 2020) by 420 mm **(Figure 4.1)**. Winter 2017-2018 (average 4.7°C) was colder than the 30-year normal (average 5.0°C) with snow cover peaking at 77 cm during a two-day snowfall event between February 17 and 18, 2017. The mean snow cover was 25 cm for the year and the amount of snow that accumulated in January and February 2017 was approximately between 1.5 and 1.7 times above the 30-year normal implying a greater volume of snowmelt runoff potential than average. A mean 43 cm of snow accumulated on the ground between January 1, 2017 to February 24, 2017; and less than 20 cm of snow had accumulated on the ground after February 24, 2017. The study period (June 14-November 14, 2017) was subdivided into the wet period of the growing season (GS-W: June 14-July 31, 2017), the dry period[f] of the growing season (GS-D: August 1-September 27, 2017) and the non-growing season (NGS: September 28-November 14, 2017).

[f] The dry period of the growing season was defined due to the observed decrease in mean daily drainage flow at both CDS 1 and 2 between August and the removal of the stop logs on September 27, 2017.

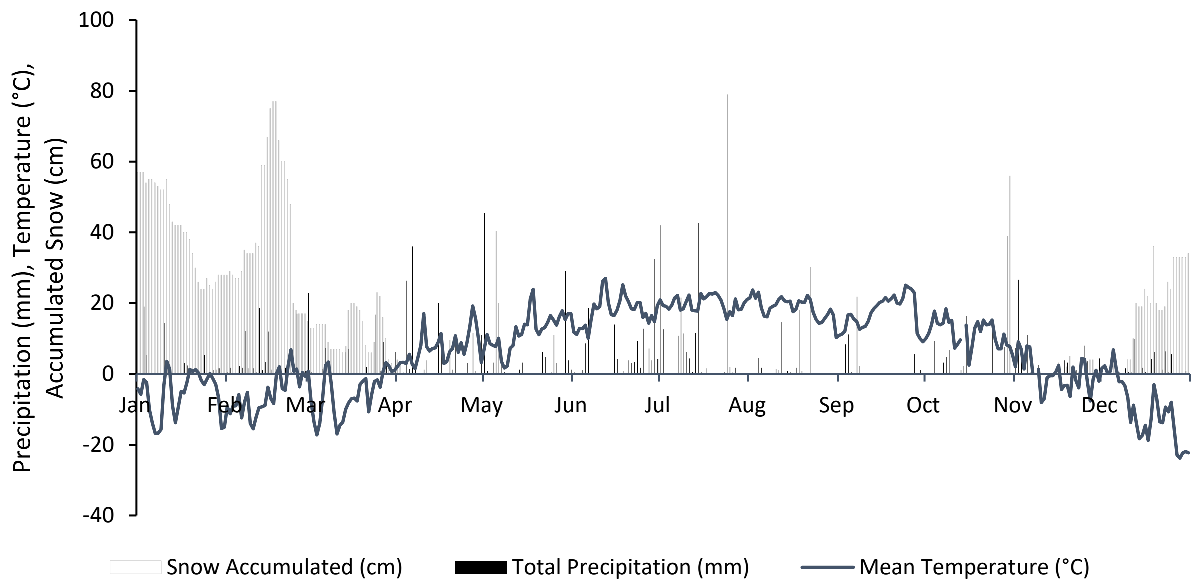


Figure 4.1: Precipitation (mm), Air Temperature (°C) and Accumulated Snow (cm) between January-December 2017 from the Meteorological Climate Station, Ottawa RCS (Environment and Climate Change Canada, 2020)

During the study period, there were 64 rainfall events averaging 9±12 mm, 7 rainfall events greater than one standard deviation from the mean (34±16 mm) and 2 rainfall events greater than two standard deviations from the mean (56±16 mm). There were 3 rainfall events greater than 21 mm during the GS-W, 3 during the GS-D and 1 during the NGS. The peak precipitation event on July 24, 2017 was 79 mm, which was a record-breaking event for that day preceded only by an extreme rainfall event that occurred on July 24, 1899 of 74 mm (Environment and Climate Change Canada, 2020). Of the 142 days in the study period, 45% were wet. On average according to the 30-year normal data, this period received a cumulative rainfall average of 522 mm, however the 2017 study period received an additional 228 mm of precipitation above the seasonal average for a total of 750 mm **(Figure 4.2).**

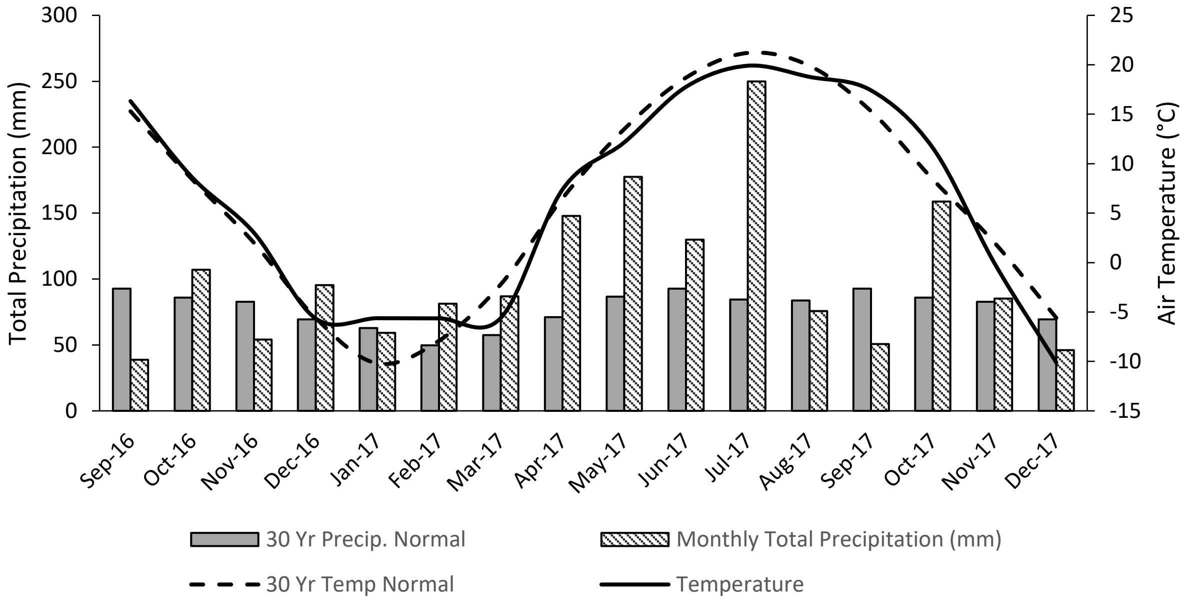


Figure 4.2: Monthly Precipitation (mm) and Average Temperature (°C) in Ottawa Compared to the 30-year Normal (1981-2010) (Environment and Climate Change Canada, 2020)

The average monthly temperature was lower than the 30-year normal between June-August 2016 and higher between September-October 2016. Compared to the 30-year normal, the average precipitation was greater during June, July, October, and November and lower in August and September. The farm received an additional 165 mm and 73 mm of rainfall in July and October 2017, respectively, compared to the 30-year normal.

A weather station was established at the Bercier farm and the temperature, precipitation, and atmospheric pressure data were compared against the Ottawa RCS weather data. The correlation between the Bercier and Ottawa RCS weather data is strong ranging from an R^2 value of 0.72 for rainfall, to 0.83 for atmospheric pressure, 0.97 for minimum temperature and 0.99 for average and maximum temperatures. The atmospheric pressure data collected at the farm that differed by greater than 0.5 kPa were replaced by the Ottawa RCS data in subsequent calculations. The comparison of Bercier data to Ottawa RCS data is presented in the **Appendix.**

4.1.1. Seasonal Variation of St. Isidore Weather Data

The average daily precipitation was 4±9 mm d^{-1} during the study period. The average precipitation (rain) was 4±9 mm d^{-1} during the GS (defined as June 14-September 27, 2017), and 3±8 mm d^{-1} during the NGS (September 28 – November 14, 2017). The GS was further divided into the wet period (June 14 - July 31, 2017) receiving an average precipitation of 6±12 mm d^{-1} and the dry season (August 1 – September 27) receiving average precipitation of 3±7 mm d^{-1}, as shown in the **Table 4.1** below. High precipitation events were defined as one standard deviation higher than the mean. The count of peak precipitation events as defined by one, two, or three standard deviations is outlined in the table below.

Table 4.1: Mean Precipitation (St. Isidore Weather Station) Criteria and Count of High Precipitation Events

Study Period	Dates	Average (μ) ± Standard Deviation (σ)	μ+1σ		μ+2σ		μ+3σ	
			P (mm d^{-1})	Count	P (mm d^{-1})	Count	P (mm d^{-1})	Count
Complete Season	June 14-November 2	9±12	21	7	33	2	45	1

The relationship of these peak events will be analyzed against flow in the subsequent section. In conclusion, the year 2017 received greater than average precipitation, while in general the temperature followed similar patterns to the 30-year normal.

4.2. **Flow**

The mean daily precipitation[g] during the study period was 9±12 mm d^{-1} while the mean flow[h] at the drainage structures (DS) varied between 0.38±0.63 mm d^{-1} to 0.54±0.38 mm d^{-1} (**Figure 4.3)**. Flow data across all DS follow similar trends with peaks corresponding to the same precipitation events. The mean daily flow during the study period was 0.75±1.46 mm d^{-1} at Weir 1 and 0.62±1.23 mm d^{-1} at Weir 4. The mean flow at the weirs was greater than that of the drainage structures, possibly due to the reception of overland and subsurface flow from a larger surface area. The flow data is highly variable across all drainage structures, as it relates to precipitation events and this is demonstrated below in **Figure 4.3**.

[g] Mean values were calculated for precipitation have been calculated using values greater than zero only.
[h] Mean values were calculated for flow have been calculated using values greater than zero only.

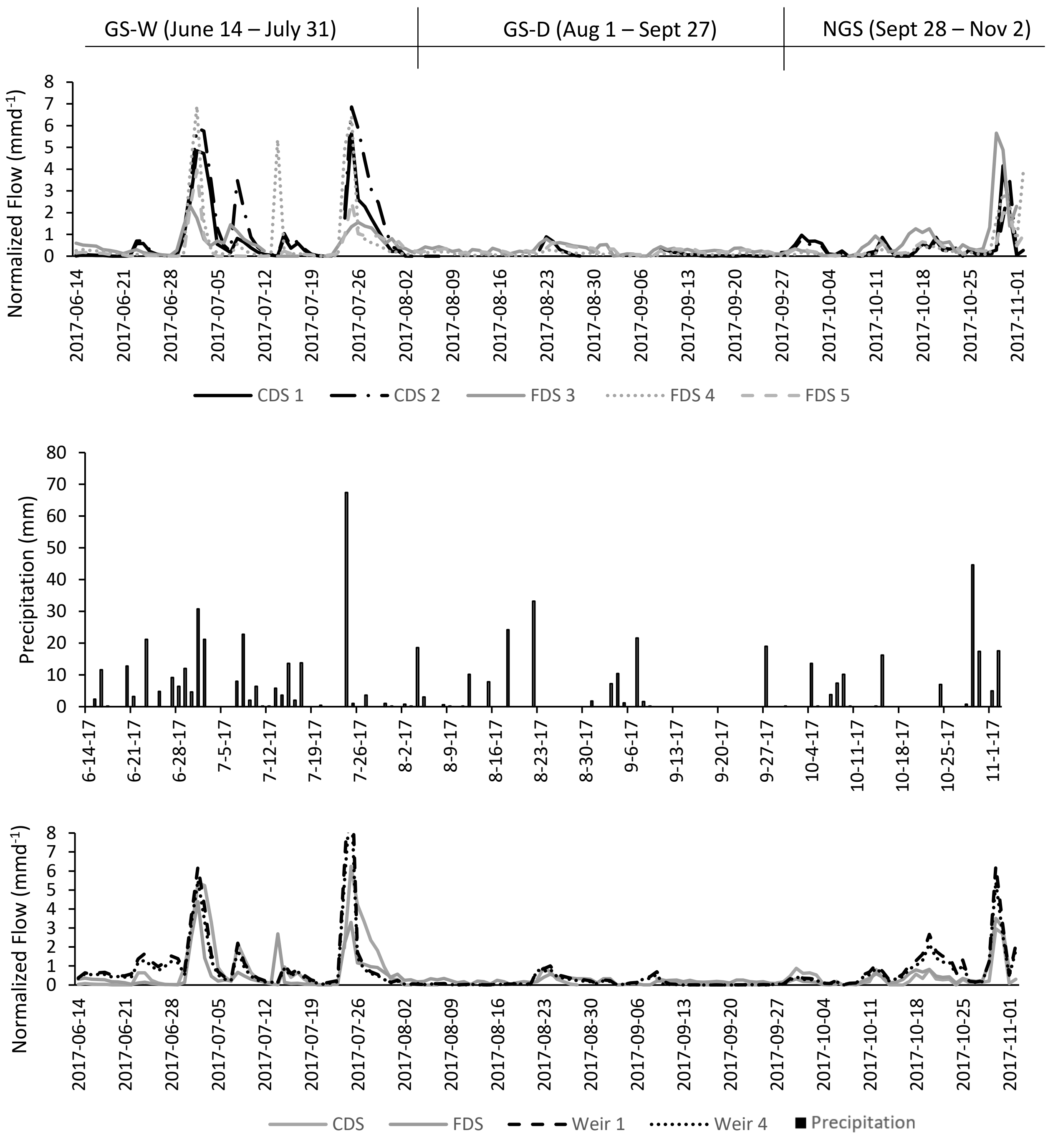


Figure 4.3: Top) Precipitation during the Study Period (June 14 – November 14, 2017); Middle) Normalized Flow (mm d^{-1}) for Controlled Drainage Structures (CDS) 1, 2 and Free Drainage Structures (FDS) 3, 4, 5 during the Study Period; Bottom) Mean Normalized Flow (mm d^{-1}) for the CDS and FDS during the Study Period

Note: CDS and FDS values were calculated from the mean CDS 1 flow and CDS 2 flow and FDS 3, 4 and 5 flows, respectively.

From **Figure 4.3**, it is evident that there is little to no flow response to precipitation events in the GS-D compared with GS-W and the NGS. The variance in the flow data is shown below in the following box and whisker plot (**Figure 4.4**).

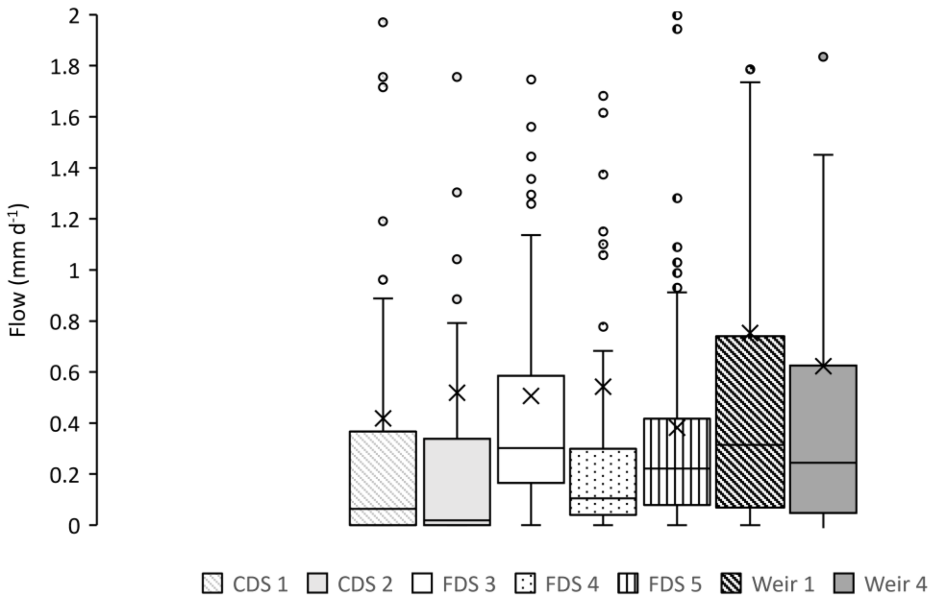


Figure 4.4: Box and Whisker Plot of Normalized Flow for Complete Season
Normalized flow at the drainage structures and pond. Drainage structures were controlled (CDS) at CDS 1 and CDS 2, and free (FDS) at FDS 3,4 and 5. A weir (Weir 1) was installed at the pond-wetland inlet and at the outlet (Weir 4). The mean flow values are shown by an X per location. The median is represented by the horizontal line in the box.

The box and whiskers plots demonstrate the skewing of the mean flow by high flow events as median values are considerably lower than the mean values at each individual DS and weir. During the complete season, the median flow for the CDS ranged from 0.02-0.06 mm d^{-1} while the median flow for the FDS ranged from 0.11-0.31 mm d^{-1}. In comparison to the FDS, the CDS reduced cumulative normalized flow by 67% only during the dry period of the growing season. The water level was controlled at 0.61 m at CDS 1 and at 0.74 m at CDS 2. A study by Lalonde et al. in Quebec, Canada (1996) showed that increasing the riser from 0.25 m to 0.50 m above the water table increased cumulative normalized flow reductions from 58.7% to 65.3% in 1992 and 41% to 95% in 1993. The findings of this present study demonstrate that controlling the water table at approximately 0.67 m above the outlet structure at the free drains resulted in a cumulative normalized flow output reduction of 67% only during the GS-D, which are comparable to those of Lalonde et al. (1996). The CDS produced 77% more cumulative outflow than the FDS during the GS-W and 25% less outflow than the FDS during the NGS.

4.2.1. Seasonal Variation in Average Flow

In order to better understand the data presented above, a consideration of mean flow values was taken over the complete study period and subdivided into GS and NGS. **Table 4.2** presents the average values and standard deviation for flow per location.

Table 4.2: Cumulative, Mean and Standard Deviation of Daily Flow at Drainage Structures and Weirs by Season

Drainage structures were controlled (CDS) at CDS 1 and CDS 2, and free (FDS) at FDS 3,4 and 5. A weir (Weir 1) was installed at the pond-wetland inlet and at the outlet (Weir 4).

	Complete Season June 14-Nov 14	Growing Season		Non-growing Season Sept 28-Nov 14
		Wet period June 14-July 31	Dry period Aug 1- Sept 27	
Precipitation (mm)	9.4±11.9	9.8±13.4	8.5±10.1	9.6±11.7
Monitoring Location	Mean Daily Flow (mm d^{-1})			
CDS 1	0.42±0.92	0.81±1.35	0.07±0.16	0.46±0.74
CDS 2	0.52±1.24	1.25±1.85	0.01±0.05	0.37±0.63
FDS 3	0.51±0.73	0.54±0.56	0.29±0.18	0.80±1.21
FDS 4	0.54±1.59	0.90±1.69	0.11±0.11	0.75±2.40
FDS 5	0.38±0.63	0.54±0.97	0.24±0.14	0.40±0.45
Weir 1	0.75±1.46	1.33±2.11	0.15±0.23	0.95±1.20
Weir 4	0.62±1.23	1.11±1.77	0.12±0.20	0.79±1.02
CDS	0.60±1.15	1.05±1.59	0.13±0.21	0.41±0.64
FDS	0.42±0.70	0.58±0.93	0.21±0.13	0.56±0.81
	Cumulative Daily Flow (mm)			
CDS	68.31	49.49	3.97	14.85
FDS	59.69	27.93	12.04	19.72

Drainage at CDS 1 and CDS 2 was controlled by implementing stop logs between June 14 and September 27, 2017. On September 27, 2017, the stop logs were removed at CDS 1 and 2, converting these structures into FDS. The study period was divided into the GS, during which the stop logs were employed and the NGS, during which the stop logs were removed. A secondary distinction was made within the GS to separate the period of inactivity and activity of the stop logs as noticed in the cumulative normalized flow. Drainage structures, CDS 1 and 2, display similar patterns of flow attenuation during the GS-D.

Over the complete season, the mean flow at CDS 1 and CDS 2 was lower or equal to most other drainage structures. Precipitation was highest during the wet period of the GS and this was generally reflected in the flow at the drainage structures and weirs. During the GS-W, the average flow at CDS 1 and 2 increased compared to the FDS. This behaviour of a lack of flow attenuation at CDS during wet periods has been described by other authors. Evans et al. (1993) reported that controlling the water table had little impact or increased peak flow during wet periods. The most important difference between the CDS and FDS was observed during the GS-D, where there is little to no flow at the CDS in the GS-D (**Table 4.2**).

The distinction between the CDS and FDS is demarcated by both the mean and cumulative normalized flows during GS-D with mean flows of 0.13±0.21 and 0.21±0.13 mm d^{-1} and cumulative normalized flows of 3.97 and 12.04 mm at the CDS and FDS, respectively. The decrease in tile drainage discharge in the summer has been described previously by Hirt et al. (2011) who attributed this phenomenon to the increased rate of evapotranspiration in the summer. Macrae et al. (2007) studied the contribution of tile discharge over one year and noted that tile discharge decreases substantially between the summer months of July-August. Since the mean precipitation was similar between the GS-D (8.53±10.06 mm d^{-1}) and NGS (9.63±11.67 mm d^{-1}), the increase in median flow at CDS 1 and 2 in the GS-D (0.00±0.00 mm d^{-1}) and the NGS (0.20±0.08 mm d^{-1}) can be attributed to the removal of the stop logs and reduced evapotranspiration during the GS-D.

4.2.2. Statistical Analysis of Flow with Considerations of Seasonality

Correlational Analysis Between Mean Flow at Drainage Structures

In order to determine the statistical similarity between the drainage structures, a correlational analysis was performed. The flow at the CDS were strongly correlated with each other during the complete season (R=0.90). Flow was moderately correlated between the FDS (0.57≤R≤0.73). Moderate correlation was observed between the flow at the FDS and CDS 2 (0.34≤R≤0.66) as well as CDS 1 (0.58≤R≤0.79). Mean flow was only statistically different during the GS-D between the drainage structures (ANOVA p<0.05). During the GS-D, there was a statistical difference between the mean flow at all DS with the exception of CDS 1 vs FDS 4 and FDS 3 vs FDS 5. The plot size of CDS 1 was larger than the other plots considered and was expected to be statistically different from all other, except CDS 2, due to the controlling of drainage. While the significant difference between CDS 1 versus CDS 2, FDS 3 and 5 was expected, statistical similarity between FDS 4 and CDS 1 was unexpected. The flow at FDS 3 was expected to be similar to FDS 5 as they are both free drains and drain plots of similar size. During the NGS, the stop logs were removed at CDS 1 and 2. The GS-D received 162 mm of rain compared to the NGS which received 144 mm of rain. A comparison of the cumulative normalized flow at CDS 1 and CDS 2 across these seasons demonstrates the effect of installing a stop log to control drainage. In comparison to the cumulative normalized flow during the GS-D, there was a 76% increase in total outflow at CDS 1 and 97% increase at CDS 2 during the NGS. The difference in total outflow is due to a combination of the effect of the stop logs as well as different evapotranspiration conditions despite similar precipitation.

4.2.3. Analysis of Flow at Controlled Drainage Structures After the Removal of Stop Logs

The stop logs were removed at CDS 1 and 2 on September 27, 2017, effectively converting the CDS to FDS and the flow response during this event is shown below. At the CDS, an increase in flow and nutrient flush was expected following the release of the stop logs. FDS 3-5 flow is shown for comparison. At the time of stop log release (14:15) on September 27, 2017, the flow increased at CDS 1 to 7.53 mm d^{-1} and to 2.1 mm d^{-1} at CDS 2. The flow subsided to its median value of 0 mm d^{-1} at CDS 2 within one hour at 15:30 and by 15:45 at CDS 1. The next precipitation event that caused a flow response was at 14:30 on September 28, 2017 with a peak of 2.78 mm d^{-1} at CDS 1-, and 1.99-mm d^{-1} at CDS 2.

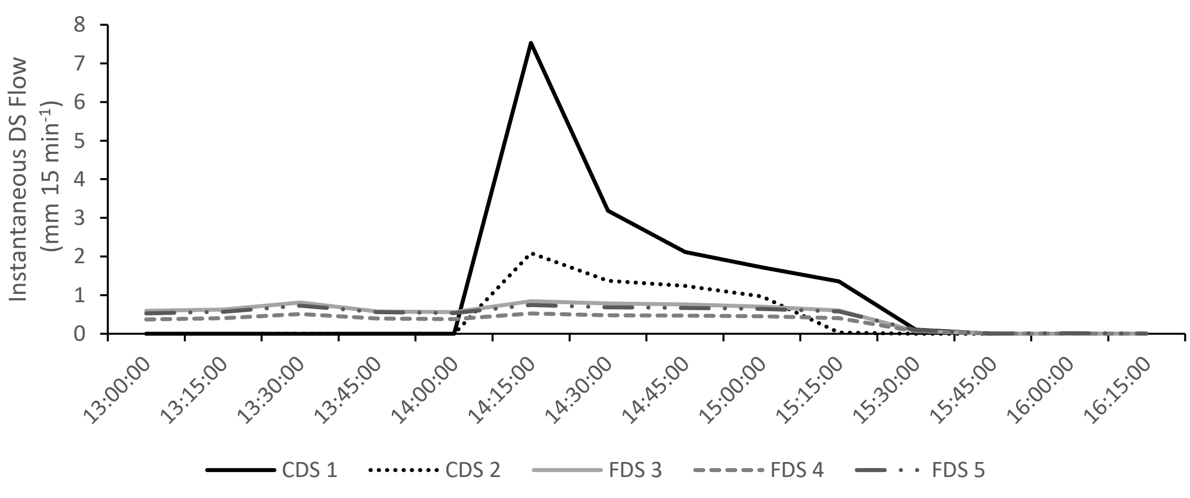


Figure 4.5: Controlled and Free Drainage Structure Flow at 15-min Intervals after the Removal of Stop Logs at CDS 1 and CDS 2 (14:15) Compared to Baseline Response at FDS 3-6 on Sept. 27, 2017.

The baseline response is seen at FDS 3-6 for the same interval. The cumulative normalized flow for this period was 2.25 mm (CDS 1) and 0.80 mm (CDS 2). Of the complete season, this represented 3% of the flow at CDS 1 and 1% at CDS 2.

4.2.4. Cumulative Normalized Flow and Cumulative Precipitation

The cumulative normalized flow and precipitation were graphed in order to interpret the general behaviour of flow per season. The drain flow mirrors the pattern of cumulative precipitation reasonably. The total cumulative drainage varied between 60-120 mm ha^{-1}, while the cumulative precipitation was 599 mm.

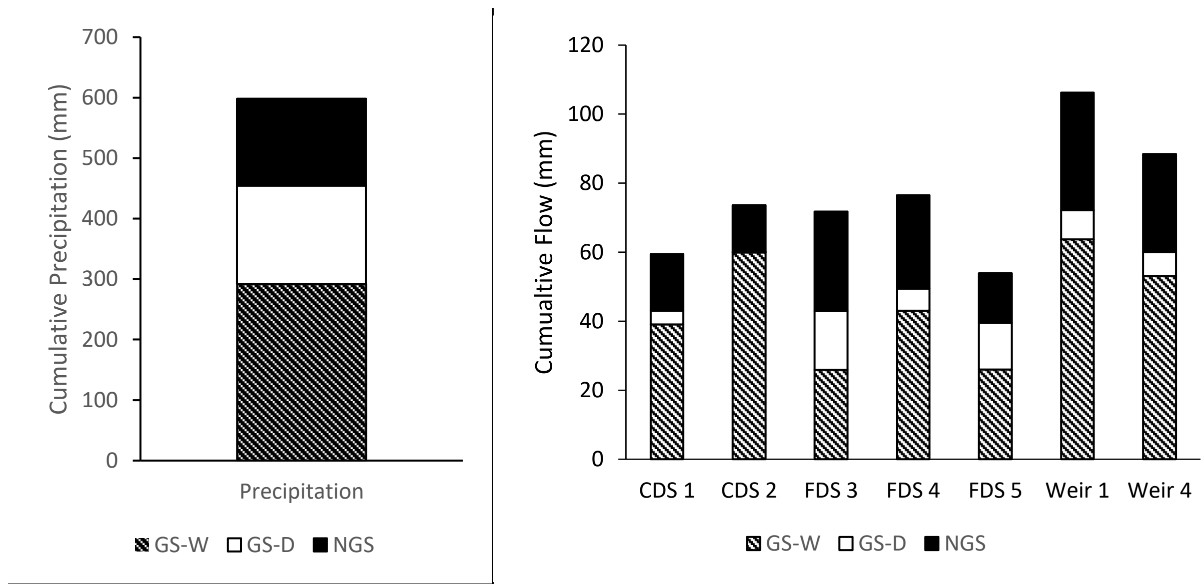


Figure 4.6: Cumulative Precipitation and Cumulative normalized flow (mm) at Drainage Structures and Pond with Seasonal Considerations
Drainage structures were controlled (CDS) at CDS 1 and CDS 2, and free (FDS) at FDS 3,4 and 5. A weir (Weir 1) was installed at the pond-wetland inlet and at the outlet (Weir 4). The study period was divided into the wet period of the growing season (GS-W: June 14 – July 31, 2017) the dry period of the growing season (GS-D: August 1 – September 27, 2017) and the non-growing season (NGS: September 28 – November 14, 2017) due to the availability of flow and concentration data at the drainage structures.

For the complete season, the cumulative precipitation between June 14 and November 24, 2017 was 598 mm. During the complete season, the cumulative normalized flow ranged from

63-124 mm d^{-1} at the flow monitoring stations. The cumulative normalized flow represented 11% of the total precipitation for the CDS and 12% for the FDS in the complete season. The cumulative normalized flow for the sum of DS 2-5 (which contribute to Weir 1) was 71 mm d^{-1} and was lower than the cumulative normalized flow at Weir 1 (106 mm d^{-1}). For the complete season, the mean cumulative normalized flow was 67 mm d^{-1} for the CDS and 79 mm d^{-1} ha^{-1} for the FDS; the cumulative normalized flow of the CDS was 16% lower than the mean flow at the FDS.

The cumulative precipitation during the GS-W was 292 mm, which represented 49% of the total precipitation during the study period. The cumulative normalized flow ranged between 39-60 mm d^{-1} at the CDS, between 26-43 mm d^{-1} at the FDS and between 53-64 mm d^{-1} at the Weirs. The cumulative normalized flow during the GS-W represented 17% of the total precipitation at the CDS, 11% at the FDS and 20% at the Weirs. During this period, the CDS produced 33% more outflow than the FDS. The flow during this period accounted for 66-81% of the total flow at the CDS, 36-56% of the flow at FDS and 60% at the Weirs. Evans et al. (1993) reported that during wet years, there may not be an effect of controlling drainage on total outflow. 49% of total precipitation for the study period occurred during the GS-W including 3 storm events greater than one standard deviation above the mean. Evans et al. (1993) reported that during wet periods, the effect of controlling drainage had little effect, or conversely increased peak flow during wet periods. Following a 67 mm rainfall on July 24, 2017, the CDS responded with an average flow increase of 6.25 mm d^{-1} the following day compared to 3.30 mm d^{-1} at the FDS. The heightened responsiveness of the CDS to high precipitation events was observed following a 31 mm rainfall on July 1 (22% higher at the CDS) and a 23 mm rainfall on July 8, 2017 (194%)

the subsequent day. The present study supports Evans et al.'s findings that the total and peak outflow can increase during wet periods with controlled drainage.

The cumulative precipitation during the GS-D is 162 mm, which represents 27% of the total precipitation during the study period. The cumulative normalized flow was 0-4 mm d^{-1} at the CDS and between 6-21 mm d^{-1} at the FDS. The cumulative normalized flow at GS-D was 1% of the precipitation for the CDS and 8% for the FDS. Of the total flow, between 1-7% of the total flow was accounted for in the GS-D at the CDS and 8-24% at FDS. In comparison to FDS, the total outflow of the CDS was 86% lower. Evans et al. (1993) summarized the impact on water quality by controlled drainage structures in various studies and reported that drainage control implemented only in the GS reduced total outflow by 15% compared to conventional subsurface drainage, whereas CD managed year-round could reduce total outflow by up to 30%. The findings of this present study show a considerably greater reduction of outflow than that reported previously in literature during the GS-D, however the higher flows were noted in the GS-W at the CDS due to high precipitation events.

The cumulative precipitation during the NGS was 144 mm, which represents 24% of the total precipitation during the study period. The cumulative normalized flow was highly variable and ranged between 13-29 mm d^{-1} at the DS. The cumulative normalized flow at the CDS was 10% (CDS) compared to 15% (FDS) of the precipitation for the NGS. The flow in this period accounted for 24-40% of the total flow at the sampling locations.

4.2.5. Evapotranspiration or Crop Water Use/Need

Evapotranspiration encompasses the movement of water to the atmosphere from waterbodies, soil, plants and canopy interception. The water balance method (OMAFRA, 2004), a method based on precipitation, soil, and crop factors, was applied to the soybean crop to estimate plant hydric stress. When the depth of water in the soil is less than the depth required to meet the water loss through evapotranspiration, the crop is stressed and therefore, implementing a CDS is useful to control the water table and ensure that crop roots have sufficient water depth through the GS. The calculations involved in calculating evapotranspiration and soil irrigation requirements are presented in the **Appendix**.

Soybean was planted on May 18, 2017 and harvested on October 17, 2017. Fertilizer was applied on September 29, 2017. The average ET values and crop factors were taken from (OMAFRA, 2004) and are presented in the **Appendix**. ET estimates were taken from OMAFRA and adjusted ET values were calculated by multiplying the crop factor with the estimated evapotranspiration data. Soybean entered a period of stress over twenty-two days between July 31, 2017 and August 21, 2017. The beginning of the soybean stress period coincides with the dry period of the growing season. The soil water balance has been graphed below.

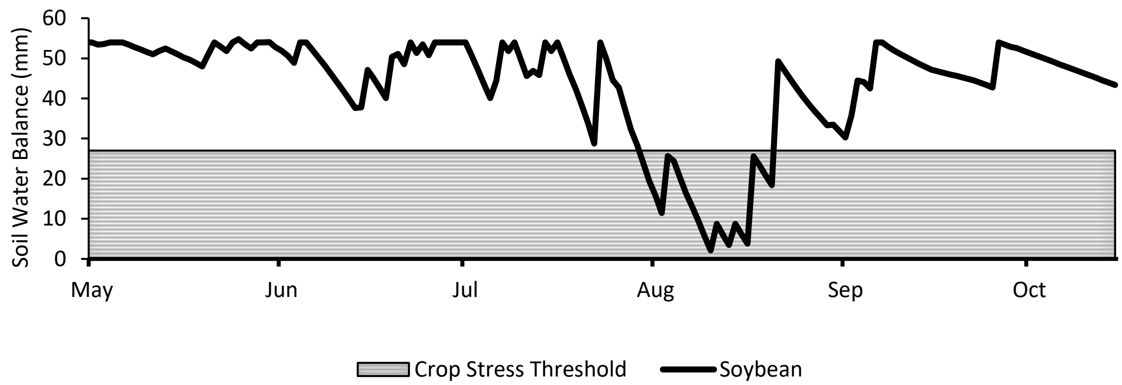


Figure 4.7: Soil Water Balance for Soybean Demonstrating that Soybean was Under Stress Conditions Between July 31 – August 25, 2017.

Soybean incurred a period of water stress over twenty-two days between July 31, 2017 and August 21, 2017 as seen in **Figure 4.7** above when the soil water balance was below 27 mm (50% of field moisture capacity). Soybean is considered to be somewhat tolerant to brief periods of drought, however, is considered to be susceptible to drought during the growth stages of germination and reproduction. The drought period seen above occurred during the reproductive stages of pod filling (R3 and R4) of soybean growth. The soybean growth stages are explained in the **Appendix**. A water deficit in the pod filling stage has been shown to decrease pod number by as much as 20%, thereby reducing seed weight and yield (Licht et al., 2013). During this period, the use of a controlled drainage system to attenuate flow and retain water in the field is useful to maintain soybean crop yield. A discussion of cumulative evapotranspiration as a proportion of cumulative precipitation follows in this section.

4.2.6. Cumulative Normalized Flow, Cumulative Evapotranspiration and Cumulative Precipitation

The substantial difference between the precipitation and drainage is given by evapotranspiration. Evapotranspiration was estimated for soybeans.

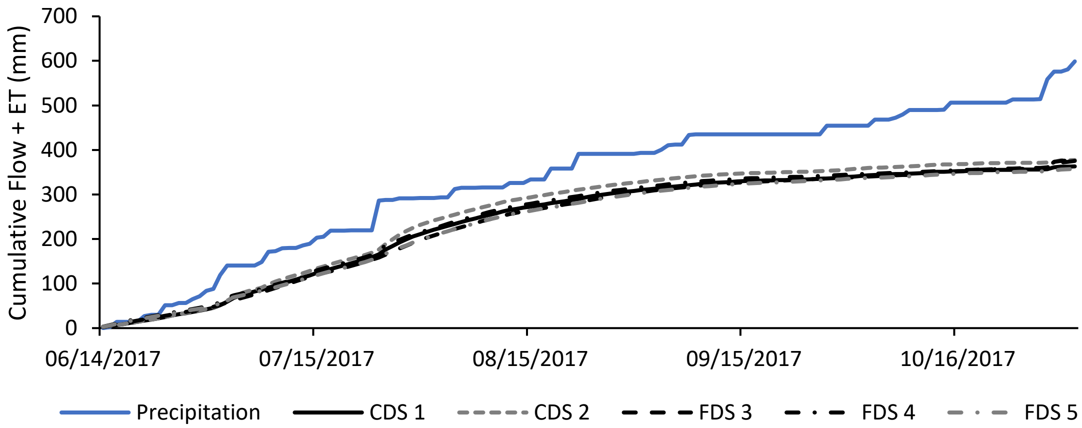


Figure 4.8: The Sum of Cumulative normalized flow and Evapotranspiration (Soybean crop) as a Function of Precipitation at All Drainage Structures and Weirs between June 14, 2017 and November 24, 2017.
Drainage structures were controlled (CDS) at CDS 1 and CDS 2, and free (FDS) at FDS 3,4 and 5. A weir (Weir 1) was installed at the pond-wetland inlet and at the outlet (Weir 4). The completed study period spanned June 14 – November 14, 2017 due to the availability of flow and concentration data at the drainage structures.

Evapotranspiration accounts for between 17% (NGS) to 82% (GS-D) of the total precipitation. Evapotranspiration accounts for the majority of the precipitation, whereas flow represents between 10-20%. In total, evapotranspiration and flow account for up to 80% of the total precipitation during the study period. Groundwater infiltration and errors in ET estimation, and to a lesser extent flow measurement, are expected to account for the difference between precipitation, flow, and evapotranspiration.

4.2.7. Responsiveness of Flow to Precipitation, with a Discussion on Seasonal Variation

To understand the relationship between precipitation and flow, the flow was compared against precipitation by season and the precipitation was time-lagged to see if there was an effect on flow of percolation through soil pores. Additionally, the behaviour of the CDS and FDS was studied in response to high precipitation events. A correlation was expected between precipitation and flow on the same day, and within a short time period after the precipitation event. The correlation ranged between $0.16 \leq R \leq 0.40$ on the same day (t), increasing to $0.40 \leq R \leq 0.69$ one day following precipitation (t+1), and decreasing to between $0.05 \leq R \leq 0.41$ two days following precipitation (t+2) indicating that the highest correlation between flow and precipitation occurred one day following precipitation for the study period. The strongest correlation was found one day following precipitation during the GS-W ($0.33 \leq R \leq 0.87$) and during the NGS ($0.58 \leq R \leq 0.79$). The correlation was moderate to strong two days following precipitation in the GS-D ($0.45 \leq R \leq 0.70$). Overall, there was a correlation between precipitation and flow, with the effect varied in strength between 0-2 days following the rainfall event depending on the season.

High precipitation events defined as precipitation events greater than one standard deviation of the norm are presented in **Figure 4.9** below where high flow events can be seen to be clustered up to five days following a high precipitation event. When high precipitation events were compared with flow on the same day (t) to seven days later (t+7), there was a moderate to strong correlation with high precipitation events and flow when time lagged up to four days ($0.31 \leq R \leq 0.92$). The strongest correlation between flow and precipitation occurred two days after the rain event at CDS 2, FDS 3-5 ($R>0.70$) and after one day at CDS 1, Weir 1 and Weir 4 ($R>0.80$). The same pattern was observed at Weirs 1 and 4 during the GS-W and the GS-D. However, strong correlations ($0.60 \leq R \leq 0.88$) were found four days following precipitation and flow at CDS 1, CDS 2, FDS 3 and FDS 5, indicating that it can take multiple days to drain the soil following large precipitation events. High precipitation events and flow events defined as greater than one standard deviation plus the mean were plotted below. The correlation described above is observable in **Figure 4.9** below.

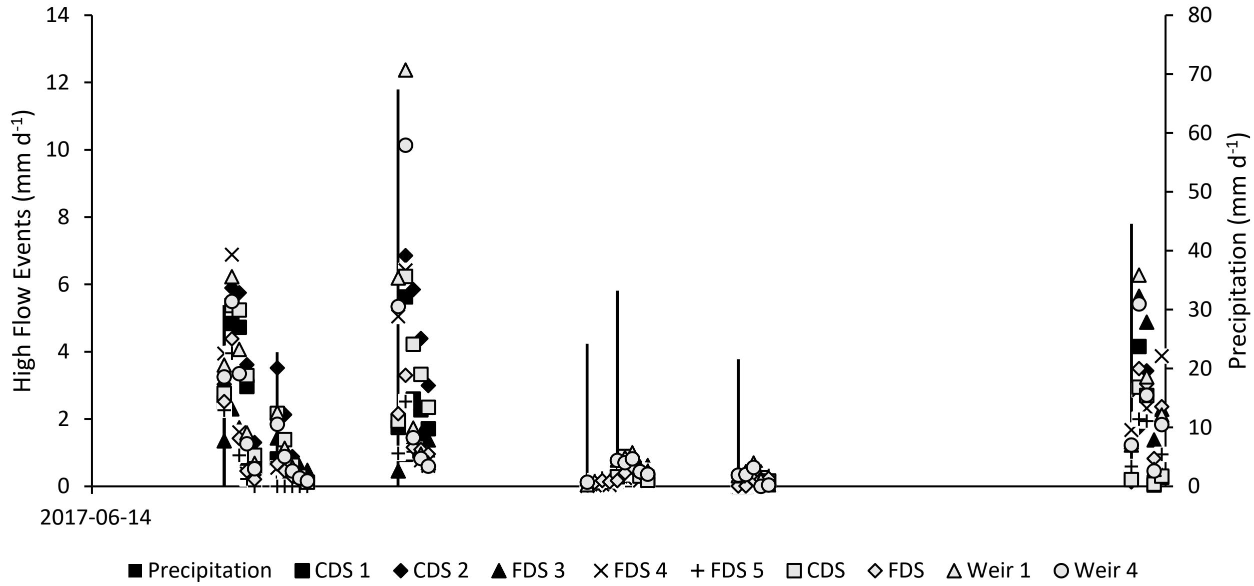


Figure 4.9: High Precipitation (mm d^{-1}) and High Flow Events (mm d^{-1}) during the Study Period (June 14 – November 14, 2017) at the Drainage Structures and Pond
Note: A precipitation event of 16.2 mm on October 15, 2017 was added to this graph to demarcate the precipitation event causing the cluster of high flow events between October 18 and October 20, 2017.

In comparison to the five days prior to the high rainfall event, the cumulative normalized flow increased by a factor ranging between 7 to 20 times for all locations during the 31 mm rainfall on July 1 and up to four days following the rainfall (+4d); between 5 to 20 times for the 67.4 mm rainfall on July 24 +4d and between 6 to 16 times for the 44.6 mm rainfall on October 29 +4d. Exceptionally, the 24.2 mm rainfall event on August 18 elicited no flow response from the CDS during the GS-W. Generally, the CDS peak flow response was between 1.2 to 3.2 times greater than the FDS in the GS-W and ranged between no response to 1.5 times greater during the GS-D and between 1.5 times greater or 1.2 lower in the NGS. There is no overall behaviour difference between the CDS and FDS to high precipitation events that can be discerned within this data set.

4.2.8. Summary

The flow was measured at five drainage structures and two weirs between June 14, 2017 and November 24, 2017. During the complete season, the flow ranged between 0.00-0.90 mm d^{-1} at the CDS and between 0.00-0.58 mm d^{-1} at the FDS. The findings of this present study show that controlling the water table at approximately 0.67 m above the outlet structure at the free drains resulted in median flow output reduction of 82%. The average flow at CDS 1 and CDS 2 decreased from 0.81±1.35 mm d^{-1} and 1.25±1.85 mm d^{-1} respectively in the GS-W to 0.07±0.16 mm d^{-1} and 0.01±0.05 mm d^{-1} in the GS-D. CDS attenuated between 91 and 99% of the outflow in the GS-D compared to the GS-W. In the GS-W, the outflow at the CDS was 33% greater than at the FDS. In comparison to the cumulative normalized flow during the dry period of the GS, there was an 76% increase in total outflow at CDS 1 and 97% increase at CDS 2 during the NGS. A summary table is shown below comparing the cumulative flow between the CDS and the FDS, and the inlet and the outlet of the pond-wetland during the individual periods considered.

Table 4.3: Cumulative Daily Flow Percent Difference at Drainage Structures and Weirs by Season

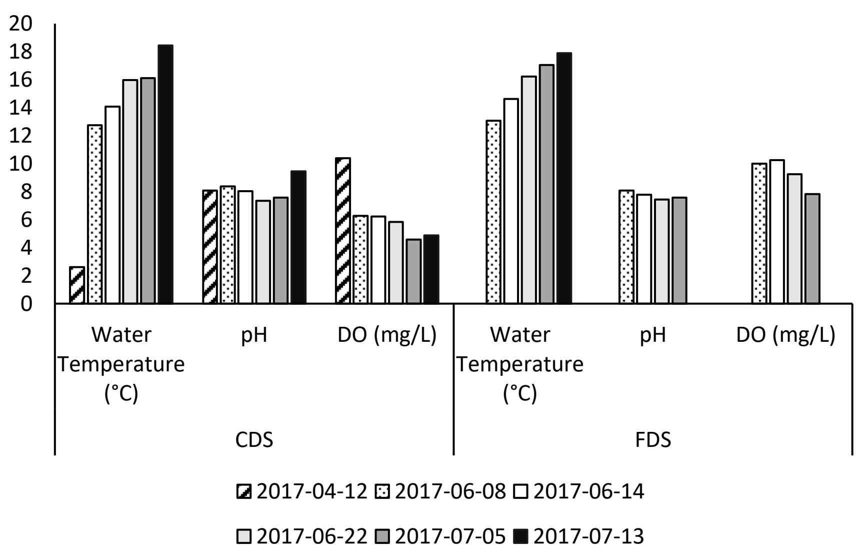
Percent Difference (%)	Study Period	GS-W	GS-D	NGS
FDS-CDS	-	-77	67	25
Pond-Wetland	17	17	19	17

The percent difference in cumulative flow between the FDS and the CDS (FDS-CDS) and between the inlet, Weir 1, and the outlet of the pond-wetland (Pond-Wetland) have been shown above. The negative percent difference observed in the GS-W is indicative of greater outflow from the CDS during the GS-W.

In comparison to the FDS, the cumulative flow at the CDS was 77% greater in the GS-W and 67% lower in the GS-D. The flow attenuation at the pond-wetland was consistent throughout the study period (17 mm).

4.3. **Monitoring Parameters**

Monitoring parameters, pH, water temperature, dissolved oxygen (DO) and electrical conductivity, were measured during the site visit at each monitoring location prior to sampling. These results have been shown below for the drainage structures and the weirs. The water temperature increased between April to July 2017, as expected, at both the controlled and free drainage structures. The pH was relatively stable, with an increase seen on July 13, 2017 at the CDS. The dissolved oxygen concentration was observed to be lower at the CDS than the FDS, though decreasing in both sample sets. Similarly, a large decrease in electrical conductivity was observed in both sampling sets in July compared to June.



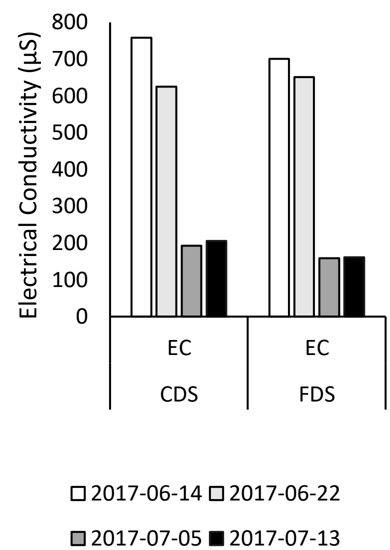


Figure 4.10: Monitoring Parameters Collected at the Drainage Structures
Monitoring parameters, Water Temperature (°C), pH, Dissolved Oxygen (DO in mg L^{-1}) and Electrical Conductivity (EC in µS/cm) in controlled drainage structures (CDS) and free drainage structures (FDS) have been presented above.

Similar to the data presented above, the monitoring parameters collected at the weirs show similar patterns. The electrical conductivity decreased sharply in June from a range of 700-900 µs cm^{-1} to a range of 100-350 µs cm^{-1}. The water temperature increased into the summer and decreased into the winter at both weirs, whereas the pH remained stable. Dissolved oxygen concentrations were supersaturated in the Spring (>8 mg DO L^{-1}) and decreased after peaking in May steadily into Fall (August-September), and increased thereafter into December at both locations.

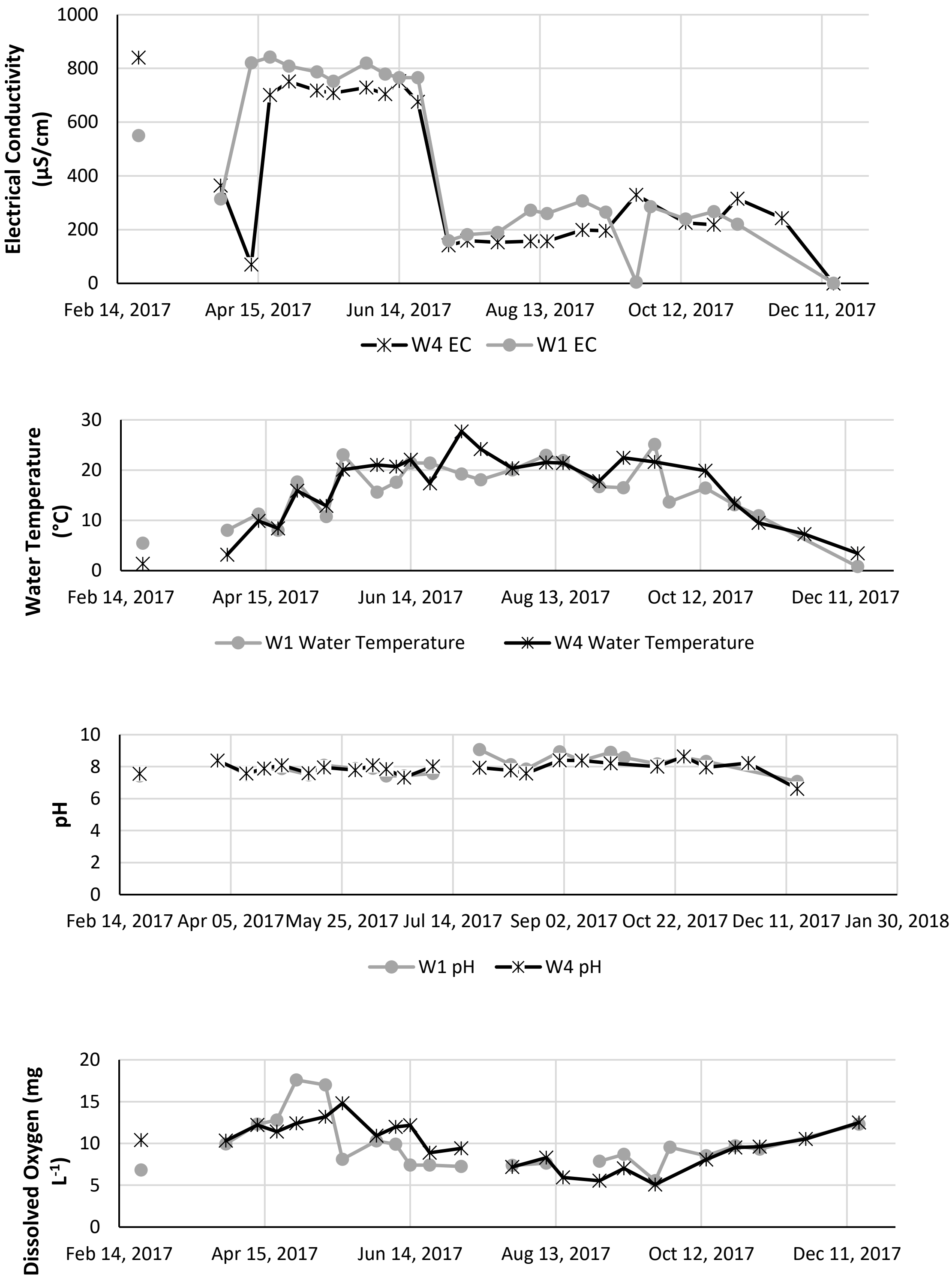


Figure 4.11: Monitoring Parameters Collected at the Weirs

Monitoring parameters, Water Temperature (°C), pH, Dissolved Oxygen (DO in mg L^{-1}) and Electrical Conductivity (EC in µS/cm) in the pond-wetland inlet (Weir 1) and pond-wetland outlet (Weir 4) have been presented above.

4.4. **Water Quality**

Three sets of analyses were performed on the collected samples categorized as: solids and organic matter [turbidity, total suspended solids (TSS) and total chemical oxygen demand (TCOD)), nitrogen (soluble nitrate (NO_3^{2-}), soluble ammonia (NH_4^+) and total nitrogen (TN)) and phosphorus (soluble reactive phosphorus (SRP) and total phosphorus (TP)]. TCOD, TN and TP analyses were completed for weir samples only.

4.4.1. Solids (Turbidity, TSS) and Organic Matter (TCOD)

i. Solids (Turbidity and TSS)

The increase of suspended solids can have numerous detrimental effects in aquatic ecosystems. Changes to the stream composition, permeability and stability can change egg-to-fry survival rates, benthic macroinvertebrate reproduction and periphyton communities (CCME, 1999). Additional downstream effects include changes in fish community structure, gill clogging, reduction in fish growth, and changes in fish coloration among others (CCME, 2002). The CCME water quality guideline allows for a maximum increase of 25 mg L^{-1} TSS and 8 NTUs from background levels for short-term exposure (≤24 h) and a maximum increase of 5 mg L^{-1} TSS and 2 NTUs for longer term exposures (24 h – 30 d) during clear flow; the same applies during high flow events for background levels between 25-250 mg L^{-1} TSS and 8-80 NTU, however, is to not increase more than 10% for background levels greater than > 250 mg L^{-1} TSS and > 80 NTU (CCME, 1999).

Total suspended solids are a measure of solids greater than 1.5 µm, while turbidity is an indicator of suspended solids within water that absorb or scatter light. Turbidity moderately correlated with TSS at the CDS (R=0.48) and at the FDS (R=0.51). Daily average TSS and turbidity at the CDS and FDS are presented with precipitation in **Figure 4.12**. Average water quality and mass flux data for CDS, FDS, and the pond-wetland system are presented in **Table 4.4** while the cumulative mass fluxes for the CDS, FDS and pond-wetland system are presented in **Figure 4.13**.

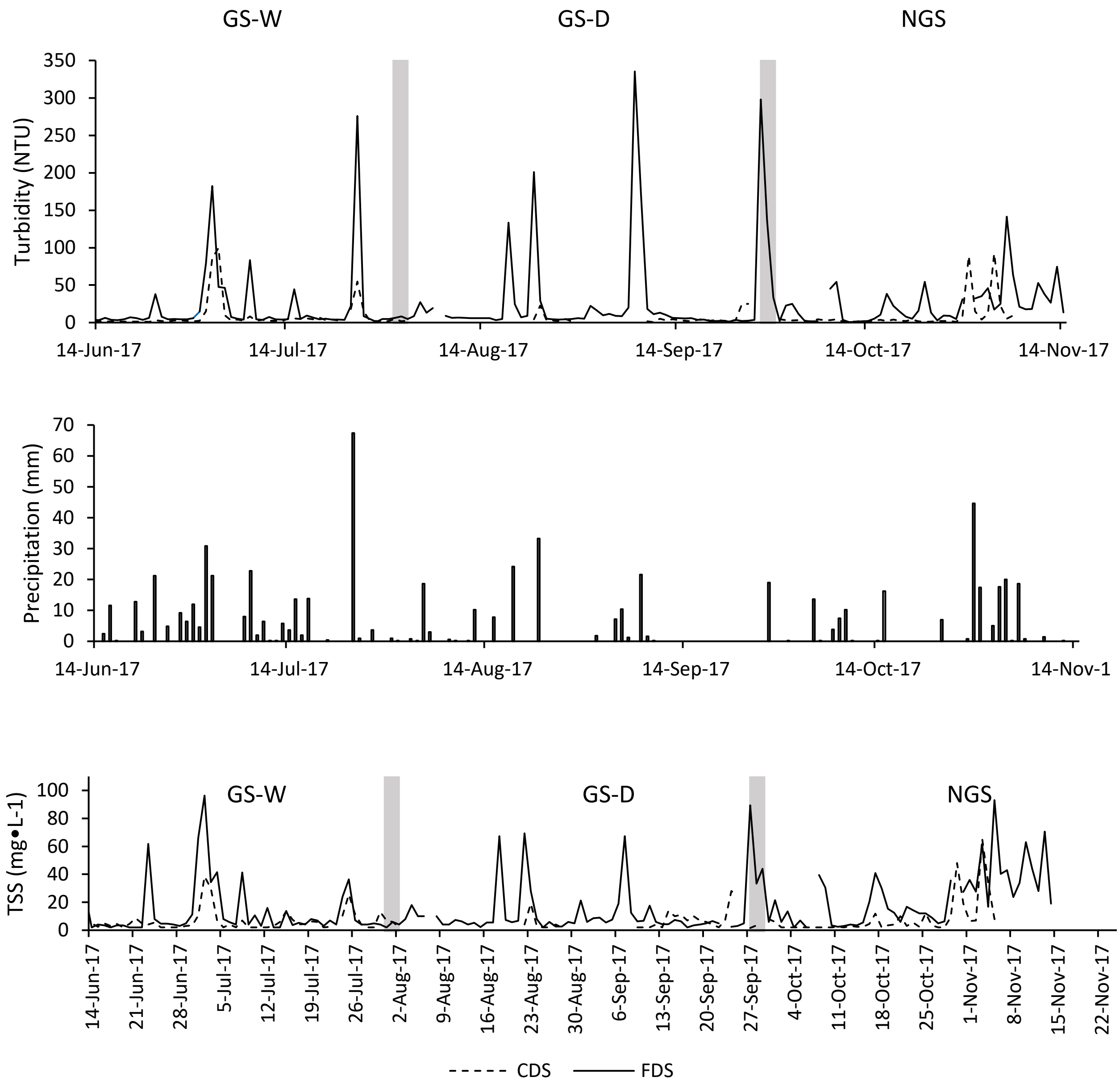


Table 4.4: Mean ± Standard Deviation and Median Daily Turbidity and Total Suspended Solids Concentration, Cumulative and Mean Daily Mass TSS Flux and Respective Percent Differences Between the Drainage Structures and Mean Removal by the Pond-Wetland During the Study Period

The drainage structure study period (June 14 – November 14, 2017) w ■ Precipitation e wet period of the growing season (GS-W: June 14 – July 31, 2017) the dry period of the growing season (GS-D: August 1 – September 27, 2017) and the non-growing season (NGS: September 28 – November 14, 2017) due to the availability of concentration data at the drainage structures.

Drainage Structures									
	Mean Turbidity			Mean TSS			Mean Daily TSS Mass Flux		
Period	FDS[b] (NTU)	CDS[a] (NTU)	Difference (%)	FDS[b] (mg L^{-1})	CDS[a] (mg L^{-1})	Difference (%)	FDS (kg ha^{-1} d^{-1})	CDS (kg ha^{-1} d^{-1})	Difference (%)
GS-W	**19±44**	**8±18**	**61**	**12±18**	**6±7**	**48**	0.21±0.82	0.20±0.52	5
GS-D	28±67	5±7	81	12±18	7±7	40	**0.02±0.04**	**0.01±0.03**	**53**
NGS	**25±32**	**9±20**	**65**	**20±29**	**8±13**	**59**	0.62±1.93	0.11±0.35	83
Pond-Wetland									
	Mean Turbidity			Mean TSS			Mean Daily TSS Mass Flux		
	Weir 1 (NTU)	Weir 4 (NTU)	Mean Removal (%)	Weir 1 (mg L^{-1})	Weir 4 (mg L^{-1})	Mean Removal (%)	Weir 1 (kg ha^{-1} d^{-1})	Weir 4 (kg ha^{-1} d^{-1})	Mean Removal (%)
Study Period	210±276	105±131	52	*210±312*	*94±157*	*55%*	0.31±0.36	0.21±0.19	33%

[a] The average of FDS 3-5 was taken to present FDS values. In the NGS, mean FDS values have been calculated using data between September 28-November 6 to compare to CDS as there is no data at the CDS after November 6, 2017.
[b] The average of CDS 1 and 2 was taken to present CDS values.
[c] Grab samples were used to calculate mean and median turbidity, TSS, TCOD, TP and TN at Weirs 1 and 4 due to the collection of unrepresentative solids in the composite weir samples.
Bold : Bolded with a grey background denotes a statistically significant difference, $p<0.05$ using a paired t-test.
Italicized: Italicized denotes a statistically significant difference, $p<0.1$ using a paired t-test.

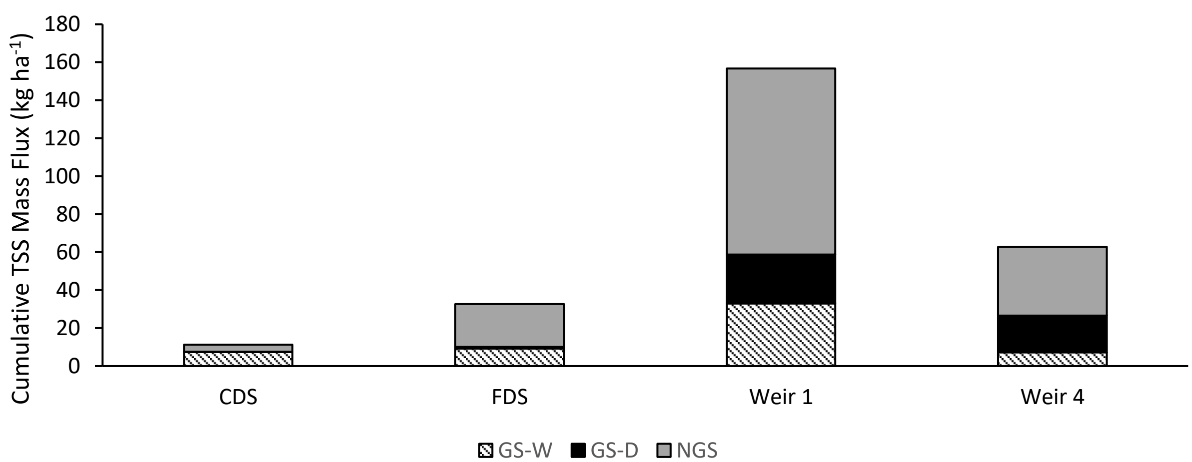


Figure 4.13: Cumulative Mass Flux by Season at the CDS, FDS, Weir 1 (Pond-Wetland Inlet) and Weir 4 (Pond-Wetland Outlet) Cumulative mass flux was calculated at the weirs using daily flow measurements and mean of preceding and antecedent concentrations values from grab samples. The drainage structure study period (June 14 – November 14, 2017) was divided into the wet period of the growing season (GS-W: June 14 – July 31, 2017) the dry period of the growing season (GS-D: August 1 – September 27, 2017) and the non-growing season (NGS: September 28 – November 14, 2017) due to the availability of concentration data at the drainage structures. The study period for the pond-wetland spanned June 14 – November 24 ,2017.

Subsurface Drainage

Effect of Precipitation on Water Quality

Turbidity and TSS responded similarly to precipitation events as presented in **Figure 4.12**. A correlation between solids and precipitation was expected, and a moderate positive correlation between precipitation and turbidity was observed at both the FDS (R=0.50) and CDS (R=0.52), while a moderate positive correlation was observed between precipitation and TSS at the FDS (R=0.48) and only a weak positive correlation at the CDS (R=0.21). An analysis of correlation by intensity of precipitation showed a strong positive correlation between TSS and precipitation for events greater than 30 mm (R=0.94) at the CDS, and a moderate negative correlation at the FDS for precipitation events $P<5$ mm, $5\text{mm}\leq P\leq 15\text{mm}$ and $P\geq 30$ mm.

Particularly in the FDS, spikes in TSS concentration (> 25 mg/L) corresponded closely with high precipitation events. There were four TSS spikes in GS-W, each relating to precipitation events of greater than 20 mm with three of four spikes trailing precipitation by 1 day. During GS-D there were also four TSS spikes, each corresponding to a precipitation event between 19-33 mm, however, with TSS spikes observed on the same day as the precipitation. In the NGS, there were two TSS flush events corresponding to lower precipitation events (7 and 16 mm d^{-1}) followed by a sustained increase in TSS from Oct 29 to Nov 13th, corresponding to sustained precipitation from Oct 29th to Nov 5th. In the FDS, a spike in TSS was observed during every precipitation event greater than 20 mm on the same day, in addition to 75% of the time within a one-day delay in the GS-W, when soils were already saturated, in comparison to 100% of the time on the same day as precipitation and 33% of the time in the GS-D when the soils were not saturated. The sustained high TSS concentrations observed from October 29th relate to saturated soil conditions after the crop was harvested, resulting in soil disturbance and lack of vegetated cover. The response in the CDS was more muted than that of the FDS with only two TSS spikes in GS-W corresponding to the two largest precipitation events (> 50 mm), none in GS-D, where the CDS were mostly not flowing, and high TSS concentrations from October 30th, which were similar to that observed at the FDS.

Effect of Controlled Drainage and Period on Water Quality

Water quality data is compared between drainage structures (CDS vs FDS) and period (GS-W, GS-D and NGS) in **Table 4.4**. The mean TSS concentration at the CDS showed no significant differences between study periods with similar values of 6±7, 7±7 and 8±13 mg L^{-1} during GS-W, GS-D and NGS, respectively. However, the mean TSS concentration at the FDS during the NGS was statistically different from the GS-W and the GS-D ($p<0.05$) as the NGS TSS concentration was approximately twice the magnitude at 12±18, 12±18 and 20±18 mg L^{-1} during GS-W, GS-D and NGS, respectively. Average concentrations and standard deviation were lower at the CDS compared with the FDS with significant differences observed in GS-W and NGS ($p<0.05$). Mean turbidity was not statistically different between the periods at the CDS or the FDS ($p>0.05$), while turbidity followed the same general pattern as TSS with higher average values and standard deviation for FDS than CDS, and significant differences observed in the GS-W and NGS.

Mean turbidity and TSS were lower at the CDS than at the FDS during all periods. This was expected during GS, while the stop logs were employed, as the installation of a CDS results in a larger depth of saturated soil for tile water to pass through resulting in decreased flow rate and therefore in decreased solids movement. Additionally, the elevation of the water table due to the implementation of a CDS reduces the potential of particulate movement through preferential flow paths caused by fissures in dry clay soil. During the dry period of the growing season, the mean turbidity and TSS were lower at the CDS than at the FDS, however, the difference was not statistically significant. The mean concentration of TSS was relatively low across all periods (TSS < 25 mg L^{-1}). However, when the stop logs were removed at the CDS, the pattern of lower TSS concentration and turbidity at the CDS continued in the nongrowing season. While the controlled drainage structures may contribute to the retention of solids, the observation that there was no significant change in TSS concentration and turbidity after the stop logs were removed at the CDS in conjunction with the observation that there is a significant difference between the CDS and FDS following the removal of the stop logs suggests that the variability between the individual plots draining into the CDS and FDS contribute more to the movement of solids into the drains than the implementation of the controlled drainage structures. The CDS met the CCME guidelines 89% of the time for turbidity and 97% for TSS, whereas the FDS met the CCME guideline 82% of the time for turbidity and 89% of the time for TSS.

Mass Flux

The mean daily TSS mass flux for the CDS and FDS are described in **Table 4.4** while the cumulative total mass flux is presented in **Figure 4.13**. The mean daily mass flux was very similar between the FDS and CDS in the GS-W, while the CDS mean daily mass flux was 53% and 85% lower than the FDS fluxes in the GS-D and NGS, respectively. The cumulative TSS mass flux was lower at the CDS during all seasons in comparison to the FDS. The solids mass flux was lower at the CDS in comparison to the FDS by 19% (GS-W), 87% (GS-D), and 81% (NGS). The higher solids mass flux during the NGS reinforces the effect of the plot itself and corroborates the likelihood that the fields draining into CDS 1 and 2 are less prone to soil movement than the fields draining into the FDS than as a result of CDS implementation. The increased TSS concentration and mass flux at the FDS during the NGS was likely a result of the harvest of crop in late September 2017 leaving the soil destabilized and prone to solids movement following precipitation events. The cumulative TSS flux for the study period was 11 kg ha^{-1} (CDS) and 33 kg ha^{-1} (FDS). In comparison, the Ontario Ministry of Agriculture, Food and Rural Affairs states that a very low soil erosion class or tolerance level of soil erosion for most soils in Ontario is 6.7 tonnes ha^{-1} yr^{-1} or 6,700 kg ha^{-1} yr^{-1} (OMAFRA, 2012). The soil migration through the subsurface drains observed in this study is below 0.5% of the tolerable level of soil erosion.

Pond-Wetland System

Water quality and mean daily TSS mass flux data for the pond-wetland system are presented in **Table 4.4** while cumulative mass flux is presented in **Figure 4.13**. TSS and turbidity values were much higher than those observed at the CDS and FDS, which contributes up to 94% of the total flow at Weir 1. This difference is partially due to surface erosion into the drainage ditch where Weir 1 is located, but also relates to sediment resuspension due to flow and wind action. An increase in solids concentration was noted within the collected samples in early August at Weir 1 and in late August to early September at Weir 4. This accumulation of solids could be due to a damming effect created by the weir following seasonal turnover of biomass in the Fall at Weirs 1 and 4. Alternatively, ponds undergo periods of episodic solids release, which may contribute to the accumulation of solids at Weir 4.

The mean TSS concentration was 200±299 mg L^{-1} at Weir 1 and 88±152 mg L^{-1} at Weir 4. An ANOVA and paired T-test performed between Weir 1 and Weir 4 TSS concentration determined that the difference was statistically significant at $p<0.1$ ($0.05< p<0.10$). The median TSS concentration percent difference of 76% between Weirs 1 and 4 accounts for the high variability caused by episodic solids events during the study period. Similarly, the mean turbidity was higher at Weir 1 (210±276 NTU) than at Weir 4 (100±127 NTU), and this difference was not statistically significant ($p>0.1$). The median turbidity was 110 NTU at Weir 1 and 44 NTU at Weir 4, with a median reduction of 60%. A strong correlation was expected between TSS and turbidity and potentially expected between TP, TN and TCOD. However, TSS only showed a strong positive correlation at Weir 1 with TCOD (R=0.90) and TP (R=0.92). The pond-wetland discharge (Weir 4) met the applicable CCME guideline for TSS 82% of the time and for turbidity 58% of the time in comparison to Weir 1 which met the CCME guideline for TSS 73% of the time and for turbidity 64% of the time.

The mean daily mass flux was 33% lower at Weir 4 than at Weir 1 during the study period, while the cumulative TSS mass flux for the study period was 157 kg ha^{-1} at Weir 1 and 63 kg ha^{-1} or 0.063 tonnes ha^{-1} at Weir 4 or a 60% reduction within the pond-wetland system. The Ontario Ministry of Agriculture, Food and Rural Affairs suggests a tolerance level for most soils in Ontario is 6.7 tonnes ha^{-1} yr^{-1} or less (OMAFRA, 2012). The cumulative input and output per year from the pond-wetland is two orders of magnitude less than the suggested tolerance level. A review of wet detention ponds by Harper and Baker (2007) reported a range of 55-94% removal of TSS mass and an average of 77% across the compared studies. A study by Md

Zahanggir et al. (2018) reported maximum reductions of TSS of 80% using new stormwater ponds in commercial areas of Western Australia with mean effluent concentrations of 63±19 mg L^{-1} TSS. A study by Lavrnić et al. (2020) studied the use of a full scale constructed wetland for agricultural drainage water treatment in Northern Italy and demonstrated a retention of TSS mass load by 69%. In comparison to this range, the Bercier pond performs below the range of the published literature for solids attenuation in 2017.

Conclusion

TSS concentrations were generally low and were observed to be lower at the CDS compared to the FDS by 48% (GS-W), 40% (GS-D) and 59% (NGS), respectively. The mean TSS concentration and turbidity was similar across the seasons at the CDS. However, the difference between the CDS and FDS was only statistically significant during the GS-W and NGS for both turbidity and TSS suggesting a potential influence on solids attenuation as a result of controlling drainage and simultaneously an effect of plot variability. The percent difference in the mean daily TSS mass flux was 5% (GS-W), 53% (GS-D) and 83% (NGS). An effect of controlling the drainage structures was seen during the GS-D between the FDS (0.02±0.04 kg ha^{-1} d^{-1}) and the CDS (0.01±0.03 kg ha^{-1} d^{-1}) resulting in a statistically significant difference of 53%. The reduction of concentration and mass flux was expected during the GS as the installation of the CDS increased the depth of saturated soil for tile water movement and therefore would result in a decreased flow as well as solids movement. However, the increased difference in TSS flux as well as the stability of TSS concentration at the CDS during the NGS suggests an effect of the field likely due to crop harvesting leaving the soil destabilized and prone to solids movement following rain events. A moderate correlation between precipitation and turbidity was noted at the CDS and FDS, and between precipitation and TSS at the FDS. A summary table is shown below comparing the cumulative TSS flux between the CDS and the FDS, and the inlet and the outlet of the pond-wetland during the individual periods considered.

Table 4.5: Cumulative Daily TSS Flux Percent Difference at Drainage Structures and Weirs by Season

Percent Difference (%)	Study Period	GS-W	GS-D	NGS
FDS-CDS	-	20	85	83
Pond-Wetland	60	78	25	63

The percent difference in cumulative TSS flux between the FDS and the CDS (FDS-CDS) and between the inlet, Weir 1, and the outlet of the pond-wetland (Pond-Wetland) have been shown above.

In comparison to the FDS, the CDS reduced TSS flux during all periods considered, with higher reduction observed in the GS-D and NGS. The pond-wetland reduced TSS flux in all considered periods, averaging annually at 60%, with lower reduction noted in the GS-D.

The solids response to precipitation was muted at the CDS compared to the FDS, in that precipitation events greater than 30 mm caused a TSS response of greater than 25 mg L^{-1} during 3 of the 4 events (24 mg L^{-1} for the fourth event) at the FDS, and a TSS response less than 11 mg L^{-1} at the CDS. The CDS met the CCME guidelines 89% of the time for turbidity and 97% for TSS, whereas the FDS met the CCME guideline 82% of the time for turbidity and 89% of the time for TSS.

Compared to Weir 1, there was a 52% reduction of turbidity, 55% reduction of mean TSS concentration ($p=0.1$) and 33% reduction of daily TSS mass flux at Weir 4 during the study period. High variability observed was attributed to episodic solids release events in the drainage ditch and the pond. The pond-wetland discharge (Weir 4) met the applicable CCME guideline for TSS 82% of the time and for turbidity 58% of the time in comparison to Weir 1 which met the CCME guideline for TSS 73% of the time and for turbidity 64% of the time. The cumulative input and output per year from the pond-wetland is two orders of magnitude less than the suggested tolerance level.

ii. TCOD

The chemical oxygen demand (COD) is an indicator of the oxidizing potential of water under the assumption that a strong oxidizing agent could fully oxidize any organic compound to carbon dioxide under acidic conditions. COD concentration, therefore, is an indicator of the organic matter in a system. Central Canadian surface waters analyzed for COD prior to 1985 were found to have a concentration range of 10-70 mg L^{-1} (NAQUADAT, 1985). COD is not regulated in Canada, however, wastewater treatment effluent regulations range globally from 125 mg L^{-1} in the European Union to between 50-120 mg L^{-1} in China (EU, 1991; Zhou et al., 2018).

The mean TCOD concentration was 23±28 mg L^{-1} (Weir 1) and 17±13 mg L^{-1} (Weir 4) while the median TCOD concentration at Weir 1 was 10 mg L^{-1} and 15 mg L^{-1} at Weir 4 during the study period. The difference in mean TCOD concentration was not statistically significant ($p>0.05$). Overall, the use of a pond or wetland system for organic matter polishing in drainage waters is not well documented, therefore, studies on stormwater runoff ponds or urban ponds with low influent concentrations have been used for comparison to literature. A study by Md Zahanggir et al. (2018) reported maximum reductions of BOD (87%) and COD (88%) using new stormwater ponds in commercial areas of Western Australia with mean effluent concentrations of 7±2 mg L^{-1} BOD and 37±25 mg L^{-1} COD. A study by Lavrnić et al. (2020) studied the use of a full-scale constructed wetland for agricultural drainage water treatment in Northern Italy and demonstrated a retention of mass load of COD by 51% (influent concentration 24±29 mg L^{-1} and effluent 24±9 mg L^{-1}) and TOC by 33%. In comparison to these values, the TCOD concentrations at the Bercier ponds are similar. A study of forty-five urban ponds across southern Ontario by McEnroe et al. (2013) reported a range of 2 to 16 mg C L^{-1} and an average of 5.3 mg C L^{-1} for dissolved organic carbon. The concentration of organic matter in the Bercier system is very low and falls within the range for the dissolved organic carbon concentrations as referenced above. The mean and median TCOD mass flux for the study period were the same at Weir 1 and Weir 4 **(Table 4.6)**. There is no net export of organic matter from the pond. However, over time, there is likely to be a release of organic matter seasonally due to the cycling of nutrients resulting from the degradation of biomass in the Fall. There was a moderate correlation between flow and TCOD at Weir 4 (R=0.39). The strong correlation between TCOD with TSS (R=0.90) and moderate correlation between TP and TCOD at Weir 1 (R=0.65) suggests that organics form a significant fraction of both the solids and total phosphorus content. The data shows the overall absence of solids movement and organic carbon within the system. In addition, there is no addition of carbonaceous materials into the system and therefore it can be inferred that any effluent carbon is sourced from the bio-degradation of wetland vegetation as it is not introduced into the system through the drainage water as demonstrated by the Weir 1 data. The major source of carbon in the system is most likely resulting from the biodegradation of aquatic plants that fix carbon dioxide from the atmosphere through photosynthesis. This suggests that carbon required for denitrification is dependent upon the accretion of organic sediment layer which would increase in thickness with pond maturity.

Table 4.6: Mean and Median TCOD Concentrations with Considerations in Seasonality

	Mean TCOD (mg L^{-1})		Median TCOD (mg L^{-1})		ANOVA p-value	Paired t-test	Mean TCOD Flux (kg $d^{-1}ha^{-1}$)		Median TCOD Flux (kg $d^{-1}ha^{-1}$)	
	Weir 1	Weir 4	Weir 1	Weir 4			Weir 1	Weir 4	Weir 1	Weir 4
Study Period	23±28	17±13	10	17	0.44	0.39	0.07±0.11	0.07±0.15	0.03	0.03

The mean TCOD concentration was 23±28 mg L^{-1} (Weir 1) and 17±13 mg L^{-1} (Weir 4) and the difference in mean TCOD was not statistically significant (p>0.05). The mean and median TCOD mass flux for the study period were the same at both Weirs 1 and 4. This indicates that the total organic carbon content of the water column is very low and comparable to background concentrations of dissolved organic carbon observed in literature and that there is no net removal of TCOD from the farm drainage waters.

4.4.2. Nitrogen: Total Nitrogen, Ammonia and Nitrate

i. Total Nitrogen

Organic nitrogen, total ammonia and nitrate from municipal effluent, total ammonia and nitrate from agricultural runoff, and NOx from atmospheric deposition are the primary anthropogenic contributors of N to surface water (CCME, 2016). The analysis of total nitrogen is an indicator of all forms of nitrogen entering and exiting the studied system. The average TN concentration for the study period was 7.36±2.98 mg N L^{-1} at Weir 1 and 4.71±3.33 mg N L^{-1} at Weir 4 (**Figure 4.14**). The pond-wetland reduced TN concentrations by 36% during the study period. There was a statistically significant difference between the mean TN concentration at Weirs 1 and 4 using ANOVA (p<0.1) and paired T-test (p<0.05).

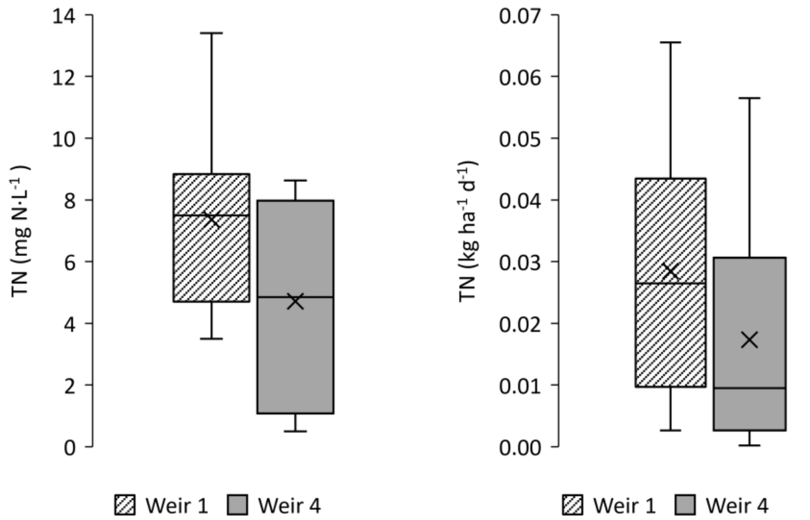


Figure 4.14: Box and Whiskers Plot of TN: Left) Concentration and Right) Mass Flux at Weir 1 (Pond-Wetland Inlet) and Weir 4 (Pond-Wetland Outlet)
The study period for the pond-wetland spanned June 14 – November 24 ,2017. The box and whisker plot depicts the range of the sample set within the box, the mean is represented by an x, the median is represented by a bar and the standard deviation is represented by the whiskers.

The average daily mass flux for TN was 0.029±0.020 kg ha^{-1} d^{-1} at Weir 1 (median 0.026 kg ha^{-1} d^{-1}) and 0.017±0.019 kg ha^{-1} d^{-1} at Weir 4 (median 0.009 kg ha^{-1} d^{-1}) for the study period (**Figure 4.14)**, achieving a mean removal of 41% and median removal of 64% between Weir 1 and Weir 4. Comparable studies have reported removal ranging between 12-63% for TN and a mean value of 37% using wet detention ponds for urban stormwater (residential and commercial) in Florida (Harper and Baker (2007)). The Bercier pond removed TN within the range of the average wet retention ponds. A cumulative 4.64 kg N ha^{-1} of total nitrogen at Weir 1 entered into the pond-wetland as tile and surface flow, while 2.07 kg N ha^{-1} exited the pond-wetland at Weir 4 resulting in a cumulative mass reduction of 55% during the study period.

Drainage water TN was expected to be composed primarily of nitrate due to nitrification in the soil. NO_3^--N represented 70% and 94% of the TN concentration while NH_4^+-N represented 3%

and 6% of the TN concentration at Weirs 1 and 4, respectively, suggesting that the system promotes ammonification and nitrification. The particulate fraction of TN was 29% at Weir 1 and 14% at Weir 4. This indicates that the pond removed a significant portion of the particulate N, likely through sedimentation.

ii. Ammonia

Ammonia is introduced into the soil through ammonification of degrading plant matter in soil, ammonia associated with migrating soil particles and the application of inorganic fertilizer (September 2017) and into the pond-wetland through plant degradation and release and internal cycling of the nitrogen cycle. It is expected that most ammonia will nitrify to nitrate within the soil column with or without the implementation of stop logs. Ammonia is easily oxidized by microorganisms through nitrification and exists in the environment in its ionized or unionized form. Ammonia ionization is dependent on pH, temperature, and the ionic strength of the water (a function of the water hardness). The concentration of total dissolved solids is correlated with water hardness and ionic strength of the water, and therefore the reduction of unionized ammonia (CCME, 2010). Unionized ammonia is understood to be more toxic to aquatic organisms due to its neutral charge that increases its ability to permeate or diffuse through cellular membranes (EPA, 1998). 48 and 96-hr LC_{50} values for freshwater invertebrates ranged between 1.10 to 22.8 mg NH_3-N L^{-1} and between 0.56 to 2.37 mg NH_3-N L^{-1} for fish species (CCME, 2010). The CCME guideline value for freshwater of 0.019 mg NH_3-N L^{-1} have been established for ammonia (CCME, 2010).

Subsurface Drainage

A review of literature shows that the effect of implementing controlled drainage structures on ammonia is under-reported, while the impact on nitrate is well-studied. Precipitation was expected to have an impact on the solids and/or ammonia concentration, which were presumed to be linked. The damming of field drainage water was presumed to have a negligible effect on ammonia movement. Metabolic pathways of ammonia include nitrification and ammonification. Ammonia nitrification generally occurs in the aerobic top layers of soil, however, the environment within the controlled drainage structures was expected to be anoxic, which would suppress nitrification. Nitrification and ammonification occur at higher rates under aerobic conditions, while the soil conditions above the tiles in the controlled drainage plots were expected to be anoxic, which would not favour nitrification or ammonification. Ammonia volatilization could occur at elevated pH, causing decreases in ammonification rates. The overall rates of ammonification or ammonia volatilization within the drainage structures is expected to be negligible as the majority of the ammonia introduced into the system was assumed to be nitrified into nitrate within the top oxic layers of the soil and soil pH is not sufficiently basic to support ammonia volatization. Therefore, an effect of periodic precipitation events on ammonia concentration was not expected within the drainage system and the ammonia concentration was expected to remain stable throughout the study period. In comparison to the pond-wetland, the internal cycling of nutrients between particulate to soluble forms within the drainage structures was expected to be negligible. Controlling the drainage structures was not expected to have a large impact on the migration of solids, and therefore ammonia migration following high flow events was not expected.

As stated previously, a difference in concentration was not expected between the controlled and free drainage structures. The expected outcome was the conversion of ammonia to nitrate through nitrification in the top aerobic layers of the soil, and a constant concentration of ammonia within the lower layers of soil, and by extension within the drains. An effect of seasonality was not expected: i.e., the concentration of ammonia was not expected to vary between the controlled and free drainage structures per season; and even if the background ammonia concentration in the soil varied within the field between the seasons, a difference was not expected between the controlled and free drainage structures.

Ammonia concentration and precipitation with time are presented in **Figure 4.15** while average ammonia concentration and daily flux data by drainage period and drainage structure and presented in **Table 4.8**. The mean NH_4^+-N concentration at the CDS was consistent across the study periods (GS-W: 0.20±0.19, GS-D: 0.20±0.18, NGS: 0.18±0.22 mg NH_4^+-N L^{-1}), whereas the NH_4^+-N concentration was highest at the FDS in the GS-W (0.39±0.42 mg NH_4^+-N L^{-1}), decreasing chronologically in the GS-D (0.24±0.68 mg NH_4^+-N L^{-1}) and the NGS (0.18±0.21 mg NH_4^+-N L^{-1}). The elevated concentration of ammonia in the GS-W at the FDS is related to the high peaks observed during this period as seen in **Figure 4.15**. The differences in mean NH_4^+-N drainage concentration were statistically significant between the CDS and FDS (ANOVA $p<0.05$) only during the GS-W, resulting in a percent difference of 49%. The difference in NH_4^+-N concentration at the FDS during the GS-W was approximately twice the magnitude of the GS-D and the NGS and was statistically significant (ANOVA $p<0.05$). The increased concentration at the FDS during the GS-W could be due to antecedent soil conditions in the FDS plots. The NH_4^+-N concentration was similar between the CDS and FDS in the GS-D and NGS. Ammonium nitrate fertilizer was applied on September 29, 2019 at 15.47 kg N ha^{-1}. A spike was expected in ammonia concentration following the application of fertilizer; however, this was not observed. The concentration of unionized ammonia met the PWQO criteria of 0.020 mg NH_3-N L^{-1} 81% of the time at both the CDS and FDS during the study period. The percentage of exceedances was higher at the CDS than the FDS only in the GS-D (CDS: 24%, FDS (13%)) and were lower at the CDS than the FDS during the GS-W (CDS: 31%; FDS: 35%) and in the NGS (CDS: 0%; FDS 8%).

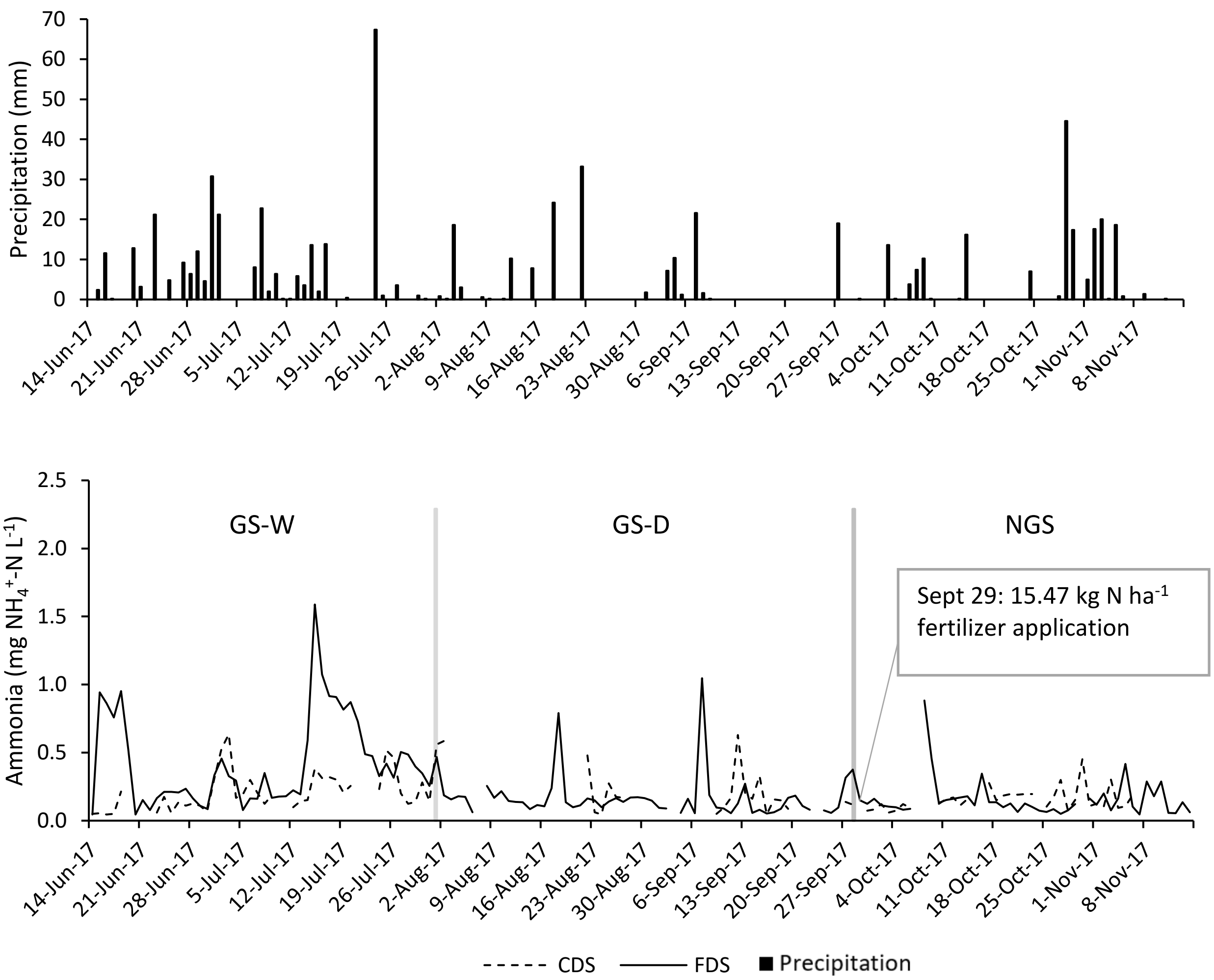


Figure 4.15: Mean Daily Ammonia Concentration at the Controlled Drainage Structures (CDS) and Free Drainage Structures (FDS) on Soybean Plots during the Study Period (June 14 to November 14, 2017).

The study period was divided into the wet period of the growing season (GS-W: June 14 – July 31, 2017), the dry period of the growing season (GS-D: August 1 – September 27, 2017) and the non-growing season (NGS: September 28 – November 14, 2017) due to the availability of flow and concentration data at the drainage structures.

Note: Samples taken by the ISCO automated sampler on days without flow have been assumed to be representative of stagnant water and have been excluded above.

Table 4.7: Mean Ammonia Concentration, Flux and Percent Change at Drainage Structures and Pond-Wetland

Period	Mean Daily Ammonia Concentration (mg NH_4^+-N L^{-1})		Difference (%)	Mean Daily Ammonia Concentration (mg NH_4^+-N L^{-1})		Difference (%)
	FDS[a]	CDS[b]		Weir 1	Weir 4	
GS-W	**0.39±0.42**	**0.20±0.19**	**49**	0.35±0.89	0.23±0.12	33
GS-D	0.24±0.68	0.20±0.18	19	**0.33±0.21**	**0.24±0.12**	**27**
NGS	0.18±0.21	0.18±0.22	0	0.17±0.08	0.34±0.84	-101
Study Period	-	-	-	0.28±0.53	0.27±0.48	3
Mean Daily Ammonia Mass Flux (kg NH_4^+-N ha^{-1} d^{-1})						
	FDS	CDS	Difference (%)	Weir 1	Weir 4	Difference (%)
GS-W	$3.1\times10^{-3}\pm7.3\times10^{-3}$	$3.9\times10^{-3}\pm9.4\times10^{-3}$	-39	0.005±0.009	0.004±0.008	16
GS-D	$5.8\times10^{-4}\pm2.1\times10^{-4}$	$2.7\times10^{-4}\pm4.0\times10^{-4}$	54	0.001±0.002	0.0003±0.0004	61
NGS	$2.8\times10^{-3}\pm8.5\times10^{-3}$	$9.2\times10^{-4}\pm2.1\times10^{-3}$	66	0.002±0.005	0.003±0.006	-12
Study Period	-	-	-	0.003±0.006	0.002±0.006	17

Note:

[a] The average of FDS 3-5 were taken to present FDS values. In the NGS, mean FDS values have been calculated using data between September 28-November 6 to compare to CDS as there is no data at the CDS after November 6, 2017.
[b] The average of CDS 1 and 2 were taken to present CDS values.
[c] Grab samples were used to calculate mean and median turbidity, TSS, TCOD, TP and TN at Weirs 1 and 4 due to the collection of unrepresentative solids in the composite weir samples.
Bold : Bolded with a grey background denotes a statistically significant difference, $p<0.05$ using an Analysis of Variance Test (ANOVA).

The mean ammonia flux was higher at the CDS by 39% (GS-W) and lower by 54% (GS-D) and 66% (NGS). The effect on flux reduction during the GS-D and NGS has been attributed partially to the implementation of the drainage structures and partially to the plots themselves. The cumulative ammonia mass flux was the greatest in descending order at the GS-W, NGS and GS-D at all locations **(Figure 4.16)**. This pattern correlates closely with the magnitude of flow observed in the same order at the CDS and FDS. The increased flow at the CDS compared to the FDS observed during high precipitation periods (such as the GS-W) had been described previously by Evans et al. (1995). The attenuation of tile discharge in July-August by the CDS has been described previously by Macrae et al. (2007). The cumulative flux was higher at the CDS than the FDS in the GS-W (-32%) and lower by 82% in the GS-D and 63% in the NGS with a net decrease of 21%.

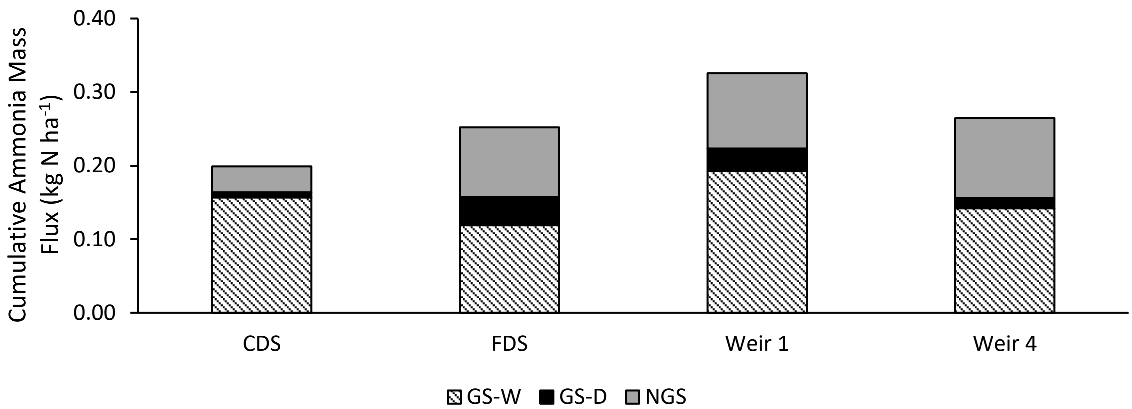


Figure 4.16: Ammonia Flux at the Controlled Drainage Structures (CDS), Free Drainage Structures (FDS) and Pond-Wetland during the Study Period
The study period was divided into the wet period of the growing season (GS-W: June 14 – July 31, 2017) the dry period of the growing season (GS-D: August 1 – September 27, 2017) and the non-growing season (NGS: September 28 – November 14, 2017) due to the availability of flow and concentration data at the drainage structures. The pond-wetland inlet has been defined as Weir 1 and the outlet as Weir 4.

The impact of environmental factors was assessed using correlational analyses. Precipitation was positively correlated with ammonia at the FDS suggesting that the associated ammonia concentration increase with rainfall is likely to be correlated with ammonia release from bound particles. Precipitation (P) events were split by intensity: P<5mm (low), 5mm≤P<15mm (medium), 15mm≤P<30mm (high) and P≥30mm (very high) with correlational analysis conducted between ammonia, turbidity and TSS as described in **Fig. 4.17**. Ammonia concentration was shown to be positively correlated with TSS and turbidity at both CDS for low, medium and high precipitation events and at the FDS for medium and high precipitation events. Ammonia concentration was not correlated with TSS or turbidity during very high precipitation events. This suggests that particulate dissolution of ammonia occurs primarily during medium and high rainfall events at both the CDS and FDS, however, this effect was superseded by the dilution effect during very high rainfall events.

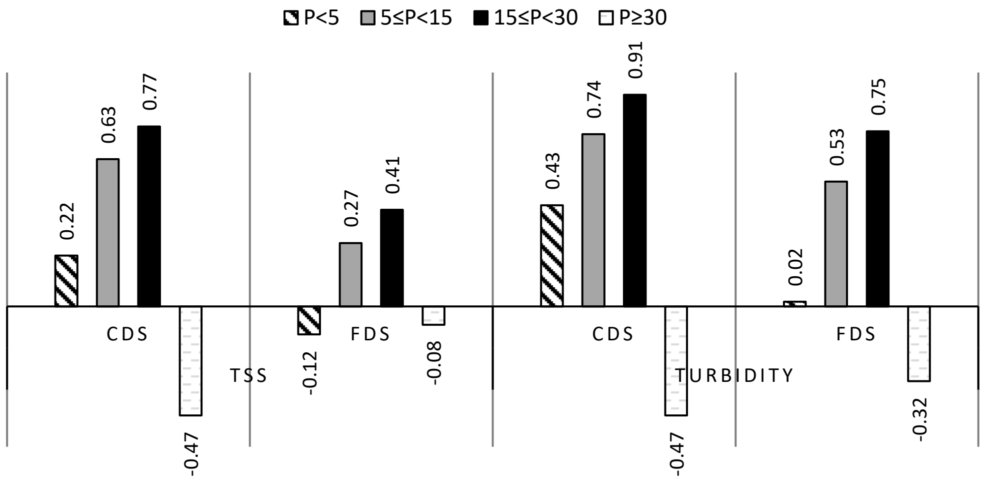


Figure 4.17: Correlation of Ammonia Concentration with Turbidity and TSS with Precipitation Intensity at the Controlled Drainage Structures (CDS) and Free Drainage Structures (FDS)
Rainfall events were categorized as low (5 mm<P), moderate (5 mm≤P<15 mm), high (15mm≤P<30mm) or very high (P≥30 mm).

Previous studies in southeastern Ontario have found ammonia concentrations to be similar between the CDS (0.05±0.12 mg NH_4^+-N L^{-1}) and the FDS (0.06±0.29 mgL^{-1} NH_4^+-N) (2016). In comparison to this study, the concentration of ammonia was 0.20±0.19 mg NH_4^+-N L^{-1} at the CDS and 0.39±0.42 mg NH_4^+-N L^{-1} at the FDS during the GS-W and was noted to be significantly different. The ammonia concentrations were found to be similar in the present study in the GS-D and the NGS, however, the concentration of ammonia was observed to be significantly higher at the FDS during the GS-W and 47% lower at the CDS. Other studies have reported daily fluxes for ammonia of $1.15 \times 10^{-4} \pm 4.99 \times 10^{-4}$ kg N ha^{-1} d^{-1} at the CDS compared to the $2.73 \times 10^{-4} \pm 1.12 \times 10^{-3}$ kg N ha^{-1} d^{-1} at the FDS, notably with CDS achieving an average daily flux reduction of 51% (Sunohara et al., 2016).

Pond-Wetland System

Average ammonia concentration and average daily flux data for the pond-wetland system are also presented in **Table 4.8**. The mean ammonia concentration over the study period at the pond-wetland inlet, Weir 1 (0.28±0.53 mg NH_4^+-N L^{-1}), was very similar to that at the pond-wetland outlet, Weir 4 (0.27±0.48 mg NH_4^+-N L^{-1}, ANOVA $p>0.05$) and represents approximately 3% of the total nitrogen in the system at Weir 1 and approximately 6% at Weir 4. Ammonia concentration reductions of 27% were observed between the pond inlet and outlet during the GS-D.

The NH_4^+-N concentration ranged between 0.05-5.68 and 0.05-5.33 mg NH_4^+-N L^{-1} at the pond inlet (Weir 1) and the pond-outlet (Weir 4), respectively. The unionized ammonia concentration was calculated and compared against the PWQO of 0.020 mg NH_3-N L^{-1} (PWQO, 1994) and CCME guideline value of 0.019 mg L^{-1}. The concentration of unionized ammonia met the PWQO criteria 65% of the time at Weir 1 and 66% of the time at Weir 4, with exceedances observed during the GS-D and the NGS. The ammonia concentration exceeded the criteria by a factor of two 20% of the time at Weir 1 and 14% of the time at Weir 4 and by a factor of three 9% of the time at Weir 1 and 2% of the time at Weir 4. The pond-wetland inlet (Weir 1) exceeded the 96-hr LC_{50} limit for freshwater invertebrates and fish species, whereas the pond-wetland outlet (Weir 4) met both the 48 and 96-hr LC_{50} limits for freshwater invertebrates and fish species in all cases (Environment Canada, 1999).

Mass Flux

Even though negligible change in concentration (3%) was observed over the total study period between Weir 1 and Weir 4, ammonia concentration was reduced in GS-W and GS-D ($p<0.05$)

by 33 and 27%, respectively, while concentrations increased in NGS by 101%. The same trend was observed with average daily flux decreasing in GS-W and GS-D, while increasing in NGS, however with a 17% decline observed over the entire study period. The reductions observed in the GS-W and GS-D could be due to a combination of aquatic plant uptake and increased nitrification during periods of increased residency time due to low precipitation. The pond-wetland released ammonia during the NGS, suggesting increased ammonification of decaying plant matter during this period.

Nitrate is the electron acceptor during both ammonification and denitrification. Aquatic systems can favour either ammonification or denitrification under different environmental conditions. A study by Kraft et al. (2014) compared the response of nitrite and nitrate incubations to favour nitrate/nitrite ammonification or denitrification and reported that the carbon/nitrogen ratio, pH, nitrite versus nitrate concentration, soil sand content, availability of fermentable carbon compounds, temperature, and sulfide concentration are environmental factors that affect nitrate pathways. As the concentration of ammonia increased by a factor of two in the NGS, the data suggests that ammonification exceeded nitrification and plant uptake in the NGS, possible due to decaying biological matter. Resuspension of particulate matter containing bound ammonia could also have played a role in the higher concentrations observed if particulate-bound ammonia concentration in runoff resulted in increased solubilization in the GS-W.

The cumulative ammonia mass flux was the greatest in descending order at the GS-W, NGS and GS-D at all locations **(Figure 4.16)**. This pattern correlates closely with the magnitude of flow observed in the same order at the Weir 1 and Weir 4. A decrease of 19% in cumulative mass flux was observed between Weir 1 and Weir 4 over the study period.

Conclusion

The ammonia concentration was consistent at the CDS through the seasons and was highest in the GS-W at the FDS decreasing to the levels at the CDS by the NGS. The elevated mean ammonia concentration at the FDS during the GS-W is related to periodic spikes at the FDS during this period presumed to result from antecedent soil conditions in the FDS plots. Ammonia concentration at the CDS was statistically different by 49% than at the FDS during the GS-W. The mean ammonia flux was higher at the CDS by 39% (GS-W) and lower by 54% (GS-D) and 66% (NGS). The effect on flux reduction during the GS-D and NGS has been attributed partially to the implementation of the drainage structures due to the retention of flow in the GS-D and partially to the plots themselves due to the reduction observed in the NGS. A correlational analysis of potential particulate ammonia movement during high intensity precipitation events suggests that particulate dissolution of ammonia occurred primarily during medium and high rainfall events at both the CDS and FDS, however, that this effect was superseded by the dilution effect during very high rainfall events. The concentration of unionized ammonia met the PWQO criteria of 0.020 mg NH_3-N L^{-1} 81% of the time at both the CDS and FDS during the study period. The percentage of exceedances was highest in the GS-D at the CDS (24%) in comparison the FDS (13%) and were lower at the CDS during the GS-W (CDS: 31%; FDS: 35%) and in the NGS (CDS: 0%; FDS 8%).

The mean ammonia concentration over the study period at the pond-wetland inlet, Weir 1 (0.28±0.53 mg NH_4^+-N L^{-1}), was very similar to that at the pond-wetland outlet, Weir 4 (0.27±0.48 mg NH_4^+-N L^{-1}) over the study period but was found to be statistically different by 27% during the GS-D ($p<0.05$). The pond-wetland removed 17% median daily ammonia flux and 23% cumulative daily flux during the study period. The mean flux removal at the pond-wetland was highest at 61%, during the GS-D. The reductions observed in the GS-W and GS-D could be due to a combination of aquatic plant uptake and increased nitrification during periods of increased residency time due to low precipitation. The pond-wetland released ammonia during the NGS, suggesting increased ammonification of decaying plant matter during this period. The concentration of unionized ammonia met the PWQO criteria of 0.020 mg NH_3-N L^{-1} 65% of the time at Weir 1 and 66% of the time at Weir 4, with exceedances observed during the GS-D and the NGS. The ammonia concentration exceeded the criteria by a factor of two 20% of the time at Weir 1 and 14% of the time at Weir 4 and by a factor of three 9% of the time at Weir 1 and 2% of the time at Weir 4. A summary table is shown below comparing the cumulative ammonia flux between the CDS and the FDS, and the inlet and the outlet of the pond-wetland during the individual periods considered.

Table 4.8: Cumulative Daily Ammonia Percent Difference at Drainage Structures and Weirs by Season

Percent Difference (%)	Study Period	GS-W	GS-D	NGS
FDS-CDS	-	-32	82	63
Pond-Wetland	21	26	56	-7

The percent difference in cumulative ammonia flux between the FDS and the CDS (FDS-CDS) and between the inlet, Weir 1, and the outlet of the pond-wetland (Pond-Wetland) have been shown above. The negative percent difference observed in the GS-W is indicative of greater outflow from the CDS during the GS-W.

In comparison to the FDS, the CDS reduced ammonia flux during the GS-D and NGS. The lack of reduction observed in the GS-W is most likely a result of the increased flow observed at the CDS during the GS-W. The pond-wetland reduced ammonia flux in the GS-W and the GS-D, averaging annually at 21% for the study period, with lower reduction noted in the NGS.

iii. Nitrate

Nitrate is the most oxidized form of nitrogen. Organic forms of nitrate can be biologically transformed into ammonia through ammonification and all inorganic forms of nitrogen can undergo nitrification for conversion to nitrate in surface water under oxic or aerobic conditions. The Canadian water quality guideline for the nitrate ion for the protection of aquatic life in freshwater is 3 mg NO_3^--N L^{-1} for long-term exposure and 124 mg NO_3^--N L^{-1} for short-term exposure (CCME, 2012). The provincial drinking water quality standards for nitrate is 10 mg NO_3^--N L^{-1} in Ontario (Canada, 2014).

Subsurface Drainage

The nitrate concentration varied considerably between 2.29 and 13.03 mg NO_3^--N L^{-1} with CDS nitrate concentration decreasing during the GS-D. FDS nitrate concentrations showed important reductions following the three largest precipitation events July 24th and Aug 2nd and Oct 29th **(Figure 4.18)**. Nitrate concentrations were significantly different between the CDS and FDS in all periods. The mean nitrate concentration at the CDS was higher than the FDS in GS-W and NGS and importantly lower by a factor of two in the GS-D (5±2 mg NO_3^--N L^{-1} (CDS) vs 9±1 mg NO_3^--N L^{-1} (FDS)), resulting in a percent difference of 43%. The reduction in CDS nitrate concentration in GS-D can be attributed to drainage water management and was most likely related to the increased plant uptake and the promotion of a denitrifying environment due to the reduction in tile flow at the CDS during the GS-D. Decreased tile flow would result in decreased oxygen diffusion from rainwater percolation through soil providing suitable anoxic conditions for the proliferation of denitrifying bacteria.

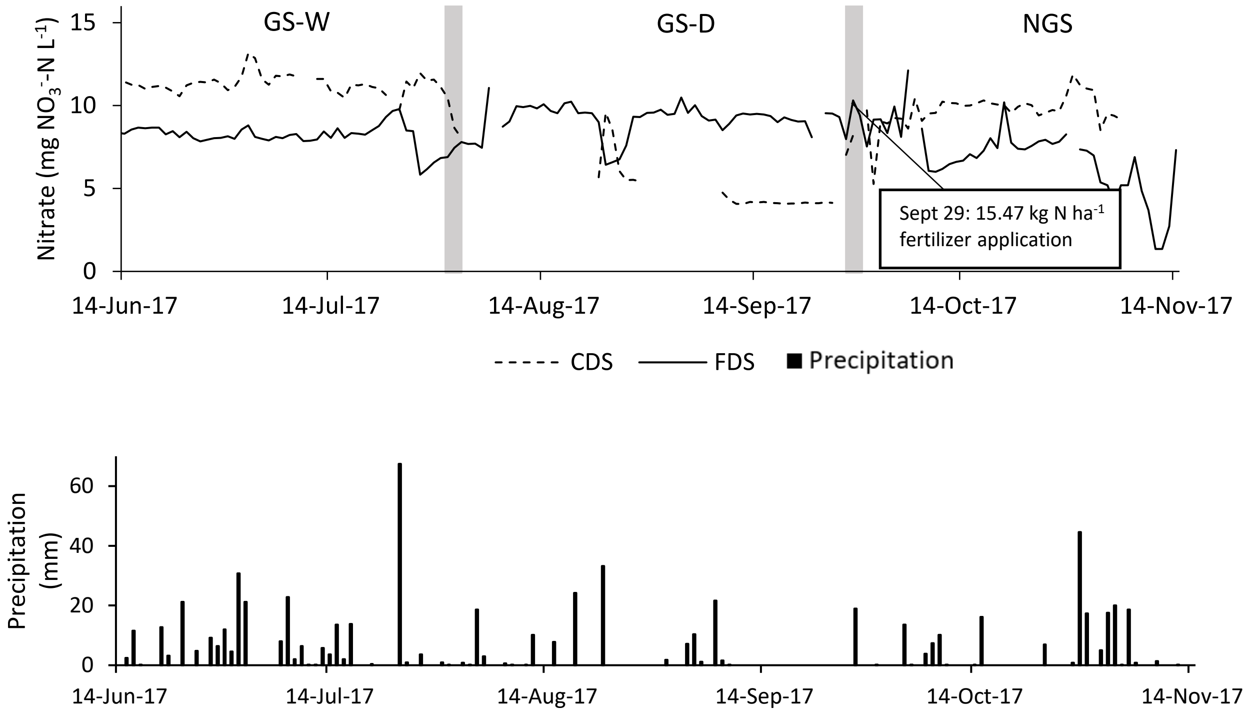


Figure 4.18: Daily Nitrate Concentration at Controlled Drainage Structures and Free Drainage Structures Between June 14 to November 14, 2017.

Note: Samples taken by the ISCO automated sampler on days without flow have been assumed to be representative of stagnant water and have been excluded from the dataset above.

The cumulative NO_3^--N mass flux was highest in the GS-W at all locations, followed by the NGS then GS-D **(Figure 4.19)**. In the GS-W, the CDS exported twice as much nitrate mass (5.1 kg NO_3^--N ha^{-1}) than the FDS (2.5 kg NO_3^--N ha^{-1}). During this period, the pond-wetland attenuated 55% of the cumulative nitrate flux. In contrast, the FDS exported more than three times the nitrate mass of the CDS during the GS-D (percent difference of 75%) and the CDS attenuated nitrate by 17% in the NGS compared to the FDS. The percent difference between the CDS and the FDS in the NGS shows that nitrate flux reduction is partly inherent to the field itself, however, accounting for the 17% in the NGS, an argument can be made that the contribution to nitrate mass flux reduction in dry periods of the CDS is 58%. The cumulative nitrate flux was similar between Weirs 1 and 4 during the GS-D (W1: 0.1; W4: 0.2 kg NO_3^--N ha^{-1}) and the NGS (both W1 and W4: 1.4 kg NO_3^--N ha^{-1}).

Table 4.9: 2017 Mean Daily Nitrate Concentration and Cumulative Nitrate Mass Flux at the Drainage Systems and Pond

Drainage structures were controlled (CDS) at CDS 1 and CDS 2, and free (FDS) at FDS 3,4 and 5. A weir (Weir 1) was installed at the pond-wetland inlet and at the outlet (Weir 4).

Period	Mean Nitrate Concentration (mg NO_3^--N L-1)					
	FDS[a]	CDS[b]	Difference (%)	Weir 1	Weir 4	Difference (%)
GS-W	**8.3±0.7**	**11.1±0.6**	**-35**	**8.1±3.4**	**5.6±2.4**	**31**
GS-D	**9.0±1.4**	**5.1±1.6**	**43**	**1.8±1.5**	**2.5±1.5**	**-42**
NGS	**7.9±1.4**	**9.6±1.6**	**-22**	**2.2±2.3**	**2.8±2.5**	**-28**
Study Period	-	-	-	**4.1±3.8**	**3.5±2.5**	**13**
	Mean Daily Mass Flux (x10^2 kg N ha^{-1})					
	FDS	CDS	Difference (%)	Weir 1	Weir 4	Difference (%)
GS-W	**5.64±10.16**	**11.75±20.26**	**-108**	0.132±0.206	0.068±0.113	48
GS-D	**1.84±1.10**	**0.99±1.92**	**46**	0.002+0.003	0.0037±0.046	-122
NGS	6.63±12.16	4.34±8.12	35	0.033±0.063	0.033±0.075	-3
Study Period	-	-	-	0.057±0.136	0.033±0.080	41

Notes: [a] The average of FDS 3-5 were taken to present FDS values. In the NGS, mean FDS values have been calculated using data between September 28-November 6 to compare to CDS as there is no data at the CDS after November 6, 2017.

[b] The average of CDS 1 and 2 were taken to present CDS values.

[c] Composite samples were used to calculate mean ammonia, nitrate and SRP at Weirs 1 and 4 due to the collection of unrepresentative solids in the composite weir samples.

Bolded*:* Bolded denotes a statistically significant difference between CDS and FDS, p<0.05 using an Analysis of Variance test.

Bold: Bolded with a grey background denotes a statistically significant difference between Weir 1 and Weir 4, p<0.05 using a paired t-test.

Italicized: Italicized denotes a statistically significant difference, p<0.1 using a paired T-test.

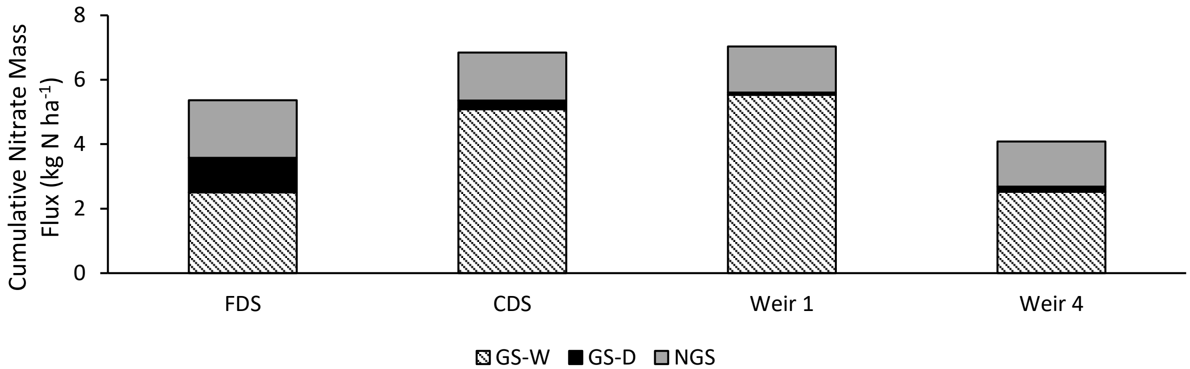


Figure 4.19: Cumulative Nitrate Flux at the Controlled Drainage Structures (CDS), Free Drainage Structures (FDS) and Pond-Wetland during the study period (June 14-November 14, 2017).
The study period was divided into the wet period of the growing season (GS-W: June 14 – July 31, 2017) the dry period of the growing season (GS-D: August 1 – September 27, 2017) and the non-growing season (NGS: September 28 – November 14, 2017) due to the availability of flow and concentration data at the drainage structures. The termination of the data set varied between November 3 -6 for the CDS and between November 11 – November 14, 2017 for the FDS. The pond-wetland inlet has been defined as Weir 1 and the outlet as Weir 4.

DWM has not shown to impact NO_3^--N concentration in the majority of previous studies. Sunohara et al. (2016) compared the effect of paired field systems of controlled and free tile drainage for nine growing seasons (May to October in 2005-2013) on NO_3^--N concentration and average daily NO_3^--N mass. During this period, the NO_3^--N concentration was 6.30 ± 2.98 mg NO_3^--N L^{-1} at the CDS and 6.33 ± 3.50 mg NO_3^--N L^{-1} at the FDS. In the present study, NO_3^--N concentration was higher in the CDS than the FDS in the GS-W and the NGS, suggesting a plot effect, and significantly lower than the FDS during the GS-D, which can be attributed to the control structures damming water in the fields. The concentration in the present study was 5.1±1.6 mg NO_3^--N L^{-1} at the CDS and 9.0±1.4 mg NO_3^--N L^{-1} at the FDS during the GS-D with an average reduction of 43%. In contrast, the concentration at the CDS during the GS-W and the NGS were 11.6±0.6 and 10.3 ± 2.4 mg NO_3^--N L^{-1} compared with concentrations at the FDS of 8.3±0.7 and 7.9±1.4 mg NO_3^--N L^{-1} for the two periods, respectively, suggesting that the implementation of drainage structures during wet periods does not affect nitrate concentrations and the CDS fields had inherently higher nitrate concentrations than the FDS fields (plot effect). In contrast to previous studies in literature, the study period of the present period was split into the three distinct sub-periods, which contributed to the observation that controlled drainage structures can promote nitrate attenuation in the dry periods of the growing season, with the likely primary mechanism of removal being denitrification and plant uptake possibly also playing a role.

Nitrate mass reduction as a result of drainage water management is well-documented in literature. A review by Skaggs et al. in 2012 compared the findings of thirteen field studies and found that the effectiveness of drainage water management on the reduction of nitrogen loss to surface waters varied between 18% to more than 75%. Daily fluxes for NO_3^--N were 1.79 x 10^{-2} ±6.37x10^{-2} kg ha^{-1} d^{-1} at the CDS compared to the 3.64 x 10^{-2}±1.26 x 10^{-1} kg ha^{-1} d^{-1} at the FDS in the study conducted by Sunohara et al. (2016) achieving an average reduction of 60% at the CDS. In this study, the mean daily NO_3^--N flux as 0.99x10^{-2}±1.92 x10^{-2} kg NO_3^--N ha^{-1} at the CDS and 1.84 x10^{-2}±1.10 x10^{-2} kg NO_3^--N ha^{-1} at the FDS in the GS-D, achieving a total reduction of 43% at the CDS. Other studies in Canadian climate have demonstrated NO_3^--N concentration reduction by controlling the water table with results similar to this study. Lalonde et al. (1996) reported a NO_3^--N concentration (mg L^{-1}) reduction of 46.9% and 19.0% by controlling the water table to 0.25 m and 0.50 m in 1992 and 37.5% and 41.7% in 1993, respectively, above the drain in an Ontario study conducted in loam (sandy loam to loam to clay loam). Similar to the present study, Lalonde et al. removed the drains in autumn to prevent cracking of pipes due to winter conditions, and the study was conducted between April-August in 1992 and between June-

November in 1993. Lalonde et al. (1993) reported a period of denitrification in November 1993 where the concentration of nitrate had decreased to 0.0 mg L N^{-1} suggesting that the implementation of controlled drains for a longer period of time may have sustained denitrification until November 1993. As samples collected during periods without flow are not presented in the present study, the denitrification stage reported in Lalonde et al. (1993) cannot be accurately compared to the present study. However, it appears that the drains implemented at 0.25 m outperformed the 0.5 m in both 1992 and 1993 suggesting an effect of the field as opposed to the depth itself. Drury et al. (2001) reported a decrease in total tile discharge by 26%, flow-weighted mean nitrate concentration (mg N L^{-1}) by 39% and total NO_3^--N loss in tile discharge (kg N ha^{-1}) by 55% of controlled versus free drainage during a continuous corn cycle and total discharge by 38%, nitrate concentration by 45% and total NO_3^--N loss by 66% in a soybean-corn rotation. During the GS-D, the reduction of NO_3^--N concentration of 43% and flux of 46% achieved at the Bercier farm is within the range reported in published literature as reported by Drury et al. (2001).

The pattern seen of NO_3^--N loss being higher at the CDS during the GS-W followed by a decrease in the GS-D and a subsequent increase in the NGS has not been described extensively in previously literature. Drury et al. (2009) observed that NO_3^--N loss in tile drainage can be variable across seasons: in 1996, Drury et al. observed the majority of NO_3^--N loss as occurring in the NGS, however, the NO_3^--N loss in tile drainage was comparable between the GS and the NGS in 2009. Elmi et al. (2005) reported nitrogen gas losses as N_2O and N_2O + N_2 and observed that N_2O + N_2 evolution rates were twice the magnitude in CDS than FDS, supporting the hypothesis that denitrification is the primary mechanism of nitrate reduction observed in GS-D in this study.

Pond-Wetland System

The mean nitrate concentrations at Weirs 1 and 4 were elevated in the GS-W (6-8 mg L^{-1}) and were lower in the GS-D and NGS (2-3 mg L^{-1}) as seen in **Table 4.9**. The mean nitrate concentration at the pond-wetland inlet, Weir 1, was 4.1±3.8 mg NO_3-N L^{-1} and statistically different from Weir 4 at 3.5±2.5 mg NO_3-N L^{-1}, resulting in net reduction of 13% during the study period (ANOVA $p \leq 0.05$). The pond-wetland reduced nitrate concentration by 31% in the GS-W, while moderately increasing in concentration during GS-D and NGS. The mean nitrate concentration was in exceedance of the provincial drinking water quality standards for nitrate of 10 mg NO_3^--N L^{-1} at the CDS in the GS-W (Government of Canada, 2014), and in exceedance of the federal CCME water quality guidelines for the nitrate ion for the protection of aquatic life (2.94 mg NO_3^--N L^{-1}) at all DS and Weir 4 across all periods of study (CCME, 2003). The mean nitrate mass loading at Weir 1 was 0.057±0.136 kg NO_3^--N ha^{-1} d^{-1} and 0.033±0.080 kg NO_3^--N ha^{-1} d^{-1} at Weir 4, achieving a mean reduction of 41% during the study period.

The concentration of nitrate was expected to be higher at the pond-inlet, Weir 1 than at Weir 4, and comparable to the concentrations observed at the CDS and the FDS. While the concentration of nitrate was similar at Weir 1 compared to the CDS and the FDS during the GS-W, the concentration was between 2-5 times lower at Weir 1 during both the GS-D and the NGS. One explanation for this phenomenon is that in addition to collecting overland flow and drainage water, the drainage ditch leading to Weir 1 was acting as a biofilter due to the presence of reeds and vegetation resulting in nitrate bio-assimilation by the vegetation upstream of Weir 1. However, this behaviour would have been more prevalent in the GS-W and the decreased nitrate concentration was observed between the GS-D and the NGS. An alternative explanation of this phenomenon would be the accretion of denitrifying sediment in the drainage ditch resulting in nitrate denitrification later in the season. Nevertheless, the data suggests that the drainage ditch itself operates as a nutrient attenuation system for nitrate in the GS-D and NGS, while the pond-wetland attenuates nitrate in the GS-W.

In a study by Bennion and Smith (2000) comparing the water chemistry at 31 shallow ponds in southeast England, nitrate displayed consistent seasonality where nitrate concentrations were highest in the winter and early spring and lowest through summer and autumn. The authors reported that this pattern is commonly observed in temperate lakes and attributed to microbial assimilation of nitrate (algae in lakes and ponds) as well as anaerobic conditions for denitrification to occur in shallow ponds decreasing the nitrate concentration during the spring and summer, and consequent increase in the winter due to decreased microbial uptake. This phenomenon was noted in both Weir 1 and 4. The elevated concentration of nitrate in the GS-W is attributed to the aerobic conditions due to high intensity precipitation and decreasing nitrate concentrations of the summer and fall to denitrification conditions.

Overall, nitrate correlated weakly with precipitation at the CDS and Weir 1 ($R<0.20$) and this correlation increased in magnitude with a time delay when comparing nitrate concentration to precipitation of the preceding day ($R<0.30$). The low correlation was unexpected and is most likely confounded by the differences in the seasonal mean nitrate concentrations at both the pond-wetland and the CDS. Flow was weakly correlated with nitrate concentration at Weir 4 and moderately at Weir 1 and the CDS; this correlation increased in magnitude with time delay at all three locations ($R<0.40$).

Conclusion

The mean nitrate concentration at the CDS was 11±1 mg NO_3-N L^{-1} and 8±1 mg NO_3-N L^{-1} at the FDS during the GS-W. The nitrate concentration at the CDS decreased in the GS-D to 5±2 mg NO_3-N L^{-1} and increased at the FDS to 9±2 mg NO_3-N L^{-1}, resulting in a percent difference of 43%. The mean nitrate concentration at Weir 1 was 4.1±3.8 mg NO_3-N L^{-1} and 3.5±2.5 mg NO_3-N L^{-1} at Weir 4. The pond-wetland achieved a mean concentration reduction of 13% during the study period. The concentration of nitrate decreased during the GS-D at the CDS and the Weirs likely as a combined result of denitrification in anoxic conditions due to lack of flow at the CDS and denitrification, algal and plant uptake in the shallow ponds. The cumulative nitrate mass loading was 6.84 kg ha^{-1} (CDS) and 5.37 kg ha^{-1} (FDS) during the study period. In comparison to the FDS, the percent difference in nitrate mass at the CDS was 75% in GS-D and 17% in the NGS. The mean nitrate mass loading at Weir 1 was $5.7 \times 10^2 \pm 13.6 \times 10^2$ kg $d^{-1}ha^{-1}$ and $3.3 \times 10^2 \pm 8.0 \times 10^2$ kg $d^{-1}ha^{-1}$ at Weir 4, resulting in a mean reduction of 41% during the study period. A strong correlation was not observed between precipitation intensity and nitrate concentration. A summary table is shown below comparing the cumulative nitrate flux between the CDS and the FDS, and the inlet and the outlet of the pond-wetland during the individual periods considered.

Table 4.10: Cumulative Daily Nitrate Flux Percent Difference at Drainage Structures and Weirs by Season

Percent Difference (%)	Study Period	GS-W	GS-D	NGS
FDS-CDS	-	-103	75	17
Pond-Wetland	42	54	-151	2

The percent difference in cumulative nitrate flux between the FDS and the CDS (FDS-CDS) and between the inlet, Weir 1, and the outlet of the pond-wetland (Pond-Wetland) have been shown above. The negative percent difference observed in the GS-W is indicative of greater outflow from the CDS during the GS-W.

In comparison to the FDS, the CDS reduced nitrate flux during the GS-D and NGS. The lack of reduction observed in the GS-W is most likely a result of the increased flow observed at the CDS during the GS-W. The pond-wetland reduced nitrate flux in the GS-W, averaging at 42% for the study period, with lower reduction noted in the GS-D and NGS. The mean nitrate concentration was in exceedance of the provincial drinking water quality standards for nitrate of 10 mg NO_3^--N L^{-1} at the CDS in the GS-W (Government of Canada, 2014), and in exceedance of the federal CCME water quality guidelines for the nitrate ion for the protection of aquatic life (2.94 mg NO_3^--N L^{-1}) at all DS and Weir 4 across all periods of study (CCME, 2003).

4.4.3. Phosphorus: Total Phosphorus and Soluble Reactive Phosphorus

iv. Total Phosphorus

Phosphorus is the limiting nutrient for algal growth in freshwater systems. Trigger ranges have been established to delineate trophic strata of lakes and rivers: ultra-oligotrophic (<4 µg L^{-1}), oligotrophic (4-10 µg L^{-1}), mesotrophic (10-20 µg L^{-1}), meso-eutrophic (20-35 µg L^{-1}), eutrophic (35-100 µg L^{-1}) and hyper-eutrophic (>100 µg L^{-1}) (CCME, 2004). These ranges are useful in assessing the trophic level of a system and allow for the prediction of environmental impacts or potential degradation. The CCME phosphorus guideline follows a framework where phosphorus concentrations should not exceed the predefined trigger ranges and increase more than 50% over the baseline levels. The Interim PWQO for TP is established as a general guideline such that average TP concentrations for the ice-free period should not exceed 20 μg L^{-1}, protection against aesthetic deterioration is provided at 10 μg L^{-1} or less, and excessive plant growth in rivers and streams can be protected at TP concentrations below 30 μg L^{-1}.

The mean daily TP concentration at Weir 1 was 0.24±0.28 mg P L^{-1} (median 0.14 mg P L^{-1}) and 0.19±0.13 mg P L^{-1} (median 0.14 mg P L^{-1}) at Weir 4 for the study period **(Table 4.11)**. The pond-wetland achieved a mean reduction of 21% and median reduction of 3% during the study period and can be classified as hyper-eutrophic. There was no statistical difference between the mean concentration of TP at Weirs 1 and 4 (paired T-test p= 0.38; ANOVA p-value: 0.50). Particulate phosphorus represented 62% of the total phosphorus concentration at Weir 1 and 56% at Weir 4.

Table 4.11: 2017 Mean Daily Concentration of Total Phosphorus between Weirs 1 and 4

	Mean TP (mg P L^{-1})		Median TP (mg P L^{-1})		Paired t-test	ANOVA p-value	Mean TP Flux (kg P $d^{-1}ha^{-1}$ x 10^{-3})		Median TP Flux (kg P $d^{-1}ha^{-1}$ x 10^{-3})	
	Weir 1	Weir 4	Weir 1	Weir 4			Weir 1	Weir 4	Weir 1	Weir 4
Study Period	0.24±0.28	0.19±0.13	0.14	0.14	0.38	0.50	0.77±0.71	0.47±0.51	0.51	0.25

Inflow into Weir 1 incorporated both tile drainage and surface runoff. Weir 1 TP concentration spanned a range of 0.07-1.10 mg P L^{-1}. Van Esbroeck et al. (2016) reported instantaneous P concentrations in tile drain effluent between <0.01 to 0.35 mg TP/L and peak TP concentrations up to 2.17 mg L^{-1} following rainstorms over a study period spanning October 2011 to April 2013. The range of TP concentration observed at the pond-wetland influent, Weir 1, falls within the range of TP concentration in drainage influent that has been previously described by other authors. The variability in the TP concentration and mass flux is demonstrated in the figure below.

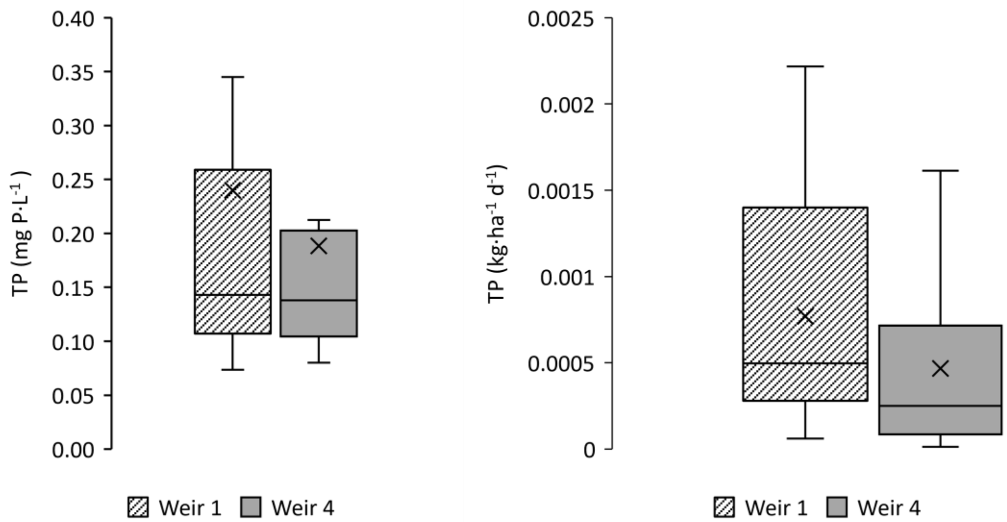


Figure 4.20: Distribution of Total Phosphorus Concentration (mg L^{-1}) at Weirs 1 and 4

The concentration of TP leaving the combined controlled drainage and pond-wetland system at Weir 4 spanned a range of 0.08-0.47 mg P L^{-1}. TP concentrations greater than or equal to 0.02-0.03 mg L^{-1} promote algal blooms (King et al., 2015). The TP concentration at the pond-wetland outlet was between 4-40 times greater than the applicable criteria.

The average TP mass flux was 0.77±0.71 $x10^{-3}$ kg d^{-1} ha^{-1} (Weir 1) and 0.47±0.51 $x10^{-3}$ kg d^{-1} ha^{-1} (Weir 4) and the median TP mass flux was $0.49x10^{-3}$ kg d^{-1} ha^{-1} (Weir 1) and 0.25 $x10^{-3}$ kg d^{-1} ha^{-1} (Weir 4) for the study period. The cumulative TP mass flux was 0.24 kg ha^{-1} at Weir 1 and 0.15 kg ha^{-1} at Weir 4 implying a removal of 0.09 kg ha^{-1} TP for the complete study period. A study by Van Esbroeck et al. (2016) quantified the total phosphorus in surface runoff and tile drainage from three reduced tillage fields in Ontario and reported that the tiles exported between 0.169 and 0.255 kg TP ha-^{1} yr^{-1} and a combined (tile and surface) TP load between 0.332 kg TP ha^{-1}

and 0.419 kg TP ha^{-1} between May 2012 and April 2013. The normalized cumulative TP flux at Weir 1 was within the range of the tile effluent export and lower than the range of the combined effluent export. The TP mass flux removal efficiency were categorized as: mean 43%, median 51% and cumulative 38%. A review of wet detention ponds by Harper and Baker (2007) reported a removal range of 39-93% for TP and a mean removal efficiency of 69%. In comparison to this study, the TP removal of the presented pond falls within this range.

A weak negative correlation was observed between TP and flow at Weir 4 (R=-0.20) and Weir 1 (R=-0.31) and between precipitation and TP at Weir 1 (R=-0.17). A weak negative correlation was observed between the fraction of particulate phosphorus and precipitation at Weir 1 (R=-0.11) and at Weir 4 (R=-0.24). It was hypothesized that precipitation events would cause the release of sediment-bound particulate phosphorus, resulting in peak concentration events correlated with peak precipitation events as seen by Van Esbroeck et al. (2016). However, the pattern of weak correlations suggests an effect of dilution by precipitation on particulate phosphorus, contradicting previous findings in literature. A strong correlation was observed between TP and TSS at Weir 1 (R =0.92). It was expected that a strong correlation would exist between TP and TSS at Weir 4 as well, however this was not found. There was a weak correlation between TP and TCOD at Weir 4 (0.17) and a moderate correlation at Weir 1 (0.65).

The mean TP concentration at Weir 1 was 0.24±0.27 mg P L^{-1} and 0.18±0.13 mg P L^{-1} at Weir 4 for the study period. The mean TP mass flux was 1.8±4.5 $x10^{-3}$ kg d^{-1} ha^{-1} (Weir 1) and 0.59±0.40 $x10^{-3}$ kg d^{-1} ha^{-1} (Weir 4) and a mean TP mass flux removal of 43%.

v. SRP

Phosphorus exists as inorganic orthophosphate, particulate phosphorus, and soluble organic phosphorus. Soluble inorganic orthophosphate ions are the only form of phosphorus that is directly taken up by aquatic plants. Aquatic plants convert inorganic phosphate into plant matter containing organic phosphate. While the filtration of a water sample for the measurement of orthophosphate overestimates the total biologically available phosphorus as all SRP following filtration may not be naturally bioavailable SRP (T. R. Fisher & Lean, 1992), a fraction of the total SRP in the sample represents the total bioavailable phosphorus to aquatic plants. Therefore, an evaluation of SRP concentration within a system is critical to the study of its eutrophication potential. Critical thresholds between 0.01-0.04 mg P L^{-1} have been reported to trigger eutrophication in freshwater systems (Zeng et al., 2016; Zhang et al., 2017). The daily concentration of SRP in drainage water at the CDS and FDS during the study period is presented below in **Figure 4.21**. The mean daily SRP concentration, flux, cumulative mass flux and mean percent change at the CDS, FDS and pond-wetland inlet and outlet have been presented in **Table 4.12**.

Subsurface Drainage

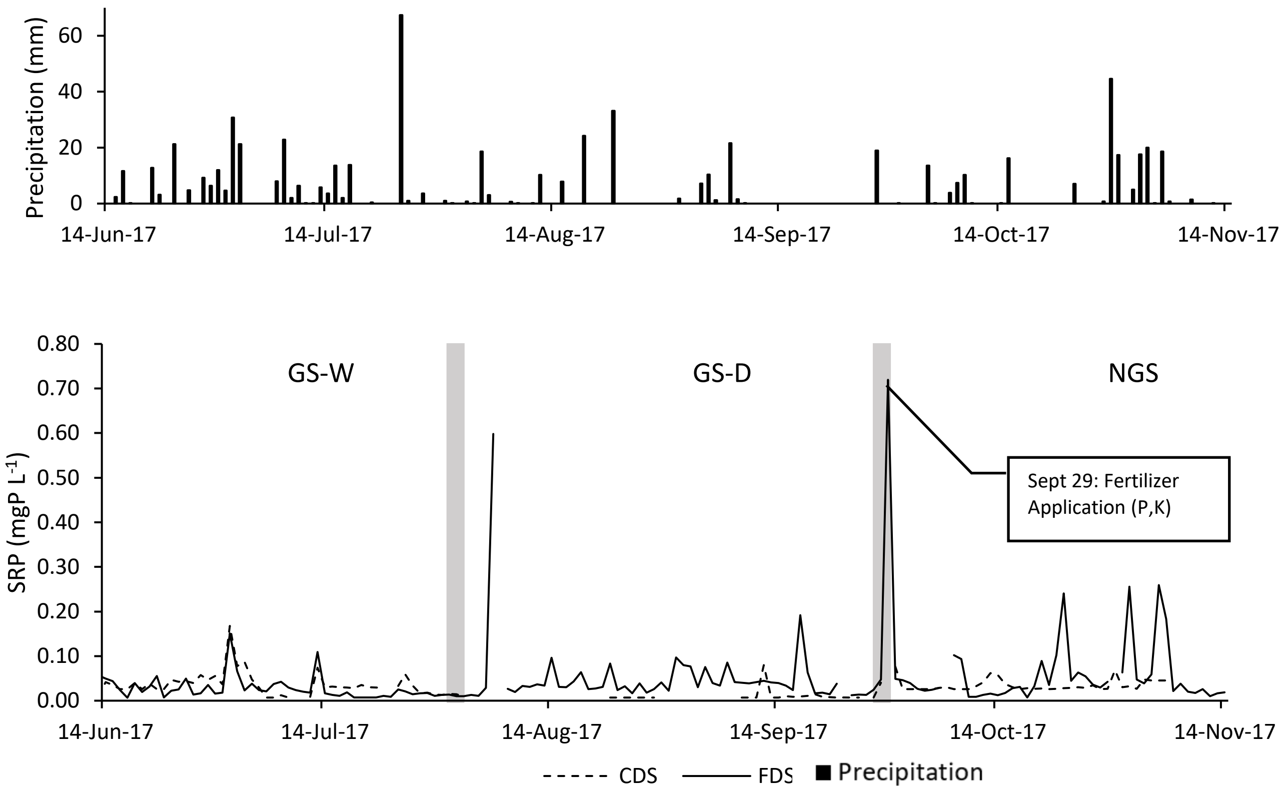


Figure 4.21: Soluble Reactive Phosphorus (SRP) Concentration (mgL^{-1}) in Daily Composite Samples from the Controlled Drainage Structures (CDS) and Free Drainage Structures (FDS) on Soybean Plots during the Study Period.
The study period was divided into the wet period of the growing season (GS-W: June 14 – July 31, 2017), the dry period of the growing season (GS-D: August 1 – September 27, 2017) and the non-growing season (NGS: September 28 – November 14, 2017) due to the availability of flow and concentration data at the drainage structures.
Note: Samples taken by the automatic sampler on days without flow have been assumed to be representative of stagnant water and have been excluded above.

Mean daily SRP concentration was higher at the CDS (0.041±0.031 mg P L^{-1}) than the FDS (0.027±0.026 mg P L^{-1}) during the GS-W (ANOVA $p>0.05$) but statistically different and lower in both GS-D (0.011±0.014 vs 0.045±0.056 mg P L^{-1}) and NGS (0.034±0.013 vs 0.084±0.170 mg P L^{-1}) (ANOVA $p<0.05$). The mean SRP concentration was lower by 76% (GS-D) and 60% (NGS) at the CDS compared to the FDS. The concentration of SRP was four times smaller at the CDS during the GS-D than during the GS-W or the NGS (GS-D $p<0.05$ compared to GS-W and NGS) as well as

76% lower than FDS indicating that damming the water had an effect on reducing SRP concentrations, potentially as a result of increased root uptake and/or increased residence time for adsorption. The significant difference observed between CDS and FDS SRP concentrations during NGS suggests a plot effect between the fields. A 19% decrease in the GS flow weighted mean DRP concentration was reported by Zhang et al. (2017) in Southwestern Ontario. Nash et al. (2015) reported that DRP concentrations were higher in the spring and an annual 60% decrease in DRP concentration was observed over a four-year period with DWM in Missouri. The higher concentrations observed in the GS-W related well with the findings of the study by Nash et al. (2015), however, the difference in SRP concentration between the CDS and the FDS appear to be greater than the averages described in literature. An increase or spike in SRP concentration was expected following the application of fertilizer on September 29, 2017 and this was observed at CDS 2 resulting in a concentration 3 times greater than background values (0.141 mg P L^{-1}) on September 30, 2017 and FDS 5 (2.079 mg P L^{-1}) resulting in a concentration 34 times greater than background values. The peaks observed at the FDS on September 29, 2017 and at the CDS on October 1, 2017 have been attributed to the application of fertilizer. The mean daily SRP concentration at the CDS met the 0.047 mg L^{-1} ecological threshold in the GS-W, the NGS and was 4 times lower in the GS-D. The FDS met this threshold in the GS-W, however, it exceeded the threshold in the GS-D and the NGS. The drainage effluent from the CDS met the second threshold for periphyton saturation in the GS-D.

The mean daily SRP flux was $1.5x10^{-5}$±$2.6\ x10^{-5}$ kg ha^{-1} d^{-1} at the CDS and $8.1x10^{-5}$±$2.8x10^{-5}$ kg ha^{-1} d^{-1} at the FDS during the GS-D resulting in a decrease in SRP mass loading of 82% at the CDS. The daily SRP flux was greater by 81% at the FDS in the GS-W and lower by 81% was seen in the NGS between the CDS and the FDS. The greater SRP flux observed during the GS-W is related to greater flow observed during this period at the CDS, and not SRP concentration. SRP loss in tile drainage was reduced by 44% with CDS in a Brookston clay loam soil in Southwestern Ontario (Zhang et al., 2017) and 80% on a Claypan soil in Missouri by Nash et al. (2015). The findings of this present study during the GS-D correlate well with the annual losses presented by Nash et al. (2015). The mean daily SRP flux showed that the pond-wetland attenuated SRP mass in the GS-W by 27% and released SRP during the other studied periods.

Table 4.12: 2017 Mean Daily Soluble Reactive Phosphorus (SRP) Concentration, Flux and Percent Change between the Drainage Structures and Pond-Wetland

Drainage structures were controlled (CDS) at CDS 1 and CDS 2, and free (FDS) at FDS 3,4 and 5. A weir (Weir 1) was installed at the pond-wetland inlet and at the outlet (Weir 4). The study period was divided into the wet period of the growing season (GS-W: June 14 – July 31, 2017) the dry period of the growing season (GS-D: August 1 – September 27, 2017) and the non-growing season (NGS: September 28 – November 14, 2017) due to the availability of flow and concentration data at the drainage structures.

Mean SRP Concentration (mg PO_4-P L^{-1})						
Period	FDS[a]	CDS[b]	Difference (%)	Weir 1	Weir 4	Difference (%)
GS-W	0.027±0.026	0.041±0.031	-41	0.06±0.03	0.08±0.08	-31
GS-D	**0.045±0.056**	**0.011±0.014**	**76**	0.11±0.11	0.16±0.20	-50
NGS	**0.084±0.170**	**0.034±0.013**	**60**	0.03±0.03	0.05±0.05	-55
Study Period	-	-		***0.07±0.14***	***0.11±0.14***	-151
Mean Daily SRP Mass Flux (x10^{-3} kg PO_4-P ha^{-1} d^{-1})						
Period	FDS	CDS	Difference (%)	Weir 1	Weir 4	Difference (%)
GS-W	*0.29±1.2*	*0.63±1.5*	*-81*	0.99±2.2	0.72±1.4	27
GS-D	**0.0081±0.2**	**0.015±0.026**	**82**	0.07±0.09	2.0±2.9	-179
NGS	**0.84±2.9**	**0.19±0.38**	**81**	4.0±7.6	6.2±1.4	-54
Total	--	--	--	0.49±1.4	0.51 ±1.1	-3

Notes: [a] The average of FDS 3-5 were taken to present FDS values. In the NGS, mean FDS values have been calculated using data between September 28-November 6 to compare to CDS as there is no data at the CDS after November 6, 2017.
[b] The average of CDS 1 and 2 were taken to present CDS values.
[c] Grab samples were used to calculate mean and median turbidity, TSS, TCOD, TP and TN at Weirs 1 and 4 due to the collection of unrepresentative solids in the composite weir samples.
Bold : Bolded and italicized in a grey background denotes a statistically significant difference between CDS and FDS, $p<0.05$ using a paired t-test.
Bold: Bolded and italicized denotes a statistically significant difference between Weirs 1 and 4, $p<0.05$ using an Analysis of Variance test.
Italicized: Italicized denotes a statistical difference using a paired t-test, $p<0.1$.

The cumulative SRP flux is presented in **Figure 4.22**. In the GS-W, the cumulative mass flux was considerably higher at the CDS compared to the FDS. Controlled drainage can increase tile flows during wet periods (Evans et al., 1995), which can partially explain this observation. In the GS-D, the controlled drains retained flow resulting in a decrease of 93% cumulative SRP mass flux at the CDS versus the free drains with both lower flows and lower concentrations contributing to the reduction. However, in NGS the SRP mass flux was lower by 79% at the CDS than the FDS, which suggests a field effect as the CDS experienced both lower flows and lower SRP concentrations than the FDS during the NGS when the stop logs had been removed.

Overall, the mean daily SRP mass flux for the study period was similar between the weirs, at 4.9 $x10^{-4}±1.4x10^{-3}$ kg PO_4-P ha^{-1} d^{-1} and 5.1 $x10^{-4}±1.1x10^{-3}$ ha^{-1} d^{-1}, however increased from the GS-W and was highest in the NGS.

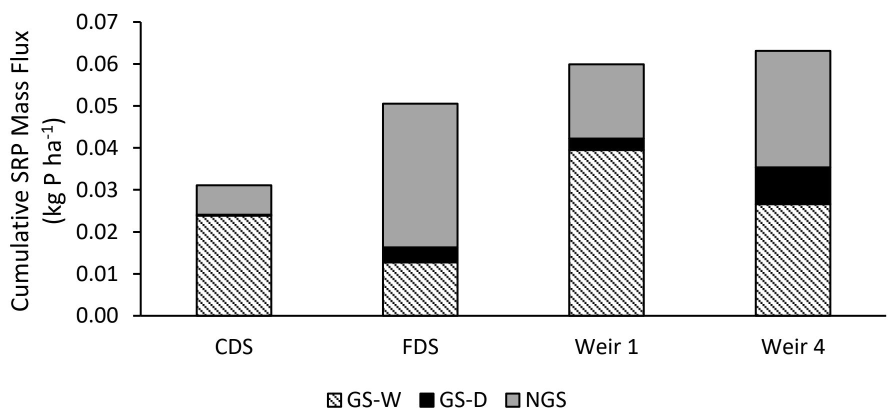


Figure 4.22: Cumulative Soluble Reactive Phosphorus (SRP) Flux at the Controlled Drainage Structures (CDS), Free Drainage Structures (FDS) and Pond-Wetland during the study period (June 14-November 14, 2017).
The study period was divided into the wet period of the growing season (GS-W: June 14 – July 31, 2017) the dry period of the growing season (GS-D: August 1 – September 27, 2017) and the non-growing season (NGS: September 28 – November 14, 2017) due to the availability of flow and concentration data at the drainage structures. The pond-wetland inlet has been defined as Weir 1 and the outlet as Weir 4.

A correlational analysis of SRP with TSS and turbidity and rainfall intensity showed moderate correlation with TSS during high and very high precipitation events at the CDS and strong correlation with TSS from medium to very high precipitation at the FDS, with similar but less pronounced correlations with turbidity **(Figure 4.23)**. This suggests that the CDS mitigated the movement of solids and related SRP resulting from medium storm events, whereas greater solids concentrations from larger precipitation events were correlated with greater SRP concentrations at the FDS, suggesting that in these events, the contributing SRP is attached to the solids or particulate-bound.

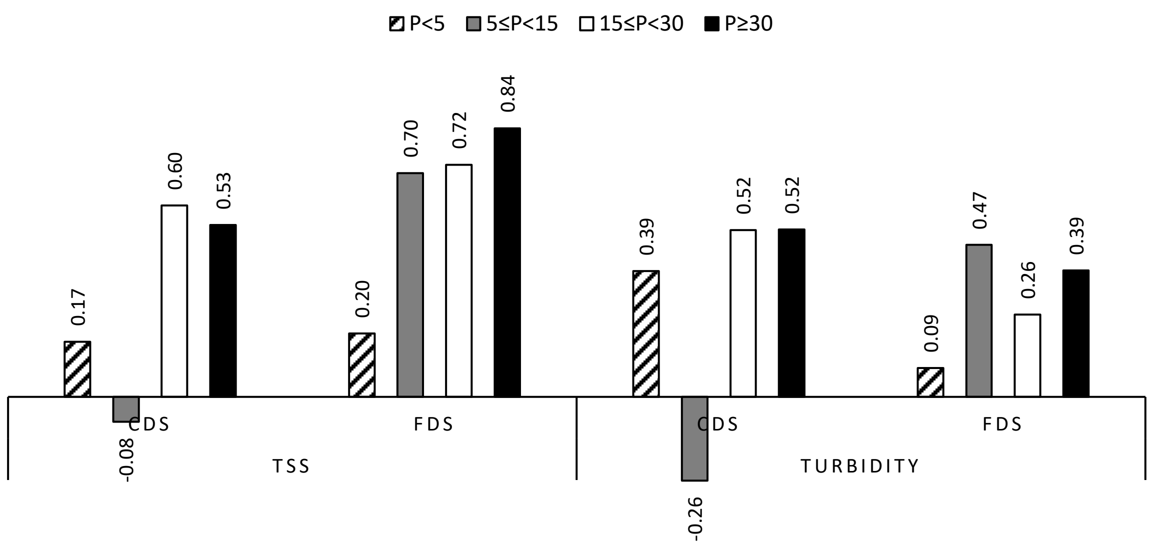


Figure 4.23: Correlation Between Total Suspended Solids (mg L^{-1} TSS) and Turbidity (NTU) and Soluble Reactive Phosphorus (SRP) Concentration at the Controlled Drainage Structures (CDS), Free Drainage Structures (FDS) categorized by Intensity of Precipitation during the Study Period

As discussed previously, the effectiveness of drainage water management on phosphorus retention has been shown to vary in previous studies. A study by Sunohara et al. (2016) reported slightly lower concentrations of DRP in drainage water and reductions of 66% for TP and 66% for DRP in drainage water fluxes in Southeastern Ontario as a result of controlling the water table in the growing season. Tan and Zhang (2011) reported a decrease of PP by 15% and TP by 12% in drainage water as a result of CDS implementation in a corn and soybean rotation on a Perth clay soil in Holiday Beach, Ontario during the GS. In this study, the mean SRP flux was 41% greater at the CDS in the GS-W, 82% lower in the GS-D and 81% lower in the NGS compared to the FDS. The greater SRP flux observed during the GS-W is related to greater flows observed during this period at the CDS, and not SRP concentration. However, high mean percent differences were observed in the NGS in concentration (60%) and in SRP mass (81%) and therefore, the observed effect is likely an effect of the variability of the fields as well as drainage water management.

Pond-Wetland System

The mean daily SRP concentration was 0.07±0.14 mg P L^{-1} at the pond-wetland inlet, Weir 1, and 0.11±0.14 mg P L^{-1} at the outlet, Weir 4, during the study period. The difference in mean concentration was statistically significant (ANOVA $p<0.05$) and highest in the GS-D. There is no regulated criterion under either the CCME or PWQO for SRP, however the interim PWQO for TP and CCME framework for the trophic levels of freshwater systems is considered to apply for SRP as well. Ecological threshold studies on biological responses to SRP have shown that concentrations less than 0.047 mg L^{-1} prevented nuisance algal growth and preserved water quality for recreational use in freshwater, whereas concentrations less than 0.015 mg L^{-1} ensured the maximum periphyton biomass remained below 100 mg m^{-2} (USEPA, 2000). The SRP concentration at the pond-wetland outlet, Weir 4, exceeded both thresholds during the study period.

Compared to Weir 1, the pond-wetland system removed 27% SRP mass during the GS-W. Harper and Baker (2007) reported a range of 39-94% for SRP removal efficiency in wet retention basis and a mean of 79% across the compared literature. A study by Md Zahanggir et al. (2018) reported maximum reductions of 26% for PO_4^{3-}-P using new stormwater ponds in commercial areas of Western Australia with mean effluent concentrations of 0.07±0.05 mg L^{-1} PO_4^{3-}-P. In comparison to this data, the removal efficiency of the Bercier pond falls squarely within the range of established literature in the GS-W. The mean daily SRP flux showed that the pond-wetland attenuated SRP mass in the GS-W by 27% and released SRP during other studied periods. While few studies have linked seasonality to SRP release in ponds, Ortuño et al. (2000) showed phosphorus release from deep wastewater stabilization ponds increased by 1.4-1.5 times under anaerobic conditions than aerobic conditions, and that P release was affected by redox and high pH conditions. Therefore, the effect seen here of seasonality may be secondary to other environmental conditions.

Wetlands have been shown in literature to display seasonal behavior, especially with respect to soluble nutrients. Wetlands may act as P sources or P sinks depending on the interactions between sediment-bound P and soluble P (Pant & Reddy, 2001). A study conducted by Steinman and Ogdahl (2011) on two new wetlands converted from abandoned celery fields through flooding in Michigan showed that TP and SRP concentrations and loads were higher downstream than upstream of the wetland between April and November 2009. The former use of the land, fertilizer application, wetland location and landscape are factors that can contribute towards whether a wetland is a nutrient sink or source.

Conclusion

The mean SRP concentration for the controlled drainage was 0.011±0.014 mg PO_4^{3-}-P L^{-1} compared to 0.045±0.056 mg PO_4^{3-}-P L^{-1} at the FDS in the GS-D, resulting in a percent difference of 76%. The concentration of SRP was four times smaller at the CDS during the GS-D than during the GS-W or the NGS (GS-D $p<0.05$ compared to GS-W and NGS) indicating that damming the water had an effect on reducing SRP concentrations, potentially as a result of increased root uptake and/or increased residence time for adsorption. The significant difference observed between CDS and FDS SRP concentrations during NGS suggests a plot effect between the fields. The daily SRP flux was greater by 81% at the FDS in the GS-W and lower by 81% in the NGS between the CDS and the FDS. The greater SRP flux observed during the GS-W is related to greater flow observed during this period at the CDS, and not SRP concentration. The mean daily SRP flux showed that the pond-wetland attenuated SRP mass in the GS-W by 27% and released SRP during the other studied periods. A correlational analysis of precipitation intensity, solids and SRP showed that the CDS mitigated the movement of solids and related SRP resulting from medium storm events, whereas greater solids concentrations from larger precipitation events were correlated with greater SRP concentrations at the FDS, suggesting that in these events, the contributing SRP is attached to the solids or particulate-bound. The mean daily SRP concentration at the CDS met the 0.047 mg L^{-1} ecological threshold in the GS-W, the NGS and was 4 times lower in the GS-D. The FDS met this threshold in the GS-W, however, it exceeded the threshold in the GS-D and the NGS.

The mean daily SRP concentration was 0.07±0.14 mg P L^{-1} at the pond-wetland inlet, Weir 1, and 0.11±0.14 mg P L^{-1} at the outlet, Weir 4. The mean daily SRP flux showed that the pond-wetland attenuated SRP mass in the GS-W by 27% and released SRP during other studied periods. Overall, the mean daily SRP mass flux for the study period was similar between the weirs, at 4.9 $x10^{-4}$±$1.4x10^{-3}$ kg PO_4^{3-}-P ha^{-1} d^{-1} (Weir 1) and 5.1 $x10^{-4}$±$1.1x10^{-3}$ ha^{-1} d^{-1} (Weir 4). Other studies have shown SRP release as a result of shifting conditions from aerobic to anaerobic, redox and high pH conditions in ponds, and it is likely that these environmental factors contributed to the SRP release observed in the GS-D and NGS. The SRP concentration at the pond-wetland outlet, Weir 4 exceeded both thresholds during the study period. A summary table is shown below comparing the cumulative SRP flux between the CDS and the FDS, and the inlet and the outlet of the pond-wetland during the individual periods considered.

Table 4.13: Cumulative Daily SRP Percent Difference at Drainage Structures and Weirs by Season

Percent Difference (%)	Study Period	GS-W	GS-D	NGS
FDS-CDS	-	-87	94	80
Pond-Wetland	-5	33	-215	-57

The percent difference in cumulative SRP flux between the FDS and the CDS (FDS-CDS) and between the inlet, Weir 1, and the outlet of the pond-wetland (Pond-Wetland) have been shown above. The negative percent difference observed in the GS-W is indicative of greater outflow from the CDS during the GS-W.

In comparison to the FDS, the CDS reduced SRP flux during the GS-D and NGS. The lack of reduction observed in the GS-W is most likely a result of the increased flow observed at the CDS during the GS-W. The pond-wetland reduced SRP flux in the GS-W, and released SRP in the GS-D and NGS.

4.5. **Effect on Nutrient Attenuation due to the Removal of Stop Logs**

The stop logs were removed from CDS 1 and 2 on September 27, 2017, effectively converting all CDS into FDS and demarcating the beginning of the non-growing season. A flush of nutrients was expected with increased flow.

The concentration of TCOD and TSS was variable, though highest at both locations shortly after the release of the stop logs. The TCOD ranged between 0 to 18 mg L^{-1} and averaged 6.4±4.8 mg L^{-1}, which was 2-4 times lower than the TCOD concentration at the Weirs and below or within the range of 10-70 mg L^{-1} observed in surface waters of Central Canada (NANQUADAT, 1985). Similarly, the TSS ranged between 0-9 mg L^{-1} and averaged 3±3 mg L^{-1}, which was lower than the TSS concentration during the GS-W (6±7 mg L^{-1}) and NGS (8±13 mg L^{-1}). This concentration was well below the maximum allowable increase of 25 mg L^{-1} from background levels between 25-250 mg L^{-1} during high flow events as required by the CCME (1999) in freshwater systems. The concentration of TCOD and TSS flushed during the release of the stop logs was very low and falls within the range observed within the study system.

The concentration of nitrate increased from 5.67 mg NO_3^--N L^{-1} to 7.61 mg NO_3^--N L^{-1} at CDS 1 and 6.65 mg NO_3^--N L^{-1} to 9.59 mg NO_3^--N L^{-1} and 2 over a 24-hour period. This range follows the increase in nitrate concentration observed from 5±2 mg NO_3^--N L^{-1} in the GS-D to 10±2 mg NO_3^--N L^{-1} in the NGS discussed previously at the CDS. The nitrate concentration increased with time, potentially due to the introduction of oxygen with flow and converting the anoxic environment conducive to denitrification into an oxic one supporting nitrification. Alternatively, the increase in nitrate concentration can be explained due to increased nitrate drainage from soil layers above the stop log level and discharge of denitrified water from the dammed soil layers. A nitrate gradation in soil from low concentration in the lower soil layers to high concentration at the water table, and a concurrent draining from low concentration to high concentration from the soil into the drains could explain this observation. The initial and final concentrations of nitrate seen during the flush period were above the CCME criteria of 3 mg NO_3^--N L^{-1} for the protection of aquatic life in freshwater but met the criteria of 10 mg NO_3^--N L^{-1} required under the Safe Drinking Water Act (CCME, 2012; Safe Drinking Water Act, 2002). The ammonia concentration at CDS 1 peaked 4 hours following stop log release and showed background variability at CDS 2. Overall, the concentration ranged between 0.03 to 0.45 mg NH_4^+-N L^{-1} and averaged 0.12±0.10 mg NH_4^+-N L^{-1}. This resulted in a mean unionized ammonia concentration of 0.00462 mg NH_3-N L^{-1} during this period, which was approximately 4 times lower in comparison to the mean unionized ammonia concentration of 0.018 mg NH_3-N L^{-1} at the CDS, effectively meeting both the PWQO of 20 µg NH_3-N L^{-1} (PWQO, 1994) and CCME guideline value of 0.019 mg L^{-1}.

A peak was noted in SRP concentration at CDS 1 within one hour of stop log release and after fourteen hours at CDS 2. The SRP concentration ranged between 0.01-0.20 mg L^{-1} and averaged 0.04±0.03 mg L^{-1} during the flush, which was comparable to the SRP concentration in the GS-W (0.04±0.03 mg L^{-1}) and the NGS (0.03±0.01 mg L^{-1}). The average SRP concentration was below the ecological threshold of 0.047 mg L^{-1} to prevent nuisance algal growth (USEPA, 2000). TP concentration showed a maximum after 7 hours at CDS 2 and was consistent at CDS 1. Overall, the TP concentration ranged between 0.01-0.40 mg P L^{-1} averaging at 0.05±0.06 mg P L^{-1}. The average TP concentration was greater than the most lenient interim PWQO objective of 0.03 mg P L^{-1} to prevent excessive plant growth in rivers and streams (PWQO, 1994).

In summary, TP and SRP concentrations at CDS 2, and ammonia and SRP concentrations at CDS 1 displayed maximums within 24 hours of the release of the stop logs. The concentrations of

TCOD at both CDS, and the concentrations of TSS at CDS 1 and ammonia at CDS 2 were variable, though highest for TSS and TCOD at the release of the stop logs.

The effect of the removal of the stop logs was immediately more obvious with a consideration of the mass flux. Nitrate, ammonia, TP and SRP flux were highest within one hour of stop log release at CDS 1 and 2 declining to a plateau within four hours and to zero within six hours. TCOD and TSS flux reached a maximum two hours following stop log release at CDS 1 and TCOD upon release at CDS 2.

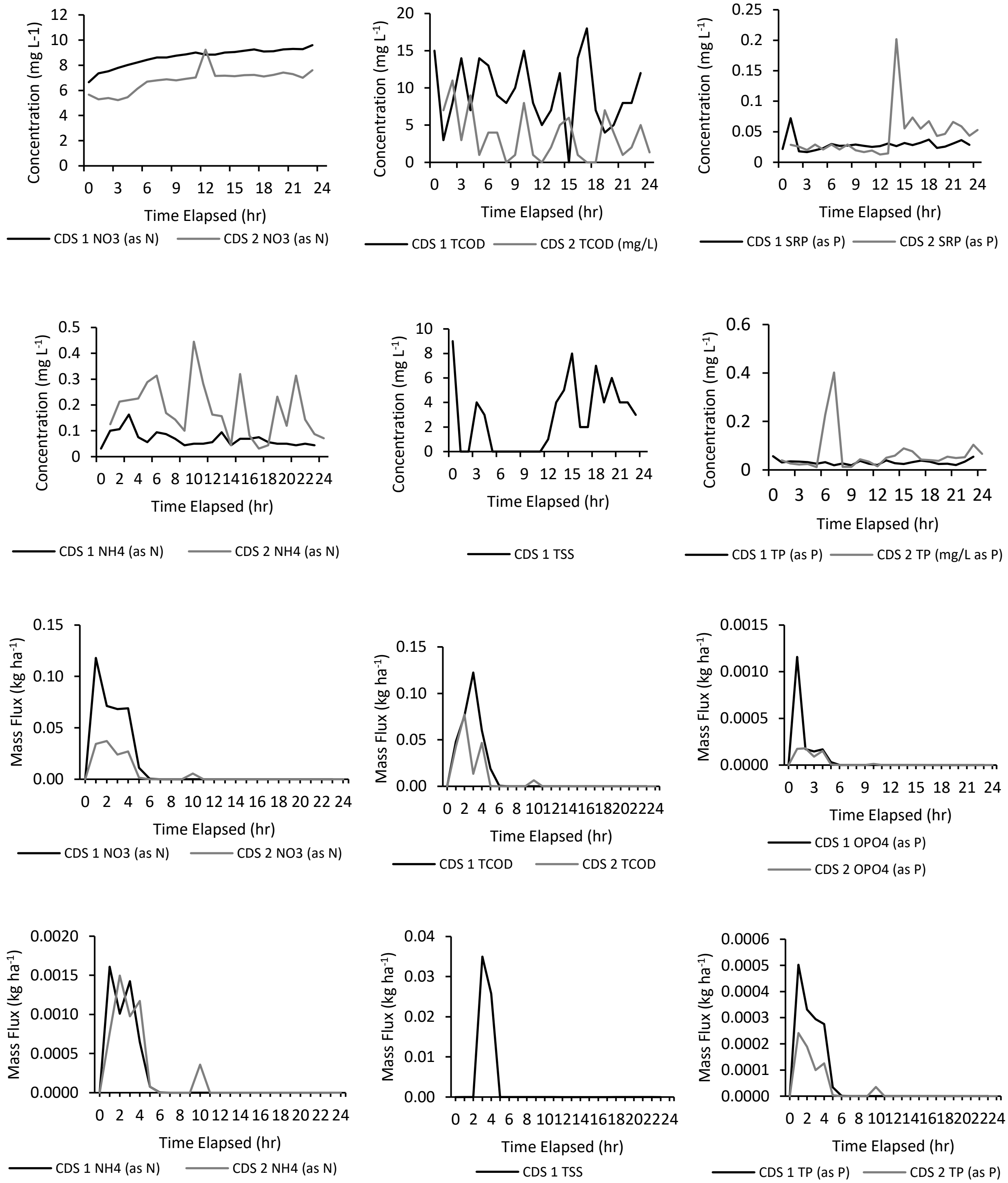


Figure 4.24: Mean daily concentration (mg L^{-1}) and mean daily mass flux per hour (kg d^{-1} ha^{-1}) of nitrate (NO_3^--N), Total Chemical Oxygen Demand (TCOD), Soluble Reactive Phosphate (PO_4^{3-}-P), Ammonia (NH_4^--N), TSS and TP (PO_4^{3-}-P) for 24 hours following the removal of stop logs from Controlled Drainage Structures (CDS) 1 and 2.

The flush represents for CDS 1 0.05% (TSS), 0.37% (SRP), 0.16% (NH_4-N) and 0.48% (NO_3-N) and for CDS 2 0.16% (SRP), 0.25% (NH_4-N) and 0.19% (NO_3-N) of the cumulative mass flux for the study period.

Overall, the expected flush of nutrients during stop log release was not observed. Maximums observed during the flush event were within the range observed during the study period. However, the increase in nitrate concentration with time observed with increasing time supports the hypothesis that during dry periods, controlled drainage structures provide suitable anoxic conditions that favour denitrification. The effect of the flush is highlighted in the mass flux data set, however, the contribution to mass during the flush event is less than 0.5% for all considered analyses.

4.6. **Yield**

Controlled drainage structures were expected to increase yield under the assumption that the elevation of the water table would increase water access for plant roots, and therefore support crop growth during periods of water stress. Soil content was evaluated in May and October.

The crop yield was on average 5.00±0.14 t^3 ha^{-1} for the controlled fields and 4.75±0.07 t^3 ha^{-1} for the free draining fields. The 5% difference in yield obtained by controlling the water table was not statistically different ($p>0.05$). The effect of DWM on soybean yield has been shown to be variable in previous studies. Soybean yield increases of 10% with DWM in North Carolina (Poole et al., 2013), 23- 58% in Ohio (Cooper et al., 1991), 68% in Ohio (M. J. Fisher et al., 1999) and decreased by 5% in southwestern Japan (Matsuo et al., 2017). A study by Mejia et al. (2000)

showed that soybean yields in eastern Ontario increased between 8.5% and 12.9% in 1995 and between 37.3% and 32.2% in 1996 by controlling the water table at 0.50 m and 0.75m, respectively, when the native water table was greater than 1.00 m from the surface. These two years were wetter than average and showed variability in yield regardless. The 5% increase in soybean yield seen in this present study, is not statistically significant, and is on the low end of the yields previously described in literature.

It is possible that as this particular year was rainy compared to average, that controlling the water table had little effect as the soil was already saturated with water regardless of the presence of CDS. The density of soybeans was 248,235 soybean plants ha^{-1} in areas with controlled drainage and 221,888 soybean plants ha^{-1} in areas with free drainage.

4.7. **Mass Balance**

Two rounds of soil testing were completed from plots draining into the CDS and FDS in May 2017 and after harvesting in October 2017 **(Figure 4.25)**. The largest proportion of nutrient content, in descending order, consisted of extractable phosphorus, nitrate and then, ammonia. In May 2017, soil nutrient content was reported in the CDS fields of 7.7±0.8 kg NH_4^+-N ha^{-1}, 24.7±1.0 kg NO_3^{2-}-N ha^{-1} and 43.0±6.9 kg P ha^{-1} extractable phosphorus and in the FDS fields of 8.1±0.8 kg NH_4^+-N ha^{-1}, 18.2±1.6 kg NO_3^--N ha^{-1} and 58.4±0.9 kg ha^{-1}. Inorganic nitrogen was higher in the CDS fields than at the FDS fields by a factor of 1.2 while the extractable phosphorus was lower in the CDS fields than the FDS fields by a factor of 0.74. Fertilizer was applied at 15.47 kg NH_4-NO_3-N ha^{-1} and 75.79 kg P_2O_5-P ha^{-1} on September 29, 2017. In October 2017, soil nutrient content of 9.7±0.5 kg NH_4^+-N ha^{-1}, 32.8±2.2 kg NO_3^--N ha^{-1} and 42.5±8.9 kg P ha^{-1} extractable phosphorus was reported in the CDS fields and 13.4±1.8 kg NH_4^+-N ha^{-1}, 21.3±0.4 kg NO_3^--N ha^{-1} and 52.5±3.1 kg ha^{-1} extractable phosphorus in the FDS fields. Similar ratios between controlled/free drainage fields were found in October of 1.2 for total inorganic nitrogen and 0.8 for phosphorus. Plant uptake was measured by taking above-ground biomass from representative plants and found to have fluxes of 173.2 kg N ha^{-1} and 16.4 kg P ha^{-1} in the CDS fields and 163.5 kg N ha^{-1} and 16.9 kg P ha^{-1} in the FDS fields. There were no significant differences between the TN and TP ratios or in the plant uptake of nutrients of controlled vs. free plots. It is interesting to note that phosphorus uptake by soybean is approximately 4 times lower than the total P applied as fertilizer, suggesting that the application of P can be reduced. Additionally, the plant uptake of N is three times larger than the soil nutrient content which can be explained by soybean nitrogen fixation. Soybean plants can obtain nitrogen from the atmosphere through a symbiotic relationship with nitrogen-fixing bacteria, *Bradyrhizobium japonicum.* A review of nitrogen uptake, fixation and response to fertilize N in soybeans concluded that on average 50-60% of soybean N demand was met by biological N_2 fixation (Salvagiotti et al., 2008). The findings of this present study show that nitrogen fixation contributed between 84% (CDS) and 87% (FDS) of soybean N demand.

To estimate that amount of nutrient loss to drains, the mean soil nutrient content in October was compared to that of the soil nutrient in May supplemented by fertilizer application. The proportion of soil nutrient content in October to the sum of the soil nutrient content of May and applied fertilizer was representative of the nutrient content of soil column. The proportion of cumulative nutrient content at Weir 1 to the sum of the soil nutrient content of May and applied fertilizer in September was representative of loss to drainage. Nearly ~100% of NH_4^+-

N, ~82% of NO_3^--N, ~39% of P and ~87% of N represents the nutrient content in the soil column compared to the historical native concentration supplemented b y fertilizer. An estimated ~14% of available P and ~12% of available N is taken up by plants. In comparison to the soil nutrient in May 2017, supplemented by the applied fertilizer in September 2017, an estimated 3% NH_4^+-N, 21% NO_3^--N, a negligible amount of P, and 21% of TN is lost as drainage, whereas 48% of P is lost as overland flow. Especially as noted in the case of the nitrogenous species, while the percentage of nutrients entering the water way is considered small, it is sufficient to cause environmental impacts.

Soybean yields can be affected by many factors including but not limited to N availability. In this present study, N uptake is estimated to range between 143-146 kg ha^{-1}. Salviagiotti et al. (2008) reported that total N uptake averaged 219 kg ha^{-1} (interquartile range of 154-280 kg ha^{-1} of N) and a maximum of 485 kg ha^{-1}, which is indicative of N being the main limiting factor in the field or the maximum N dilution. The N uptake presented in this study appears to be within the lower 25 percentile reported by Salviogiotti et al. (2008) indicating the yield is limited by factors other than N.

The sum of ammonia and nitrate soil content were similar between the CDS and FDS fields in May at 32 and 26 kg N ha^{-1}, respectively, as well as in October at 43 and 35 kg N ha^{-1}, respectively. A recent soil survey conducted by OMAFRA in 2020 on 93 silty loam soil samples collected in the Ottawa region showed that TN ranged between 0.03-0.81% with an average of 0.24±0.03% and that the available P content ranged between 1.2-11.2 mg kg^{-1} with an average value of 15.5±12.1 mg kg^{-1} (OMAFRA, Ontario Ministry of Agriculture, 2020). Residual soil N at the end of the growing season was shown to range between 20-30 kg N ha^{-1} in Quebec and 30-50 kg N ha^{-1} in Ontario farmlands between 1981 and 2006 by De Jong et al. (2009). Loam soils are expected to have cationic exchange capacities between 7-25 cmol/kg and are not expected to bind strongly to cations (OMAFRA, 2018). Phosphorus binds strongly with iron or aluminum in acidic soils and magnesium or calcium in alkaline soils to form insoluble or slightly insoluble complexes, that reduces the bioavailability of P to plant roots. A study of P export in organic grain farms reported available P levels of 10-20 kg ha^{-1} in soil from 14 farms in Manitoba (R. Martin et al., 2007). A cumulative P balance over 40 years between 1961-2011 showed a range between 0-100 and 100-300 kg ha^{-1} within the various areas in the Ottawa valley (Reid & Schneider, 2019). The average extractable P content of the soil was 49 kg ha^{-1} across the fields between the two sampling sessions and falls within the former range proposed by Reid and Scheider (2019).

The amount of phosphorus in the soil is relatively constant between in May and October 2017. Fertilizer was applied in September and there is no observable increase or decrease in soil P between the GS and NGS. It is possible the soil P was depleted following plant uptake in the GS and that the application of fertilizer replenished the depleted soil P to the original concentration, however, there is insufficient data to conclude that soil P was depleted or that it remained the same throughout the study period. It is interesting that the amount of P that is added as fertilizer is the same concentration as what is already present in the soil. It is suggested that soil cores be taken down to the water table to assess the saturation of P in the soil and that that the storage capacity of the soil be assessed in order to determine the ability of the soil to retain the P, as well as the likelihood of the soil to lose nutrients through drainage.

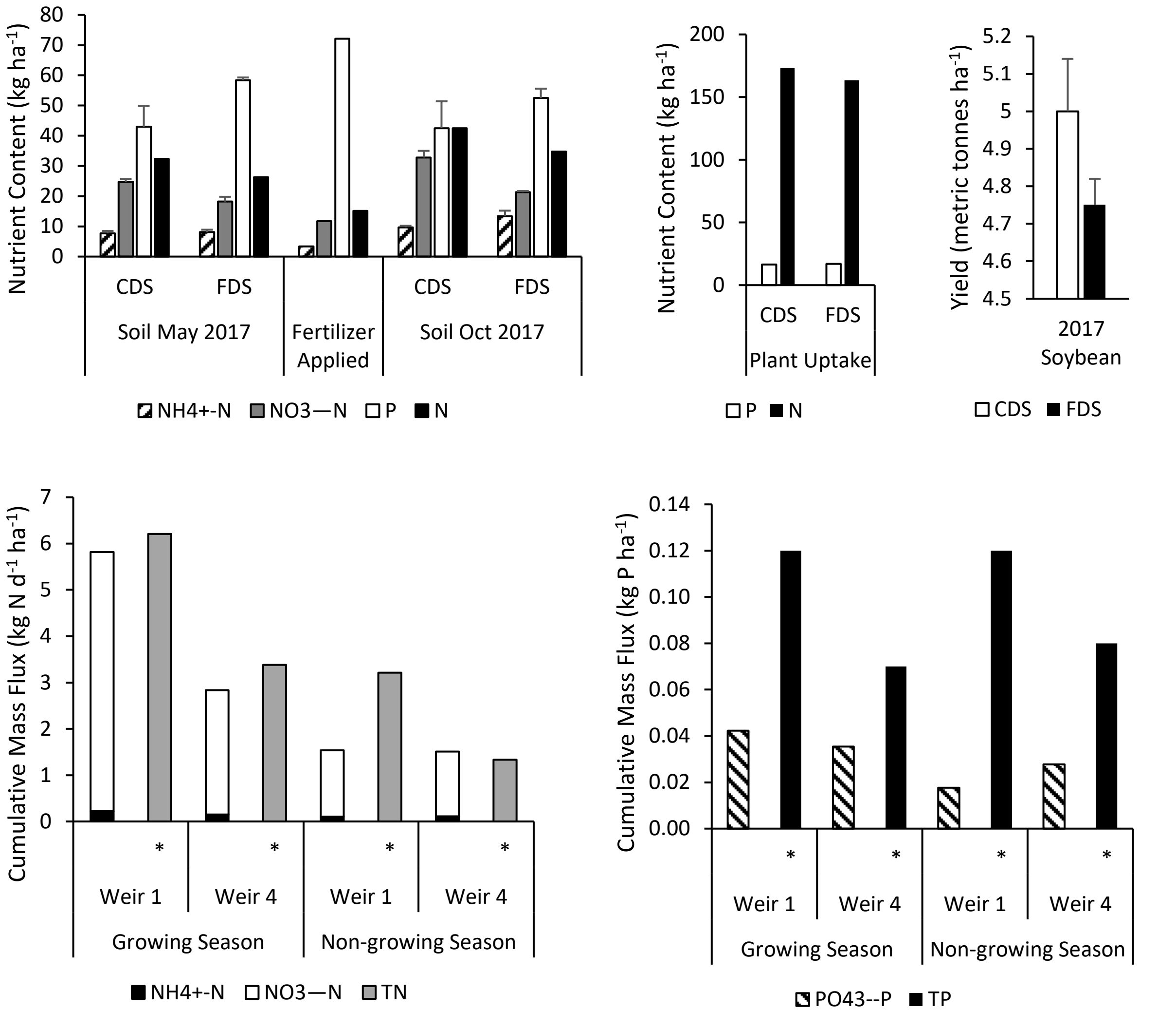


Figure 4.25: Top left) The Nutrient Content (kg ha^{-1}) of Soil Sampled from Plots Draining into the Drainage Structures (DS Plots) in May 2017, Nutrient Content of Fertilizer Applied on September 29, 2017 and Soil Sampled from DS Plots in October 2017; Top middle) Nutrient Content (kg ha^{-1}) of Representative Plants Sampled from DS Plots; Top Right) Yield (metric tonnes ha^{-1}) of Soybean in DS Plots; Bottom Left) Cumulative Mass Flux (kg ha^{-1}) of nitrogen in the Pond with Seasonal Considerations; and Bottom Right) Cumulative Mass Flux (kg ha^{-1}) of Phosphorus into the Pond with Seasonal Considerations.

Drainage structures were controlled (CDS) at CDS 1 and CDS 2, and free (FDS) at FDS 3,4 and 5. A weir (Weir 1) was installed at the pond-wetland inlet and at the outlet (Weir 4). The study period was divided into the wet period of the growing season (GS-W: June 14 – July 31, 2017) the dry period of the growing season (GS-D: August 1 – September 27, 2017) and the non-growing season (NGS: September 28 – November 14, 2017) due to the availability of flow and concentration data at the drainage structures.

Note: The standard deviation for plant uptake measurement was not provided.

*: Grab samples used to calculate particulate analytes including total nitrogen and total phosphorus.

5. Conclusion

Agricultural runoff and drainage are significant contributors to the deterioration of water quality in receiving water bodies. Controlled drainage can maintain water levels above the drainage lines and can provide an essential source of water to plant roots during dry periods in the growing season. Additionally, CD has been proven as an effective method of flow reduction with commensurate reductions in both nitrogen and phosphorus loading to surface waters. Ponds and constructed wetlands improve water quality through the attenuation of solids and nutrients. A drainage water management system and pond-wetland system were installed on a 64-acre seed farm in St. Isidore, Ontario. The drainage management system had the twin objectives of providing soil moisture to crops during dry periods and reducing nutrient migration to surface waters, while the pond-wetland system was designed with the dual objectives of increasing ecosystem habitat while attenuating nutrient migration from farm fields. The objective of this study was to investigate the effectiveness of the two beneficial management practices to attenuate nutrient concentration during the growing season (GS) and non-growing season (NGS) of 2017, and in particular, the effectiveness of the CDS in reducing flow and increasing yield. The effectiveness of CD on increasing yield is well documented, whereas the effect on nutrient attenuation is less well studied. The GS was subdivided into a wet period (GS-W) and dry period (GS-D) to account for the impacts of seasonality.

To address the potential for flow attenuation by the drainage structures and weirs, water level loggers were implemented at all sample points to measure fluctuations in pressure and temperature. The average daily precipitation was 3.95±8.86 mm d^{-1} and the average daily flow at the drainage structures were similar during the GS-W between CDS (0.29±0.11 mm d^{-1}) and the FDS (0.21±0.17 mm d^{-1}) and significantly different between the CDS (0.00±0.00 mm d^{-1}) and the FDS (0.23±0.11 mm d^{-1}) during the GS-D. In the NGS, all drainage structures were free and in comparison, to the GS, however, there was less flow at the CDS in comparison with the FDS. In this study, a decrease in flow was observed during the GS-D due to the implementation of controlled drainage structures. The mean daily flow was higher at Weir 1 than Weir 4 across all the seasons. Composite flow data indicate that on average, the pond-wetland system attenuated 17% of the inflow over the study period.

The effect of solids attenuation is understudied in drainage structures, and therefore reductions in turbidity or TSS were not anticipated at the CDS. Nitrate attenuation by CDS is well documented in literature, where attenuation of phosphorus and other forms of nitrogen are less studied. Reductions in turbidity (81%), and concentrations of TSS (40%), NH_4^+-N (19%) NO_3^--N (43%), SRP (78%), and mean daily mass flux were noted of TSS (53%), NH_4^+-N (54%), NO_3^--N (46%), SRP (82%) in the dry period of the growing season between the CDS and the FDS. The CDS appeared to be active in the GS-D and effective at reducing flow, solids, soluble nutrient concentration and flux. The effect of DWM on soybean yield has been shown to be variable in previous studies. In this study, there was no significant effect on yield as a result of controlling the water table.

The solids settling capacity of ponds is established in literature. Over the complete study period, the pond-wetland system achieved reductions in turbidity (52%), TSS (55%), TP (21%) and NH_4^+-N (27%). The combined flow and nutrient attenuation contributed to effective mass removal of nutrients daily and seasonally. On average, the pond-wetland system achieved mean mass flux reductions of 33% TSS, 43% TP, 41% TN, 61% NH_4^+-N. The pond-wetland attenuated NO_3-N (48%) and SRP (27%) mass in the GS-W and released both nutrients in the GS-D and NGS suggesting an effect of seasonality for nitrate and SRP attenuation in small pond-wetland systems.

Additionally, a flush of nutrients was expected following the removal of stop logs at the drainage structures. A gradual increase of nitrate concentration and increases in NO_3^-, TCOD, SRP, NH_4^+, TSS and TP flux was observed within 6 hours of stop log release, however, this flush represented only 0.05% to 0.37% of total nutrient flux for the study period.

There are limited studies on ponds and wetlands attenuating agricultural drainage and runoff from grain farms. In this study, the controlled drainage system was observed to attenuate nutrients, especially high concentrations of nitrate by 43% and nitrate flux by 46% in the GS-D. The pond-wetland system was observed to attenuate nitrate flux by 48% in GS-W. In comparison, the drainage structures attenuated SRP concentrations by 78% and SRP flux by 82% in the GS-D, while the pond-wetland system attenuated 27% of SRP in the GS-W. Overall, these results show that a combined controlled drainage and pond-wetland system can be a beneficial tool to reduce the impact of nutrient migration from farmlands with a low economic footprint, especially in the context of particulate-bound nutrients and nitrate.

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7. Appendices

Meteorological Conditions

Comparison of St. Isidore Farm Weather Station Data to Ottawa RCS Data

The maximum, minimum and mean temperature, rain and average humidity recorded from January 1, 2017 to December 4, 2017 on the Bercier weather station were compared against weather data available from the Ottawa RCS weather station and plotted below. The correlational coefficient was strong for rainfall (R^2=0.72) and pressure (R^2=0.83) and very strong for minimum temperature (R^2=0.98), maximum temperate (R^2=0.99) and mean temperature (R^2=0.99).

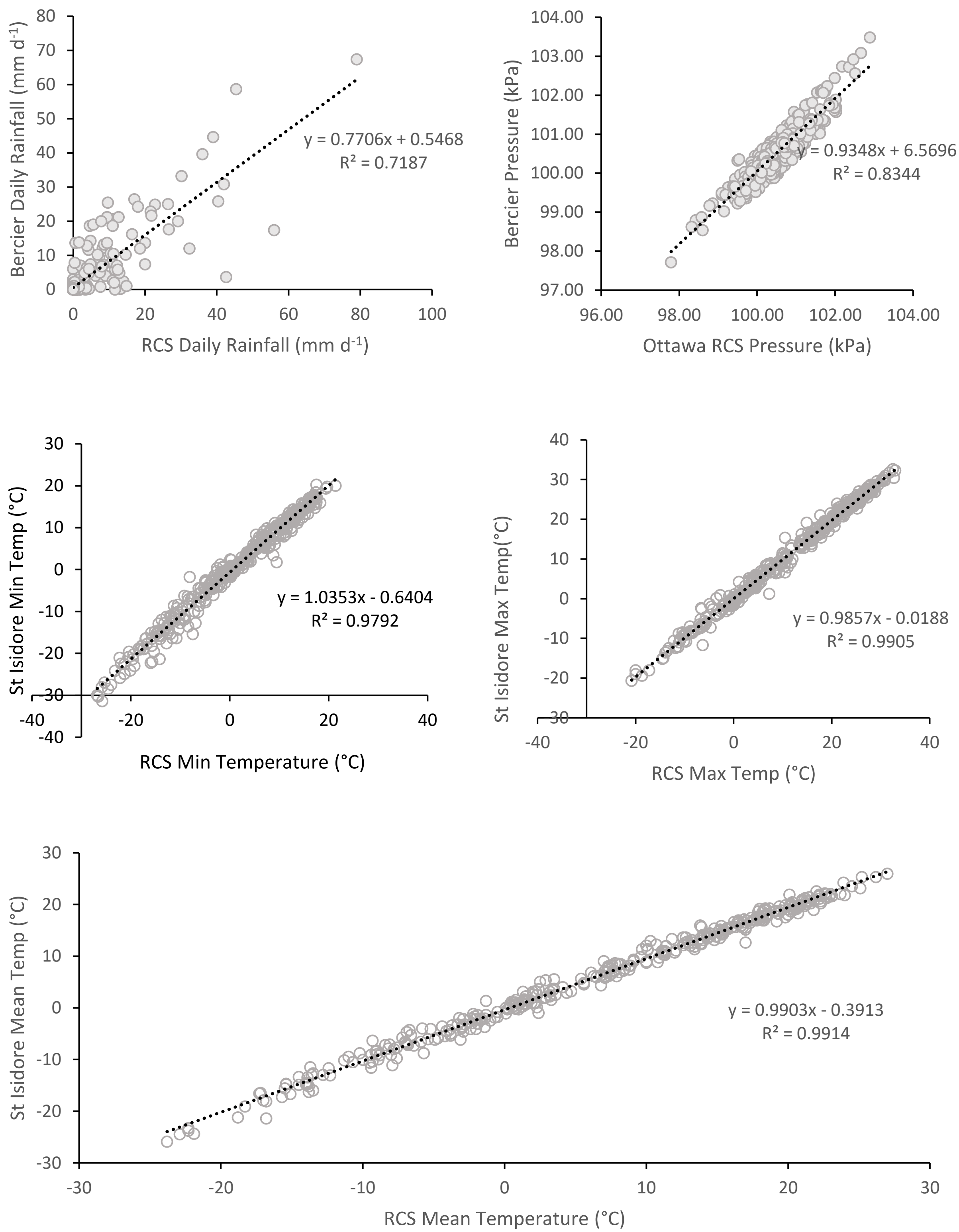

Figure 7.1: Comparison of Bercier Atmospheric Pressure and Temperature to Ottawa RCS. Monthly precipitation and temperature were used from the Environment Canada Historical Weather Data (Environment and Climate Change Canada, 2020).

CDS Parameters

The height of the installed stop logs and important parameters are given below by season.

Table 7.1: Height of Corresponding Component of Drainage Structure by Season

	Component	Height (m)					
		CDS 1	CDS 2	FDS 3	FDS 4	FDS 5	FDS 6
Growing Season (GS)	Stop Log# 4 (Top)	0.178	0.178	Same as NGS			
	Stop Log# 3	0.128	0.128				
	Stop Log# 2	0.178	0.128				
	Stop Log# 1	0.128	0.178				
	Base Log	0.178	0.128				
	V-notch weir	0.178	0.178				
	Top of V-notch weir to base of CDS	0.790	0.918				
	Base of V-notch weir to base of CDS	0.658	0.763				
	Max height at which water flows through the triangular weir	0.790	0.918				
	Total Height of CDS	2.411					
Non-growing Season (NGS)	V-notch weir log	0.178			0.178	0.178	
	Total height from base of CDS to top of V-notch weir	0.178			0.225	0.178	
	Height from base of weir to base of weir lock	0.047			0.047	0.047	
	Max height at which water flows through the weir	0.178			0.356	0.178	

Flow

Water Height Calibration

Water pressure measurements were taken using a barometric level logger (HOBO Onset U20) and converted to water height as described in the **Section 3.1**. This water height was calibrated against field measurements taken at the CDS and plotted against each other and shown below. The following equations were applied to correct the height at their respective locations:

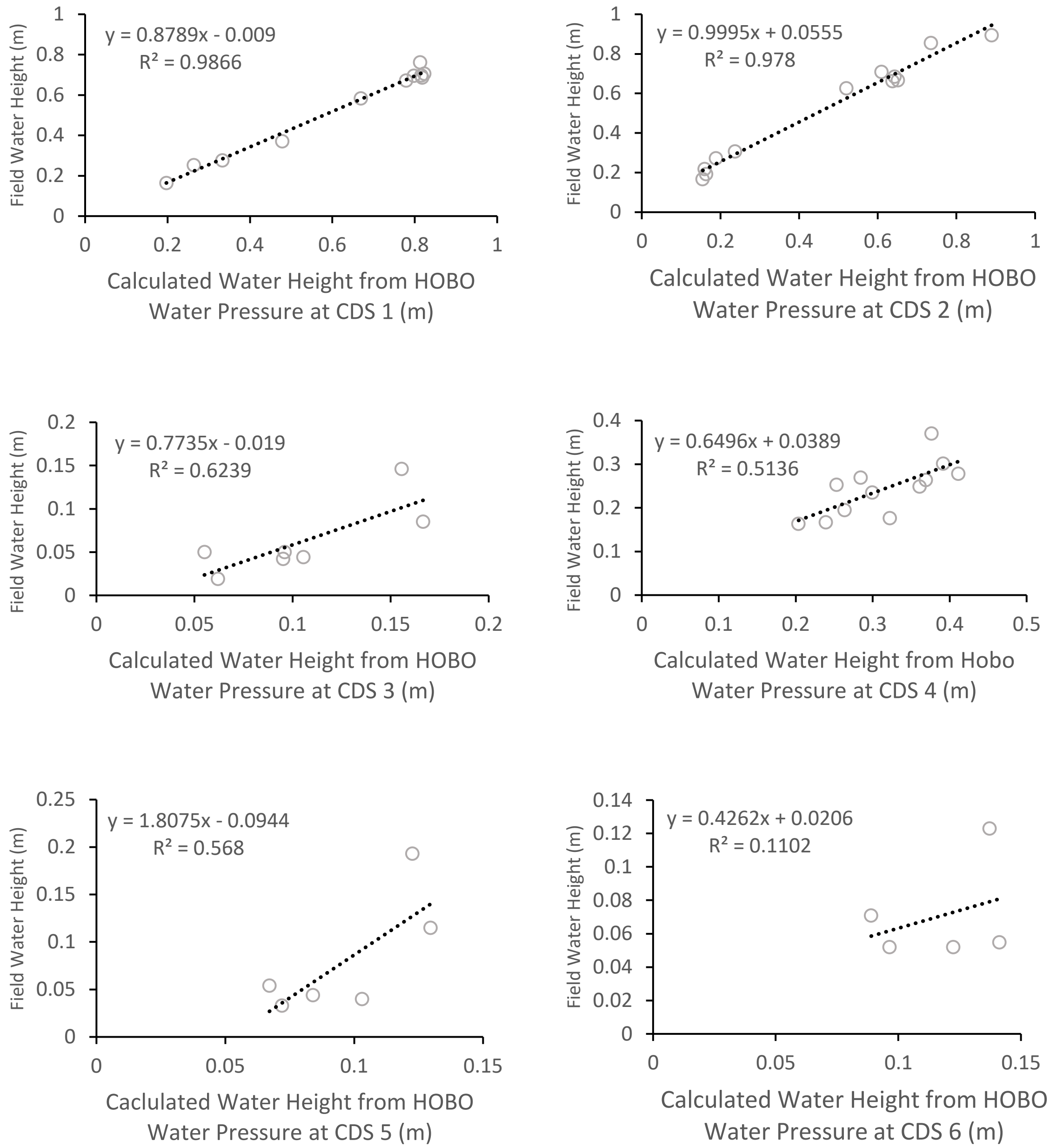

Figure 7.2: Flow Correction using Field Measurements for Drainage Structures CDS 1-6. (Bista, 2018)

Calculation of Flow

Equation 2 Constants and Coefficients for the CDS and Weir 1

The values for C_e, h_e and k_h can be calculated using Equations 2B, 2C and 2D respectively; and also estimated empirically use the **Figure 3.6**.

Equation 2B: $C_e = \theta\,(0.02286\,\theta - 0.05734) + 0.6115$

Equation 2C: $h_e = h_u + k_h$

Equation 2D: $k_h = 0.001\,[\theta * (1.395\,\theta - 4.296) + 4.135]$

Where:

θ is the weir angle in radians

These values can also be approximated empirically, as below.

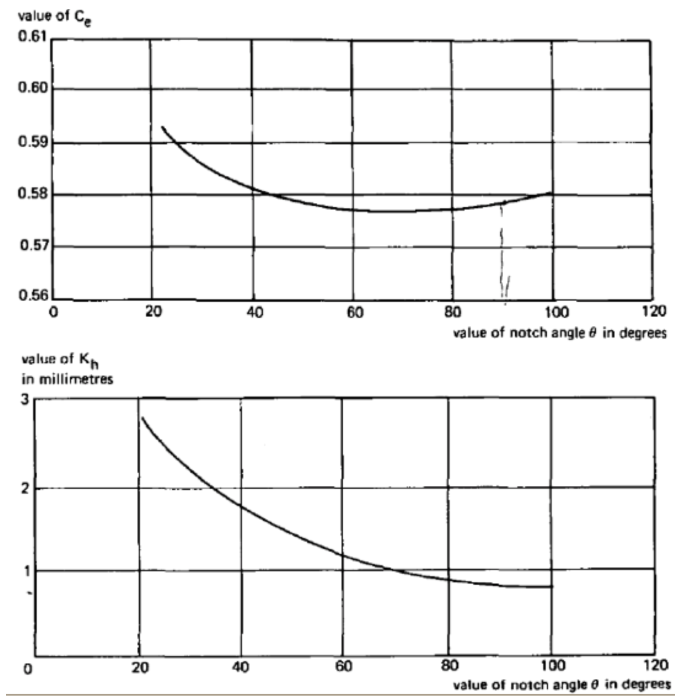

Figure 7.3: Empirical Determination of constants C_e and K_h in Triangular Weir Discharge Equation (U. S. Dept of the Interior, 2001).

For CDS, the weir angle is 22.5 degrees and as such, the constant C_e can be approximated at 0.5925 and K_h at 2.66 mm or 0.0266 m using **Figure 6.3**. The calculated values as per the equations are below in **Table 6.2**:

Table 7.2: Calculated Components of Triangular Weir Equation for CDS and Weir 1

Parameter	General Equation	Constants for CDS	Constants for Weir 1
C_e (dimensionless)	$\theta\,(0.02286\,\theta - 0.05734) + 0.6115$	0.5925	0.5778
K_h (m)	$0.001\,[\theta * (1.395\,\theta - 4.296) + 4.135]$	0.002663	0.0008
θ (radians)		0.3927	1.5709

Equation 4 Constants and Values Used for the Calculation of Flow over A Suppressed Weir in the CDS

The discharge characteristics are based on The Kindsvater-Carter method, which defines an equation for a rectangular, sharp-crested weir as:

$$\text{Equation 4A: } Q = C_e L_e H_e^{\frac{3}{2}}$$

Table 7.3: Components of Equation 4A

Where:	In these relationships:
Q is the discharge (flow rate over the weir) in ft^3/s	k_b is a correction factor to obtain effective weir length
e is a subscript denoting "effective"	L is the length of the weir crest in ft
C_e is the effective coefficient of discharge in $ft^{1/2}/s$	B is the average width of the approach channel in ft
$L_e = L + k_b$	H is the head measured above the weir crest in ft
$H_e = H + k_h$	k_h is a correction factor having a value of 0.003 ft

k_b, is dependent on the ratio of L/B, the length of the weir crest in ft/ average width of the approach channel in ft and is defined by the following graph:

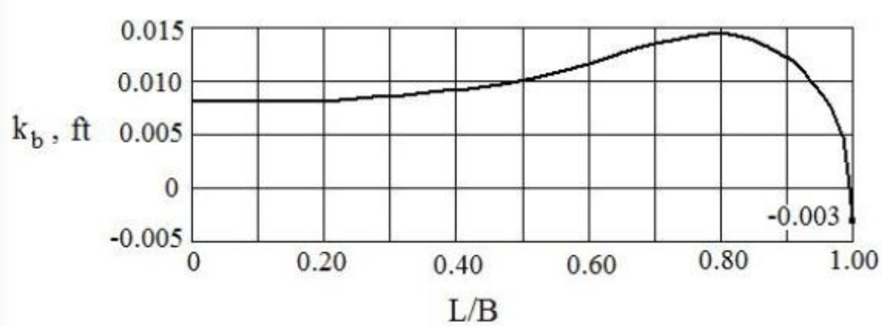

Figure 6. k_b as a function of L/B (as given in *Water Measurement Manual*)

Figure 7.4: Calculation of kb for the Calculation of Flow over a Rectangular Weir (U. S. Dept of the Interior, 2001).

In a suppressed weir, L = B and therefore, L/B = 1 and k_b = -0.003 as per the graph above.

Similarly, C_e can be calculated in relation to H/P where L/B=0. Using the table below, where L/B = 1, C_1 = 0.4 AND C_2 = 3.220.

Table 1. Values of C_1 & C_2 for equation (6) (from *Water Measurement Manual*)

L/B	C_1	C_2
0.2	-0.0087	3.152
0.4	0.0317	3.164
0.5	0.0612	3.173
0.6	0.0995	3.178
0.7	0.1602	3.182
0.8	0.2376	3.189
0.9	0.3447	3.205
1.0	0.4000	3.220

Figure 7.5: Calculation of C1 and C2 for the Calculation of Flow over a Rectangular Weir (U. S. Dept of the Interior, 2001).

Equation 4B: $C_e = C_1 (H/P) + C_2$; or

Equation 4C: $C_e = 0.400 (H/P) + 3.220$

Therefore, **Equation 4D:** $Q = \left(0.4000 * \left(\frac{H}{P}\right) + 3.200\right) * (L - 0.003) * (H + 0.003)^{3/2}$

Or alternatively, **Equation 4E:** $Q = 1.84BH^{\frac{3}{2}}$ if $\frac{H}{P} \leq 0.33, or\ \frac{H}{B} \leq 0.33$, where

Q is in m^3/s; and, B, H are in m.

It can be recalled from **Table 6.4** that, the values of B, or the average width of the approach channel are standardized for the CDS weirs and Weir weirs and are shown below:

Table 7.4: Components of Rectangular Weir Equation for CDS and Weir 1

Location	B, Weir Width (m)	Outer CDS Width (m)	Height (m)	Maximum Value of H for Equation 4E (m)
CDS 1	0.314	0.335	-	0.104
CDS 2	0.162	0.197	-	0.0535
CDS 3			-	-
CDS 4			-	-
CDS 5			-	-
CDS 6			-	-
Weir 1	0.918	-	0.14	0.303
Weir 4	0.594 L	-	0.10	0.196 L
	0.918 R		0.12 R	0.303 R

Equation 3 Constants and Values Used for the Calculation of Flow over a Rectangular Weir at Weir 4

As Weir 4 is a rectangular weir, the following assumptions were used in the calculation of flow.

The Kindsvater-Carter rectangular weir equation was used.

$$\text{Equation 3: } Q = \frac{2}{3} C_e \sqrt{2g}(b + K_b)(h + K_h)^{\frac{3}{2}}$$

Table 7.5: Constants and Values Used in the Rectangular Weir Equation

Where:	Constants	Values Used
h = Head [L]	H (L)	0.075
P = height from base of weir to notch (m)	P (m)	0.1
b = Notch Width [L]	b (L)	0.594
Q = Discharge [L^3/T]	B (L)	1.512
g = Acceleration of gravity [L/T^2]	h/P	variable
	b/B	0.39
C_e = Discharge Coefficient	C_e	0.6
K_b and K_h account for effects of viscosity and surface tension [L]	K_b	0.0275

C_e is a function of h/P and b/B as defined below.

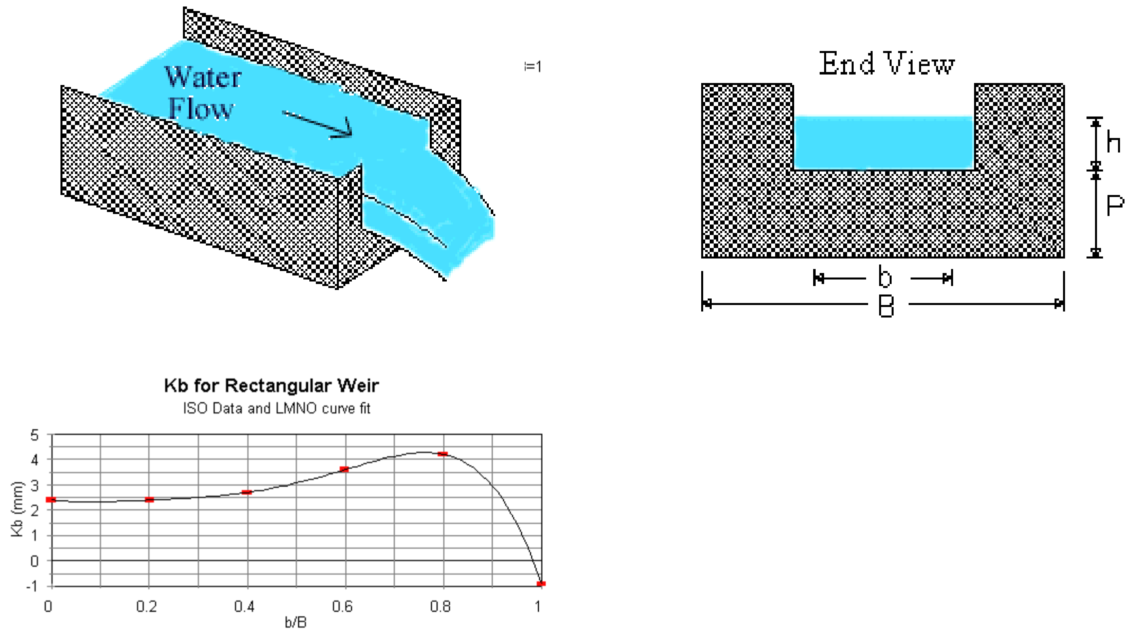

Figure 7.6: Left) Rectangular Weir Right) Discharge Coefficient and Kb for Rectangular Weir (U. S. Dept of the Interior, 2001).

Evapotranspiration Calculations

The water balance method was used to determine the likelihood of water stress on crop roots (i.e. to assess the potential of using to irrigation to alleviate plant stress) during the study period using evapotranspiration data. The following assumptions were made: 1) the water column in the soil was available to plants; 2) field capacity was reached when the reservoir was full[i] 3) crop water use (evapotranspiration) removed water from the reservoir; 4) rainfall and irrigation added water to the reservoir (OMAFRA, 2004). The following essential information was required about the operation to calculate evapotranspiration rates.

[i] The amount of water retained in the soil following a saturating rainfall and the draining of excess water is termed as the reservoir.

Table 7.6: Essential Information to Calculate Root Stress Using Soybean Common Rooting Depth of 300 mm

Item	Crop	Details
Weather station	-	St. Isidore, on-farm
Soil Texture	-	Silty clay loam
Available water capacity for soil texture (mm of water/ mm of soil)	-	Average 0.18 Range 0.15-0.20
Crop	-	Soybean and corn
Common Rooting Depth	Corn	600 (mm)
	Soybean	300 (mm)
Estimate of maximum crop-available soil water in the root zone (field capacity)	Corn	=0.18*600 =108 mm
Available water capacity of the soil texture x crop rooting depth =0.18 mm/mm	Soybean	=0.18*300 =54 mm
Allowable soil water depletion in the root zone (irrigation point)	Corn	=0.5*108mm =54 mm
50% crop-available soil water	Soybean	=0.5*54 mm =27 mm

Evapotranspiration (ET) or crop water use is the amount of water that is extracted from the soil root zone by the root system and no longer present in the soil. Crop water use is the depth of water that is needed to meet the water loss through evapotranspiration. Crop water needs are influenced by the temperature, humidity and windspeed of the study area. Crop factor is a variable that is part of the measurement of the evapotranspiration and a crop factor of 0.3 + 0.00365t for corn and 0.2 + 0.01t for soybean were used to fit the following curves and table.

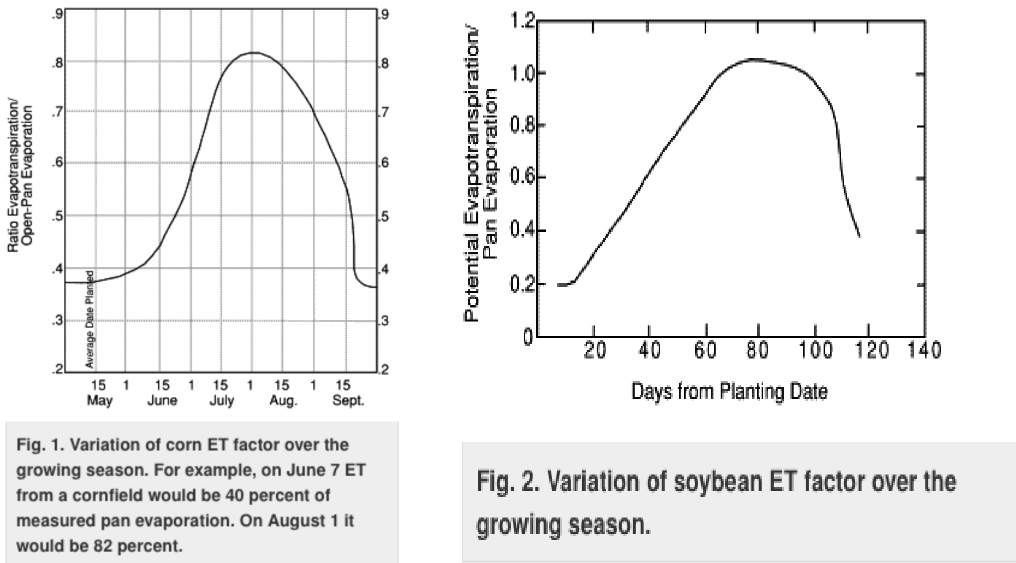

Figure 7.7: Corn and Soybean Evapotranspiration Factor Trend Across the Summer (Al-Kaisi, 2019)

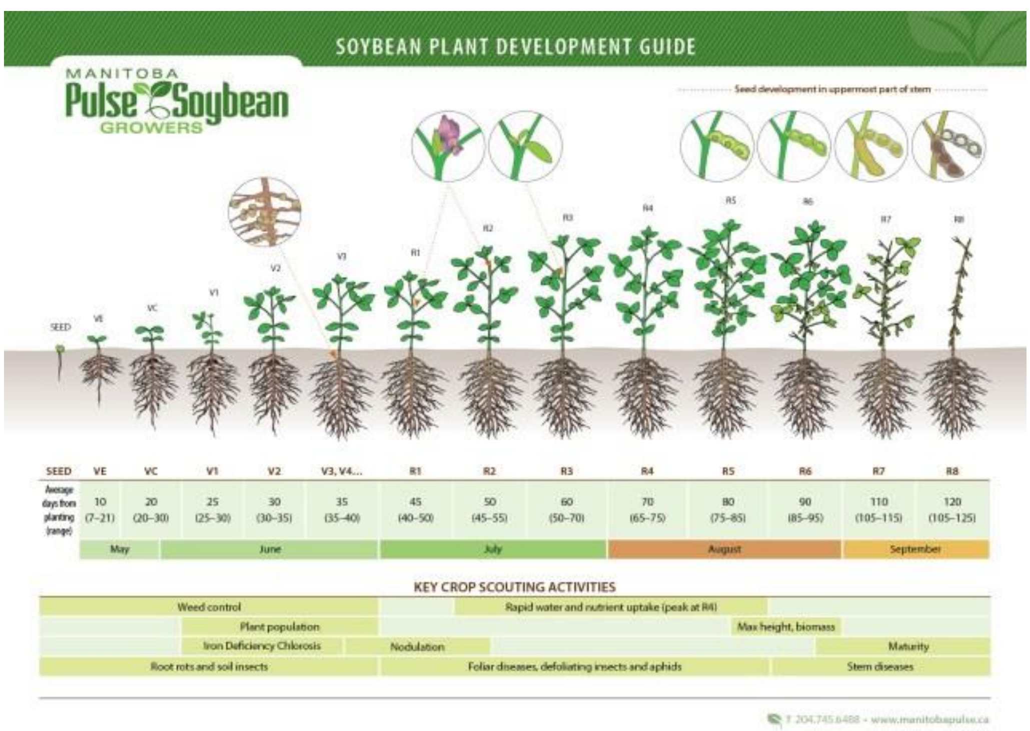

Figure 7.8: Growth Stages of Soybean (MPDG, 2019) Used to Allocate Crop Factor

Table 7.7: Literature Crop Factor

Item	Crop Factor	Comments

Bare soil (OMAFRA, 2008)	0.2	-
Corn	0.3	Emergence
	0.6	July 1
	0.75	July 15 to silk
	0.80	After pollination
Soybean	0.6	40 days after planting (Emergence)
	0.9	60 days after planting (when canopy closes (Reproductive Stage)
	1.1	70 days through leaf turning (Reproduction)

The crop factors that were used in the calculation for evapotranspiration in this study for corn and soybean have been shown below.

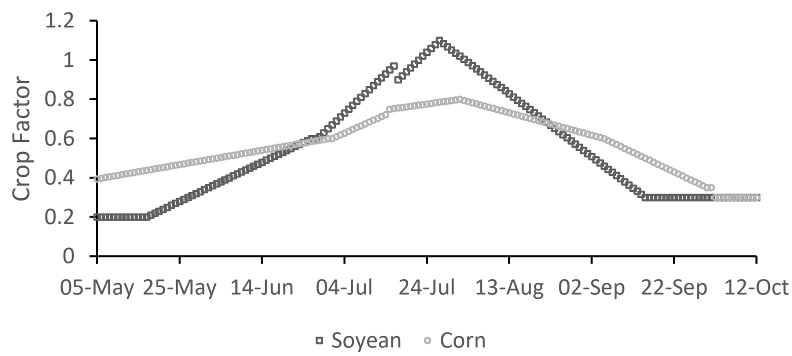

Figure 7.9: Used Crop Factor for the Calculation of the Soil Water Balance

Table 7.8: Literature ET Values for Ottawa, Ontario (OMAFRA, 2008)

Date	ET Ottawa	Date	ET Ottawa	Date	ET Ottawa
May 7	3.0	*July* 2	4.7	*September 3*	3.5
14	3.7	9	5.0	10	2.4
21	4.2	16	4.3	17	1.3
28	3.5	23	4.9	24	1.9
June 4	4.6	30	4.5		
11	4.6	*August 6*	4.3		
18	4.6	13	3.2		
25	4.5	20	3.4		
		27	3.1		

Concentration

Standard Curves

TSS

The Mettler Toledo Classic Plus Model AB204-s/fact analytical balance was calibrated as below by using calibration weights and comparing the calibrated weight to measured weight (mg).

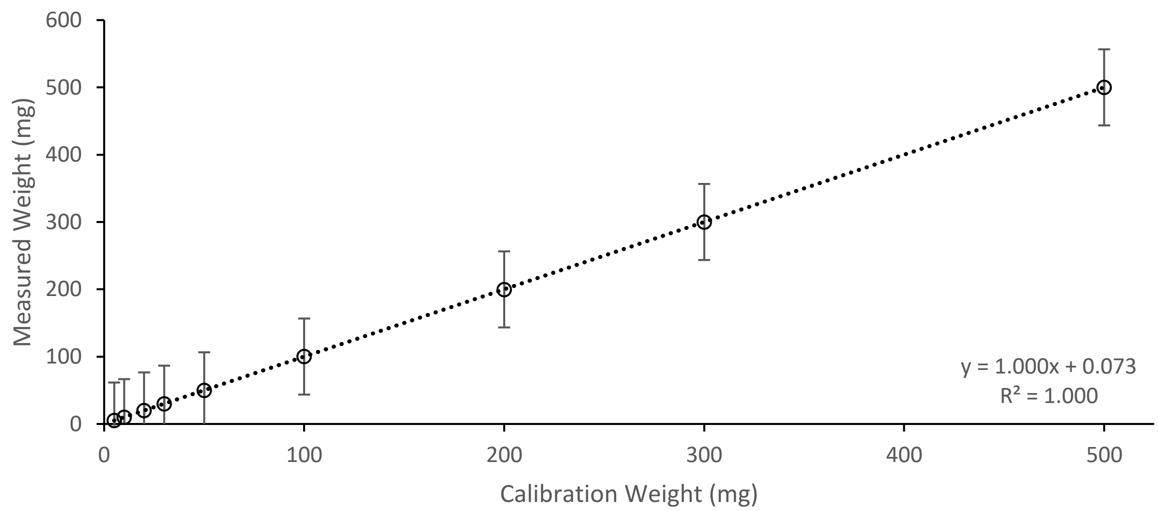

Figure 7.10 Calibration Curve Comparing Measured and Actual Weight of the Laboratory Weight Scale

The above chart demonstrates very strong correlation ($R^2 = 1$) between actual and measured weight, reinforcing confidence in the TSS data. The Limit of Detection (LOD) was calculated by analyzing successive blanks to determine the error inherent to the methodology. Successive blanks are defined samples consisting of 100 mL of distilled water only. LOD determination for TSS is demonstrated in the table below. LOD was determined at 4 mg L^{-1} and TSS concentrations of samples with values less than 0.5LOD (2 mg L^{-1}) were removed from the data set for further analysis.

Table 7.9 TSS Limit of Detection Determination Based on Successive Blanks

Successive Trials	Pre-weight (g)	Post-weight (g)	TSS (mg L^{-1})

1	2.1917	2.1915	-2
2	2.1695	2.1694	-2
3	2.2303	2.2304	1
4	2.2951	2.2952	1
5	2.2431	2.2431	0
6	2.3092	2.3091	-2
7	2.318	2.3181	2
8	2.3163	2.3163	0
9	2.2747	2.2745	-2
Average (μ)			0
Stdev (σ)			2
LOD = μ+3σ			4
LOQ = μ+10σ			15

TCOD

The standard curve for Low Range COD for concentrations ranging between 0 to 140 mg L^{-1} is shown below. The detection range for this method using the HACH DR 6000 spectrophotometer stored program 430 COD LR is 3 mg L^{-1}.

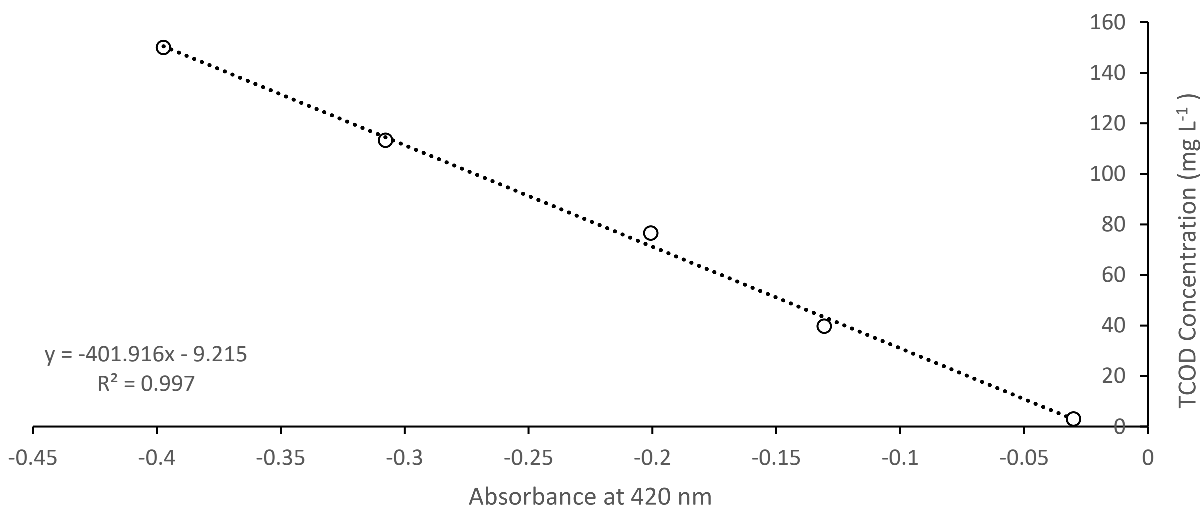

Figure 7.11 Low-Range COD Calibration Curve

Total Phosphorus

The standard curve for TP is shown below for concentrations ranging from 0.05 to 4 mg PO_4^{3-} L^{-1}. LOD was calculated by analyzing the variability absorbance of successive dilutions as low as mg PO_4^{3-} L^{-1}. Eight of ten, nine of ten and five of ten successive trials were observed to be within the range of the expected absorbance for concentrations of 0.05, 0.01 and 0.005 mg PO_4^{3-} $L^{-1.}$ The LOD was determined at 0.01 mg L^{-1} mg PO_4^{3-} L^{-1}. Concentrations of samples were screened against 0.5LOD (0.005 mg PO_4^{3-} L^{-1} or 0.002 mg P L^{-1}) and concentration values less than 0.5LOD were removed from the data set for further analysis.

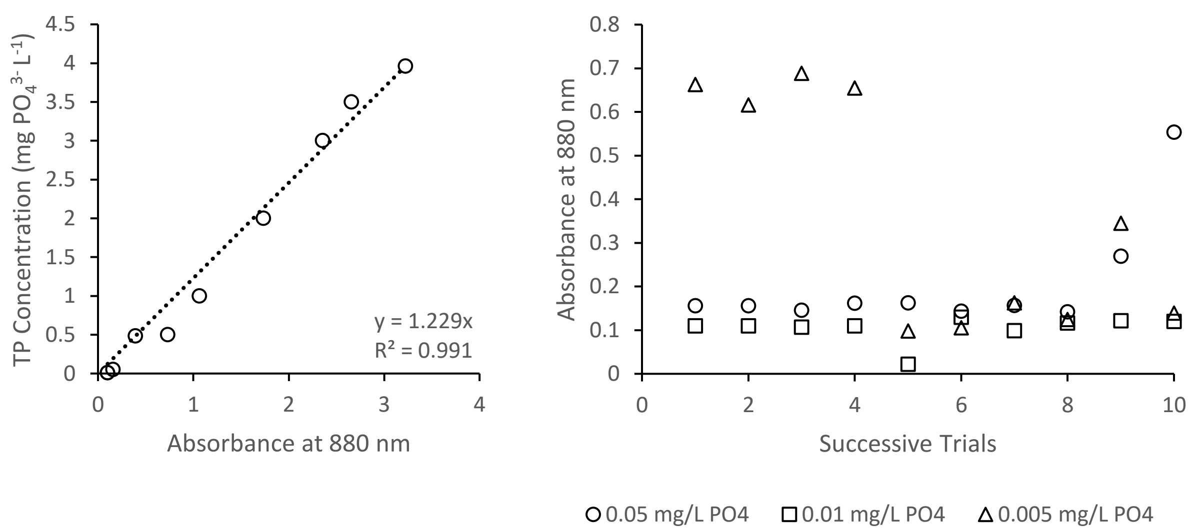

Figure 7.12 Left) Calibration Curve for Total Phosphorus and Right) Successive Repeats at Decreasing Concentrations of PO_4

Orthophosphate

The standard curve for SRP of concentrations between 0 to 3 mg PO_4^{3-} L^{-1} was calculated as below.

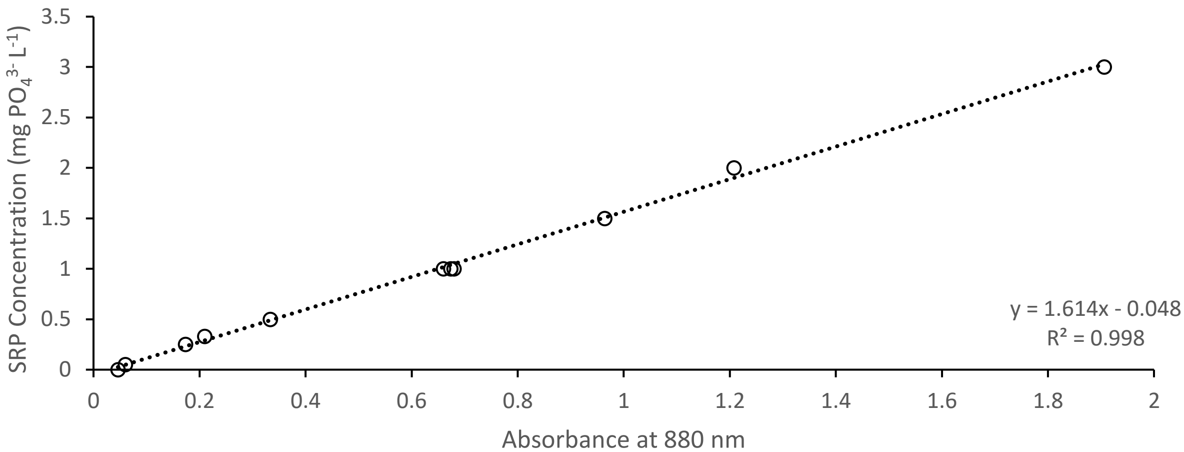

Figure 7.13 Standard Curve for Soluble Reactive Phosphate

The limit of detection was determined to be 0.043 mg PO_4^{3-} L^{-1} or 0.014 mg P L^{-1} using successive blanks. The data has been screened for half the LOD as 0.0215 mg L^{-1} PO_4 or 0.0070 mg L^{-1} P.

Table 7.10: Absorbance at 880 nm of Successive Blanks

Trial	Absorbance at 880 nm of Successive Blanks	Concentration (mg PO_4^{3-} L^{-1})
1	0.045	0.024
2	0.048	0.029
3	0.046	0.026
4	0.046	0.026
5	0.045	0.024
6	0.044	0.023
7	0.041	0.018
8	0.031	0.002
9	0.046	0.026
10	0.044	0.023
11	0.045	0.024
12	0.045	0.024
13	0.047	0.027
Average (μ)	0.04	0.023
Stdev (σ)	0.00	-0.042
LOD = μ+3σ	0.06	0.043
LOQ = μ+10σ	0.09	0.092

Total Nitrogen

The standard curve for total nitrogen (0.5-25 mg N L^{-1}) is shown below. The detection range for this method using the HACH DR 6000 spectrophotometer stored program 350 N, Total LR TNT, is 0.5 to 25.0 mg N L^{-1}.

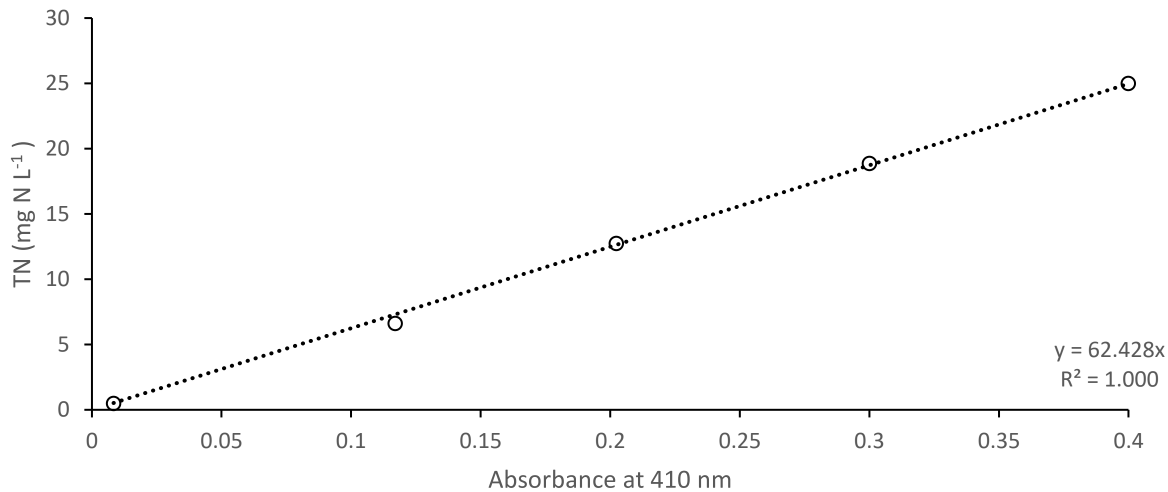

Figure 7.14 Standard Curve for Total Nitrogen

Ammonia

The standard curve for ammonia concentration ranging from 0 to 10 mg NH_4-N L^{-1} is shown below.

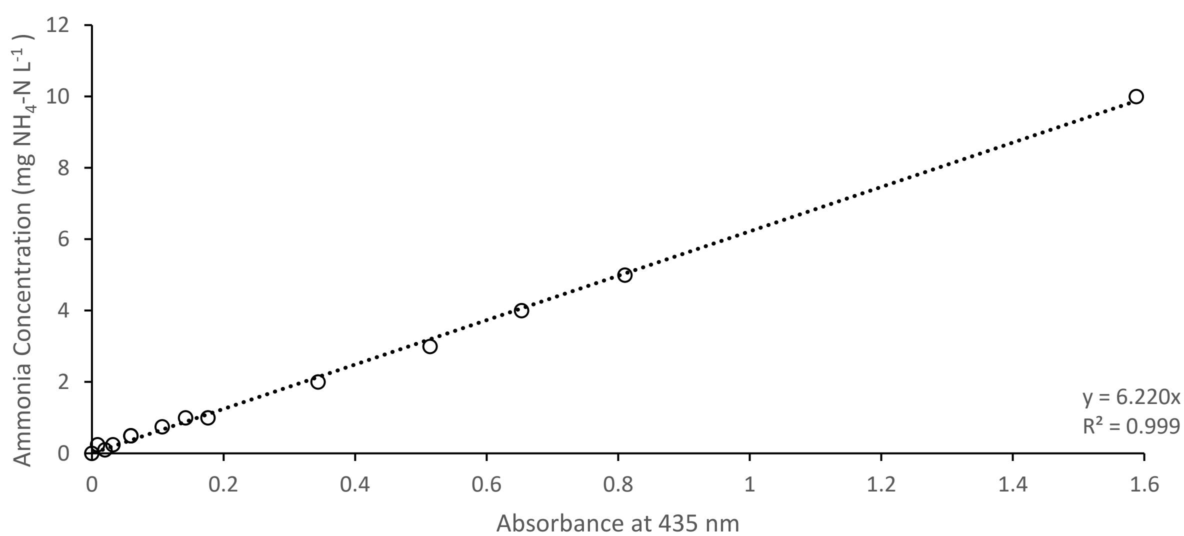

Figure 7.15 Standard Curve for Ammonia

The limit of detection was determined at 0.09 mg NH_4-N L^{-1} (shown in table below). Samples were screened against a value of 0.5LOD (0.045 mg NH_4-N L^{-1}) and values less than 0.5LOD were removed from the data set.

Table 7.11 Determination of the Limit of Detection for Ammonia

Trial	Absorbance at 420 nm	Concentration (mg L^{-1} NH_4^+-N)
1	-0.01	-0.03
2	-0.01	-0.03
3	-0.01	-0.01
4	-0.01	-0.02
5	-0.01	-0.01
6	-0.01	-0.02
7	-0.01	-0.01
8	0.00	0.07
9	0.00	0.03
10	-0.01	-0.01
Average (μ)	-0.01	-0.01
Stdev (σ)	0.01	0.03
LOD = μ+3σ	0.01	**0.09**
LOD = μ+10σ	0.04	0.30

Nitrate

The standard curve for nitrate is shown below for concentrations ranging from 0 to 10 mg NO_3-N L^{-1}. The LOD for nitrate was not calculated as the sample nitrate concentration ranged between 3-11 mg NO_3-N L^{-1} and the minimum (3 mg NO_3-N L^{-1}) is within the range of the accuracy of the standard curve (R^2=0.997).

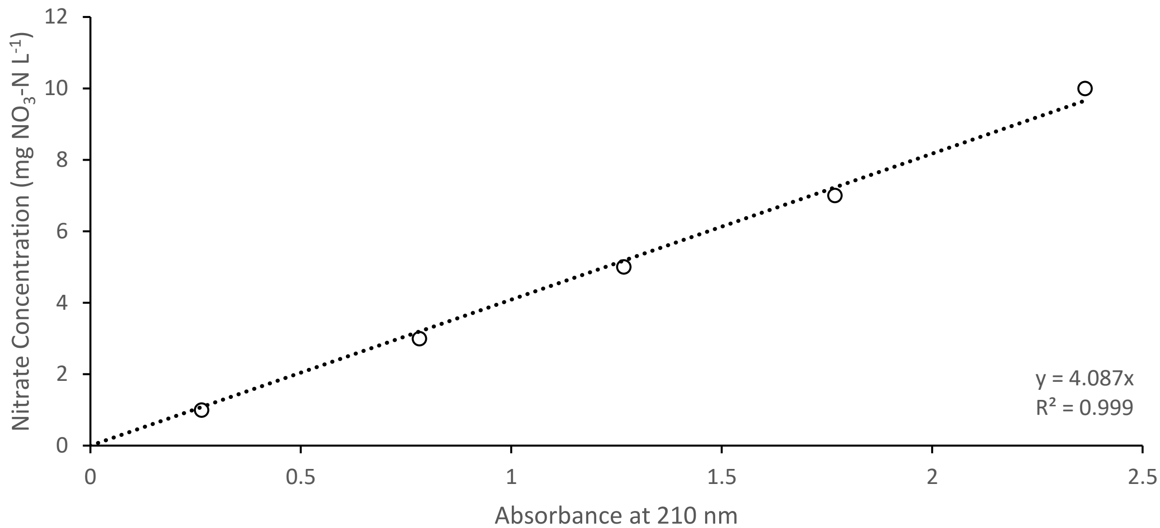

Figure 7.16 Standard Curve for Nitrate