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Evaluation of the Impacts of De-Icing Salts on the Performance of Bioretention Media in Retaining Phosphorus From Urban Stormwater

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A thesis submitted in partial fulfillment of the requirements for the Master of Engineering Science degree in Civil and Environmental Engineering

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Abstract

Bioretention systems are a low impact development system that can remove pollutants such as phosphorus (P) from urban stormwater. P retention in bioretention systems is complicated in cold climate regions due to factors such as inputs of road de-icing salts. This study evaluates the impact of prolonged and periodic salt inputs on P retention by conducting column experiments using three different bioretention media with and without an amendment added. Non-amended columns showed net P release, whereas amended columns showed net P retention. While some non-amended columns showed prolonged salt exposure increases P release, the largest P release for all columns occurred during the freshening period following the switch from high to low salt influent. High porewater pH (> 9) observed during the freshening period may be causing the high P release. This study provides new insights needed to improve year-round P retention in bioretention systems installed in cold climates.

Keywords

Stormwater Management, Low Impact Development (LID), Bioretention, Green Infrastructure, Phosphorus, Road Salt, Cold Climate, Runoff, Biogeochemical Processes, Sorption, Water Treatment Residuals

Summary for Lay Audience

As rainwater is collected on the streets of urban areas it picks up many pollutants including phosphorus and transports them to streams, rivers, and lakes. While phosphorus is essential for plant and animal growth, it can also lead to toxic algal blooms. This can cause serious public health, economic and environmental problems. Bioretention systems are a low impact development engineering approach that promotes the infiltration of stormwater into the ground. As the stormwater infiltrates, physical and chemical processes can remove phosphorus from the water, thereby improving water quality. However, these systems do not always perform as designed and can release high levels of phosphorus under certain conditions. It is still unclear what controls the behavior of phosphorus within bioretention systems and what conditions promote phosphorus retention. To address this, water treatment residuals (WTRs), a by-product of drinking water treatment plants, are a promising material that can be added to bioretention media to improve phosphorus retention. The behaviour of phosphorus within the system is further complicated by the use of de-icing roads salts used during the winter months in cold climate regions. The impact of de-icing road salts on phosphorus retention in bioretention media with and without WTRs is unclear.

In this study, laboratory columns with bioretention media (with and without an aluminum WTR added) were exposed to artificial stormwater with high and low salt concentrations. Columns without WTR were found to release phosphorus, whereas columns with WTR were found to remove phosphorus. The highest release of phosphorus occurred when the columns switched from receiving water with high salt concentrations to no salt. The pH also increased during this switch from high salt input to no salt input indicating that pH may be a major control on the behaviour of phosphorus in bioretention media exposed to de-icing road salts. This study provides important new insights into the impact of de-icing salts on the ability of bioretention systems to remove phosphorus as needed to improve the year-round performance of these systems in cold climate environments.

Co-Authorship Statement

This thesis is the result of collaboration between Dr. Clare Robinson, Jaeleah Goor, and Brennan Donado. The candidate is responsible for the design of the laboratory column experiments, collection and analysis of data, and writing the drafts of all chapters of this thesis. Dr. Clare Robinson provided the initial motivation and background for this research, provided suggestions for data analysis, and provided revisions for improvements of the thesis. The co-authorship breakdown of Chapter 3 is as follows:

Chapter 3:

Authors: Brennan Donado, Clare Robinson, Jaeleah Goor

Contributions:

Brennan Donado designed the laboratory column setup, collected and analyzed water quality data, interpreted the results, and was the lead author for writing the chapter.

Clare Robinson supervised column data collection, analysis, provided insight and interpretation of results, and reviewed the draft chapter.

Jaeleah Goor assisted with data collection, analysis, provided insight and interpretation of results, and reviewed the draft chapter.

Acknowledgments

I would like to express my sincere gratitude to my supervisor, Dr. Clare Robinson, for your invaluable advice, continuous support, encouragement, and patience over the past years. This research would not have been possible without your passion, dedication, and immense knowledge. I truly value your mentorship and the opportunity to take on this project and learn from you. I am beyond grateful to have been able to call you, my supervisor.

Thank you to NSERC, OCI (Ontario Centre of Innovation), and C.F. Crozier & Associates Inc. for providing funding for this work and supporting this project.

I would like to thank Dr. Jason Gerhard, Dr. Chris Power, and all of the RESTORE research group, for the incredible friendships, inspiration, and support. I am proud to have been part of such a welcoming and amazing group of people. I would like to express my gratitude to Jaeleah Goor, Meghan Vissers, Shuyang Wang, Sabina Rakhimbekova, Dillon Vyn, Chris Jobity, Anna Duong, and Natalie Connors for your tireless effort and patience while running and analyzing all my complicated samples in the lab. I would also like to extend a thank you to Caitlin Corcoran for your knowledge and all the time you spend guiding and teaching all of us how to use and troubleshoot the analytical machines.

Finally, I would like to thank my friends and family for their unconditional love, support, and motivation. Thank you for always believing in me and challenging me to step out of my comfort zone. A special thank you to my parents, I can't begin to express how thankful I am for everything you have done for me.

Dedication

This thesis is dedicated to my family.

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List of Abbreviations

Abbreviation	Full Description
AA	Atomic Adsorption
Al-WTR	Aluminum Water Treatment Residual
ASTM	American Society for Testing and Materials
CEC	Cation Exchange Capacity
DIP	Dissolved Inorganic Phosphorus
DOC	Dissolved Organic Carbon
DOP	Dissolved Organic Phosphorus
DP	Dissolved Phosphorus
EC	Electrical Conductivity
FIA	Flow Injection Analysis
GLWQA	Great Lakes Water Quality Agreement
HDPE	High Density Polyethylene
HPLC	High-Performance Liquid Chromatography
LID	Low Impact Development
ORP	Oxidation Reduction Potential
PP	Particulate Phosphorus
SRP	Soluble Reactive Phosphorus
TDP	Total Dissolved Phosphorus
TP	Total Phosphorus
US EPA	United States Environmental Protection Agency
UV/Vis	Ultraviolet Visible
WTR	Water Treatment Residual

Chapter 1

1 Introduction

1.1 Research Background

Urbanization places increasing stress on urban stormwater management systems by replacing natural pervious surfaces with hard impervious surfaces (Liu et al., 2014). This modifies the natural hydrologic cycle by reducing infiltration and increasing stormwater runoff volumes delivered to downstream receiving watersheds (Adhikari et al., 2016). The stormwater also transports pollutants from the urban environment (e.g., from road surfaces, vehicles, lawns) to receiving watersheds which can degrade downstream water quality and impair aquatic ecosystems (Davis et al., 2001).

Various pollutants of concern are found in urban stormwater including sediments, metals, chloride, and nutrients including nitrogen (N) and phosphorus (P) (Dietz & Clausen, 2005). This thesis focuses specifically on the performance of urban stormwater systems in retaining P. While P is a naturally occurring element and is an essential nutrient for animal and plant growth, excessive P loads to surface waters can cause eutrophication leading to harmful algal blooms and hypoxic events (Environment and Climate Change Canada and the Ontario Ministry of the Environment and Climate Change, 2018). This can have severe economic and ecological implications by directly impacting recreational and commercial activities, clogging municipal drinking water intakes, and impairing ecosystem function and biodiversity (Environment and Climate Change Canada and the Ontario Ministry of the Environment and Climate Change, 2018). Eutrophication is a major challenge for many freshwater environments worldwide including in Lake Erie which is one of the largest freshwater bodies in the world. Since P is generally the limiting nutrient in freshwaters, it is the typically the main target for nutrient management plans aimed at reducing eutrophication of fresh surface waters (Komlos & Traver, 2012). Non-point P sources including urban stormwater are recognized as an important contributor to P loads to receiving watersheds and reducing their contribution are now a focus for watershed nutrient management plans.

Over the last two decades urban stormwater management has seen a shift from “traditional” management focused primarily on reducing floods downstream (controlling stormwater volumes and timing) to a more holistic approach called low impact development (LID). LID aims to mimic natural processes to mitigate the impacts of stormwater runoff and pollution by treating stormwater runoff as close to its source as possible (Credit Valley Conservation, 2010; Goulden et al., 2018). Bioretention systems are an increasingly popular type of LID that are now used worldwide including in many Canadian municipalities (Trowsdale & Simcock, 2011). These systems are small-scale shallow vegetated depressions made with an engineered soil media consisting of sand, topsoil, and organic matter (herein referred to as bioretention media). These systems are used to reduce peak runoff volumes and retain pollutants found in urban stormwater (Hatt et al., 2008; LeFevre et al., 2015; J. Li & Davis, 2016). However, the performance of bioretention systems with respect to removing P from urban stormwater is highly variable. While some studies have shown total P (TP) retention within the systems (Davis et al., 2006; Komlos & Traver, 2012; Liu & Davis, 2014; Lucas & Greenway, 2008), other studies have shown that bioretention systems, specifically the bioretention media, can act as a source of TP with effluent TP concentrations being higher than influent TP concentrations (Dietz & Clausen, 2005; Hatt et al., 2008; Hunt et al., 2006; H. Li & Davis, 2009). TP is composed of particulate phosphorus (PP) and dissolved phosphorus (DP). DP is further broken into dissolved organic phosphorus (DOP) and soluble reactive phosphorus (SRP). SRP and some DOP forms are bioavailable, meaning they are available to be taken up by primary producers and thus contribute to algal growth (Ellison & Brett, 2006; LeFevre et al., 2015). While DP and PP are often found in equal amounts in urban stormwater, in some cases DP has been observed to be up to 90% of the TP load (LeFevre et al., 2015; Marvin et al., 2020). Bioretention systems have been found to be highly effective in retaining PP by physical filtration mechanisms, but the mechanisms governing the retention and release of DP are more complex (Liu & Davis, 2014). Considering the contrasting results reported previously with respect to TP retention in bioretention systems there is a need to better understand the factors that affect TP retention in these systems.

To increase the performance and consistency of bioretention systems with respect to P retention recent studies have examined the effectiveness of using various amendments to “enhance” the bioretention media (Marvin et al., 2020; O’Neill & Davis, 2012a). Water treatment residuals (WTRs) are a by-product of drinking water treatment plants produced during the coagulation-filtration treatment step (Ippolito et al., 2011; Soleimanifar et al., 2016). WTRs have been shown to increase the P sorption capacity of the bioretention media, and thus increase P retention in bioretention systems compared to systems with non-amended bioretention media (Ippolito et al., 2011; Marvin et al., 2020; O’Neill & Davis, 2012b).

In cold climate regions which are characterized by cold (below freezing) temperatures, freeze-thaw cycles, and snow, the function of bioretention systems is complicated by decreased biological activities in colder months, increased sediment and pollutant concentrations and high runoff volumes during snowmelt periods, and the potential impacts of road de-icing salts (Khan et al., 2012; Kratky et al., 2017). It is estimated that municipalities in the United States spend around \$US 2 billion every year for winter road maintenance and as part of that maintenance, approximately 1.5 million tons of de-icing salts, typically sodium chloride, are applied to roads during the winter (U.S. EPA, 2001). The impact of high salt inputs on the efficiency of bioretention systems to retain P is unclear with prior studies reporting conflicting findings. For instance, Szota et al. (2015) found from column experiments that increasing salt concentrations in influent water resulted in lower effluent TP concentrations. In contrast, Géhéniau et al. (2015) showed from their monitoring of a full-scale bioretention system that effluent TP concentrations increased during winter when salt concentrations were high in the influent stormwater, and Søbørg et al. (2020) found that high salt loading decreased TP retention but had no effect on DP retention in their bioretention column experiments. Other column experiments have also shown that effluent TP concentrations may increase in response to high salt loading but show different timings of when the TP is released. For instance, McManus & Davis (2020) observed that effluent TP concentrations may spike when bioretention media is flushed with stormwater with low salt concentration following a short duration period of high salt stormwater input. More recently, Goor et al. (2021)

showed from their monitoring of a field bioretention system combined with column experiments that high salt loading may increase TP release mostly in the form of DP. However, they concluded that the high TP release may have occurred due to prolonged duration of high salt loading over the winter rather than due to flushing of the media with low salt concentration influent. Additionally, no prior literature has evaluated the performance of AI-WTR “enhanced” bioretention media exposed to stormwater with high salt concentrations.

Due to variable findings from prior studies, there is a need to further evaluate and understand the mechanisms responsible for the retention and release of P in bioretention media including understanding the potential impact of high salt loading on the ability of bioretention media and “enhanced” bioretention media to retain P.

1.2 Research Objectives

The overall objective of this research thesis is to address knowledge gaps regarding the performance of bioretention media in retaining P, in particular SRP, in urban stormwater under prolonged and periodic salt loading conditions. Despite the popularity of bioretention systems, the impact of de-icing salts on the ability of bioretention media to retain P including the potential impacts of salt on enhanced WTR-amended bioretention media are unclear. To address these knowledge gaps, this thesis is divided into three sub-objectives:

1. Assess the impact of prolonged and periodic high salt loading on SRP retention in bioretention media including switching between stormwater influent with high salt and low salt concentrations.
2. Assess the impact of prolonged and periodic high salt loading on SRP retention in bioretention media amended with Al-WTR.
3. Identify possible geochemical controls affecting SRP retention and release in bioretention media exposed to stormwater influent with prolonged and periodic salt concentrations.

The findings from this study are needed to provide insight into seasonal variations in the performance of bioretention systems, and thus improve the design and maintenance of bioretention systems installed in cold climate environments to ensure sustained year-round P retention.

1.3 Thesis Outline

This thesis is written in “Integrated Article Format.” A brief description of each chapter is presented below.

Chapter 1: Introduction to the research background, motivation for research, and the research objectives.

Chapter 2: A synopsis on stormwater management, bioretention system design, the impacts of P in the environment, and P transformations within bioretention systems. This chapter also provides a review on prior literature that has explored the performance of bioretention media with respect to P retention, the impacts of de-icing salts on this performance, and the use of an Al-WTR as an amendment in bioretention systems.

Chapter 3: Presents the methods and results of column experiments conducted to evaluate the performance of bioretention media collected from three operational bioretention systems. The mechanisms controlling P retention/release in the bioretention media, the impacts of de-icing salts, and benefits of using bioretention media amended with Al-WTR are assessed.

Chapter 4: Summarizes the research results and provides recommendations for future work.

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Chapter 2

2 Literature Review

Phosphorus (P) is an essential nutrient for animal and plant growth. In freshwater aquatic systems, excess P can lead to eutrophication which can have negative environmental, societal and economic consequences (Correll, 1999; Environment and Climate Change Canada, 2020; Environment and Climate Change Canada and the Ontario Ministry of the Environment and Climate Change, 2018). Water quality management programs across Canada have historically focused on reducing P loading from point sources including wastewater treatment plants. As a result, non-point P sources, including urban stormwater runoff, are now the dominant contributors of P to surface waters and management programs need to address these more complex sources (Scavia et al., 2014).

Bioretention systems are an increasingly popular type of low impact development stormwater management system designed to reduce the quantity and improve the quality of urban stormwater runoff (Khan et al., 2012a; LeFevre et al., 2015). Prior studies have illustrated the benefits of using bioretention systems for the removal of pollutants found in urban stormwater including sediments, metals, and nutrients including nitrogen (N) and P (Davis et al., 2006; Hunt et al., 2006; Khan et al., 2012b; Komlos & Traver, 2012; Kratky et al., 2017). However, a number of studies have also shown that retention of pollutants, especially P, can be inconsistent over time and between bioretention systems (Dietz & Clausen, 2005; Hager et al., 2019; Hatt et al., 2008; H. Li & Davis, 2009). Additionally, the impact of cold climate factors such as inputs of road de-icing salts remains unclear with previous studies reporting conflicting findings. For instance, some studies have observed decreased P retention with high salt loading (Géhéniau et al., 2015; Sjøberg et al., 2020), while others have reported increased P retention (Szota et al., 2015). With bioretention systems now being installed widely including in municipalities with cold climates there is a need to better understand the impacts of de-icing salt inputs on the retention of P in these systems to ensure they are able to provide year-round water quality improvements. This thesis focuses on assessing the performance of the engineered soil media used in bioretention systems (herein referred to as bioretention media) in reducing

P loads from urban stormwater with time-varying low and high salt (sodium chloride, NaCl) loading. This chapter reviews the impacts of P on aquatic systems, P transformations in porous media, bioretention system design and their performance with respect to P retention including the use of soil amendments, and the potential impacts of road de-icing salts on P retention in bioretention systems.

2.1 Phosphorus in the environment

P is a naturally occurring element that is an essential nutrient for animal and plant growth. However, excessive P loads to surface waters create eutrophic conditions which can lead to harmful algal blooms and hypoxic events (Correll, 1999; Environment and Climate Change Canada, 2020; Environment and Climate Change Canada and the Ontario Ministry of the Environment and Climate Change, 2018). Eutrophication is a major challenge in many freshwater systems around the world including large lakes in Canada such as Lake Erie and Lake Winnipeg. Eutrophication can have severe economic, societal and environmental impacts by directly impacting recreational and commercial activities, clogging municipal drinking water intakes, and leading to impaired ecosystem function and biodiversity loss (Correll, 1999; Environment and Climate Change Canada and the Ontario Ministry of the Environment and Climate Change, 2018). For instance, Smith et al. (2019) estimated the economic costs of algal blooms in Lake Erie to be \$272 million (in 2015 prices) per year over a 30-year period.

In aquatic systems, plant and bacterial growth is limited by the availability of an essential element, referred to as the “limiting nutrient” (Correll, 1999). As P is naturally the limiting nutrient in many fresh surface water systems (e.g., lakes, reservoirs, and streams) (Correll, 1999; Komlos & Traver, 2012) increased P loading to surface waters from human activities often results in eutrophication. As such, water quality management efforts in freshwater environments often focus on limiting P inputs from anthropogenic sources (Correll, 1999; Environment and Climate Change Canada and the Ontario Ministry of the Environment and Climate Change, 2018). For example, Canada and the United States have worked together to reduce P loads to Lake Erie since the 1970’s as part of the Great Lakes Water Quality Agreement (GLWQA). Initial efforts found

success in controlling point sources such as municipal wastewater treatment effluent and industrial effluent (Environment and Climate Change Canada and the Ontario Ministry of the Environment and Climate Change, 2018; Scavia et al., 2014). However, since the 1990's there has been a re-emergence of harmful algal blooms in Lake Erie due to a changing climate and changes in land use such as increased urbanization and intensification of agriculture (Environment and Climate Change Canada and the Ontario Ministry of the Environment and Climate Change, 2018). To address the re-emergence of algal blooms, Canada and the United States recently committed to reducing total phosphorus (TP) and soluble reactive phosphorus (SRP) loads entering Lake Erie by 40% from 2008 levels by 2025 (Environment and Climate Change Canada and the Ontario Ministry of the Environment and Climate Change, 2018). As non-point sources are now thought to be responsible for the majority of P loads entering the lake (Environment and Climate Change Canada, 2020), nutrient management plans need to focus on reducing P loads from non-point sources including agriculture and urban stormwater runoff.

2.1.1 Forms of phosphorus and transformations

Total P (TP) is present in the environment as particulate P (PP) and dissolved P (DP) (Figure 2-1) (Marvin et al., 2020). PP is the fraction of P that is attached to particles and is retained on a 0.45- μm filter (Broberg & Persson, 1988; Ellison & Brett, 2006). DP is the remaining fraction of P that passes through the filter. DP can be further broken into dissolved organic phosphorus (DOP) and dissolved inorganic phosphorus (DIP). DIP is often referred to as soluble reactive phosphorus (SRP) and the main form of DIP is orthophosphate (PO_4^{3-}) (Broberg & Persson, 1988; Ellison & Brett, 2006; LeFevre et al., 2015). SRP and some DOP types are the forms of P that are bioavailable, meaning they are available to be taken up by primary producers and thus may contribute to the growth of algal blooms. As such, these forms of P are often the target for nutrient water quality management programs (Ellison & Brett, 2006; Komlos & Traver, 2012; LeFevre et al., 2015).

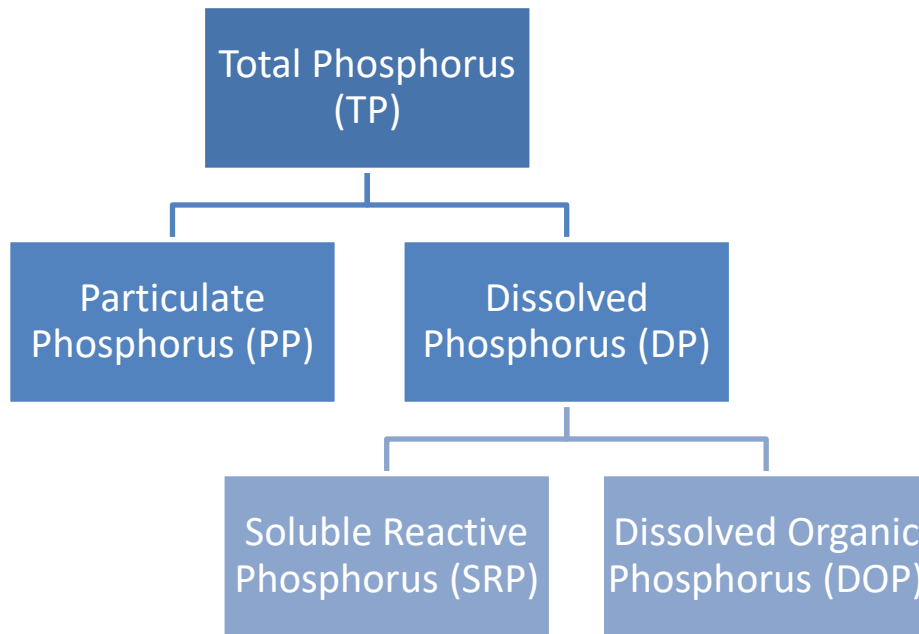


Figure 2-1: Forms of P in the environment.

P cycles between its inorganic and organic forms in aquatic systems with P transformations affected by geochemical conditions including pH, temperature, salinity, and the presence of oxygen (redox conditions) (Bai et al., 2017; Ellison & Brett, 2006; Mackey et al., 2019; Prasad & Chakraborty, 2019) (Figure 2-2). In porous media, including within bioretention systems, the main P transformation processes are immobilization and mineralization, plant uptake, weathering, precipitation and dissolution, and adsorption and desorption (Mackey et al., 2019; Prasad & Chakraborty, 2019).

Mineralization is the process by which enzymes produced by microbes convert organic P (organisms and vegetation) in the soil into inorganic P (Prasad & Chakraborty, 2019). In the reverse process of immobilization, inorganic forms of P are transformed into organic forms by being absorbed into the living cells of soil microbes. Additionally, during the growing season, plants can take up inorganic P from the soil and store it in their biomass thereby converting it into organic P (Mackey et al., 2019; Prasad & Chakraborty, 2019). Immobilization is often considered to be “transitory” as mineralization can occur rapidly after the death of plants and cells which re-release DP into the system (Mackey et al., 2019). The biological processes of mineralization and immobilization are sensitive to

changes in soil moisture, temperature, pH, and microbial populations (Prasad & Chakraborty, 2019).

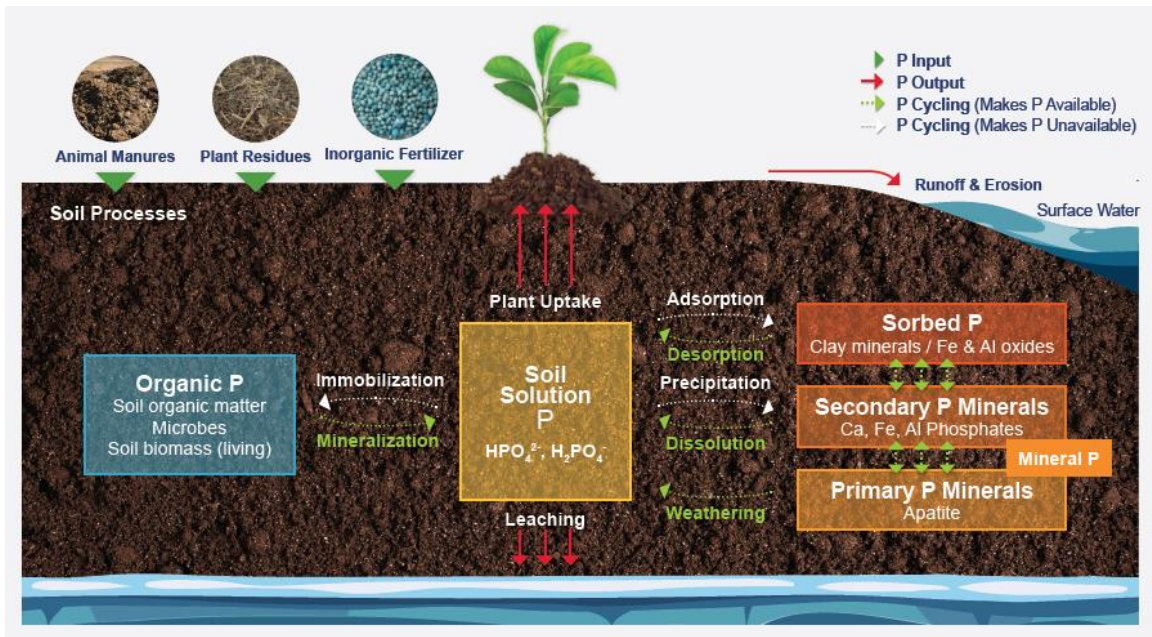


Figure 2-2: Main P transformations in porous media (Prasad & Chakraborty, 2019).

DOP and SRP can also be produced by the weathering of P-rich primary minerals (e.g., apatite) and the dissolution of secondary minerals (e.g., Ca, Fe, Al, and Mn phosphates) (Hyland et al., 2005; Mackey et al., 2019; Prasad & Chakraborty, 2019). Weathering is generally considered an irreversible process whereby primary minerals (rock material) break down due to physical processes (mechanical weathering) or processes that alter the chemical structure of the minerals (chemical weathering) (Mackey et al., 2019; Prasad & Chakraborty, 2019). Dissolution of secondary minerals is considered a reversible process whereby minerals may also precipitate depending on the dissolved chemical concentrations and geochemical conditions. For instance, SRP can co-precipitate with Ca^{2+} in alkaline calcareous environments or co-precipitate with metal ions including Al^{3+} , Fe^{3+} , and Mn^{2+} in acidic environments (Hyland et al., 2005; J. Li & Davis, 2016; Mackey et al., 2019; Prasad & Chakraborty, 2019). While secondary minerals tend to be relatively stable in the environment, precipitation-dissolution of secondary phosphate minerals is influenced by pH, redox conditions, and metal ion concentrations. Changes in these

conditions can cause the minerals to slowly dissolve or precipitate, thereby affecting the SRP concentration (Mackey et al., 2019; Prasad & Chakraborty, 2019).

SRP and organic phosphate ions can also be removed from porewater and associated with solid phases through adsorption, a process by which these ions attach to the surface of solid phases including clay minerals and Mn-, Al- and Fe-oxides (Lucas & Greenway, 2011; Mackey et al., 2019). Adsorption can occur as fast and reversible outer sphere ion-exchange reactions with Mn-, Fe-, and Al-oxide minerals surfaces, as well as slower and less reversible inner sphere adsorption reactions forming mono- and bidentate complexes. There is a continuous transition between the inner- and outer-sphere complexes and as the slower adsorption reactions occur P can be transferred from outer-sphere complexes to inner-sphere irreversible sites, increasing the availability of the more rapid and reversible adsorption sites (Lucas & Greenway, 2008; Marvin et al., 2020; O'Neill & Davis, 2012a). The adsorption capacity of a soil is influenced by the amount of available adsorption sites and therefore, the soil's capacity for further P retention decreases as adsorption occurs (J. Li & Davis, 2016). Soils with higher clay content also have higher adsorption capacity due to an increased surface area (Prasad & Chakraborty, 2019). The adsorption-desorption processes are influenced by redox conditions as the dissolution of metal oxides and release of SRP is often caused by the onset of reducing conditions (Bai et al., 2017; Mackey et al., 2019). pH can also affect the adsorption capacity of soils since Fe- and Al-oxides surfaces have variable charge, depending on pH. Above a certain pH, mineral surfaces go from being positively charged, which attracts anions, to negatively charged, which repels negatively charged PO_4^{3-} species (Schlesinger & Bernhardt, 2020). Finally, the tendency of P to adsorb is also influenced by the presence and concentration of other anions that can bind and compete with phosphates for adsorption sites (Schlesinger & Bernhardt, 2020).

2.2 Bioretention systems

2.2.1 Stormwater management and low impact development

Rapid urbanization and urban sprawl increase imperviousness and change the natural hydrology of watersheds (Abebe et al., 2018; Fletcher et al., 2013; Hager et al., 2019).

Reduced infiltration leads to decreased groundwater recharge, increased stormwater runoff volumes, flooding, and increased transport of pollutants to downstream surface waters and subsequent impairment of aquatic ecosystems (Fletcher et al., 2013; Hager et al., 2019; H. Li & Davis, 2009). Pollutants commonly found in urban stormwater include suspended solids, metals (copper, cadmium, nickel, chromium, and zinc), oil and grease, nutrients such as P and N, pesticides, pathogens, and petroleum hydrocarbons (LeFevre et al., 2015; H. Li & Davis, 2009). Traditional stormwater management approaches use “end-of-pipe” methods such as detention ponds that focus on flood reduction and provide limited water quality benefits or restoration of the pre-development hydrological conditions (Khan et al., 2012a). These detention and conveyance-based stormwater management systems are now thought to be insufficient for water balance control, and protection of water quality and ecosystems (Fletcher et al., 2013). As such, over the last decade there has been a shift from traditional stormwater management systems to a more holistic and sustainable approach that focuses on addressing water quantity and water quality challenges simultaneously (Fletcher et al., 2013; Hager et al., 2019).

Low impact development (LID) is a stormwater management approach which aims to manage both water quantity and quality (Davis & McCuen, 2005; Hager et al., 2019). LIDs (i.e., green infrastructure) are manmade features that rely on natural processes to make the post-development hydrologic and water quality characteristics of a watershed the same as pre-development conditions (Davis et al., 2006; Davis & McCuen, 2005; Hager et al., 2019; Khan et al., 2012a). In contrast to traditional stormwater management approaches, LIDs aim to provide both water quantity and quality benefits by capturing and treating stormwater close to the source by the implementation of small-scale water management structures that allow water to infiltrate into subsurface rather than becoming runoff (Davis & McCuen, 2005; Khan et al., 2012a). LID features include infiltration swales and trenches, permeable pavements, green roofs, and bioretention systems. Bioretention systems are an increasingly popular LID feature now used worldwide including in many Canadian municipalities (Davis & McCuen, 2005; Khan et al., 2012a; Trowsdale & Simcock, 2011).

2.2.2 Design of bioretention systems

Bioretention systems are a type of LID stormwater management system that promote the infiltration of stormwater and in doing so they are able to reduce runoff volumes, peak flows, and pollutant concentrations (Davis & McCuen, 2005; Khan et al., 2012a; LeFevre et al., 2015). These systems are shallow basins with vegetation and underlying soil media. As stormwater infiltrates through the soil media pollutant concentrations can be decreased through a combination of physical, chemical, and biological processes (Davis & McCuen, 2005; Khan et al., 2012a). The flexible size and design of bioretention systems has resulted in their widespread installation for management of stormwater runoff from a variety of sources including small residential lots, large parking lots and roads (Davis & McCuen, 2005; Sustainable Technologies Evaluation Program, 2021).

According to Sustainable Technologies Evaluation Program (2021), for optimal performance bioretention systems should ideally receive runoff from impervious areas that are between 5 to 20 times their own surface area. Generally, bioretention systems have a 0.05 to 0.1 m deep layer of mulch or topsoil on the surface to promote vegetation growth (Figure 2-3). Vegetation used in bioretention systems often includes grasses, shrubs, and sometimes small trees that can provide additional pollutant uptake as well as promote evapotranspiration and biological activity (Davis & McCuen, 2005). Below the topsoil or mulch layer, a 0.3 to 1.0 m deep layer of bioretention media promotes infiltration, acts as temporary water storage, and provides water quality treatment. Below the bioretention media layer, there is typically a layer of pea gravel or clean annular aggregate that prevents the migration of the finer bioretention media to the underlying gravel storage layer below (Davis & McCuen, 2005; Sustainable Technologies Evaluation Program, 2021). In permeable environments, bioretention systems are designed so that stormwater infiltrates into the subsurface below the system. However, when the native soil infiltration rates are less than 15mm/hr, a perforated underdrain pipe is typically used to connect the gravel layer to the storm sewer network (Khan et al., 2012a; Kratky et al., 2017; Sustainable Technologies Evaluation Program, 2021).

The composition of the bioretention media is an important aspect of the bioretention system design because the media needs to support plant growth, enable infiltration, and also impacts the effectiveness of these systems to remove pollutants (Hunt & Lord, 2006). The recommended composition of the bioretention media depends on whether the overall priority of the system is infiltration or water quality treatment. For the latter, the bioretention media is typically composed of three parts sand, two parts topsoil, and one-part organic matter (Sustainable Technologies Evaluation Program, 2021). However, even for systems focused on improving water quality, a high infiltration rate is critical to reduce excessive ponding and avoid bypassing the bioretention system through the overflow system (Davis & McCuen, 2005). As such, the particle size distribution of the bioretention media is recommended to be less than 25% silt- and clay-sized particles combined. Additionally, the saturated hydraulic conductivity of the system should be between 25- to 300-mm/hr (Sustainable Technologies Evaluation Program, 2021). While organic matter is essential to support vegetation growth on the bioretention system, it can also leach nutrients into the stormwater as it infiltrates through the bioretention system. Therefore, 3-10% organic matter by weight is recommended (Hunt & Lord, 2006; Sustainable Technologies Evaluation Program, 2021). To ensure that the media can support vegetation without leaching P, the plant available P (i.e., the extractable P) should be between 12- to 40-ppm. Lastly, the cation exchange capacity (CEC) which indicates the ability of the bioretention media to adsorb exchangeable cations in the soil is typically recommended to be greater than 10 meq/100g (Ketterings et al., 2007; Schlesinger & Bernhardt, 2020; Sustainable Technologies Evaluation Program, 2021). Amendments can also be added to bioretention media to enhance the removal of pollutants including P. The addition of amendments is discussed in Section 2.3.1.

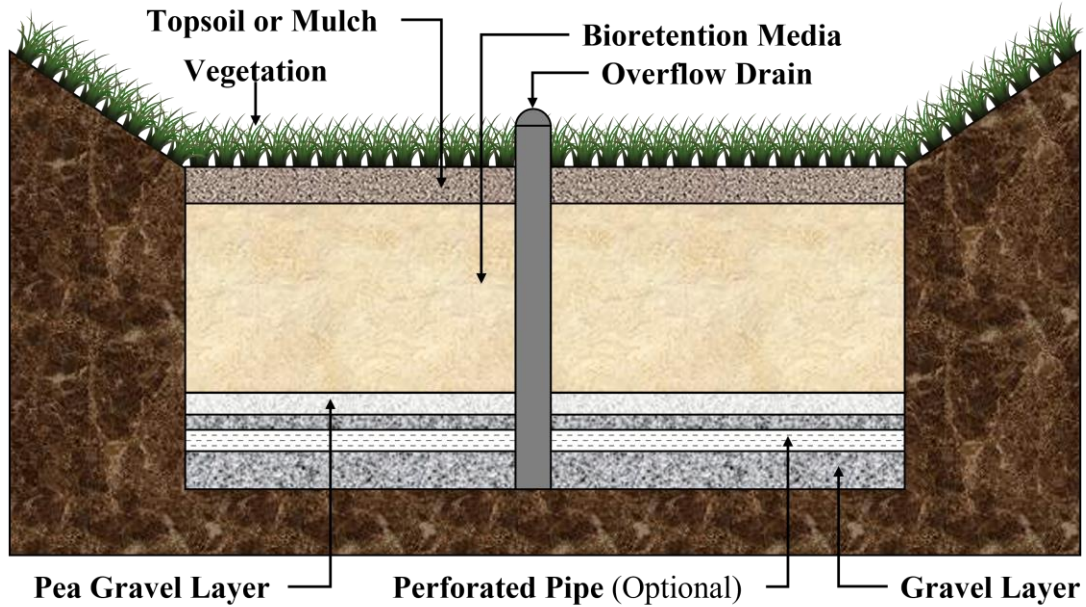


Figure 2-3: Typical bioretention system design.

2.3 P retention in bioretention systems and controlling factors

The performance of bioretention systems with respect to removing P from urban stormwater is highly variable. For example, Davis et al. (2006), reported 70 - 85% TP retention in their combined mesocosm and field-scale bioretention study. This study is consistent with other observations of TP retention in bioretention systems (Komlos & Traver, 2012; Lucas & Greenway, 2008). In contrast, a study of two field bioretention systems by Dietz & Clausen (2005) showed that effluent TP concentrations were greater than influent TP concentrations, although both the influent and effluent concentrations generally decreased over the 56-week monitoring period. This study is consistent with other studies that have shown that bioretention systems can act as a source of TP with greater TP concentrations in the effluent compared to the influent (Goor et al., 2021; Hatt et al., 2008; Hunt et al., 2006; H. Li & Davis, 2009).

In addition to understanding the performance of bioretention systems with respect to TP retention, it is important to understand the effectiveness of bioretention systems in retaining the different forms of P including PP and SRP. Studies have found that bioretention systems are effective in retaining PP due to physical filtration (H. Li &

Davis, 2009; J. Li & Davis, 2016; Liu & Davis, 2014; Marvin et al., 2020). The few studies that have analyzed for SRP, observed removal efficiencies ranging from 97 to -584% and suggest SRP retention is likely due to adsorption processes (Mangangka et al., 2015; Shrestha et al., 2018). However, as P can cycle between its particulate and dissolved phases (both organic and inorganic) depending on environmental conditions (Liu & Davis, 2014), detailed understanding of P behaviour within bioretention systems is needed to understand the processes that govern the removal of P.

The processes that control the forms and transformations of P in the natural environment also affect the fate of P in bioretention systems. As such, many factors such as pH, redox conditions, and metal ion concentrations can affect P behaviour, and more specifically SRP retention in bioretention systems. pH is an important factor in the adsorption and precipitation reactions that control SRP retention and release. In more alkaline environments, SRP removal is largely through co-precipitation reactions with Ca, while SRP is primarily removed through Al- and Fe-oxide adsorption processes in more neutral or acidic environments (Marvin et al., 2020). For example, Davis et al. (2006) reported desorption of P in the upper ports of their bioretention box laboratory experiments where the pH was either greater than 8 or less than 6. In contrast they observed no P desorption in the lower ports due to pH buffering effects. Similarly, O'Neill & Davis (2012a) conducted batch adsorption tests and concluded that pH effects on P adsorption were minimal in a pH range of 4.6 to 7.2. Redox conditions also play an important role in P retention. For example, reducing conditions can promote the reductive dissolution of Fe (III)-oxides releasing Fe (II) and SRP to the porewater (Mackey et al., 2019; Shrestha et al., 2018). Mineralization of organic matter can also be an important source of SRP in bioretention systems (Hsieh et al., 2007; J. Li & Davis, 2016). Bratieres et al. (2008) performed 125 large column tests and found that TP retention was high in all columns, but media with increased organic matter (in the form of compost and mulch) leached SRP and decreased TP retention from over 90% to about 40%. Studies have found that vegetation can improve the retention of SRP in bioretention systems as well as extend the lifetime of the bioretention media (Davis et al., 2006; Marvin et al., 2020). This is because vegetation can not only take up SRP, but it can also be an important factor

controlling redox conditions in a bioretention system since the roots of plants can provide oxygen to the system preventing the onset of reducing conditions which can decrease the adsorption capacity of the bioretention media (due to dissolution of metal oxides) (Lucas & Greenway, 2008; Marvin et al., 2020).

2.3.1 Addition of amendments to bioretention media

While the retention and release of SRP in bioretention media is influenced by many processes, adsorption is often the dominant retention mechanism (Lucas & Greenway, 2011; Marvin et al., 2020). As such, recent studies have shown that the effectiveness of bioretention systems in retaining P can be improved by adding amendments to the bioretention media which increase its adsorption capacity (Adhikari et al., 2016; Duranceau & Biscardi, 2015; Lucas & Greenway, 2011; Marvin et al., 2020). Many amendments including waste products (by-products of industrial activities such as water treatment residuals [WTR], a by-product of drinking water treatment plants produced during the coagulation-filtration treatment step), natural materials (such as rocks, minerals, and seashells), processed materials (commercial products such as iron filings or steel wool), and proprietary products (media designed for P removal from water such as Sorbtive Media and Bold & Gold) containing Al-, Fe-, and Ca-compounds have been investigated for their ability to improve the P retention capacity in bioretention media (Marvin et al., 2020). For example, in a study of eleven different amendment materials, Adhikari et al. (2016) used batch tests to determine the P adsorption capacity of the amendments and reported that alum and lime sludges had P removal efficiencies of up to 76% and 94%, respectively, while the remaining materials had less than 25% removal efficiency. Similarly, Lucas & Greenway (2011) showed the effectiveness of aluminum water treatment residuals (Al-WTR) comparing its performance against red mud and Krasnozem soil in bioretention mesocosm studies. They observed 99%, 97%, and 91% SRP retention after an equivalent of more than 30 years of P loading with the Al-WTR, red mud, and Krasnozem soil, respectively. Duranceau & Biscardi (2015) evaluated the ability of Al-WTR, fly ash, Sorbtive Media, and Bold & Gold to remove P from surface water and showed through batch and column experiments that P retention was highest for the media amended with Al-WTR and Sorbtive Media. Liu & Davis (2014) investigated

the impact of WTRs on P retention in a field-scale bioretention system. They found that the amended bioretention media was effective at retaining TP due to reduced leaching of DP from the media when compared to the results of a previous study on the same bioretention system before amendments (H. Li & Davis, 2009). Overall, studies examining bioretention media amended with WTRs have found WTRs to be effective in increasing the adsorption capacity of the bioretention media and thus increasing P retention in bioretention systems (Ippolito et al., 2011; Marvin et al., 2020; O'Neill & Davis, 2012b; Soleimanifar et al., 2016). WTRs also present a unique opportunity to recycle a waste product, which provides both environmental and economical benefits, since they are a low-cost and readily available material (Adhikari et al., 2016; Wendling et al., 2013).

2.3.2 P retention in bioretention systems in cold climates and impacts of de-icing salts

In cold climates factors including cold temperatures, freeze-thaw cycles, short growing seasons, de-icing salts, and snowmelt can further impact the performance of bioretention systems with respect to P retention (Kratky et al., 2017). For example, a 1-year field study in Montreal, Canada observed the highest effluent TP concentrations in May compared to the rest of the year, indicating a seasonal release of TP in the spring (Géhéniau et al., 2015). However, this study did not examine the potential factors that may have contributed to the observed seasonal variability. In contrast, a cold climate field study in Calgary, Canada observed a 95.6% mass retention rate of TP over the 15-month monitoring period and concluded that cold climate conditions do not have a significant impact on bioretention systems (Khan et al., 2012a, 2012b). Similarly, Kratky et al. (2018) studied the impact of freeze-thaw cycles on the performance of bioretention media using column experiments. They found that SRP was effectively removed in all columns during both regular operation (no freeze-thaw cycles) and cold season operation (freeze-thaw cycles) with an SRP concentration reduction greater than 89% for both column experiments.

De-icing salts, typically sodium chloride, are often applied in high quantities to keep roads clear of snow and ice and minimize the risk of collisions (Green et al., 2008; U.S.

EPA, 2001). However, studies show that high salt levels can have severe negative impacts on soils, vegetation, as well as ground- and surface waters (Amrhein et al., 1992; Green et al., 2008; Kakuturu & Clark, 2015; Kazemi et al., 2018; Kratky et al., 2017; Sjøberg et al., 2017; Szota et al., 2015). High salt concentrations in infiltrating stormwater may also alter the chemical properties of bioretention media including its ability to retain pollutants (Green et al., 2008; Kazemi et al., 2018). For example, in their study of roadside soils, Bäckström et al. (2004) observed that high Na concentrations caused H^+ ions to be released through ion exchange which lowered the porewater pH. The lower pH can then facilitate the release of metals and SRP. High Na concentrations can also cause soil dispersion and changes in soil structure that can reduce the infiltration capacity of the soil and, in some cases, impair plant growth (Kazemi et al., 2018).

Despite the well documented impacts of de-icing salts on roadside soils and vegetation, the impact of high seasonal salt loads on the retention of P in bioretention systems remains unclear. For instance, Kakuturu & Clark (2015) conducted flow cell experiments with salt water and examined the chemical characteristics of bioretention media before and after salt input. They observed reduced concentrations of plant available P from their media extractions, but also reported an instance of increased plant available P and suggested that the result could be coincidental due to the complexity of ion-exchange processes. Some field and laboratory studies have found that high salt loading may decrease TP retention (Géhéniau et al., 2015; Sjøberg et al., 2020). For instance, in their pilot-scale bioretention columns, Sjøberg et al. (2020) observed decreasing TP retention with increasing salt concentrations but found that DP retention was not significantly affected by salt. In contrast, Szota et al. (2015) dosed vegetated bioretention media columns with synthetic stormwater and observed both effluent TP and SRP concentrations to decrease with increasing salt concentration.

More recently studies have shown that the influence of salt on the retention of P in bioretention media may be due to either its prolonged application (over winter and spring) or may be associated with the switching between stormwater with high salt and low salt concentrations. Goor et al. (2021) monitored field bioretention systems combined with column experiments and reported increased TP release, mostly in the

form of SRP, during early spring. They conducted column experiments that suggested that the increased P release in early spring may have been caused by prolonged high salt loading. A recent mesocosm study by McManus & Davis (2020) exposed bioretention media to synthetic stormwater that was periodically dosed with high salt concentrations. They found that effluent TP concentrations rapidly spiked as the bioretention media was exposed to stormwater with low salt concentration immediately after a period of high salt concentration input. These studies highlight that salt inputs influence the P retention in bioretention media, but further research is needed to clarify the effects of salt including the underlying geochemical mechanisms.

2.4 Research Gaps

This chapter has reviewed prior studies that have evaluated the performance of bioretention systems with respect to their ability to retain P from urban stormwater. It is evident that despite the popularity of bioretention systems for urban stormwater management, their performance with respect to P retention, particularly in cold climates, remains unclear. Prior studies report contradicting results with respect to P retention which suggests that a better understanding of the geochemical controls on P retention and release is needed to improve the design and performance of these systems. The impact of de-icing salts on these systems is not well understood although this is needed to ensure the year-round performance of these systems in cold climates. Finally, while amendments including WTRs are now being proposed to be added to bioretention media to enhance P retention, the effects of de-icing salts on amended bioretention media have not previously been examined. When evaluating the overall performance of bioretention systems to retain P in cold climates, there is a need to better understand the way in which de-icing salts may influence the geochemical conditions within bioretention systems that govern their ability to retain P.

Chapter 3 of this thesis aims to address these knowledge gaps by presenting laboratory column experiments conducted to i) evaluate the effects of prolonged and periodic high salt loading (including the switch from stormwater influent with high and low salt concentrations) on both non-amended and Al-WTR amended bioretention media, and ii)

identify the possible geochemical processes governing P retention in media exposed to prolonged and changing salt concentrations. The findings from this thesis are needed to enhance understanding of P retention and release in bioretention media installed in cold climate environments such that the design of the systems can be improved to ensure they provide higher and more consistent P retention year-round.

2.5 References

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Chapter 3

3 Performance of bioretention media in retaining phosphorus from urban stormwater under the influence of de-icing salts

3.1 Introduction

Urbanization increases impervious surfaces which leads to greater stormwater volumes and subsequent stress on infrastructure and downstream environments (J. Liu et al., 2014). Urban stormwater can degrade downstream water quality and impair aquatic ecosystems by delivering high loads of pollutants including nutrients (phosphorus [P] and nitrogen [N]), total suspended solids, pathogens, and metals to downstream water bodies (Davis et al., 2001; Davis & McCuen, 2005; J. Liu et al., 2014). High P loads are of particular concern in many freshwater environments, including the Laurentian Great Lakes Basin, as excessive P loads can trigger eutrophication which can lead to harmful algal blooms and hypoxic events (Environment and Climate Change Canada and the Ontario Ministry of the Environment and Climate Change, 2018). Eutrophication can have severe economic and ecological consequences including impacts to recreational and commercial activities, clogged municipal drinking water intakes, and impaired ecosystem function and biodiversity loss (Environment and Climate Change Canada and the Ontario Ministry of the Environment and Climate Change, 2018).

Bioretention systems are a popular type of low impact development (LID) urban stormwater management system. They are shallow vegetated depressions designed to promote stormwater infiltration, thereby reducing runoff volumes, peak flows, and concentrations of some pollutants (Khan et al., 2012; LeFevre et al., 2015). Bioretention systems typically consist of vegetation, a surface cover layer (mulch, topsoil, or stone), and a layer of engineered soil media (herein referred to as bioretention media) that is typically 0.3 to 1.0 m deep (Khan et al., 2012; Kratky et al., 2017; Sustainable Technologies Evaluation Program, 2021). Some bioretention systems installed in native low permeability soils also have underdrains that enable excess infiltrated water to be transported to the storm sewer system. Pollutants can be removed through physical,

chemical, and biological processes as the stormwater infiltrates through the surface cover and bioretention media layers (Khan et al., 2012).

The performance of bioretention systems with respect to P removal from urban stormwater has been shown to be highly variable over time and between systems (Dietz & Clausen, 2005; Hunt et al., 2006; J. Li & Davis, 2016). While some studies have shown total P (TP) retention within a bioretention system (Davis et al., 2006; Komlos & Traver, 2012; J. Liu & Davis, 2014; Lucas & Greenway, 2008), other studies have shown that bioretention systems, specifically the bioretention media, can act as a source of TP with effluent TP concentrations being higher than TP concentrations in the influent stormwater (Dietz & Clausen, 2005; Hatt et al., 2008; Hunt et al., 2006; H. Li & Davis, 2009). TP includes particulate phosphorus (PP) and dissolved phosphorus (DP). DP can be further broken into dissolved organic phosphorus (DOP) and soluble reactive phosphorus (SRP). SRP and some DOP forms are bioavailable, meaning they are available to be taken up by primary producers and thus contribute to algal growth (Ellison & Brett, 2006; LeFevre et al., 2015). While DP and PP are often found in similar amounts in urban stormwater, in some cases DP has been observed to be up to 90% of the TP load (LeFevre et al., 2015; Marvin et al., 2020). Bioretention systems have been found to be highly effective in retaining PP by physical filtration processes, but the processes governing the retention and release of DP are more variable and complex (J. Liu & Davis, 2014).

To address the variable performance of bioretention systems in retaining DP, recent studies have demonstrated that P retention can be considerably increased by adding water treatment residuals (WTRs) to the bioretention media (Duranceau & Biscardi, 2015; Lee et al., 2015; O'Neill & Davis, 2012a, 2012b). WTRs are a by-product of water treatment plants produced during the coagulation process (Soleimanifar et al., 2016). In particular, adding aluminum-based WTRs (Al-WTRs) to bioretention media has shown considerable promise for improved P retention, with Al-WTRs having higher P adsorption capacity compared to other amendment materials that have been tested (e.g., fly ash, red mud, zeolite, perlite, pine mulch) (Lee et al., 2015; Zhang et al., 2018). For instance, Adhikari et al. (2016) conducted batch tests to compare ten typical amendment materials used in

bioretention media and found bioretention media amended with Al-WTRs had a 94% P removal efficiency. The high retention of P in bioretention media amended with Al-WTR compared to non-amended bioretention media has also been observed in column (Lee et al., 2015; O'Neill & Davis, 2012b) and field studies (Houle et al., 2017; J. Liu & Davis, 2014).

De-icing salts, typically sodium chloride (NaCl), are often applied in high quantities for winter road safety in cold climate regions (U.S. EPA, 2001). The use of de-icing salts may alter the performance of bioretention systems in retaining pollutants including P (Kazemi et al., 2018). However, previous studies report conflicting findings on the impact of de-icing salts on P retention in bioretention media. For instance, Sørberg et al. (2020) found that high salt loading decreased TP retention but had no effect on DP retention in their pilot-scale bioretention columns. Similarly, Géhéniau et al. (2015) monitored a field bioretention system in Montreal, Canada over a one-year period and found effluent TP concentrations increased when salt loading was high, with TP concentrations highest during spring. In contrast, Szota et al. (2015) conducted column experiments with bioretention media that showed that higher salt concentrations in the influent led to lower effluent TP concentrations. More recently, McManus & Davis (2020) conducted mesocosm experiments in which bioretention media was exposed to artificial stormwater that was periodically spiked with high salt concentrations. Their results showed effluent TP concentrations rapidly increased immediately following a period of high salt stormwater input as the bioretention media was exposed to stormwater with low salt concentrations (McManus & Davis, 2020). Goor et al. (2021) also recently concluded from monitoring of a field bioretention system combined with column experiments that high salt loading may increase TP release mostly in the form of SRP. In contrast to McManus & Davis (2020), Goor et al. (2021) concluded that the increase in TP release may have been caused by the prolonged duration of high salt loading over the winter and into the early spring rather than due to freshening of the influent stormwater (i.e., a switch from high salt to low salt stormwater influent as would occur in mid- to late spring at their field site). The different timing of P release in these studies suggests that multiple mechanisms may affect the release and retention of P when de-icing salts are

applied. With widespread application of de-icing salts on roads in cold climates, there is a need to clarify how P retention in bioretention systems is influenced by seasonal road de-icing salt application. Further, with recent studies illustrating the benefits of using Al-WTR amended bioretention media to improve P retention, there is a need to evaluate how the P retention performance of this amended bioretention media may be impacted by de-icing salts. The impact of de-icing salts on P retention in amended bioretention media has not previously been examined.

To address these research gaps, the objectives of this study were: i) assess the influence of prolonged and periodic high salt loading on SRP retention in non-amended bioretention media, including the effects of switching between stormwater influent with high and low salt concentrations; ii) assess the impact of prolonged and periodic high salt loading on SRP retention in bioretention media amended with Al-WTR; iii) identify the geochemical conditions influencing SRP retention and release in bioretention media exposed to prolonged and periodic high salt loading. These objectives were addressed by conducting laboratory column experiments with bioretention media (with and without Al-WTR added) that were collected from three different operational field bioretention systems. Column influent, effluent, and porewater were sampled to determine the impact of prolonged and periodic high salt loading and possible geochemical controls on SRP retention and release. This study focuses on SRP retention and release from the bioretention media rather than TP as SRP is the bioavailable form of P that is taken up by primary producers, thus leading to eutrophication (Ellison & Brett, 2006; Komlos & Traver, 2012; LeFevre et al., 2015), and Goor et al. (2021) observed that high seasonal salt loads led to high release of SRP (rather than other P fractions). The findings from this study are needed to provide insight into the effects of road de-icing salts on the performance of bioretention systems in retaining P, and thus to improve the design and operation of bioretention systems to ensure year-round P retention in cold climates.

3.2 Methodology

3.2.1 Column Experiment Setup

Laboratory column experiments were performed to evaluate the retention and release of SRP from bioretention media exposed to stormwater influent with periods of high salt (NaCl) concentrations. The column experiments were conducted using eight 30-cm long acrylic columns with a 5.08-cm inner diameter (Figure 3-1).

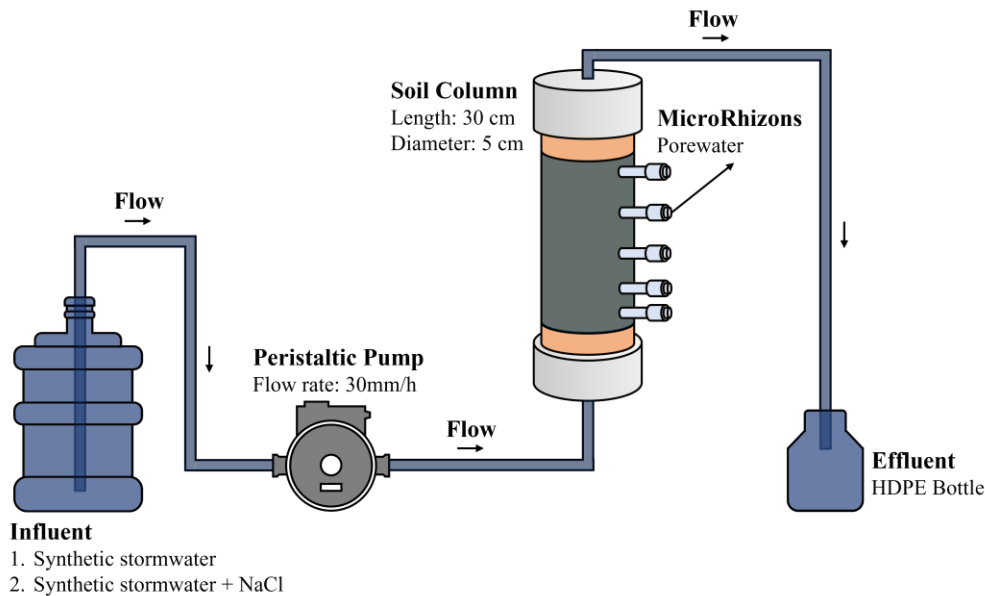


Figure 3-1: Schematic of experimental column setup.

Bioretention media was collected with a split core soil sampler from three mature and operational field bioretention systems in southern Ontario, Canada. These bioretention systems are herein referred to as the Sarnia, Dorchester, and Dundas systems. The cores were collected in October 2020 (Sarnia and Dorchester systems) and November 2020 (Dundas system). After collection, the sediment cores were wrapped in plastic to avoid exposure to the air, transported to the laboratory, and stored in a fridge before being packed into the columns. The disturbed soil cores were placed into the columns by dry packing the bioretention media in 0.5-cm lifts using a circular tamping device. The bioretention media was lightly scarified before adding another 0.5-cm lift to ensure hydraulic connectivity between layers. Two columns were packed with bioretention media from the Sarnia system (these columns are named Sarnia-Control and Sarnia-1,

respectively), one column was packed with bioretention media from the Dorchester system (column named Dorchester), and one column was packed with bioretention media from the Dundas system (column named Dundas). Three paired columns were packed with each of the three bioretention media with Al-WTR added (columns named Sarnia-WTR, Dorchester-WTR, and Dundas-WTR). An eighth column was packed with “fresh” bioretention media that was collected when the Sarnia bioretention systems were constructed in 2017 (column named Sarnia-2). The performance of the Sarnia bioretention system in retaining P, including SRP, over a one-year period was previously examined by Goor et al. (2021), and the behaviour of SRP within the Dorchester and Dundas systems were evaluated by Y. Liu et al. (2021). These three sites were also chosen as they represent common bioretention media compositions and had different ages. Key characteristics of the three bioretention systems including the bioretention media used in each of these systems are provided in Table 3-1 with additional details provided in Goor et al. (2021) and Y. Liu et al. (2021).

Table 3-1: Key characteristics of bioretention systems from which bioretention media was collected.

	Sarnia	Dorchester	Dundas
Installation year	2017	2016	2013
Location	London, ON	Dorchester, ON	Mississauga, ON
Design media composition	85-88% sand 8-12% soil fines 3-5% leaf mulch	85-88% sand 8-12% soil fines 3-5% leaf mulch	85-88% sand 8-12% soil fines 3-5% leaf mulch
Measured media composition	91% sand 9% silt/clay 3% organic matter (woodchips)	2% gravel 90% sand 8% silt/clay	20% gravel 76% sand 4% silt/clay
P content	171 ppm (TP)	286 ppm (SRP)	636 ppm (SRP)

The Al-WTR mixed into the bioretention media was provided by Lake Huron Water Treatment Facility in Grand Bend, ON which uses aluminum sulphate (alum) in its coagulation treatment process. Characteristics of the Al-WTR are provided in Table 3-2. The chemical composition of the Al-WTR was determined using total acid digestion (U.S. EPA, 2007), and the amorphous Al and Fe contents were determined using an

oxalate extraction (0.2 M ammonium oxalate and 0.2 M oxalic acid solution at pH 3) (McKeague & Day, 1966). Eluent samples were analyzed for dissolved Al and Fe using atomic absorption spectroscopy analysis (AA: Agilent Technologies 200 Series AA). Before the Al-WTR was added to the bioretention media it was oven dried at 105°C over a 48-hour period and crushed and sieved (American Society for Testing and Materials [ASTM] sieves). Following the Sustainable Technologies Evaluation Program guidelines for bioretention media composition (Sustainable Technologies Evaluation Program, 2021), Al-WTR particle sizes less than 2.36 mm were well-mixed into the three collected bioretention media at a ratio of 10% Al-WTR by weight.

Table 3-2: Characteristics of Al-WTR from Lake Huron Water Treatment Facility.

Characteristic	Value
Moisture Content (%)	74
Total Acid Digestion	
Iron (g/kg)	14
Aluminum (g/kg)	1,564
Sodium (g/kg)	2.1
Calcium (g/kg)	524
Manganese (g/kg)	2.9
Oxalate Extraction	
Al _{ox} (g/kg)	728
Fe _{ox} (g/kg)	6.5

3.2.2 Column Experiment Operation

The columns were run under upward flow saturated conditions with a peristaltic pump continuously delivering synthetic stormwater at a rate of 30 mm/hr. This flow rate was selected to mimic the design bioretention media infiltration rate for the Sarnia bioretention system (Goor et al., 2021). A schematic of the experimental setup is shown in Figure 3-1. All columns were run continuously for between 111 – 309 days with the experiments divided into four main periods: i) Maturation period to establish baseline conditions during which columns received synthetic stormwater with no added NaCl; ii) Salt period during which columns received influent synthetic stormwater spiked with 1000 mg/L NaCl (influent electrical conductivity [EC] > 1700 µS/cm); iii) Freshening period during which columns received synthetic stormwater with no added NaCl and EC was greater than 180 µS/cm; iv) Regular period during which the columns continued to

receive synthetic stormwater with no added NaCl and the effluent EC was below 180 $\mu\text{S}/\text{cm}$. The length of each period varied slightly between each column experiment but on average the maturation period was 46 days, the salt period was 48 days, the freshening period was 5 days, and the regular period was 23 days. Each period except the freshening period lasted until the columns were observed to reach steady state conditions based on effluent SRP concentrations and overall geochemical conditions within the columns (as determined based on pH and oxidation-reduction potential [ORP]). The freshening period lasted until the high salt influent was flushed through the columns and the effluent EC was below 180 $\mu\text{S}/\text{cm}$. Three of the columns (Sarnia-1, Sarnia-2, and Dorchester) underwent multiple salt-freshening-regular cycles to ensure the effects of the high salt concentrations on SRP release were adequately captured and consistent between consecutive cycles.

Synthetic stormwater was used rather than real stormwater runoff collected from the field sites to provide greater control over the influent chemistry and thus geochemical conditions in the columns. The composition of the synthetic stormwater used as influent for all column experiments was based on chemical characterization of stormwater runoff samples collected in the field at the Sarnia (Goor et al., 2021), Dorchester, and Dundas bioretention systems (Y. Liu et al., 2021). The synthetic stormwater was made using Milli Q water (Thermo Fisher Scientific Barnstead EASYpure II UV) with the concentrations of chemicals added provided in Table 3-3.

Table 3-3: Chemical compositions of synthetic stormwater influent.

Parameter	Target Concentration	Source
pH	7	HCl/NaOH
Organic Nitrogen	0.48 mg/L as N	Glycine
Ammonia	0.13 mg/L as N	NH ₄ Cl
Nitrate	0.24 mg/L as N	KNO ₃
Nitrite	0.08 mg/L as N	NaNO ₂
Total Phosphorus	0.075 mg/L as P	K ₂ HPO ₄
Salt*	1000 mg/L	NaCl
Na ₂ CO ₃	21.52 mg/L	Na ₂ CO ₃

*Salt period only. ACS grade (assay $\geq 99.5\%$) NaCl.

Column influent and effluent samples were collected at least twice a week over the duration of each experiment. In addition, porewater samples were collected once per week using Micro-Rhizon samplers that were inserted horizontally into the columns. These samplers were 5-cm in length and 1-mm in diameter and were located at depths of 2.5, 5, 9.5, 15.5, and 23.5-cm from the bottom inlet of each column. The sampling frequency was increased at the start of the freshening period to four and two samples per week for influent and effluent, and porewater, respectively, to capture the effects of switching from high salt influent to no salt influent.

3.2.3 Analytical methods

All influent, effluent and porewater samples were analyzed immediately for EC, pH, and ORP using a HACH HQ40d multimeter with IntelliCAL® CDC401, PHC201, and MTC101 probes, respectively. All samples were then filtered with 0.45 µm cellulose acetate membrane filters into two 30 mL acid-washed HDPE sample bottles. One sample bottle was acidified with nitric acid and stored in a fridge until cation analysis (Al, Ca, Fe, Mn, and Na) using Atomic Absorption Spectroscopy (AA: Agilent Technologies 200 Series AA). The other sample bottle was refrigerated until the sample was analyzed for SRP within 48 hours of collection. SRP was analyzed using a Lachat QuickChem 8500 Flow Injection Analysis Machine (FIA). Additional influent and effluent samples were collected up to three times during each of the maturation, salt, and freshening periods, for dissolved organic carbon (DOC) analysis. These samples were collected in 20 mL glass amber vials, refrigerated, and samples were analyzed for DOC within one week of collection using a Shimadzu TOC-V with ANSI-V auto-sampler. Additional details on analytical methods including QA/QC are provided in Appendix A.

3.3 Results

3.3.1 SRP

The SRP concentrations in the influent and effluent for all column experiments (non-amended and Al-WTR amended columns) that were exposed to varying influent salt concentrations are provided in Figure 3-2. The SRP concentrations for the Sarnia-Control column experiment are provided in Appendix B. Considering all column experiments, the

mean influent SRP over the experimental periods was $64 \pm 13 \mu\text{g P/L}$ which was slightly lower than the target influent concentration ($75 \mu\text{g P/L}$). There was some variability in the influent SRP, particularly during salt periods during which the influent SRP concentrations were slightly lower (mean = $56 \pm 16 \mu\text{g P/L}$). This decrease in SRP concentrations with increasing salt concentration in the influent was similarly observed by Szota et al. (2015) and may have been due to co-precipitation of SRP with metal impurities in the NaCl chemical compound used.

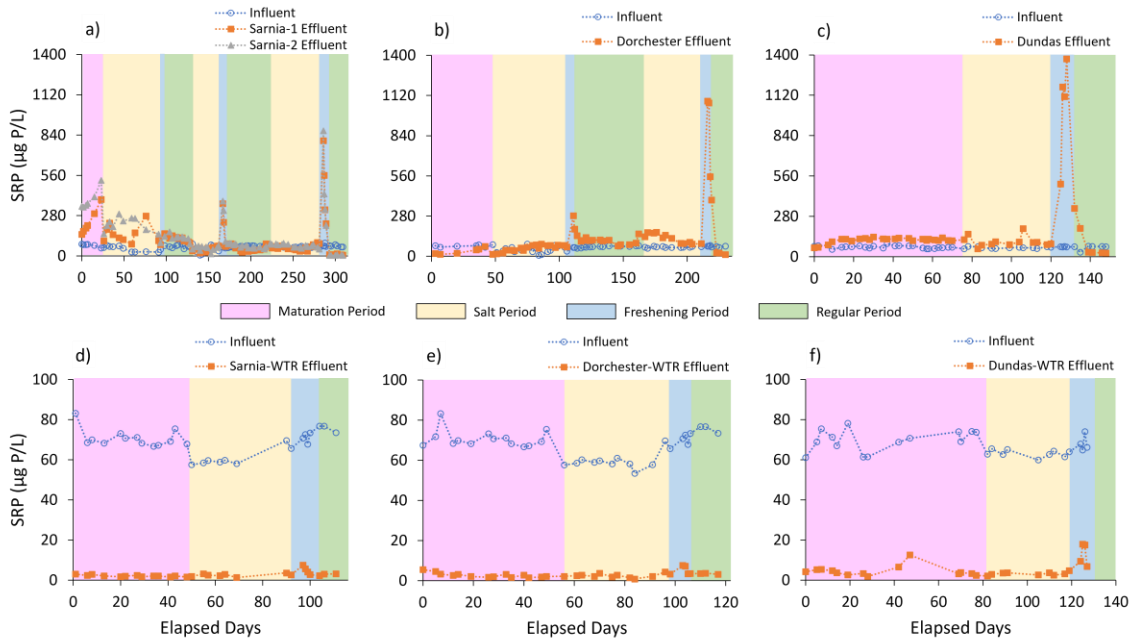


Figure 3-2: Influent and effluent SRP for (a) Sarnia-1 and Sarnia-2, (b) Dorchester, (c) Dundas, (d) Sarnia-WTR, (e) Dorchester-WTR, and (f) Dundas-WTR columns. The pink, yellow, blue, and green shaded regions represent the maturation, salt, freshening, and regular periods, respectively. Note the different y-axis scales used in (a) – (c) compared with (d) – (f).

Overall, all non-amended columns (Sarnia-Control, Sarnia-1, Sarnia-2, Dorchester, and Dundas) showed the field bioretention media acted as a source (rather than sink) of SRP during all periods of the experiment (Appendix B and Figure 3-2). The mean effluent SRP for the Sarnia-Control, Sarnia-1, Sarnia-2, Dorchester, and Dundas columns were 131 ± 82 , 111 ± 123 , 138 ± 140 , 131 ± 195 , and $187 \pm 278 \mu\text{g P/L}$, respectively, over the experimental period. For all non-amended columns, high effluent SRP concentrations

were observed during the freshening period (maximum SRP of up to 800, 870, 1080, and 1370 $\mu\text{g P/L}$ for the Sarnia-1, Sarnia-2, Dorchester, and Dundas columns, respectively). As expected, no similar effluent SRP increases were observed for the Sarnia-Control column which was not exposed to high salt influent (see Appendix B). For the columns exposed to high salt influent, the spike in effluent SRP that occurred during the freshening period typically lasted two to five days with the maximum effluent SRP concentration usually occurring within 24 hours of switching from high salt to no salt influent. Following the spike in effluent SRP, the SRP concentrations returned to concentrations similar to those observed before the salt period or in some cases decreased to concentrations below the influent, indicating SRP retention in the column (e.g., Day 167 – 173 and Day 286 – 293 for Sarnia-1 and Sarnia-2, Day 216 – 223 for Dorchester, Day 125 – 139 for Dundas). The Sarnia (Sarnia-1 and Sarnia-2) and Dorchester columns showed larger spikes in effluent SRP during their third and second freshening periods, respectively, compared to during earlier freshening periods. It is important to note that no spike in effluent SRP concentrations was observed during the first freshening period for the Sarnia-1 and Sarnia-2 columns. This is likely because the sampling resolution during this first freshening period was too low with samples only collected two days after the switch from high salt to no salt influent. Despite the prolonged duration of the salt periods, for all non-amended columns the effluent SRP concentrations were similar to those observed before each salt period with only small differences in mean effluent SRP concentrations observed in some columns. For example, the mean effluent SRP concentration for the Dorchester column during the salt period was $123 \pm 31 \mu\text{g P/L}$ compared to $106 \pm 22 \mu\text{g P/L}$ during the equivalent (duration) regular period immediately before. In contrast, the mean effluent SRP concentration for the Dundas column was lower during the salt period ($104 \pm 35 \mu\text{g P/L}$) compared to the equivalent regular period immediately before ($121 \pm 8 \mu\text{g P/L}$).

The porewater SRP concentrations for the Sarnia-1, Dorchester, and Dundas columns for select sampling days during the regular, salt, and freshening periods are provided in Figures 3-3 and 3-4. Porewater SRP concentrations for other sampling times and for the Sarnia-Control and Sarnia-2 columns are provided in Appendix B. Consistent with the

effluent SRP concentrations, the porewater SRP concentrations were similar or only slightly higher during salt periods compared to the regular periods (Figures 3-3a and d, 3-4a and d). For example, mean porewater SRP concentrations during the regular and salt periods were $68 \pm 58 \mu\text{g P/L}$ and $69 \pm 36 \mu\text{g P/L}$ for Sarnia-1, $82 \pm 69 \mu\text{g P/L}$ and $86 \pm 42 \mu\text{g P/L}$ for Sarnia-2, $69 \pm 34 \mu\text{g P/L}$ and $90 \pm 90 \mu\text{g P/L}$ for Dorchester, and $43 \pm 32 \mu\text{g P/L}$ and $66 \pm 30 \mu\text{g P/L}$ for Dundas. However, consistent with the effluent concentrations, the greatest increases in porewater SRP concentrations occurred during the freshening periods in all the non-amended columns. The mean porewater SRP concentrations during freshening periods were 149 ± 151 , 204 ± 191 , 268 ± 121 , and $572 \pm 263 \mu\text{g P/L}$ for Sarnia-1, Sarnia-2, Dorchester, and Dundas, respectively. During the freshening periods porewater SRP concentrations did not increase consistently with depth highlighting the complexity and heterogeneity of the bioretention media and processes governing SRP release (Figures 3-3a and d, 3-4a and d).

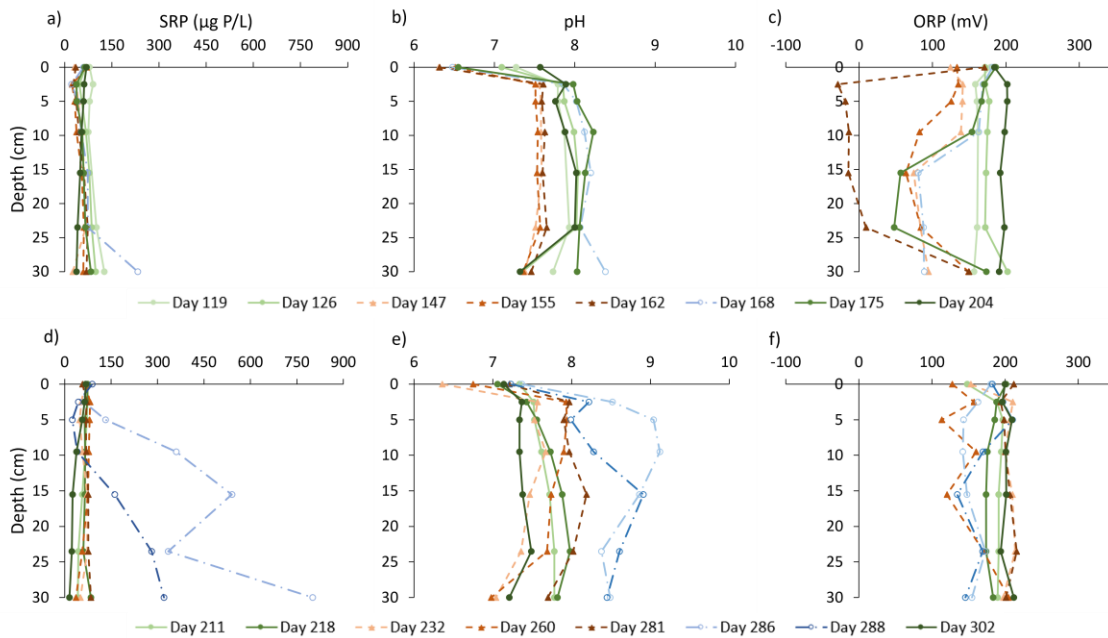


Figure 3-3: Porewater a) SRP concentrations, b) pH, and c) ORP for Sarnia-1 column before, during, and after the second salt period, and porewater d) SRP concentrations, e) pH, and f) ORP for Sarnia-1 column before, during, and after the third salt period. The green, orange, and blue colors represent regular, salt, and freshening periods, respectively. Depth of 0- and 30-cm represent the influent and effluent samples, respectively.

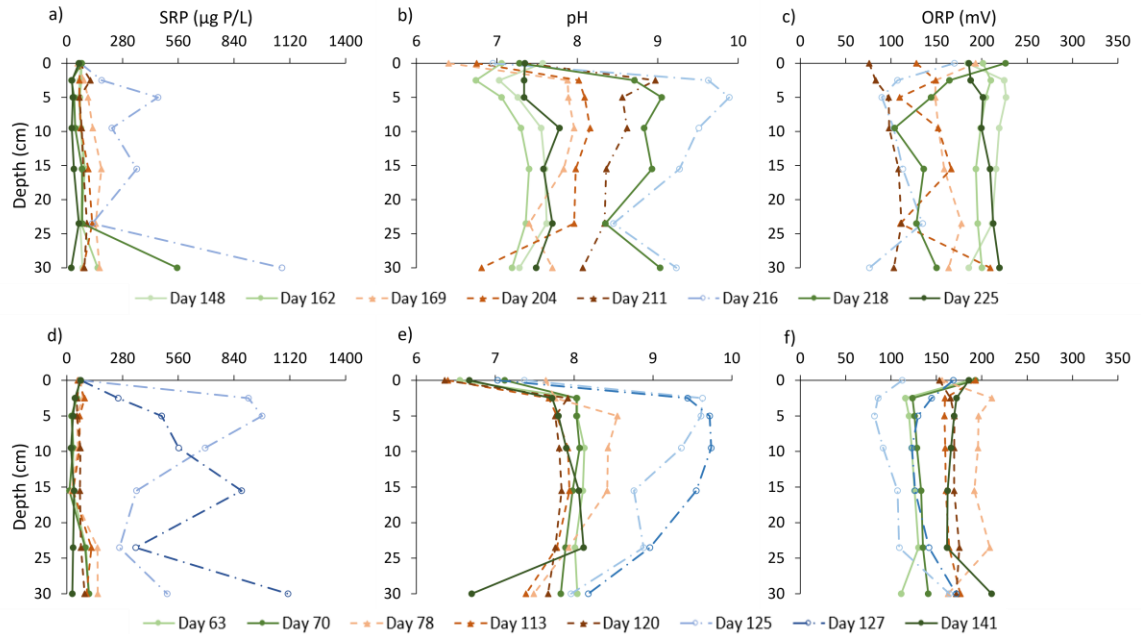


Figure 3-4: Porewater a) SRP concentrations, b) pH, and c) ORP for the Dorchester column before, during, and after the second salt period, and porewater d) SRP concentrations, e) pH, and f) ORP for the Dundas column. The green, orange, and blue colors represent regular, salt, and freshening periods, respectively. Depth of 0- and 30-cm represent the influent and effluent samples, respectively.

The columns amended with Al-WTR showed much greater and more consistent SRP retention compared to their non-amendment counterparts (Figure 3-2d-f). Mean effluent SRP concentrations over the experimental periods for Sarnia-WTR, Dorchester-WTR, and Dundas-WTR were 2.7 ± 1.2 , 3.0 ± 1.5 , and 5.2 ± 4.1 µg P/L, respectively, which were considerably lower than the mean influent SRP concentrations (69 ± 6 , 67 ± 7 and 67 ± 5 µg P/L, respectively). No changes in effluent SRP concentrations were observed between the regular period and salt period despite the prolonged duration of the salt period. The effluent SRP concentrations slightly increased during the during the freshening periods (compared to the regular and salt periods) for the amended columns with concentrations reaching up to 7.4, 7.5, and 18 µg P/L for Sarnia-WTR, Dorchester-WTR, and Dundas-WTR, respectively. However, these effluent SRP concentrations were still considerably lower than the influent SRP concentrations indicating that the Al-WTR amendment was able to prevent the rapid release of SRP that occurred during the

freshening period for the non-amended bioretention media. The high SRP retention throughout the experiments including the freshening periods are also evident from the measured porewater SRP profiles for the amended columns (Figure 3-5). It is important to note that for the amended columns the porewater SRP increased up to 70 $\mu\text{g/L}$ close to the influent of the columns (< 10 cm depth) during the freshening period suggesting less retention of SRP at shallow depths.

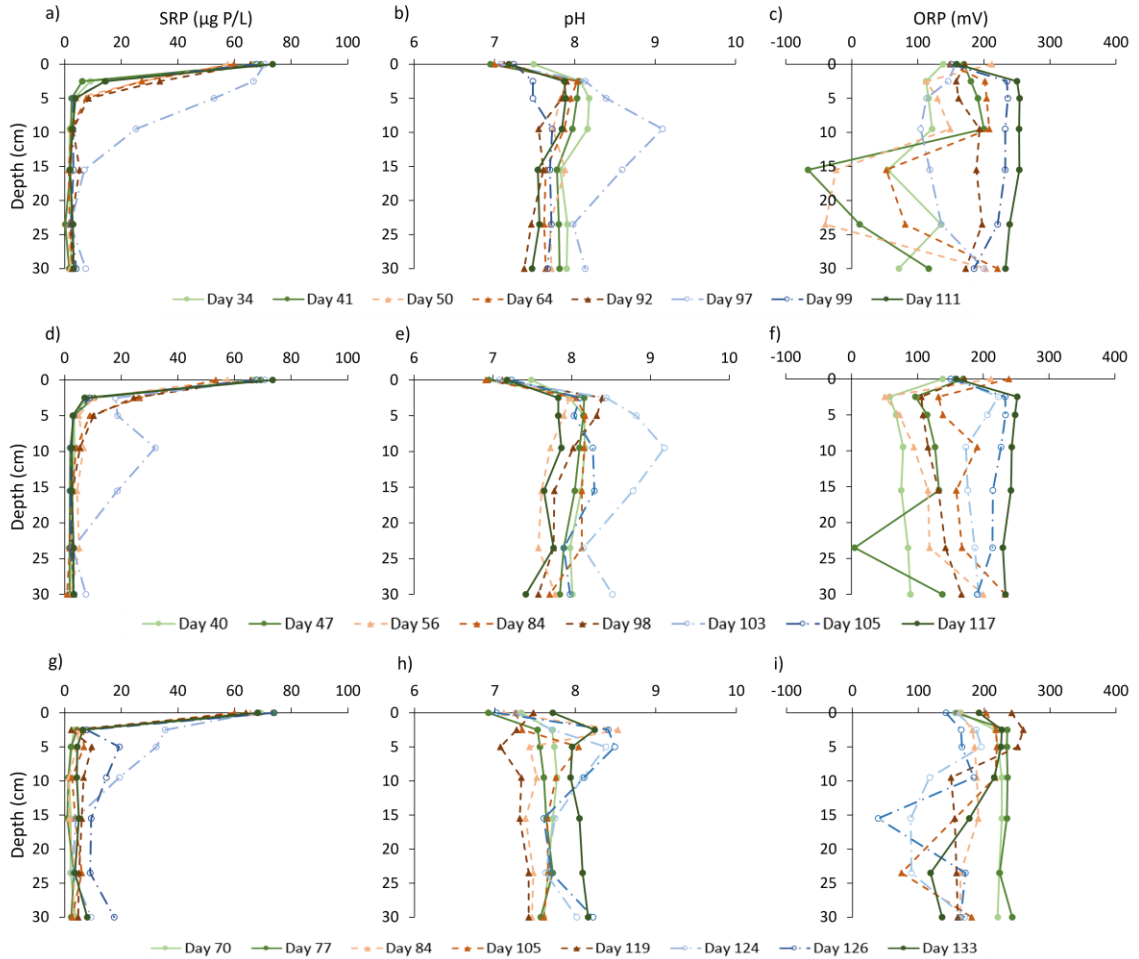


Figure 3-5: Porewater a) SRP concentrations, b) pH, c) ORP for Sarnia-WTR, porewater d) SRP concentrations, e) pH, and f) ORP for Dorchester-WTR, and porewater g) SRP concentrations, h) pH, and i) ORP for Dundas-WTR. The green, orange, and blue colors represent regular, salt, and freshening periods, respectively. Depth of 0- and 30-cm represent the influent and effluent samples, respectively.

3.3.2 pH and ORP

All columns (amended and non-amended) showed similar patterns of pH in the influent, effluent, and porewater through the different stages of the experiments. Influent pH for all columns was 7.0 ± 0.5 . For all columns, the porewater pH increased as the synthetic stormwater entered the bioretention media (over the initial 10 cm) during both the regular and salt periods before remaining relatively stable through the rest of the column (Figures 3-3b and e, 3-4b and e, 3-5b, e, and h). Porewater pH for other sampling times for all columns and for all sampling times for the Sarnia-Control column are provided in Appendix C. The mean porewater pH over the experimental period for Sarnia-Control, Sarnia-1, Sarnia-2, Dorchester, Dundas, Sarnia-WTR, Dorchester-WTR, and Dundas-WTR were 7.6 ± 0.4 , 7.8 ± 0.4 , 7.9 ± 0.4 , 7.9 ± 0.5 , 8.0 ± 0.5 , 7.8 ± 0.3 , 7.9 ± 0.3 , and 7.7 ± 0.3 , respectively. The pH of the effluent was slightly lower compared with the porewater pH with a mean effluent pH of 7.4 ± 0.6 and 7.6 ± 0.3 for the non-amended and amended columns, respectively. The most notable change in pH occurred at the start of the freshening period with the porewater pH increasing sharply to between 9 to 9.5 within the first 10 cm of all non-amended and amended columns, except for Dundas-WTR and Sarnia-1 (second freshening period only). The mean effluent pH was also considerably higher during the freshening periods compared to the salt and regular period (8.2 ± 0.6 and 8.0 ± 0.3 for the non-amended and amended columns, respectively). Similar to the rapid increase and decrease in effluent and porewater SRP concentrations observed during the freshening periods (Figure 3-2), the high pH levels rapidly returned to “normal” conditions ($\text{pH} < 8.5$) within seven days of switching from the high salt to no salt influent – this coincided with the end of the freshening period ($\text{EC} < 180 \mu\text{S}/\text{cm}$). It is important to note that the smaller increase in porewater and effluent pH for Sarnia-1 during the second freshening period compared to the third freshening period is consistent with the smaller increase in effluent SRP concentrations observed during the second freshening period (Figure 3-2).

Porewater ORP data was variable within individual columns and between columns. Generally, the conditions in the columns were oxic with the mean porewater ORP of the non-amended columns measured to be $156 \pm 53 \text{ mV}$ considering the entire experimental

period. The most notable change in the porewater ORP occurred during some of the salt periods for Sarnia-1 and Sarnia-2. The porewater ORP decreased during the first and second salt periods for Sarnia-1 reaching an ORP of -30 mV (see Figure 3-3c for second salt period). Sarnia-2 also exhibited low ORP in the porewater during all salt periods reaching an ORP of -70 mV. Porewater ORP for other sampling times for Sarnia-1 and for Sarnia-Control and Sarnia-2 are provided in Appendix D. The decrease in ORP observed during the salt periods in Sarnia-1 and Sarnia-2 was not observed in all columns and was also not observed in Sarnia-1 during the third salt period (Figure 3-3f). Overall, the porewater ORP in the amended columns were similar to the non-amended columns with the mean porewater ORP of the amended columns measured to be 161 ± 69 mV considering the entire experimental period. For the amended columns, the ORP was relatively stable except for Sarnia-WTR and Dorchester-WTR during the regular periods when the porewater ORP decreased below 50 mV. The porewater ORP did not decrease during the salt periods for the non-amended columns as observed during the salt periods for the Sarnia-1 and Sarnia-2 columns.

3.3.3 Metals (Fe, Mn, Al, Ca, Na)

Dissolved Fe, Mn, Al, and Ca concentrations in the porewater and effluent were measured as these metals are often closely linked with SRP retention and release through precipitation-dissolution and adsorption-desorption reactions. Sodium (Na) concentrations were also measured as Na affects ion exchange processes that may in turn affect SRP retention and release. Together with pH and redox conditions, these data can provide insight into the possible mechanisms governing P retention and release from the bioretention media.

Overall, the effluent Fe concentrations for Sarnia-1, Sarnia-2 and Dorchester during the regular and salt periods were low with 72% of samples below the detection limit of 0.06 mg/L (Q75 = 0.07 mg/L; Figure 3-6a-b). Similarly, effluent Fe concentrations were low during the regular and salt periods for all the Al-WTR amended columns with 56% of samples below the detection limit (Q75 = 0.07 mg/L). The highest effluent Fe concentrations during the regular and salt periods were observed for the Dundas column

with mean Fe concentration of 0.23 ± 0.16 mg/L and 0.49 ± 0.37 mg/L, respectively (Figure 3-6c). Importantly, the effluent Fe concentrations increased during the freshening periods for Dorchester, Dundas, Dundas-WTR and for the third freshening period only for Sarnia-1 with Fe concentrations reaching 2.7, 3.0, 1.6 and 1.2 mg/L, respectively. Similar to the observed spike in effluent SRP concentrations, the high effluent Fe concentrations decreased over the freshening period. Porewater Fe concentrations in the non-amended columns were low except during the freshening periods for Sarnia-1, Dorchester, and Dundas – this is consistent with the higher porewater SRP concentrations also observed during the freshening periods for these columns (Figure 3-7a, c, and d). Porewater Fe concentrations for the Al-WTR amended columns were low over the entire experimental period including during the freshening periods (Figure 3-7e-g; 75% of samples < detection limit of 0.06 mg/L, Q75 = 0.06 mg/L). Porewater Fe concentrations for Sarnia-Control are provided in Appendix E.

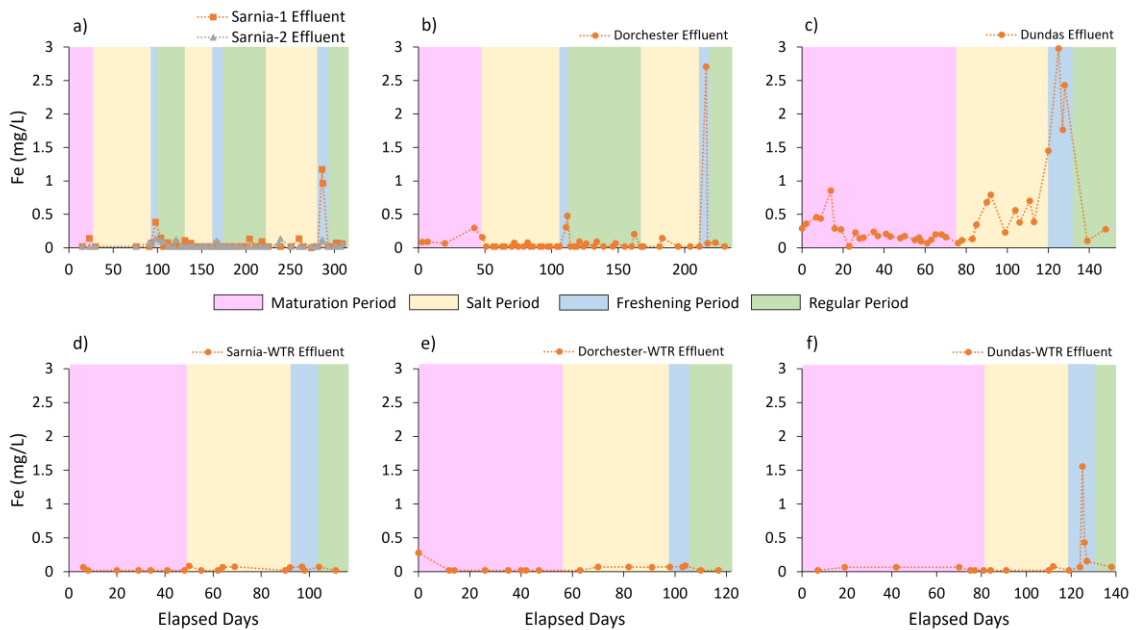


Figure 3-6: Effluent Fe concentrations for (a) Sarnia-1 and Sarnia-2, (b) Dorchester, (c) Dundas, (d) Sarnia-WTR, (e) Dorchester-WTR, and (f) Dundas-WTR columns. The pink, yellow, blue, and green shaded regions represent maturation, salt, freshening, and regular periods, respectively. Note that Fe concentrations in the influent were negligible.

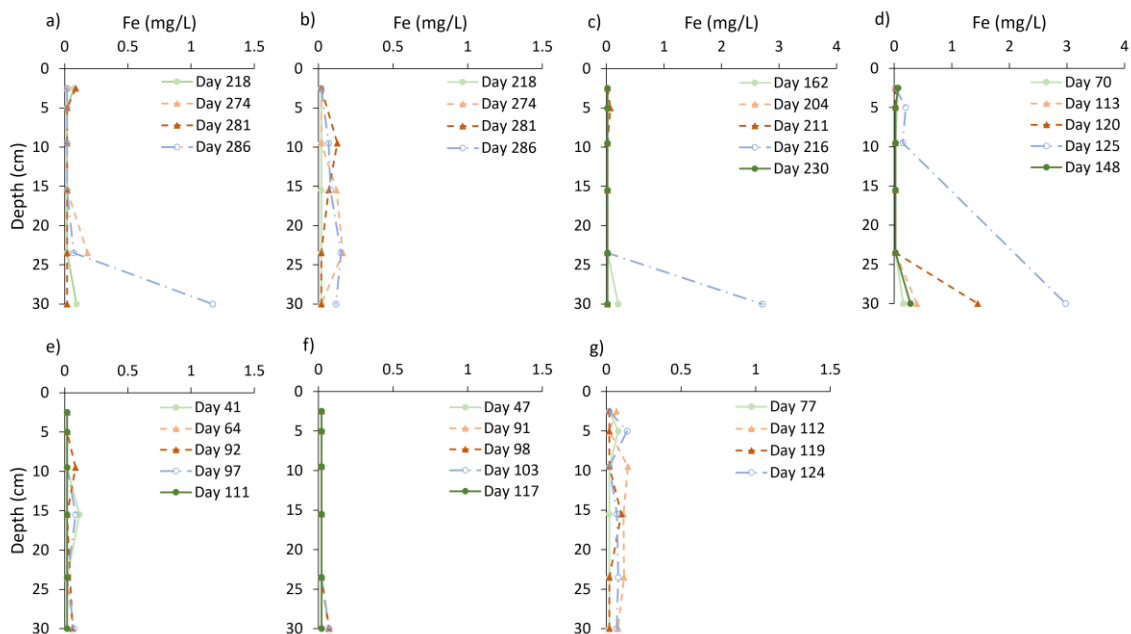


Figure 3-7: Fe porewater concentrations for a) Sarnia-1 (before during and after third salt period), b) Sarnia-2 (before, during and after second salt period), c) Dorchester (before, during and after second period), d) Dundas, e) Sarnia-WTR, f) Dorchester-WTR, and g) Dundas-WTR. The green, orange, and blue colors represent regular, salt, and freshening periods, respectively. Depth of 30-cm represents the effluent sample.

Mean Mn effluent concentrations for Sarnia-1, Sarnia-2, Dorchester, and Dundas during the regular periods were 0.04 ± 0.05 , 0.05 ± 0.03 , 0.02 ± 0.02 , and 0.05 ± 0.01 mg/L, respectively (Figure 3-8a-c). In contrast to the effluent Fe concentrations, the effluent Mn concentrations increased during some salt periods reaching up to 0.45 mg/L during the first and second salt periods for Sarnia-1 and Sarnia-2 and the first salt period for Dorchester (Figure 3-8a-b). This was not observed during the subsequent salt periods for these columns or for Dundas. For Dundas, the highest effluent Mn concentration (0.15 mg/L) was observed during the freshening period. In the amended columns, the mean Mn effluent concentrations were stable over the entire experimental period (mean = 0.12 ± 0.06 , 0.07 ± 0.04 , and 0.11 ± 0.04 for Sarnia-WTR, Dorchester-WTR, and Dundas-WTR, respectively). During the freshening period, the mean Mn effluent concentrations in all the amended columns decreased (mean = 0.03 ± 0.02 , 0.02 ± 0.02 , and 0.06 ± 0.03 mg/L

for Sarnia-WTR, Dorchester-WTR, and Dundas-WTR, respectively) and no spikes in effluent Mn concentrations were observed.

Porewater Mn concentrations were generally consistent with the effluent concentrations for all columns (Figure 3-9). The Mn concentrations in the porewater during the first and second salt periods for Sarnia-1 and Sarnia-2, and for the first salt period for Dorchester were higher (mean = 0.18 ± 0.17 , 0.18 ± 0.1 mg/L and 0.09 ± 0.1 mg/L for Sarnia-1, Sarnia-2, and Dorchester respectively) compared to during the regular periods (mean = 0.03 ± 0.06 , 0.08 ± 0.09 , and 0.02 ± 0.06 , respectively) and during the subsequent salt periods (50% of samples < detection limit of 0.02 mg/L, Q75 = 0.03 mg/L). In contrast, the porewater Mn concentrations were low in all stages of the experiment for Dundas (50% of samples < detection limit of 0.02 mg/L, median = 0.02 mg/L) and for Sarnia-WTR and Dorchester-WTR (29% of samples < detection limit of 0.02 mg/L, median = 0.03 mg/L and 60% of samples < detection limit of 0.02 mg/L, Q75 = 0.03 mg/L, respectively).

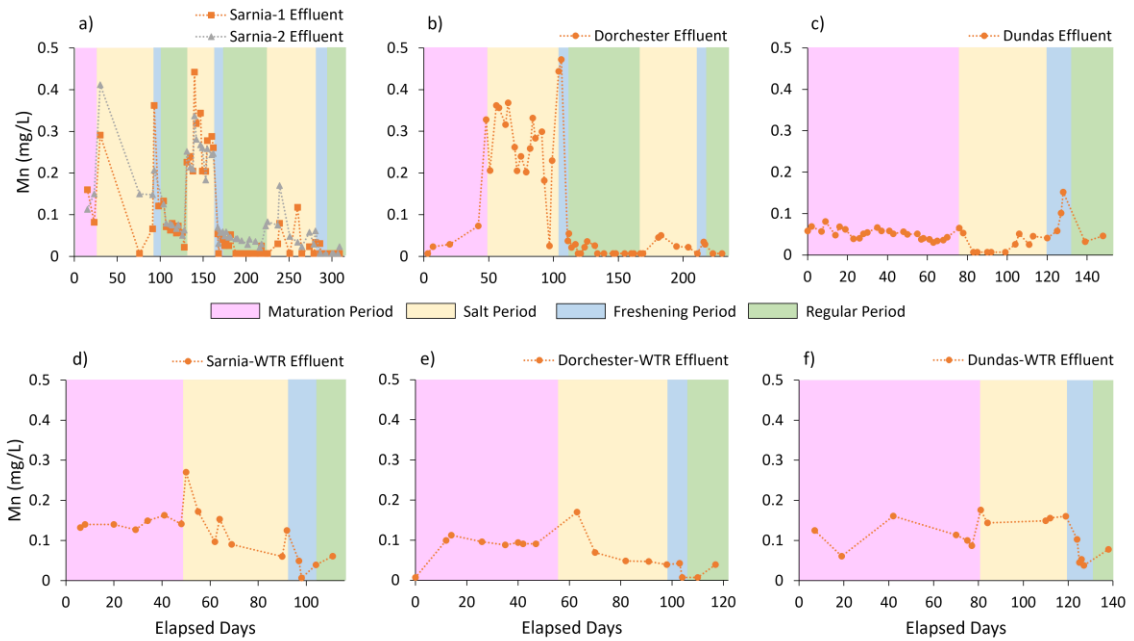


Figure 3-8: Effluent Mn concentrations for (a) Sarnia-1 and Sarnia-2, (b) Dorchester, (c) Dundas, (d) Sarnia-WTR, (e) Dorchester-WTR, and (f) Dundas-WTR columns. The pink, yellow, blue, and green shaded regions represent maturation, salt, freshening, and regular periods, respectively. Note that Mn concentrations in the influent were negligible.

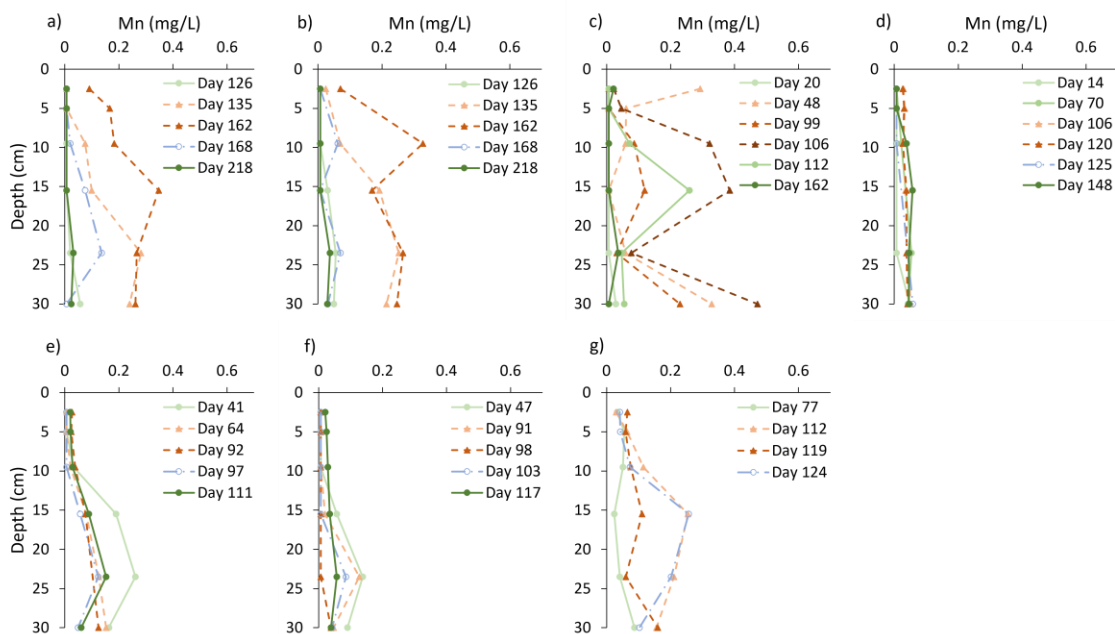


Figure 3-9: Mn porewater concentrations for a) Sarnia-1 (before, during and after second salt period), b) Sarnia-2 (before, during and after second salt period), c) Dorchester (before, during and after first period), d) Dundas, e) Sarnia-WTR, f) Dorchester-WTR, and g) Dundas-WTR. The green, orange, and blue colors represent regular, salt, and freshening periods, respectively. Depth of 30-cm represents the effluent sample.

Mean effluent Al concentrations for Sarnia-Control, Sarnia-1, Sarnia-2, Dorchester, and Dundas were 1.0 ± 0.7 , 1.1 ± 0.7 , 1.0 ± 0.8 , 1.2 ± 1.2 , and 2.0 ± 1.8 mg/L, respectively, considering the entire experimental period. The effluent Al concentrations for Sarnia-1 and Sarnia-2 remained low (< 3.5 mg/L) throughout the experimental period and were similar to the Sarnia-Control column which was not exposed to high salt influent (Figure 3-10 and Appendix E). Effluent Al concentrations increased up to 9.0 mg/L during the freshening period for Dundas and during the second freshening period for Dorchester. Similar to the spike in SRP concentrations observed during the freshening period, the high Al concentrations decreased to below 3.5 mg/L within seven days after the start of the freshening period. In the amended columns, the effluent Al concentrations were low (< 3.5 mg/L) during all stages of the experiment (mean = 1.4 ± 0.7 , 1.7 ± 0.9 , and 0.6 ± 0.5 mg/L for Sarnia-WTR, Dorchester-WTR, and Dundas-WTR, respectively). The

highest effluent Al concentrations for Sarnia-WTR and Dorchester-WTR (2.7 mg/L and 4 mg/L, respectively) occurred during the freshening periods. While the maximum effluent Al concentration did not occur during the freshening period in the Dundas-WTR column, a spike in effluent Al concentration to 1.4 mg/L was observed during this period.

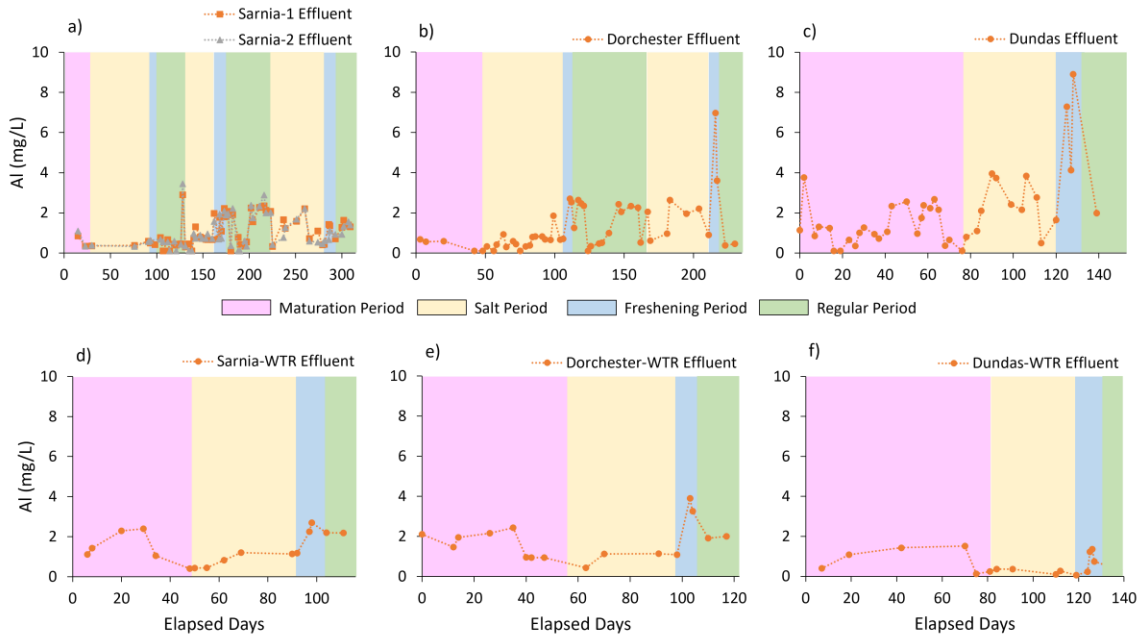


Figure 3-10: Effluent Al concentrations for (a) Sarnia-1 and Sarnia-2, (b) Dorchester, (c) Dundas, (d) Sarnia-WTR, (e) Dorchester-WTR, and (f) Dundas-WTR columns. The pink, yellow, blue, and green shaded regions represent maturation, salt, freshening, and regular periods, respectively. Note that Al concentrations in the influent were negligible.

In the non-amended columns, effluent Ca concentrations during the salt periods (mean concentrations of 38 ± 24 , 36 ± 21 , 34 ± 15 , and 32 ± 11 mg/L for Sarnia-1, Sarnia-2, Dorchester, and Dundas, respectively) were slightly higher compared to the regular periods (23 ± 10 , 24 ± 22 , 26 ± 21 , and 22 ± 10 mg/L; Figure 3-11). This may be a possible effect from the impurities in the NaCl used for this study. Effluent Ca concentrations reached over 90 mg/L for Sarnia-1 and Sarnia-2 during the first and second salt periods. The effluent Ca concentrations did not increase during the freshening period for the non-amended columns. Overall Ca effluent concentrations for Sarnia-WTR and Dorchester-WTR showed similar behaviours to the non-amended columns with

slightly lower effluent Ca concentrations observed during the regular periods (mean = 36 ± 22 and 25 ± 11 mg/L for Sarnia-WTR and Dorchester-WTR, respectively) compared with the salt periods (mean = 42 ± 20 , 47 ± 10 mg/L for Sarnia-WTR and Dorchester-WTR, respectively). In contrast, the effluent Ca concentrations for the Dundas-WTR column were higher during the regular period (mean = 42 ± 25 mg/L) compared to the salt period (mean = 29 ± 8 mg/L).

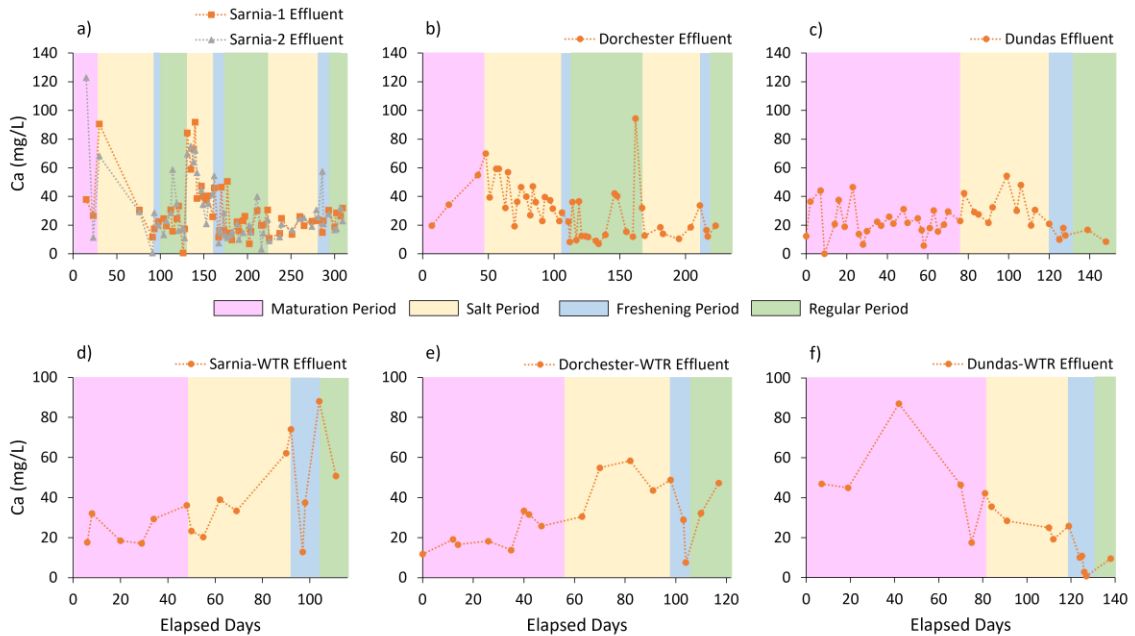


Figure 3-11: Effluent Ca concentrations for (a) Sarnia-1 and Sarnia-2, (b) Dorchester, (c) Dundas, (d) Sarnia-WTR, (e) Dorchester-WTR, and (f) Dundas-WTR columns. The pink, yellow, blue, and green shaded regions represent maturation, salt, freshening, and regular periods, respectively.

Mean Na effluent concentrations during regular periods for Sarnia-1, Sarnia-2, Dorchester, and Dundas were 9.8 ± 2.2 , 10.1 ± 2.7 , 10.2 ± 3.9 , and 10.5 ± 3.2 mg/L, respectively (Figure 3-12). During salt periods, the mean effluent Na concentrations increased to 311 ± 76 , 313 ± 70 , 307 ± 88 , and 348 ± 71 mg /L for Sarnia-1, Sarnia-2, Dorchester, and Dundas, respectively. This was expected as the target Na concentration in the high salt influent was 393 mg/L. The amended and non-amended columns showed similar behaviour with respect to effluent Na concentrations. Na effluent concentrations during the regular periods for Sarnia-WTR, Dorchester-WTR, and Dundas-WTR were 11

± 1.8 , 18 ± 24 , and 10 ± 1.6 mg/L, respectively. As expected, the Na effluent concentrations increased during the salt periods (379 ± 29 , 373 ± 24 , and 394 ± 12 mg/L, for Sarnia-WTR, Dorchester-WTR, and Dundas-WTR, respectively) and were similar to the target Na influent concentration (393 mg/L).

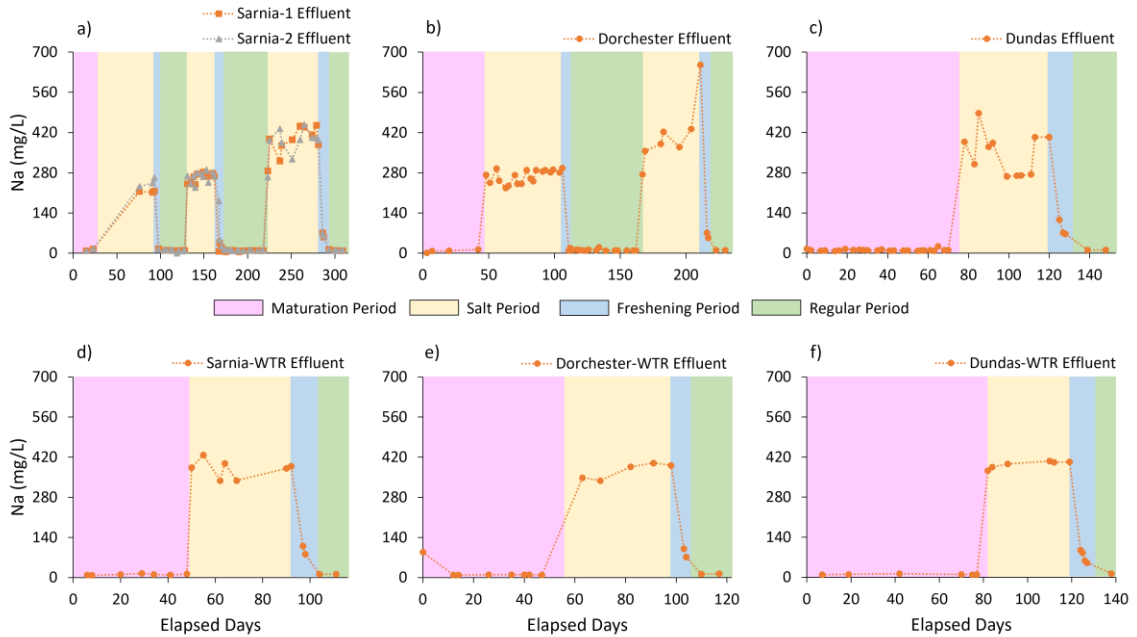


Figure 3-12: Effluent Na concentrations for (a) Sarnia-1 and Sarnia-2, (b) Dorchester, (c) Dundas, (d) Sarnia-WTR, (e) Dorchester-WTR, and (f) Dundas-WTR columns. The pink, yellow, blue, and green shaded regions represent maturation, salt, freshening, and regular periods, respectively.

3.3.4 DOC

DOC was measured as a proxy for dissolved organic matter as it can release SRP if mineralized and can also affect the redox conditions and pH within the columns (Amrhein et al., 1992; Y. Liu et al., 2021). Effluent DOC concentrations were relatively constant between the different stages of the experiments for all columns except for Dundas-WTR. The effluent DOC concentrations for Sarnia-1, Sarnia-2, Dorchester, and Dorchester-WTR (mean = 44 ± 5 , 51 ± 8 , 50 ± 5 , and 54 ± 4 mg C/L, respectively [Figure 3-13a, b, and e]) were only slightly higher than the mean influent concentration (38 ± 5 mg C/L). The effluent DOC concentrations were considerably higher than the

influent concentrations for Dundas and Sarnia-WTR with mean concentrations of 129 ± 13 mg C/L and 119 ± 15 mg C/L, respectively. Dundas-WTR was the only column for which the DOC effluent concentrations varied over the experiment with high DOC effluent concentrations (up to 160 mg C/L) observed during the freshening period compared to the remainder of the experiment (mean effluent DOC = 50 ± 5 mg C/L; Figure 3-13f). The DOC concentrations for the Sarnia-Control column experiment are provided in Appendix F.

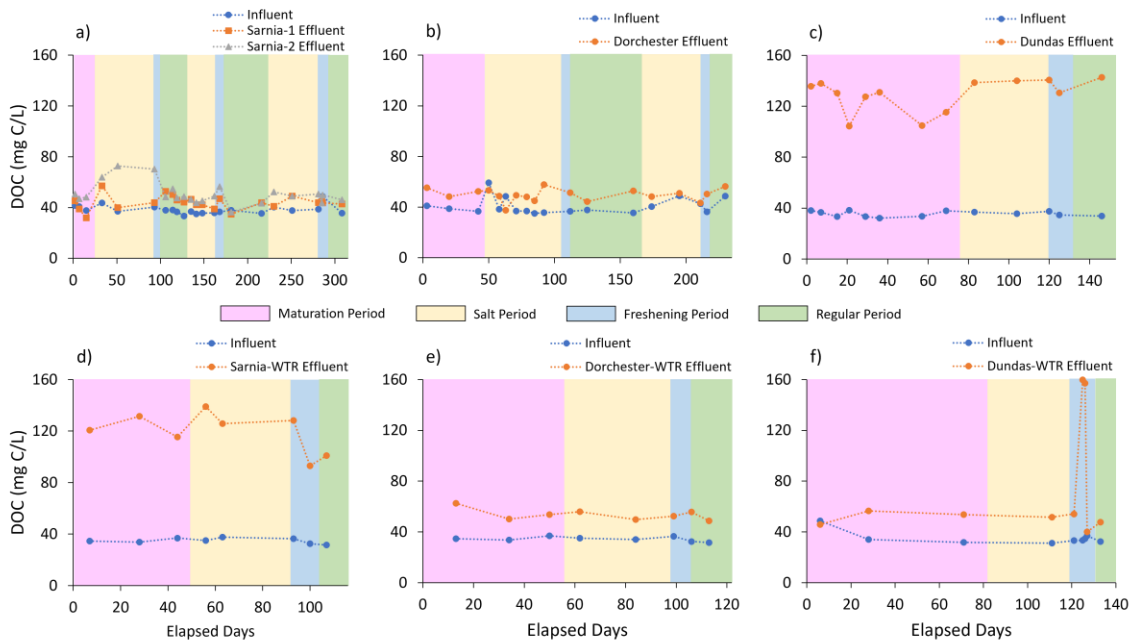


Figure 3-13: Effluent DOC concentrations for (a) Sarnia-1 and Sarnia-2, (b) Dorchester, (c) Dundas, (d) Sarnia-WTR, (e) Dorchester-WTR, and (f) Dundas-WTR columns. The pink, yellow, blue, and green shaded regions represent maturation, salt, freshening, and regular periods, respectively.

3.4 Discussion

3.4.1 Overall performance of bioretention media in retaining SRP

The performance of bioretention media in retaining SRP from urban stormwater has been shown to be highly variable in prior studies with the performance governed by the specific media composition and in situ geochemical conditions (Mangangka et al., 2015; Shrestha et al., 2018). Variable SRP retention was also observed between the three non-

amended bioretention media examined in this study, although overall, it was found that the three media acted as sources and released SRP. Considering the entire experimental period, Sarnia-Control, Sarnia-1, Sarnia-2, Dorchester, and Dundas released a cumulative SRP mass of 7.3, 5.8, 8.9, 6.2 and 8.4 mg P, respectively (Appendix G). Interestingly, Dundas had the second highest SRP release although it had the shortest experiment length (148 days for Dundas, compared with 309 days for Sarnia-Control, Sarnia-1 and Sarnia 2, and 230 days for Dorchester). The Dundas bioretention media had the highest measured extractable P content of 636 ppm (SRP) compared to 171 ppm (TP) and 286 ppm (SRP) for the Sarnia and Dorchester field systems, respectively, and was from the oldest field system (system installed in 2013). Dundas also consistently had the highest effluent DOC concentrations for the non-amended columns (Figure 3-13) suggesting potential mobilization of organic matter which may have released SRP if mineralized. The composition of the media also varied between the three bioretention systems. For example, Dundas had the lowest amount of fine material (silt/clay) at 4% compared to 9% and 8% for Sarnia and Dorchester, respectively. Lower silt/clay content can mean lower available mineral surface area for P adsorption, and this may have contributed to the higher P release from the Dundas media (Lucas & Greenway, 2011; Mangangka et al., 2015; Shrestha et al., 2018). Comparing the experimental results to available field data, the overall release of SRP from Sarnia-Control, Sarnia-1 and Sarnia-2 is consistent with Goor et al. (2021) who reported net release of SRP from the Sarnia field systems over a 12-month monitoring period. The Dorchester and Dundas field systems were monitored by Y. Liu et al. (2021) with SRP concentrations found to be similar in the porewater compared to the influent for field systems. In contrast, in our laboratory column experiments, the porewater and effluent SRP concentrations were higher than the influent concentrations for both Dorchester and Dundas indicating release of SRP from the media. This difference could be due to the continuous operation of the columns (saturated flow conditions) but also highlights the complexity and heterogeneity of bioretention media even within a single bioretention system. Importantly, the addition of Al-WTR amendments to the bioretention media considerably improved P retention with the total SRP mass retained in Sarnia-WTR, Dorchester-WTR and Dundas-WTR over the experiments calculated to be 2.7, 3.1, and 2.7 mg P, respectively. The Al-WTR used in

this study had an aluminum content (1,564 g/kg) that is ten times greater than the contents reported in other studies (Lee et al., 2015; O'Neill & Davis, 2012a; Zhang et al., 2018). Future experiments should explore the retention capacity of amended media if a lower Al-WTR content is used.

3.4.2 Effect of prolonged salt inputs

Overall, SRP effluent and porewater concentrations were similar between the salt periods and regular periods for all columns indicating that SRP release from the columns was not increased during a period of prolonged high salt input. The exception to this was Dorchester during the first salt period. Dorchester was observed to retain SRP for the first 27 days of the first salt period (until around day 75), after which it began to consistently release SRP for the remainder of the experiment (Appendix G). This is similar to the experimental column results of Goor et al. (2021) which used Sarnia media and suggested that prolonged salt input may cause increased release of TP.

The porewater and effluent data indicate that the increased SRP release observed over the first salt period for Dorchester may have been due to the onset of Mn reducing conditions. This may promote SRP release if Mn oxide minerals, which can adsorb SRP, undergo reductive dissolution. The onset of Mn reducing conditions in Dorchester is supported by the decrease in porewater ORP to less than 80 mV (Appendix D), and the increase in Mn concentrations in the effluent and porewater to 0.47 mg/L during the first salt period (Figures 3-8 and 3-9). The porewater and effluent Fe concentrations did not increase during the first (and subsequent) salt periods for Dorchester indicating that high salt inputs caused the column to become Mn reducing but not Fe reducing. The low porewater ORP (down to -70 mV) and high porewater Mn concentrations (up to 0.4 mg/L), and high effluent Mn concentrations (up to 0.45 mg/L) also suggest that Sarnia-1 and Sarnia-2 columns became Mn-reducing during the first and second salt periods (Figures 3-3, 3-8, and 3-9). While speculative, it is possible that enhanced SRP release did not occur during the salt periods for the Sarnia columns as SRP may have been more associated with other mineral phases including Fe- and Al-oxides in the Sarnia media rather than Mn-oxides (Marvin et al., 2020). The onset of Mn reducing conditions in the

Sarnia and Dorchester columns during the salt periods may have been caused by the high Na^+ concentrations increasing mobilization and availability of organic matter (Amrhein et al., 1992). However, as the DOC effluent concentrations were stable between the regular and salt periods for the Sarnia and Dorchester columns (Figure 3-13) it is challenging to confirm the role of organic matter based on the data available.

3.4.3 Effect of variable salt inputs (freshening periods)

Our column experiments indicate that the highest release of SRP from all columns occurred when the bioretention media was flushed with no salt influent immediately after a prolonged high salt period. Maximum SRP effluent concentrations during these events were 801, 869, 1080, and 1373 $\mu\text{g P/L}$ for the Sarnia-1, Sarnia-2, Dorchester, and Dundas columns, respectively (Figure 3-2). These concentrations are of concern as they are considerably higher than the hypereutrophic threshold of 100 $\mu\text{g/L}$ (Canadian Council of Ministers of the Environment, 2004). A similar phenomenon was observed by (McManus & Davis, 2020) in their bioretention mesocosm experiments in which bioretention media was periodically exposed to stormwater with salt concentrations of 2,000, 5,000, and 10,000 mg/L . However, interestingly our columns that were exposed to multiple high salt periods (Sarnia-1, Sarnia-2 and Dorchester) saw larger spikes in SRP in the later freshening periods (Figure 3-2). The AI-WTR amended columns showed much greater retention of SRP compared to the non-amended columns including during the freshening periods. While these columns experienced some increase in SRP effluent concentrations during the freshening periods (SRP up to 18 $\mu\text{g P/L}$; Figure 3-2), these increases were minor compared to that observed for the non-amended bioretention media and overall SRP was still retained in the columns during the freshening periods (i.e., influent SRP concentrations were higher than effluent concentrations). These findings support the enhanced SRP retention provided by AI-WTR as reported in prior studies (Duranceau & Biscardi, 2015; Lee et al., 2015; O'Neill & Davis, 2012b).

Various mechanisms may have contributed to the increased release of SRP from the bioretention media during the freshening periods. Most notably, porewater pH was observed to increase during the freshening periods for all columns except for Dundas-

WTR and Sarnia-1 (second freshening period) with pH increasing to above 9 (compared with pH 7.5 – 8 during the regular and salt periods). It is possible this increase in pH may have been caused by cation exchange. During the salt periods, high Na⁺ concentrations may have displaced H⁺ ions from surface exchange sites (Schlesinger & Bernhardt, 2020) causing a decrease in porewater pH. As the high Na⁺ concentration rapidly decreased during the freshening periods, H⁺ may have preferentially re-attached to the exchange sites (Schlesinger & Bernhardt, 2020), causing the observed increase in porewater pH. Prior studies have shown that pH (> around 8.5) can promote release of SRP from sediment by desorption from metal (Mn, Fe, Al) oxide surfaces and dissolution of phosphate-bearing minerals (Davis et al., 2006; O'Neill & Davis, 2012a). Increases in effluent Fe (Dorchester, Dundas, Dundas-WTR and the third freshening period for Sarnia-1) and Al (Dundas and the second freshening period for Dorchester) concentrations also observed during the freshening periods (Figures 3-6 and 3-10) suggest the high SRP concentrations may have been associated with the dissolution of Fe- and Al-phosphate minerals. It is possible that SRP desorption from Fe- and Al-oxides at high pH may also have contributed to enhanced release of SRP during the freshening periods since above neutral pH (pH of zero point of charge) these mineral surfaces repel negatively charged phosphate (PO₄³⁻) species (Schlesinger & Bernhardt, 2020). For example, Y. Liu et al. (2021) reported high SRP concentrations in one of their monitored field bioretention systems which also had high porewater pH (> 8), and Davis et al. (2006) found P desorbed from bioretention media at high pH (> 8) in their mesocosm-scale study. While high pH conditions are also favourable for precipitation of calcium phosphate minerals, it is not expected that this was a dominant control on SRP behaviour in these systems as this would have led to lower, rather than the observed higher SRP concentrations during the freshening periods.

While the amended columns were observed to retain SRP during the freshening periods, it is interesting that Dundas-WTR, which had higher maximum effluent SRP concentrations during the freshening period (18 µg/L) compared with Sarnia-WTR and Dorchester-WTR (7.4 µg/L and 7.5 µg/L, respectively; Figure 3-2) also showed a coincident spike in effluent DOC (Figure 3-13). It is unclear why this spike in effluent

DOC occurred during the freshening period for Dundas-WTR, however, it highlights the need for further investigation of the impact of periodic high salt inputs on organic matter immobilization and mineralization.

3.4.4 Limitations of column experiments

Soil-column experiments are often used as representations of field-scale systems as they provide increased control, monitoring and sample collection compared to field monitoring (Gibert et al., 2014). However, replicating field conditions with column experiments can be challenging with the results a function of the construction and operation of the soil columns (Lewis & Sjöstrom, 2010). Our study used packed soil columns (disturbed media from field systems were packed into the columns), rather than placing intact sediment cores into columns. While the use of packed soil columns avoids the formation of stratifying layers or preferential flow pathways and therefore can improve the reproducibility of the results, it is possible intact sediment cores may have provided better representation of the field conditions (Lewis & Sjöstrom, 2010). The difference in moisture dynamics between the soil columns and field systems may also limit the applicability of the column results to the field systems. For instance, the bioretention media in field systems has variable moisture content with intermittent infiltration events, whereas our columns were run under saturated conditions. This may alter the geochemical conditions between the field systems and columns including the redox conditions.

It is possible that the use of a continuous flow set up may have exposed the bioretention media in our columns to more salt than the field systems receive over a winter period. To examine this, we used field data collected by Goor et al. (2021) for the Sarnia field system to compare the total mass of Cl input normalized based on pore space volume between the column salt periods and the Sarnia field system. For the column experiments, between 336 and 727 pore volumes with high salt concentrations were infiltrated through the columns during each salt period, considering the influent rate of 1.44 L/day, 0.13 L of pore space within a column, and a minimum and maximum salt period of 31 and 67 days, respectively. This is equivalent to the Sarnia field system receiving an equivalent total

mass of Cl input between 373 and 806 kg, assuming it has a pore space volume of 14,000 L (see Appendix H for details of calculations). Based on Cl concentrations from road runoff samples collected in the middle of precipitation events and first flush road runoff Cl concentrations, it is estimated that the Sarnia field system actually received between 60 and 510 kg of Cl over a winter period (Goor et al., 2021). Although a number of assumptions were used in this calculation (e.g., no dead pore spaces, road runoff infiltrated equally across the bioretention system), these estimates suggest that the operation of our column experiments may have over-exposed the columns to salt. To address this limitation, we recommend additional column experiments be conducted with shorter duration salt periods and also recommend monitoring of field scale systems with sampling focused on rain events in early spring when our column experiments suggest enhanced SRP release may occur.

3.5 Conclusions

Five non-amended and three Al-WTR amended laboratory bioretention media columns were run to evaluate the influence of prolonged and periodic high salt inputs on SRP retention, and to identify the possible geochemical processes influencing SRP retention. While data indicate that prolonged high salt loading may have caused higher release of SRP for one of the non-amended columns, the impact of switching from high salt influent to no salt influent led to much higher SRP release for all columns. These results suggest that bioretention systems installed in cold climates where road de-icing salts are used may release high SRP loads during spring freshet rain events. Importantly, bioretention media amended with Al-WTR showed high capacity to retain SRP even during the freshening periods, thus supporting the benefits of using Al-WTR as a bioretention media amendment. Detailed porewater chemistry data indicate that the redox conditions became Mn reducing in three of the columns during the salt periods, and this may have promoted SRP release. It is possible that conditions could become Fe reducing in field bioretention systems in response to prolonged salt inputs and this could promote even higher SRP release (due to desorption of SRP from Fe oxides). This high SRP release that occurred during the freshening periods was associated with a large increase in porewater pH suggesting that pH-driven precipitation-dissolution and adsorption-desorption processes

may be controlling the retention and release of SRP from bioretention media during this period. Overall, this study provides new insights into the performance and ability of bioretention media exposed to prolonged and periodic high salt inputs on P retention in bioretention systems. This information can be used to improve bioretention system design as needed to ensure the year-round performance of these systems installed in cold climates where de-icing road salts are applied.

3.6 References

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Chapter 4

4 Summary and Recommendations

4.1 Summary

In freshwater systems, high inputs of phosphorus (P) can lead to eutrophication which has negative environmental, societal and economic consequences (Correll, 1999; Environment and Climate Change Canada, 2020; Environment and Climate Change Canada and the Ontario Ministry of the Environment and Climate Change, 2018). Non-point P sources, including urban stormwater runoff, are important contributors of P to surface waters, and must be addressed to restore and protect downstream surface waters (Scavia et al., 2014). Bioretention systems are a popular low impact development stormwater management system used to reduce peak runoff volumes and retain pollutants found in urban stormwater (Khan et al., 2012; LeFevre et al., 2015; Trowsdale & Simcock, 2011). However, prior studies report variable performance of bioretention systems with respect to their ability to retain P from urban stormwater and the geochemical processes governing P fate within these systems remains unclear (Dietz & Clausen, 2005; Hunt et al., 2006; Li & Davis, 2016). Further the impact of de-icing road salts, that are widely used in cold climates, on the retention of P in bioretention systems is not well understood. Lastly, while amendments including aluminum-based water treatment residuals (Al-WTRs) have been shown to considerably improve P retention in bioretention systems (Marvin et al., 2020; O'Neill & Davis, 2012), no prior studies have evaluated the performance of Al-WTR amended bioretention media exposed to stormwater with high and variable salt concentrations. This study addresses these knowledge gaps by conducting laboratory column experiments using three bioretention media (with and without Al-WTR amendment) exposed to artificial stormwater with periodically high salt concentrations.

The first and second objectives to assess the impact of prolonged and periodic high salt stormwater inputs on the retention of soluble reactive phosphorus (SRP) in non-amended and Al-WTR amended bioretention media were addressed by collecting and analyzing

influent, effluent, and porewater SRP concentrations from the columns. Overall, all non-amended media columns had a net release of SRP over the experimental periods, whereas the Al-WTR amended media had net retention of SRP. Importantly, although some non-amended columns showed increased SRP release during prolonged exposure to high salt influent stormwater, the largest SRP releases observed in all columns occurred during the freshening periods immediately following the switch from high salt to low salt influent stormwater. During this time effluent SRP concentrations reached more than 800 $\mu\text{g P/L}$ which is considerably higher than concentrations of 35 to 100 $\mu\text{g P/L}$ that trigger eutrophic conditions in surface waters (Canadian Council of Ministers of the Environment, 2004). In bioretention systems installed in cold climate environments, this result indicates that large releases of P could occur during rain events in early spring when de-icing salts are no longer applied.

The third objective was to identify the possible geochemical processes influencing SRP retention and release in bioretention media exposed to prolonged and periodic high salt stormwater influent. This objective was accomplished through detailed sampling and analysis of porewater for pH, ORP, and chemical species (Fe, Mn, Al, Ca, Na, DOC) related to P retention. Data indicate that while conditions in the columns were generally oxic (ORP > 140 mV), some columns became Mn reducing during periods of prolonged exposure to high salt influent. This was associated with higher SRP concentrations in the effluent (up to 280 $\mu\text{g/L}$) which may have been due to reductive dissolution of Mn oxides and associated SRP desorption. It is also possible that high Cl concentrations during the prolonged salt periods may also have promoted SRP desorption through anion exchange processes. For all columns, high porewater pH up to 9 (compared to pH 7-8 for the remainder of the experimental periods) was observed during the freshening periods when the highest SRP release occurred. It is possible that cation exchange processes associated with changes in Na concentrations may have caused the increase in porewater pH during the freshening periods. High pH may have promoted the dissolution of Fe- and Al-phosphate minerals that are less stable in alkaline environments (Schlesinger & Bernhardt, 2020). This mechanism is supported by the high porewater, and effluent Fe and Al concentrations observed during the freshening periods. Additionally, high pH may

also trigger desorption of SRP from Fe- and Al-oxide surfaces due to a change in the mineral surface charge (from positively to negatively charged). However, this mechanism does not explain the high dissolved Fe and Al concentrations also observed during the freshening period coincident with the high pH and SRP concentrations (Schlesinger & Bernhardt, 2020).

Overall, the findings from the laboratory column experiments illustrate the impact of road de-icing salts on P retention in bioretention systems and the complexity of the geochemical conditions that govern SRP retention in these systems. The findings provide new insight of the factors and conditions that may promote the release of SRP as needed to improve the year-round performance of bioretention systems in cold climates.

4.2 Recommendations

Recommendations for further research needed to improve understanding of P retention in bioretention systems installed in cold climates are as follows:

- Conduct column experiments with monolithic (intact soil) columns and intermittent flow regimes that may better represent field conditions including variably saturated conditions and more realistic periods of salt exposure.
- Future experiments should assess if the retention capacity of Al-WTR amended media is as high including during freshening periods if lower Al-WTR contents are used.
- Conduct monitoring of field-scale bioretention systems installed in cold climates with a focus on high resolution influent, effluent and porewater sampling during periods of prolonged salt input and freshening. This will help confirm the large releases of SRP observed during the freshening periods in this study and better understand the impact of high de-icing salt inputs on P retention in field-scale systems.
- Monitor field bioretention systems amended with Al-WTR to better understand the benefits of this amendment for SRP retention. This study shows that use of

Al-WTRs in bioretention media considerably improves the performance of the media with respect to its ability to retain SRP even under the impact of de-icing salts.

- Further investigate the impact of de-icing salts on organic matter mobilization and decomposition, and its influence on SRP release from bioretention media at the column and field scale. While columns with higher effluent DOC concentrations were observed to release more SRP during the freshening periods and over the entire experimental period, the stable effluent DOC concentrations in these columns over the experimental period made it challenging to determine the role of organic matter in the release of SRP. As field-scale bioretention systems often use organic-rich topsoil, the impact of de-icing salts on organic matter mobilization and mineralization may considerably affect SRP retention in these systems.

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Appendices

Appendix A: Supplemental details on analytical methods

All influent, effluent and porewater samples were analyzed immediately following collection for electrical conductivity (EC), pH and oxidation reduction potential (ORP) using HACH HQ40D multimeter, IntelliCAL® CDC401 probe, IntelliCAL® PHC201 probe and IntelliCAL® MTC101 probe.

SRP was analyzed with LaChat QuickChem 8500 Flow Injection Analysis Machine (FIA) method 10-115-01-1-M within 48 hours of collection. Detection limit of 1 – 100 µg P/L. Six standards of known concentrations were used to create a calibration curve ($r^2 > 0.95$). Quality control was completed with duplicates run every six to ten samples and immediately followed by a standard of known concentration. Sample duplicates and quality control standards had high accuracy with differences less than 10%. Duplicates with greater than 10% difference were re-run.

Samples for Al, Ca, Fe, Mn, and Na analysis were stored at 4°C and acidified with HNO₃ before analysis. Concentrations of these analytes were determined using Atomic Absorption Spectroscopy (AA: Agilent Technologies 200 Series AA). Detection limits of 0.3 – 250 mg Al/L, 2 – 800 mg Ca/L, 0.06 – 15 mg Fe/L, 0.02 – 5 mg Mn/L, and 2 – 400 mg Na/L. Five standards of known concentration were used to create a calibration curve ($r^2 > 0.99$). Quality control was completed with standards of known concentrations run every 20 samples with machine re-calibration set for every 50 samples.

DOC samples were stored at 4°C in glass amber vials and analyzed within one week of collection with a Shimadzu TOC-V with ANSI-V auto-sampler with detection limit 0.1 – 30,000 mg/L. Ten standards of known concentration were used to create a calibration curve ($r^2 > 0.995$). Quality control was completed with duplicates run every six samples. Duplicates with greater than 10% difference were re-run.

Appendix B: Supplemental SRP data

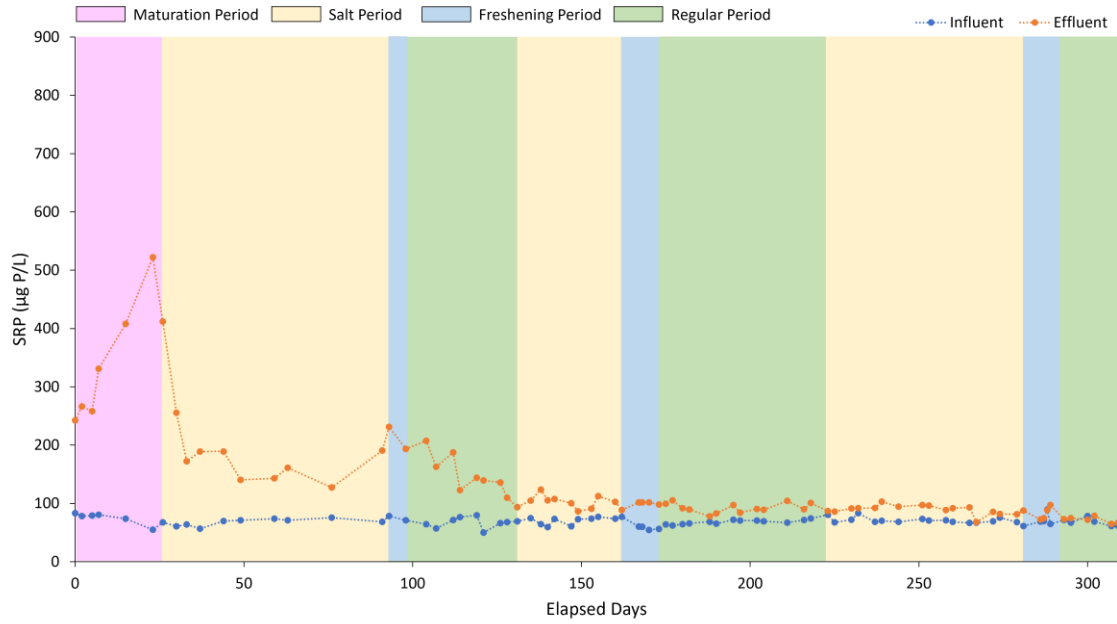


Figure B-1: Influent and effluent SRP for Sarnia-Control. The pink, yellow, blue, and green shaded regions represent maturation, salt, freshening, and regular periods, respectively.

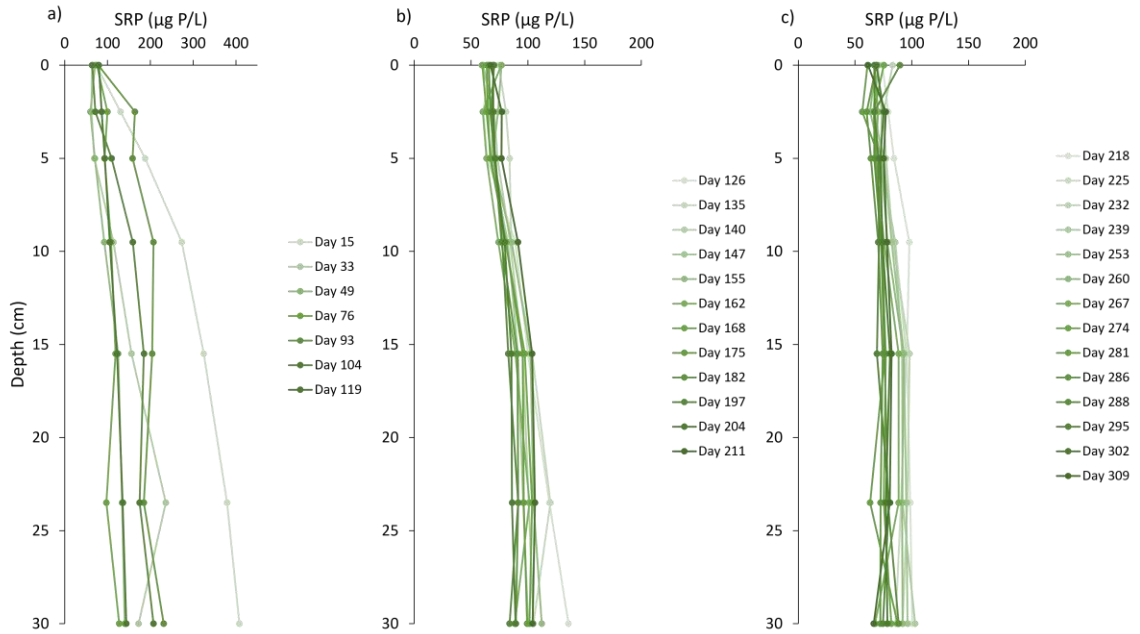


Figure B-2: Porewater concentrations for Sarnia-Control before, during, and after the a) first salt period, b) second salt period, c) third salt period. Sampling depths of 0- and 30-cm represent the influent and effluent samples, respectively. Note the different x-axis scales between the subplots.

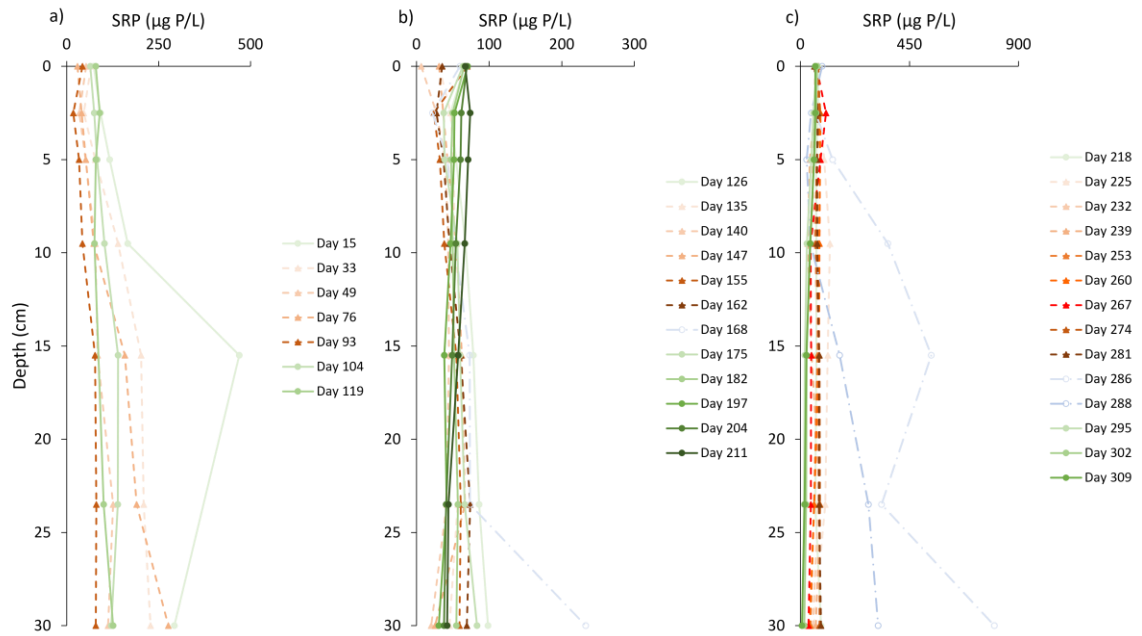


Figure B-3: Porewater concentrations for Sarnia-1 before, during, and after the a) first salt period, b) second salt period, c) third salt period. The green, orange, and blue colors represent regular, salt, and freshening periods, respectively. Sampling depths of 0- and 30-cm represent the influent and effluent samples, respectively. Note the different x-axis scales between the subplots.

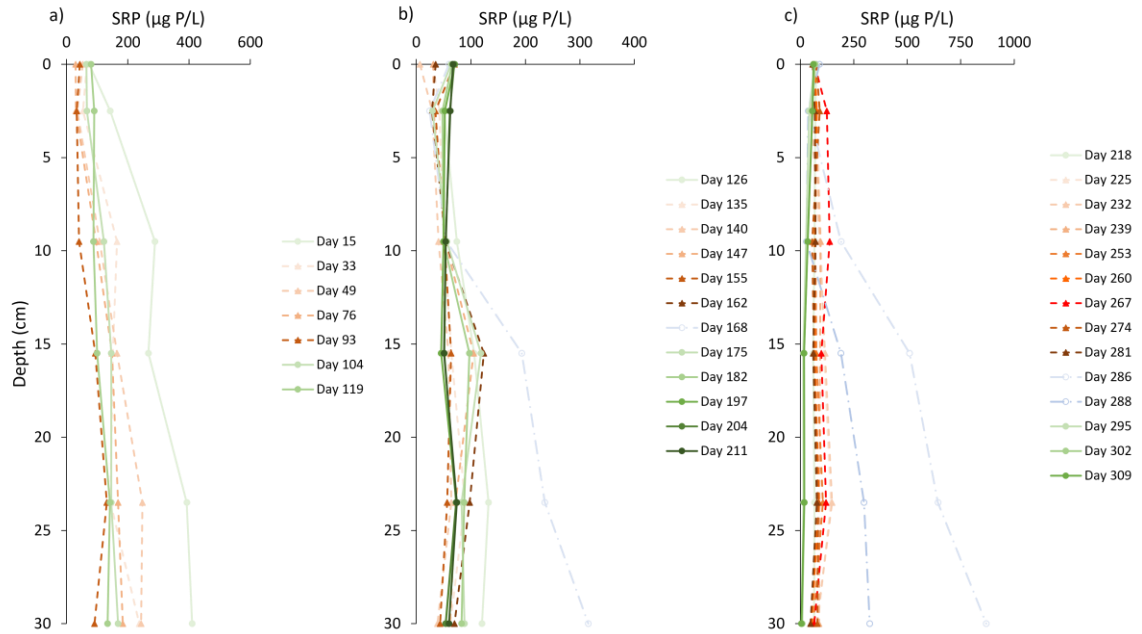


Figure B-4: Porewater concentrations for Sarnia-2 before, during, and after the a) first salt period, b) second salt period, c) third salt period. The green, orange, and blue colors represent regular, salt, and freshening periods, respectively. Sampling depths of 0- and 30-cm represent the influent and effluent samples, respectively. Note the different x-axis scales between the subplots.

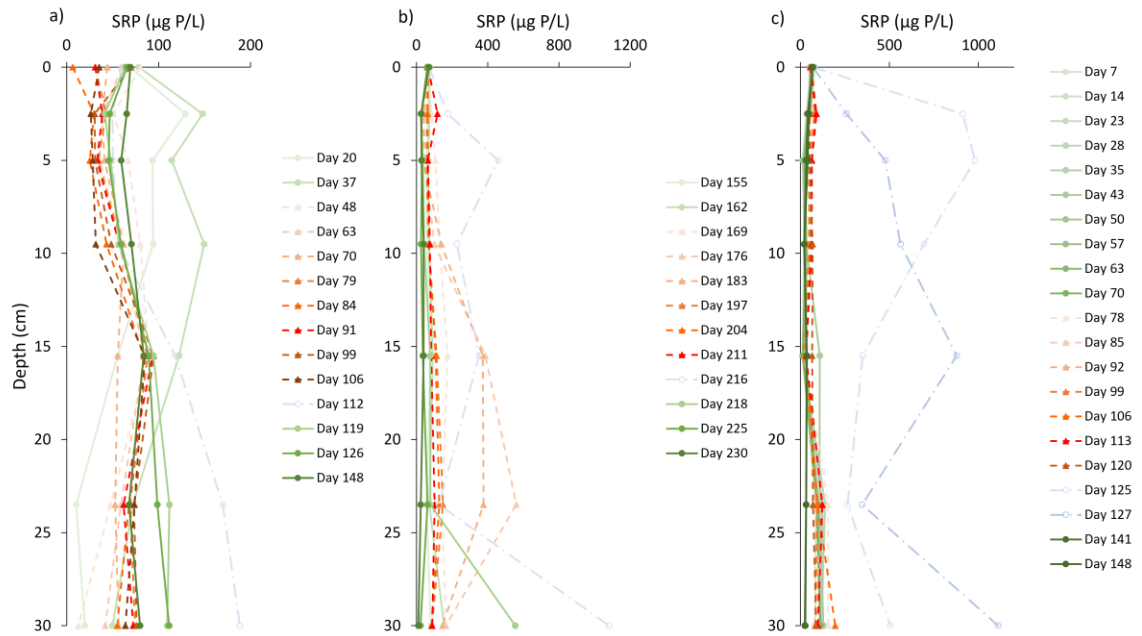


Figure B-5: Porewater concentrations for a) Dorchester (before, during, and after the first salt period), b) Dorchester (before, during, and after the second salt period), and c) Dundas. The green, orange, and blue colors represent regular, salt, and freshening periods, respectively. Sampling depths of 0- and 30-cm represent the influent and effluent samples, respectively. Note the different x-axis scales between the subplots.

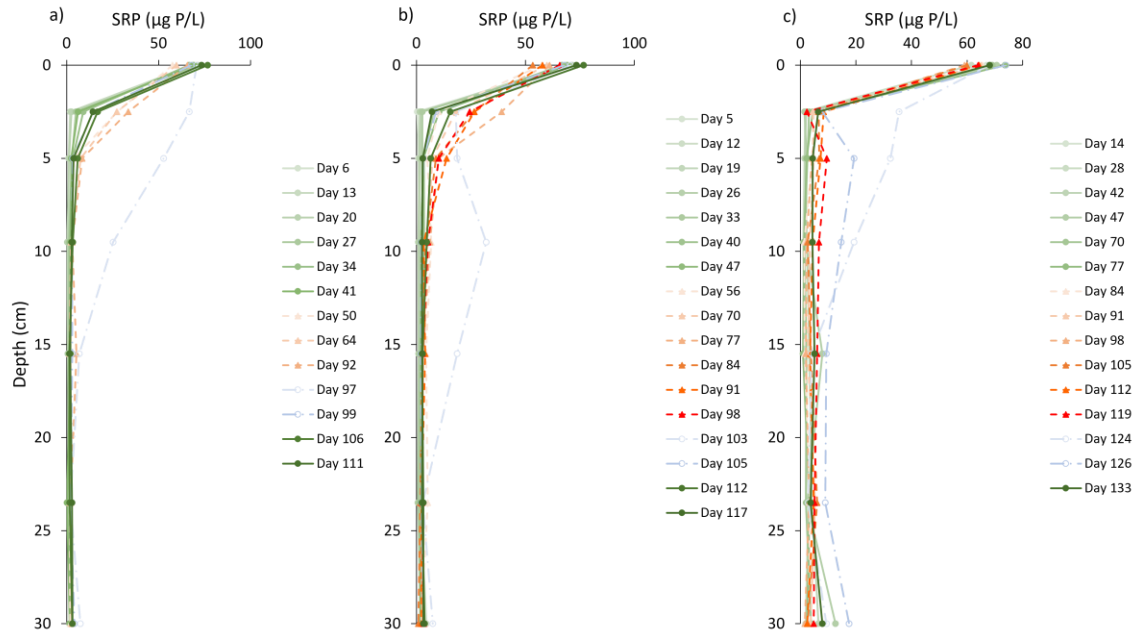


Figure B-6: Porewater concentrations for a) Sarnia-WTR, b) Dorchester-WTR, and c) Dundas-WTR. The green, orange, and blue colors represent regular, salt, and freshening periods, respectively. Sampling depths of 0- and 30-cm represent the influent and effluent sample, respectively. Note the different x-axis scales between the subplots.

Appendix C: Supplemental pH data

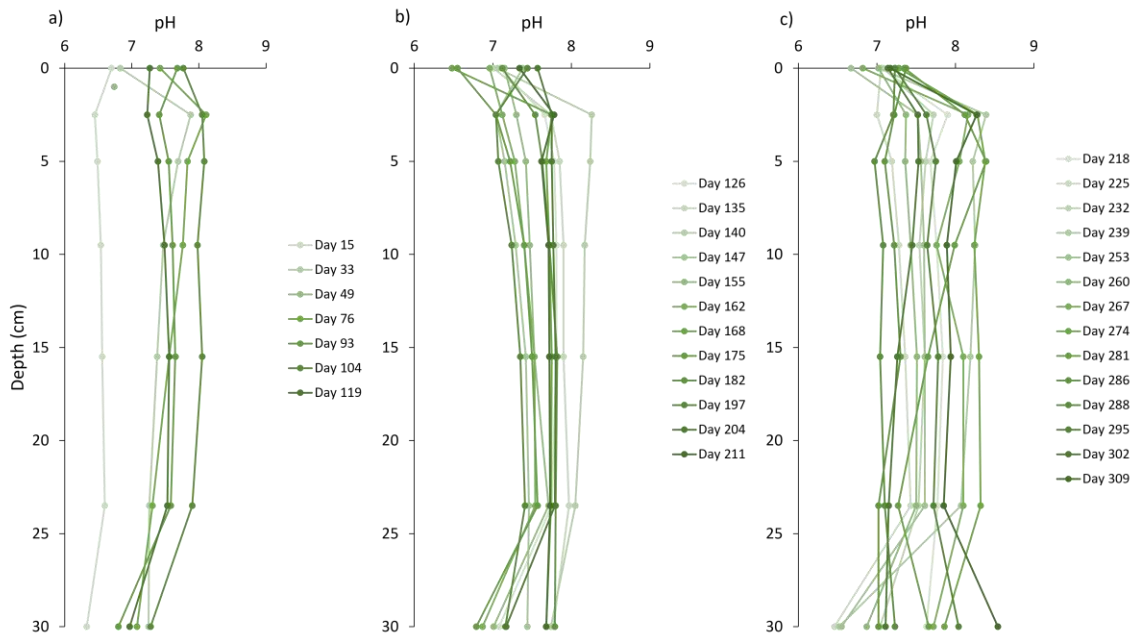


Figure C-1: Porewater pH for Sarnia-Control before, during, and after the a) first salt period, b) second salt period, c) third salt period. Sampling depths of 0- and 30-cm represent the influent and effluent samples, respectively.

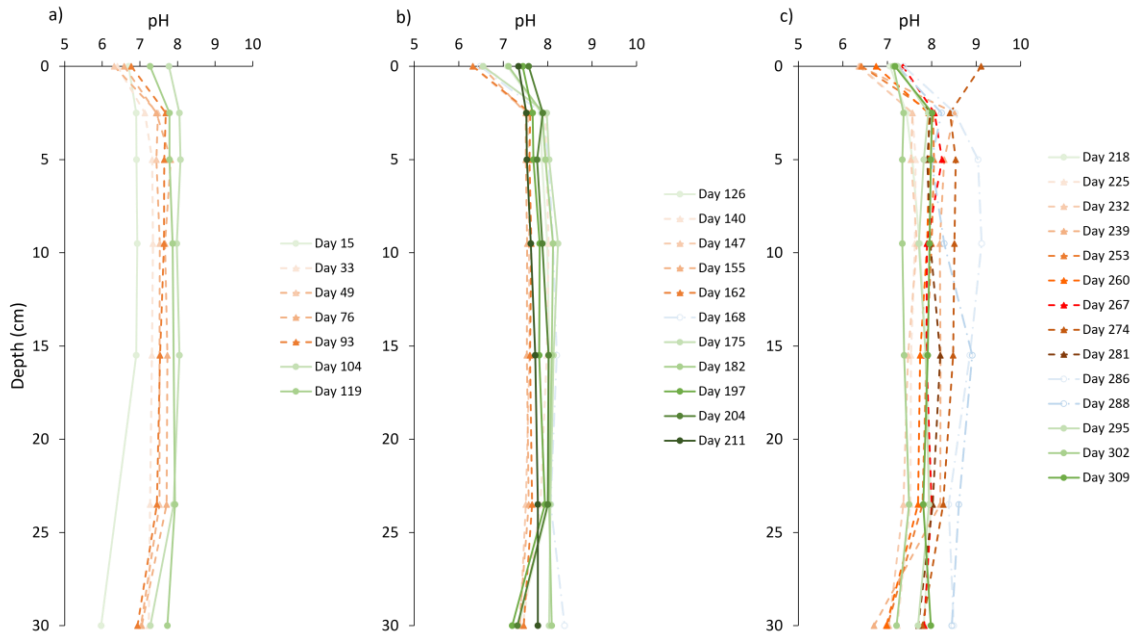


Figure C-2: Porewater pH Sarnia-1 before, during, and after the a) first salt period, b) second salt period, c) third salt period. The green, orange, and blue colors represent regular, salt, and freshening periods, respectively. Sampling depths of 0- and 30-cm represent the influent and effluent samples, respectively.

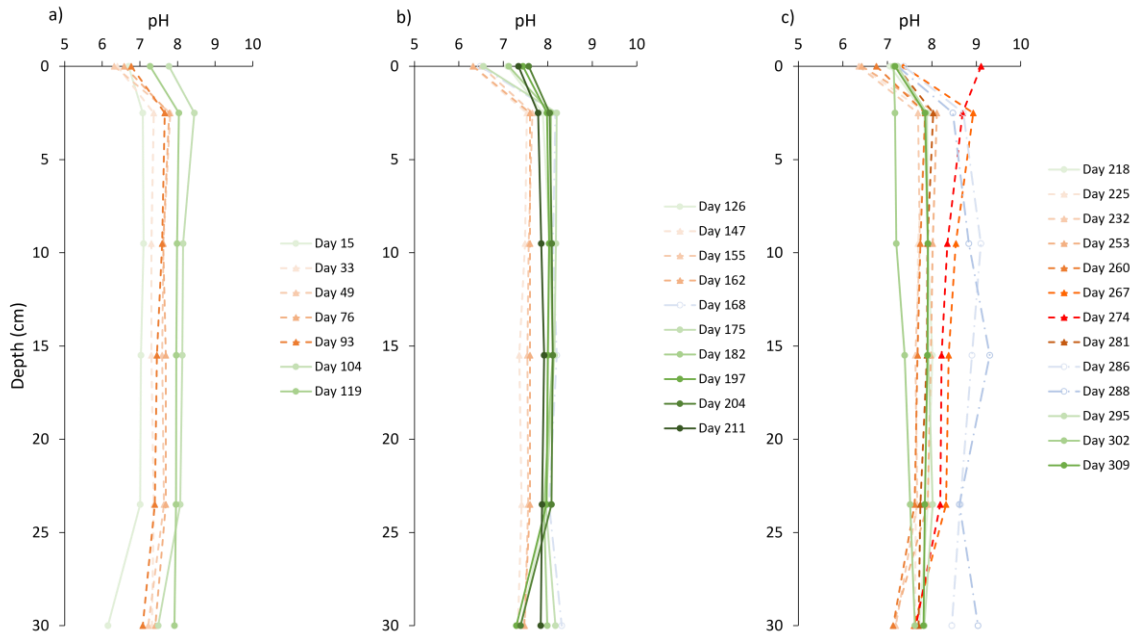


Figure C-3: Porewater pH for Sarnia-2 before, during, and after the a) first salt period, b) second salt period, c) third salt period. The green, orange, and blue colors represent regular, salt, and freshening periods, respectively. Sampling depths of 0- and 30-cm represent the influent and effluent samples, respectively.

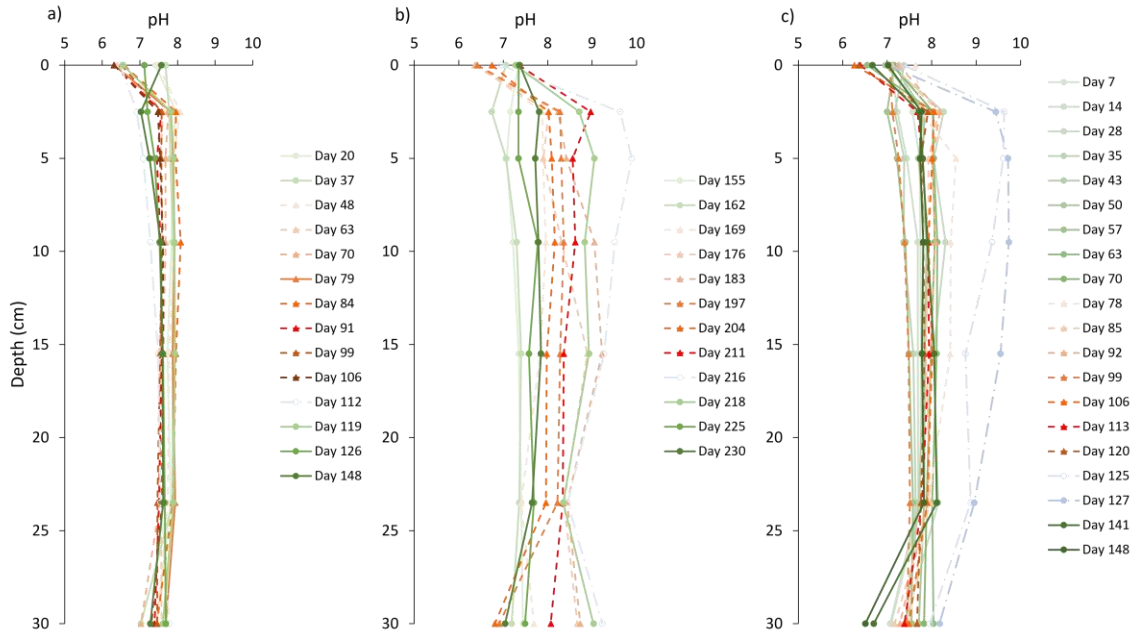


Figure C-4: Porewater pH for a) Dorchester (before, during, and after the first salt period), b) Dorchester (before, during, and after the second salt period), and c) Dundas. The green, orange, and blue colors represent regular, salt, and freshening periods, respectively. Sampling depths of 0- and 30-cm represent the influent and effluent samples, respectively.

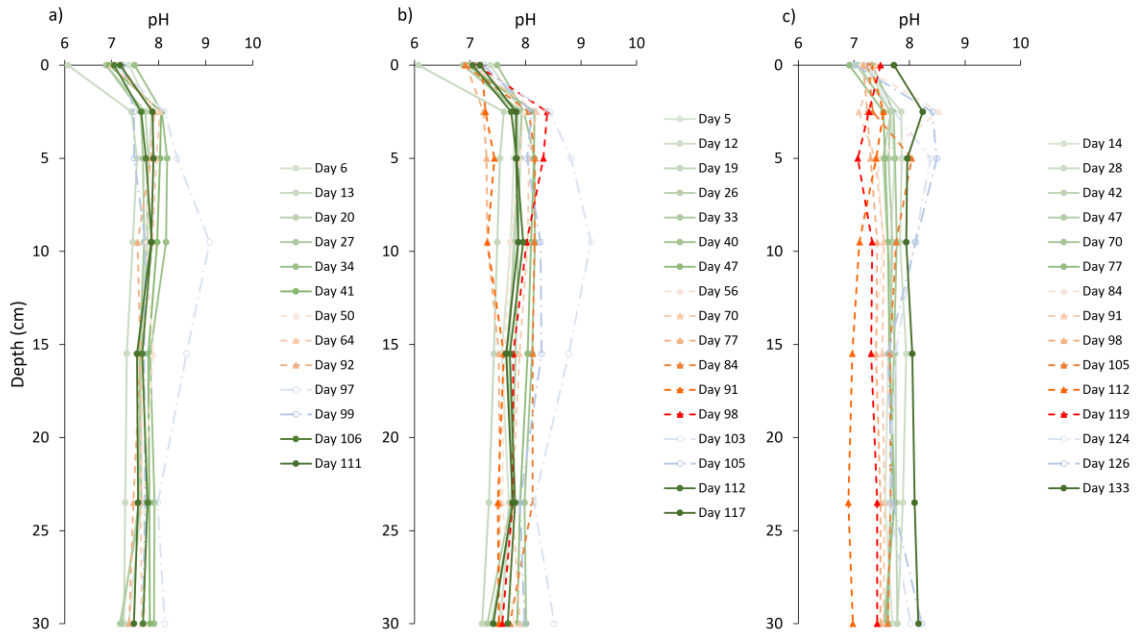


Figure C-5: Porewater pH for a) Sarnia-WTR, b) Dorchester-WTR, and c) Dundas-WTR. The green, orange, and blue colors represent regular, salt, and freshening periods, respectively. Sampling depths of 0- and 30-cm represent the influent and effluent sample, respectively.

Appendix D: Supplemental ORP data

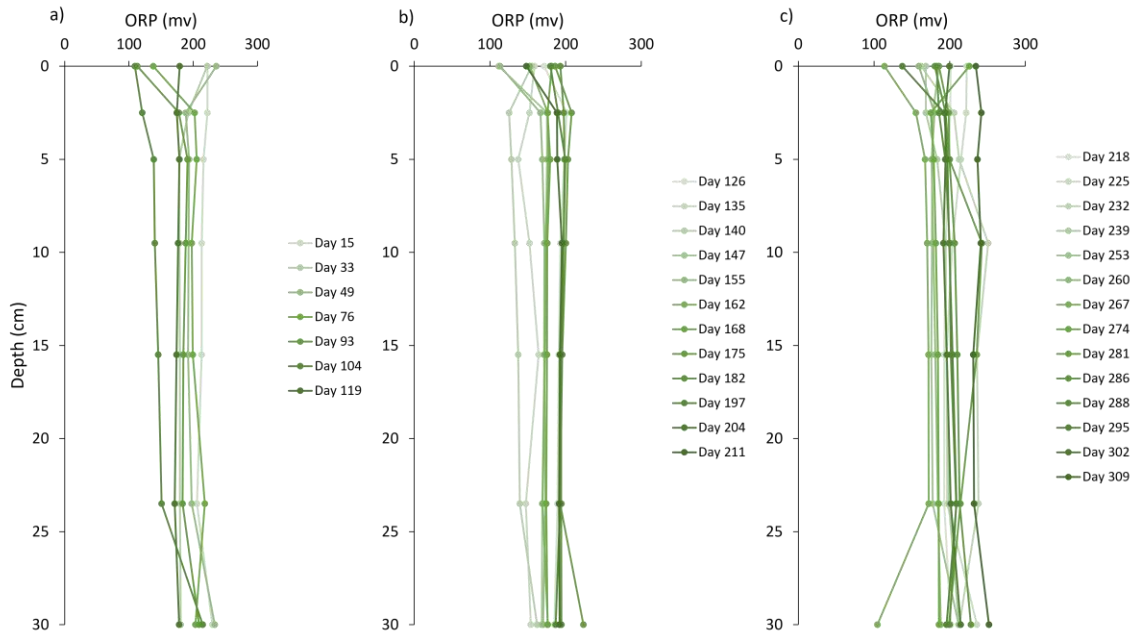


Figure D-1: Porewater ORP for Sarnia-Control before, during, and after the a) first salt period, b) second salt period, c) third salt period. Sampling depths of 0- and 30-cm represent the influent and effluent samples, respectively.

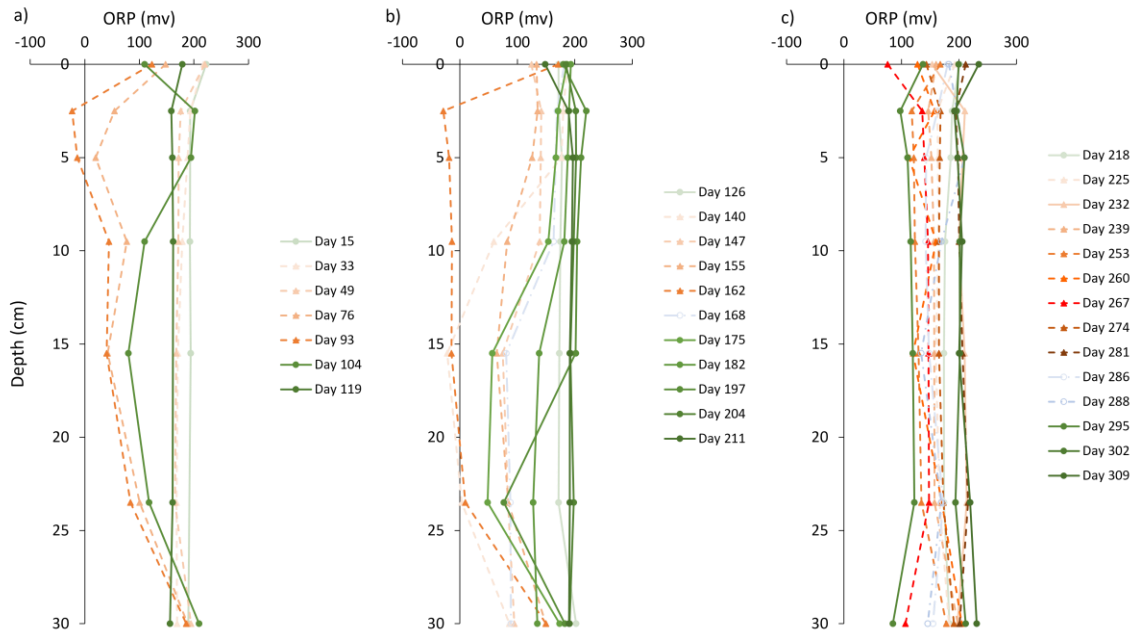


Figure D-2: Porewater ORP for Sarnia-1 before, during, and after the a) first salt period, b) second salt period, c) third salt period. The green, orange, and blue colors represent regular, salt, and freshening periods, respectively. Sampling depths of 0- and 30-cm represent the influent and effluent samples, respectively.

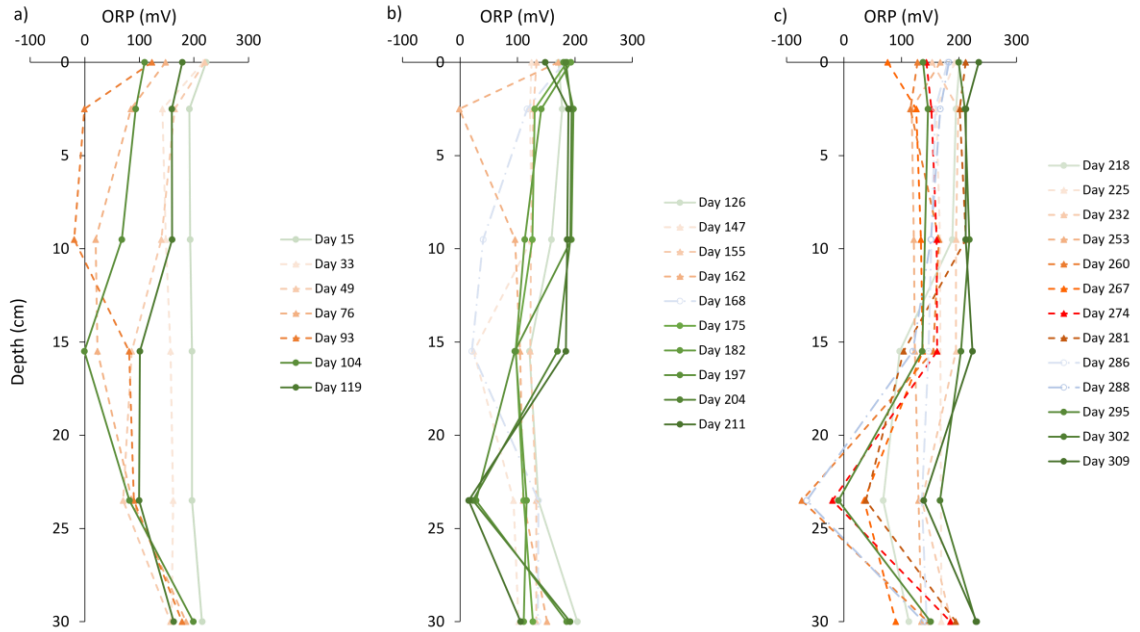


Figure D-3: Porewater ORP for Sarnia-2 before, during, and after the a) first salt period, b) second salt period, c) third salt period. The green, orange, and blue colors represent regular, salt, and freshening periods, respectively. Sampling depths of 0- and 30-cm represent the influent and effluent samples, respectively.

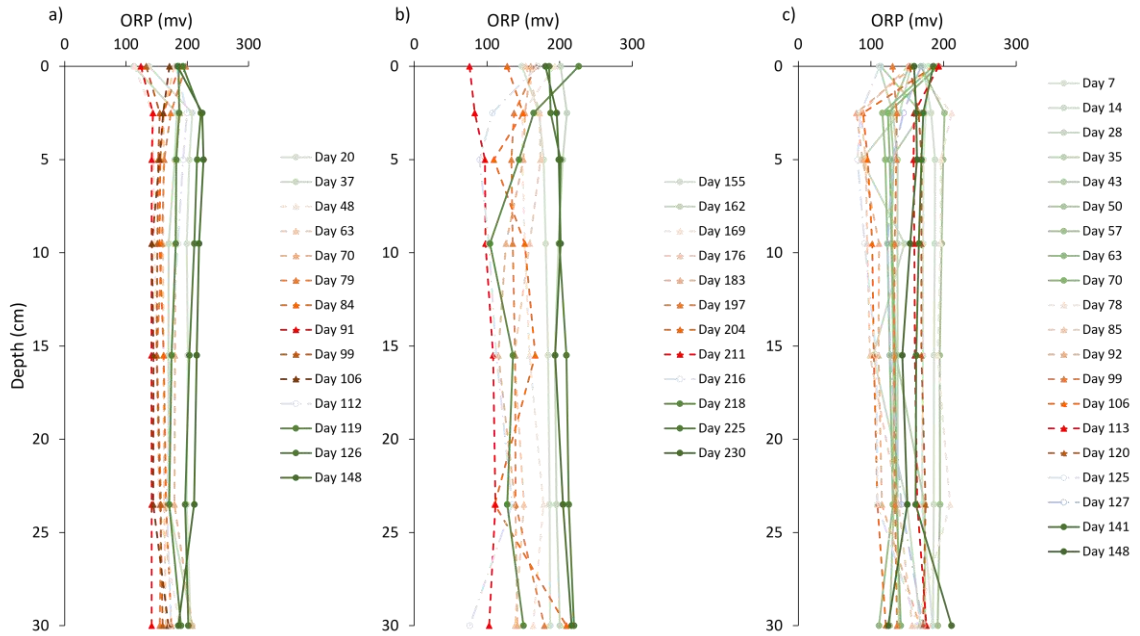


Figure D-4: Porewater ORP for a) Dorchester (before, during, and after the first salt period), b) Dorchester (before, during, and after the second salt period), and c) Dundas. The green, orange, and blue colors represent regular, salt, and freshening periods, respectively. Sampling depths of 0- and 30-cm represent the influent and effluent samples, respectively.

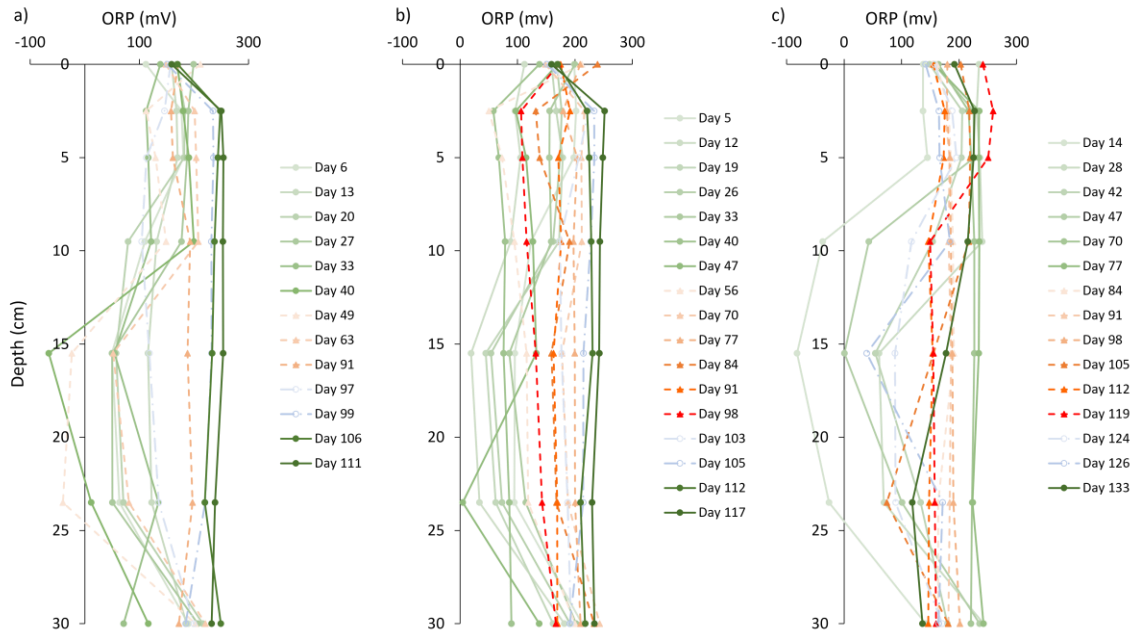


Figure D-5: Porewater ORP for a) Sarnia-WTR, b) Dorchester-WTR, and c) Dundas-WTR. The green, orange, and blue colors represent regular, salt, and freshening periods, respectively. Sampling depths of 0- and 30-cm represent the influent and effluent sample, respectively.

Appendix E: Supplemental Metal Data

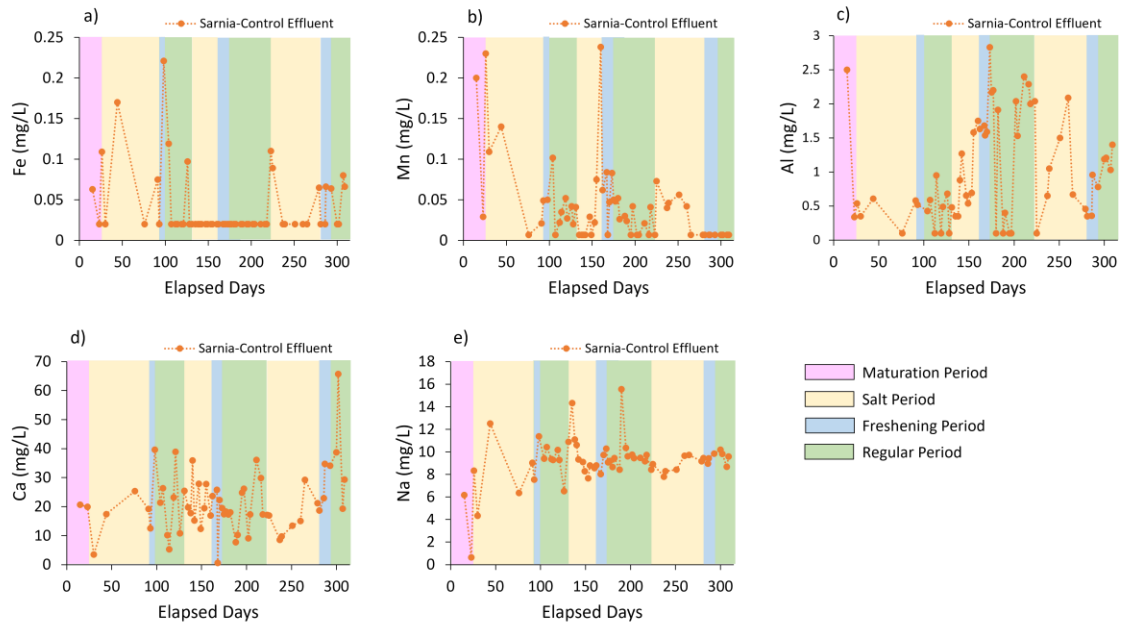


Figure E-1: Effluent a) Fe, b) Mn, c) Al, d) Ca, and e) Na concentrations for Sarnia-Control. The pink, yellow, blue, and green shaded regions represent maturation, salt, freshening, and regular periods, respectively.

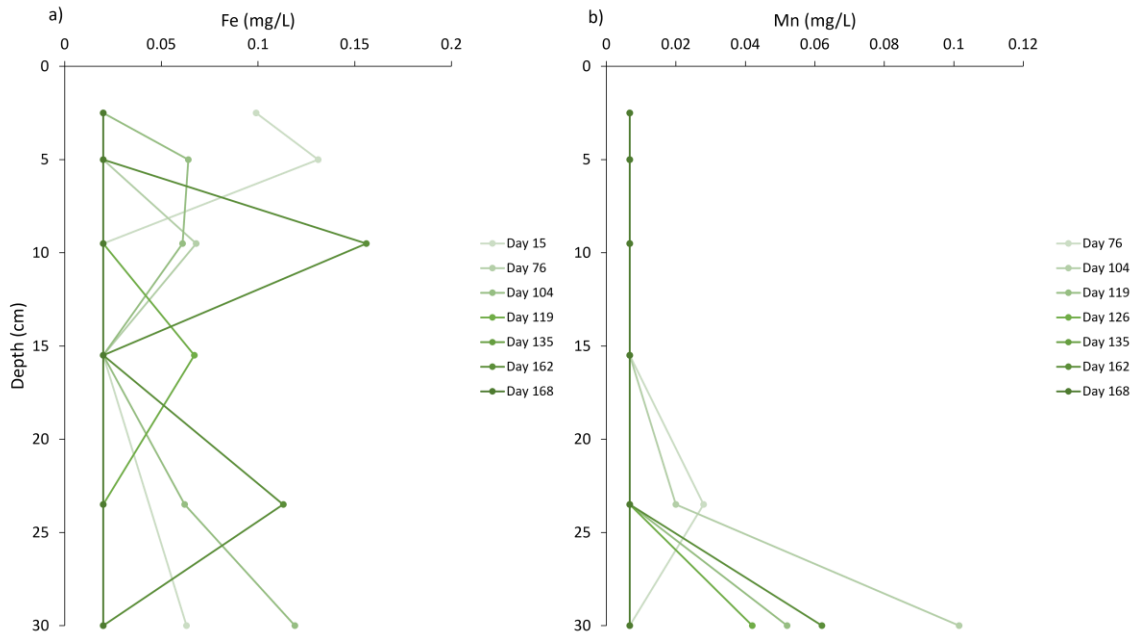


Figure E-2: Porewater a) Fe and b) Mn concentrations for Sarnia-Control. The green represents regular period. Sampling depths of 0- and 30-cm represent the influent and effluent samples, respectively.

Appendix F: Supplemental DOC data

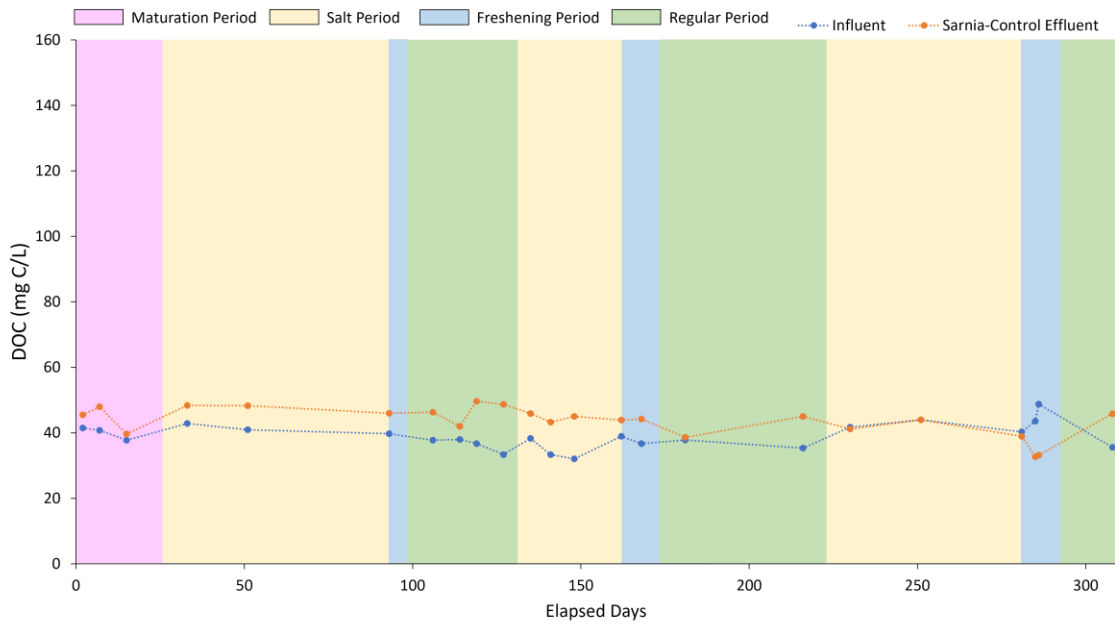


Figure F-1: Influent and effluent DOC for Sarnia-Control. The pink, yellow, blue, and green shaded regions represent maturation, salt, freshening, and regular periods, respectively.

Appendix G: SRP cumulative mass released

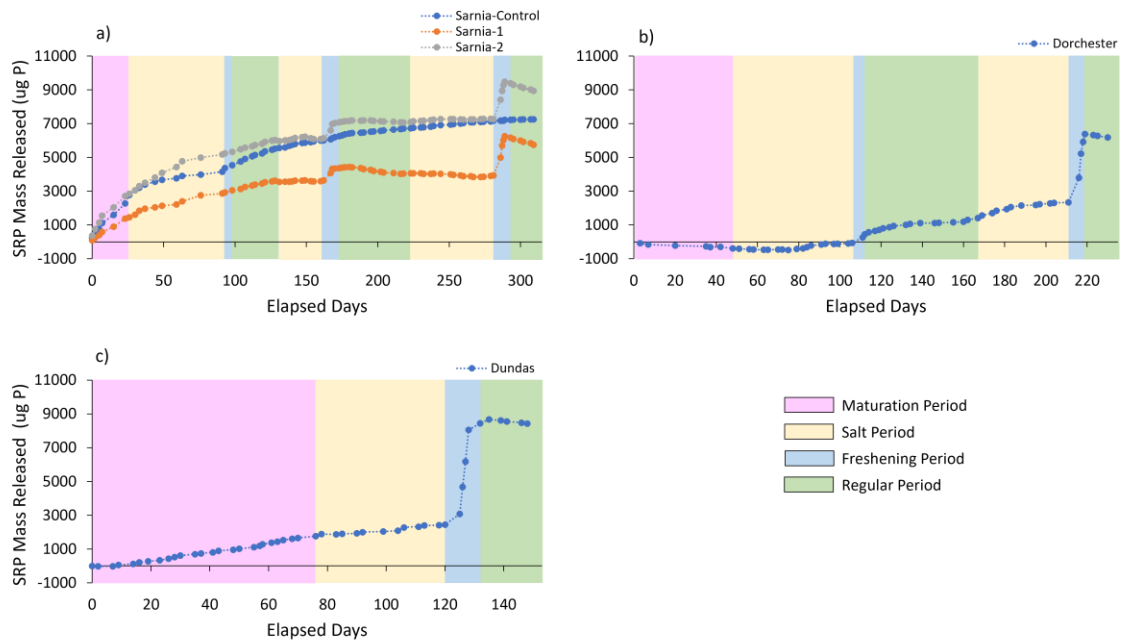


Figure G-1: Cumulative SRP mass released for a) Sarnia-Control, Sarnia-1, Sarnia-2, b) Dorchester, and c) Dundas. The pink, yellow, blue, and green shaded regions represent maturation, salt, freshening, and regular periods, respectively. Note that a negative release indicates SRP retention within the column.

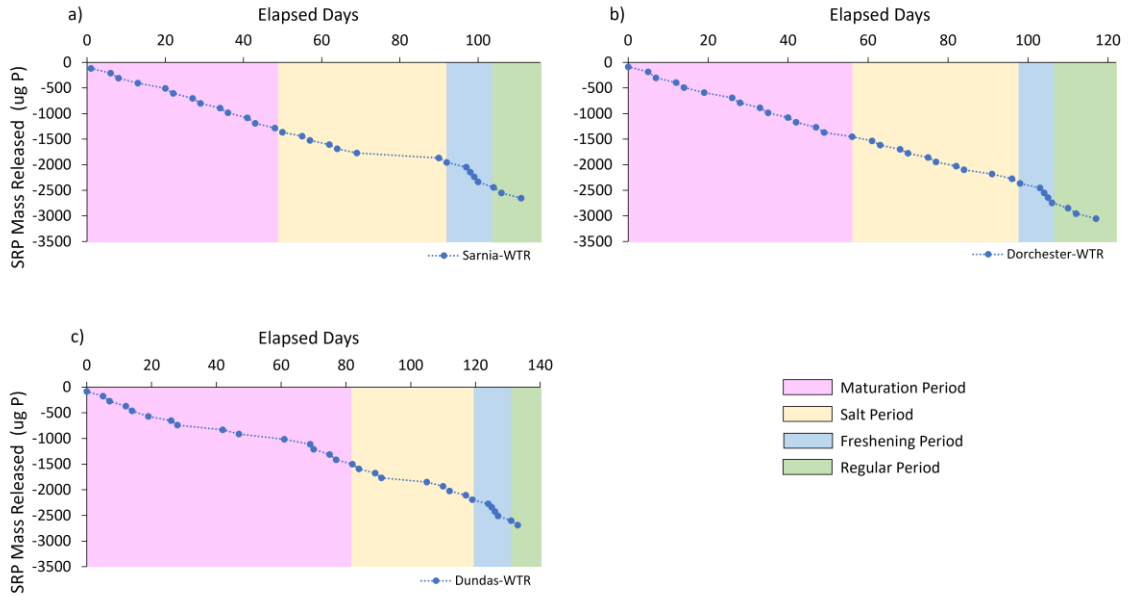


Figure G-2: Cumulative SRP mass released for a) Sarnia-WTR, b) Dorchester-WTR, and c) Dundas-WTR. The pink, yellow, green, and blue shaded regions represent maturation, salt, freshening, and regular periods, respectively. Note that a negative release indicates SRP retention within the column.

Appendix H: Calculations for salt mass input

Table H-1: Calculation of total chloride mass per total pore space flush in column experiments

Column experiment	Calculation	Assumptions
Volume of media in column (m ³):	5.11E-04	0.05m diameter, 0.26m height
Volume of pore space in column (m ³)	1.33E-04	0.26 porosity
Volume of pore space in column (L)	1.33E-01	
Infiltration rate (L/day)	1.44	
Pore volumes/day	10.85	
Salt Period Lengths		
Sarnia-1 and Sarnia-2: 1st salt event (days)	67	
Pore Volumes Flushed in 67 days	727	Use for maximum calculation
Sarnia-1 and Sarnia-2: 2nd salt event (days)	31	
Pore Volumes Flushed in 31 days	336	Use for minimum calculation
Sarnia-1 and Sarnia-2: 3rd salt event (days)	58	
Pore Volumes Flushed in 58 days	629	
Sarnia-WTR salt event (days)	43	
Pore Volumes Flushed in 43 days	467	
Water volume to flush pore space 727 times (L)	96	
Water volume to flush pore space 336 times (L)	45	
Influent NaCl concentration (mg/L)	1000	
Influent Cl concentration (mg/L)	606.6	
Total Cl mass in 727 pore space flushes (mg)	58,525	
Total Cl mass in 336 pore space flushes (mg)	27,079	
Cl mass per total pore space flush (mg)	81	
Cl mass per total pore space flush (mg)		

Table H-2: Calculation of total chloride mass per total pore space flush based on column-scale chloride loading

Field Calculations (Equivalent)		
Volume of media in Sarnia East cell (m3):	53	53m ² footprint, 1m depth
Volume of pore space in cell (m3):	13.78	0.26 porosity
Volume of 727 [total cell pore spaces] (m3):	10,016	
Volume of 336 [total cell pore spaces] (m3):	4,634	
Volume of 727 [total cell pore spaces] (L):	10,016,360	
Volume of 336 [total cell pore spaces] (L):	4,634,435	
Cl mass per 727 [total pore spaces] flush (mg)	8.06E+08	
Cl mass per 336 [total pore spaces] flush (mg)	3.73E+08	
Cl mass per 727 [total pore spaces] flush (kg)	806	
Cl mass per 336 [total pore spaces] flush (kg)	373	

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Honours and Awards: J.D. Hole Global Opportunities Travel Award
2016

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Related Work Experience Graduate Research Assistant
The University of Western Ontario
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