Persistence of Artificial Sweeteners, Phosphorus and Nitrogen in Three Septic System Plumes with Differing Redox Conditions

by

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Statement of Contributions

I completed most of the data collection and the analysis myself with the assistance of field staff. Reporting of the results was completed by myself.

William D. Robertson designed the work, contributed to the interpretation of results and provided revisions to this thesis.

Abstract

Septic systems are widely used for on-site wastewater treatment throughout Canada, including at most of Ontario’s provincial parks. They are frequently located in unconfined aquifer systems that may also be used for water supplies, thus the potential for contamination from constituents such as nitrate (NO_3^-), phosphate (PO_4^{2-}) and more recently, pharmaceutical compounds and personal care products is a concern. Degradation rates for these constituents vary in differing subsurface environments and remain poorly understood. In order to establish degradation potential, there is a need for tracer compounds that can clearly identify groundwater impacted by wastewater and, additionally, techniques must be available that allow age estimates for such impacted groundwater so that rates can be determined. Unfortunately, conventional groundwater age dating techniques such as use of tritium, tritium/helium or carbon 14, are ineffective for dating young groundwater less than several years old, which is the time frame of greatest interest with respect to degradation potential. In this study, a novel approach was undertaken for obtaining age estimates for 'young' septic system impacted groundwater. Sampling was undertaken at three septic system sites (campgrounds) where wastewater loading occurs only during the summer season, then monitoring was continued throughout the winter period as the plume water aged. Using this approach, plume samples were acquired that ranged in age from a few days to eight months, which is the critical timeframe needed for revealing degradation potential.

Artificial sweeteners such as potassium acesulfame (ACE) and sucralose (SUC) have been found to persist during wastewater treatment and in groundwater flow systems and have been proposed as powerful wastewater tracers because they are unique to this source. However,

additional insight into their degradation potential in groundwater environments is required to more fully exploit this potential.

The objective of the current investigation was to gain new insight into degradation rates of N, P and artificial sweeteners in septic system plumes. Three study sites, which are seasonal use campgrounds, were specifically selected to represent a range of redox conditions. Craigleith is the nitrate rich (NO_3^-) site; Six Mile Lake is the ammonium (NH_4^+) rich and high iron (Fe^{2+}) site; and Long Point is a NO_3^- depleting site. Extensive groundwater sampling took place at each of the three sites from multilevel piezometers, during both the on-loading and off-loading periods from 2015 to 2017. Groundwater ages were established based on loading rates, migration distances, seasonal breakthrough of electrical conductivity (EC) and time lags after termination of sewage loading in the fall.

Artificial Sweeteners

Acesulfame (ACE) and Sucralose (SUC) decay trends with increasing groundwater age were compared to modeled decay curves that would be expected for first order decay rates with half-lives of 4 and 12 months. Trends were further refined by correcting values for dilution based on chloride (Cl^-) concentrations. Rapid ACE and SUC decay were observed in the unsaturated zone, whereas ACE and SUC became much more persistent once they entered the groundwater flow system. Between the three sites, half lives (t1/2) in the unsaturated zone for ACE and SUC ranged from 0.15-2 months and 0.2-2 months, respectively. Half-lives in the groundwater zone for ACE and SUC ranged from 4-35 months and 2-35 months, respectively.

Nitrogen

The wastewater plume at the Craigleith site is well oxidized and nitrogen occurs almost completely as NO_3^--N. As groundwater aged in the distal zone during the non-loading period, isotopic enrichment of both $\delta^{18}O\text{-}NO_3^-$ and $\delta^{15}N\text{-}NO_3^-$ was observed. The ratio of enrichment (R^2=0.81-0.83) indicated that denitrification was likely occurring, but at a very slow rate (t1/2 = 70 months). In contrast, at the Six Mile Lake site where the wastewater is only partially oxidized due to the shallow water table, a greater amount of N attenuation occurred in the proximal tile bed zone (~ 80 %) and at a faster rate with half lives ranging from 3-8 months in the groundwater zone. It is likely that anammox contributes to the robust N attenuation observed at the Six Mile Lake site.

Phosphorus

Phosphorus, as soluble reactive phosphorus (SRP) was highly attenuated in the vadose zones and/or the groundwater zones at all three sites. Phosphorus depletion occurred at a rapid rate in the unsaturated zones, where half-lives were less than a few weeks at both the Craigleith and Six Mile Lake sites. Chemical equilibrium modelling and electron imaging of sand grains indicated mineral precipitation reactions, in the form of Fe-P minerals which likely contribute to P attenuation at Six Mile Lake. The decay rates in the vadose zone (<0.1-0.2 months) and groundwater zone (1-7 months) demonstrate that P attenuation occurs rapidly after the wastewater enters the subsurface, which is consistent with mineral precipitation.

Monitoring during the off-loading period provides insight into artificial sweetener, nitrogen and phosphorus loss in groundwater by observing concentration differences between initial concentrations in young wastewater during active loading and aging wastewater during inactive loading. This approach of monitoring seasonal use septic systems during the off season, has proved very useful in providing new insight into degradation potential for these critical wastewater parameters.

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Table of Contents

Abbreviations

ACE- Acesulfame

CR- Craigleith Site

CYC- Cyclamate

Cl^- - Chloride

DO- Dissolved Oxygen

DOC- Dissolved Organic Carbon

EC- Electrical Conductivity

LP- Long Point Site

N- Nitrogen

$\delta^{15}N\text{-}NO_3^-$ – Nitrate-15 Isotope from nitrate.

N_2- Nitrite

NO_3^-N- Nitrate

NH_4^+-N- Ammonium

$\delta^{15}O\text{-}NO_3^-$ – Oxygen-18 Isotope from nitrate.

P- Phosphorus

Redox- Reducing-Oxidizing Reaction

SAC- Saccharin

SUC- Sucralose

SM- Six Mile Lake Site

SRP- Soluble Reactive Phosphorus

TP- Total Phosphorus

List of Figures

List of Tables

Chapter 1:

Introduction to Septic System Components and Artificial Sweeteners

1.1 Introduction

Septic systems are widely used for on-site wastewater treatment throughout rural areas of Canada, including at many of Ontario's provincial parks. It is estimated that as of 2006, 15% of Canadian households had private systems such as wells and septic systems (Statistics Canada, 2015). Potential contaminants of concern include nitrate (NO_3^-), phosphorus (PO_4^{2-}), human pathogens (Wilhelm et al., 1994), and more recently a number of pharmaceutical compounds that have been found to persist in wastewater during treatment and in groundwater flow systems (Van Stempvoort et al., 2013). Septic systems are often located on unconfined aquifer systems that are also used for potable water supplies (Aravena et al, 1993), thus the potential for contamination of drinking water supplies is significant. Additionally, nutrient loading from septic systems has been implicated in the eutrophication of surface water bodies, particularly in relation to phosphorus loading to lakes (Stollenwerk et al., 1996; Nicholls et al., 1993) and nitrogen loading to marine coastal environments (Schindler et al., 2008; Kane et al., 2014). This perception of contaminant risk can play an important role in planning decisions related to options for wastewater treatment (i.e. on-site treatment vs. installation of communal sewers). Also, the perceived risk of contamination usually plays a pivotal role when existing septic systems are decommissioned in favour of communal sewers. Yet, septic systems usually provide wastewater treatment at lower capital cost and with lower energy consumption compared to communal sewers and can otherwise be the preferred option in some case. It is thus important to understand the true risk that septic systems represent to groundwater supplies. However, several factors combine to complicate the understanding of this risk. Two of the key contaminants, nitrogen and phosphorus, are highly reactive compounds that can undergo a variety of transformations in the subsurface that greatly affect their contaminant risk. For example, inorganic nitrogen (NH_4^+ and NO_3^-) has the potential to be converted to innocuous nitrogen gas (N_2) by processes such as denitrification (Aravana et al., 1993) and anammox (Robertson et al., 2012) and phosphorus can be immobilized by mineral precipitation reactions (Chen et al., 2015). Yet these reactions remain poorly understood in septic system plumes and there is often reluctance by regulators to acknowledge their potential. Part of the reason is that septic system plumes, from households for example, are relatively small scale and can be difficult to trace in groundwater flow systems unless very detailed monitoring networks are installed (Robertson et al., 1991). Also, wastewater plumes may be masked by contaminants from other sources, such as from agricultural operations, which can have similar chemical signatures (Robertson et al., 1991). Consequently, predicting the fate of these key contaminants in septic system plumes remains uncertain.

Campgrounds in Ontario are usually located in rural areas and consequently they are serviced by septic systems. Campground septic systems offer a special opportunity to gain insight into septic system plume behaviour. These systems generally provide wastewater treatment for dozens to hundreds of occupants, thus loading rates are high and wastewater composition remains relatively consistent because it is an average generated by several occupants. Consequently, the groundwater plumes that are generated are relatively large scale and easier to trace and any chemical changes that occur are more likely to be the result of degradation reactions, rather than from variations in wastewater composition. Secondly, most campgrounds in Ontario are seasonal use, with no sewage loading during the six-month period from November to May. Consequently, any chemical changes that occur over this period can be more confidently attributed to degradation reactions, rather than from influx of fresh wastewater. In this study, septic system plumes were monitored at three seasonal use provincial parks located in southern Ontario; Long Point, Craigleith and Six Mile Lake. Special emphasis was placed on plume behaviour during the inactive loading period to gain insight into natural attenuation processes for N and P and for a suite of four artificial sweeteners (ACE, SUC, SAC and CYC). These sweeteners are specific to domestic sewage and have recently been recognized as potentially powerful wastewater tracers because they persist during wastewater treatment and during subsurface flow (Van Stempvoort, et al., 2011). However, areas of intensive agricultural activities could be a potential source of artificial sweeteners. For instance, pig feed contains and SAC additive and therefore, pig manure can be a potentially source of SAC to the environment (Spoelstra et al., 2017). However, it is unlikely that manure/fertilizer was a source of artificial sweeteners in this study, because agricultural activity did occur at the provincial parks selected for the current investigation. Sweeteners have emerged as wastewater tracers in surface waters (Spoelstra et al., 2013; Oppenheimer et al., 2011), but only a few studies have examined its usefulness as a tracer in groundwater (Robertson et al., 2016). Sucralose (SUC) has been more recently suggested to be the dominant sweetener in groundwater and surface water indicating its usefulness as tracers of domestic wastewater (Robertson et al., 2016; Robertson et al., 2016; Snider et al., 2017; Spoelstra et al., 2013). However, ACE has also been exhibited persistent traits and has been suggested to be a powerful tracer for domestic wastewater assisting in identifying sources of nitrate contamination in groundwater (Robertson et al., 2016).

1.2 Objectives

The objective of this study was to observe the behaviour of N, P and the four artificial sweeteners, particularly during the six months non-loading period at these sites, to gain new insight into degradation rates, or lack thereof. Monitoring networks were previously available at Long Point (Robertson et al., 2013), while the second (Craigleith) and third site (Six Mile Lake) was instrumented as part of the current study. As a result of the high sewage loading rates at these sites, the plume zones of interest in the current study which are located below the infiltration beds and immediately down gradient are comprised of relatively undiluted wastewater during most times of the year (Verstraeten et al, 2005). This study was initiated under the assumption that plume redox conditions would strongly influence degradation processes and rates. Consequently, sites were specifically selected to represent a range of redox conditions (Craigleith, NO_3^- rich; Long Point, denitrifying; Six Mile Lake, NH_4^+rich, Fe reducing; Fig. 1.1). This is the first study we are aware of, that has taken this investigative approach for assessing contaminant degradation in septic system plumes. In particular, this study will provide new insight into the potential for degradation of the artificial sweeteners acesulfame and sucralose in a well oxidized groundwater plume (Craigleith site), which has not yet been well documented. Cyclamate (CYC) was not detected in most of the samples throughout the investigation and therefore was excluded from analysis. Additionally, concentrations of SAC are generally reduced in wastewater effluent and more susceptible to biodegradation (Buerge et al., 2009) and therefore was also excluded from the current investigation.

1.3 Septic System Operation

Septic systems are a means of disposing of domestic wastewater on-site, usually in a relatively passive manner, rather than having it discharged to a communal sewer network. Wastewater is first collected in a septic tank where anaerobic digestion of waste occurs (McCray et al., 2005). Effluent from the septic tank is then discharged to a subsurface infiltration bed through a set of distribution tiles/pipes. The effluent from the tile bed then percolates downward, through the vadose zone, where a series of biological and geochemical treatment reactions occurs prior to the effluent reaching the water table (McCray et al., 2005).

1.4 Redox Zonation in the Subsurface

Degradation of sewage contaminants in the subsurface is dependent on redox conditions within specific treatment zones (Wilhelm et al., 1994). Redox reactions involve the transfer of electrons, often by microorganisms that gain energy by catalyzing the oxidation of reduced compounds and can strongly influence the geochemistry of septic effluent and groundwater (Wilhelm et al., 1994). The first redox zone encountered is within the septic tank itself, where the wastewater is usually retained for a period of several days. Here anaerobic conditions occur, causing dissolution of organic matter, and mineralization of organic N to ammonium (NH_4^+) (Wilhelm et al., 1994). Septic tanks also serve as primary settling chambers, removing solids from the sewage. After exiting from the septic tank, the effluent then flows into the aerobic unsaturated sediments of the tile bed, where it encounters the second major redox zone. In the tile bed, microorganisms use O_2 as the electron acceptor in the oxidation of organic C to CO_2 and of NH_4^+ to NO_3^- (E.q. 1.1 and E.q. 1.2). Nitrate concentrations generated in this zone often exceed the drinking water limit, and these high concentrations can sometimes persist in septic system plumes for large distances (Wilhelm et al., 1994; Caschetto et al., 2018). A third redox zone that is encountered in some plumes is where denitrification occurs (Aravena et al., 1998). Denitrification requires anaerobic conditions and an electron donor. NO_3^- is used as an electron acceptor in the oxidation of organic C producing N_2, CO_2 and alkalinity (E.q. 1.3).

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \qquad \text{(E.q. 1.1)}$$

$$NH_4^+ + O_2 + H_2O \rightarrow NO_3^- + 6H^+ + 4e^- \qquad \text{(E.q.1.2)}$$

$$4NO_3^- + 5CH_2O + 4H^+ \rightarrow 2N_2 + 5CO_2 + 7H_2O \qquad \text{(E.q.1.3)}$$

1.5 Nutrient Contamination in Septic System Plume

Septic systems, even those from individual households, have the potential to produce large-scale contaminant plumes in sand and gravel aquifers, which can pose potential risks to the drinking water supplies (Robertson et al., 1991). Also, excess loading of nutrients such as P and NO_3^- have become a significant environmental problem leading to the eutrophication of surface waters, posing several health risks (Rivett et al., 2008). Phosphorus concentrations in septic tank effluent (typically 1-22 mg/L; McCray et al., 2005) are orders of magnitude higher than the minimum levels needed to stimulate algae growth (0.01-0.10 mg/L, McCray et al 2005). Furthermore, some studies have shown plume P values that approach the effluent values (Robertson, 2003). However, other studies have shown substantially lower plume values (~0.3 mg/L, Cape Cod plume, Parkhurst et al., 2003; 0.01 mg/L, Muskoka plume, Zurawsky et al., 2004) where natural attenuation reactions in the subsurface have resulted in P concentrations that meet or exceed the normal treatment level of 1 mg/L total phosphorus (TP) required for most sewage treatment plants in Ontario (MOE, 2016).

Elevated nitrate levels in shallow groundwater in southern Ontario are often attributed to agricultural activity (Rudolph et al., 1998). However septic tank effluent normally has NH_4^+-N concentrations in the range of 40-100 mg/L (McCray et al., 2005), which can potentially lead to NO_3^--N concentrations well above the drinking water limit of 10 mg/L in septic system plumes (Robertson et al, 1991). Furthermore, in rural agricultural areas serviced by septic systems, water supply wells are often present nearby. Consequently, when well water nitrate contamination is observed, there is often a suspicion that septic systems could be the cause, even at sites where N loading from agricultural operations greatly exceeds that from septic systems (Spoelstra et al., 2017). Thus, there is a need for tracers that can definitively distinguish contamination from septic systems.

1.6 Artificial Sweeteners

History of Artificial Sweeteners

Artificial sweeteners are used worldwide as a sugar substitute in several food, beverage, drugs and sanitary products (Lange et al., 2012). Acesulfame (ACE) was approved for consumption in Canada in 1988 (Robertson et al., 2013). SUC is the newest of the commonly used artificial sweetener, as it was approved for consumption in Canada in 1992 (PepsiCo Canada, 2010), SUC use has likely rapidly increased since 2005 (Robertson et al, 2013). It is estimated that SUC concentrations in wastewater will increase within the next 20 years up to a factor of 8 compared with the concentration in 2009 (Lange et al., 2012). Neither SUC or ACE is metabolized by the body and pass through unchanged after consumption. Another sweetener, saccharin (SAC) is less commonly used in Canada because previous studies raised concerns about potential carcinogenic effects, and it was de-listed as a food additive in Canada (Government of Canada, 2018).

However, since 2006, SAC was re-allowed as a food additive, due to more recent studies that reveal non-toxicological effects to humans (Government of Canada, 2018). Similarly, cyclamate (CYC) has been banned as a food additive in Canada since 1960, due to potential carcinogenic effects (CFIA, 2018) and is only permitted as a non-food product under specific conditions (Government of Canada, 2018). Additionally, it has been shown that CYC and SAC are usually degraded by more than 90% during wastewater treatment (Lange et al., 2012). Aspartame is one of the most commonly used artificial sweetener used in Canada and is broken down following consumption into phenylalanine, aspartic acid, and methanol (Prodolliet et al., 1993). Therefore, aspartame is less suitable as a trace for domestic wastewater.

Artificial Sweeteners in Surface waters and Groundwater

Tracing the fate of wastewater in urban settings is challenging given the spatial variability in exchange of water and contaminants between surface waters, groundwater and urban infrastructure. Wastewater constituents such as nutrients and chloride have been used as tracers, however both have other natural and anthropogenic sources, such as landfills, road salt, or fertilizers, which can limit their usefulness (Van Stempvoort et al, 2013). Although CYC and SAC degrade during wastewater treatment, SUC and ACE are more persistent and have the ideal characteristics of a wastewater indicator such as: source specificity, sustained effluent release due to limited ability for degradation, sensitive analytical methodology, minimal attenuation during transport and little to no background concentrations (Oppenheimer et al, 2011; Van Stempvoort et al, 2013).

The range of concentrations of artificial sweeteners in untreated and treated municipal wastewater treatment plants (WWTP) have been well documented. ACE has been detected up to

57 µg/L in Singapore to as low as 0.06 µg/L in Vietnam in WWTP influent (Snider et al., 2017). In addition, SUC levels have been detected up to 27 µg/L in Canada (Robertson et al., 2016) and to as low as 0.08 µg/L in Singapore WWTP (Snider et al., 2017). Only recently have these sweeteners been considered as wastewater tracers in groundwater (Buerge et al., 2009; Van Stempvoort et al., 2011; Robertson et al., 2013)

ACE has been demonstrated to be persistent in the environment. In Switzerland, ACE was consistently detected in untreated and treated wastewater at concentrations ranging from 12-46 µg/L in most surface waters, and in 65% of groundwater samples (Buerge et al., 2009). In Canada, ACE was detected in >50% of the samples from groundwater from near the Long Point Provincial Park septic system (Van Stempvoort et al., 2011a). ACE occurred throughout the plume core in the Long Point septic plume over a distance of 200 m, at concentrations > 8 µg/L and showed little degradation compared to the septic tank values (Robertson et al., 2013). However, ACE degradation has been previously reported during some treatment processes such as photolysis by UV light and ozonation. Falas et al (2016) observed significant removal of ACE (80%; Table 6.3) in aerobic batch reactors, where the removal of ACE was attributed to biological degradation. Additionally, considerable removal of ACE (70 %) was reported during full-scale treatment in a sand filter, receiving water from the River Ruhr, Germany (Castronovo et al., 2017), and Kattel et al. (2017) exhibited successful ACE degradation by H_2O_2/Fe^{2+} and $S_2O_82^{-}/Fe^{2+}$ in wastewater effluent and groundwater at a pH of 3.

Sucralose has also been widely detected in surface waters receiving wastewater inflows due to its persistence during wastewater treatment. For example, concentrations up to 1 µg/L were detected in 120 river samples from 23 European countries (Lange et al., 2012). A large quantity of sucralose was also in the Grand River, located in southern Ontario, Canada, where up to 21 µg/L was detected (Spoelstra et al., 2013). Additionally, SUC was consistently detected in wastewater effluent in the U.S (Florida, Texas, norther/southern California, Illinois, and Michigan), where the average concentration of sucralose detected was 27 µg/L (Oppenheimer et al., 2011). Thus, the persistence of SUC in U.S wastewater effluents showcased its suitability as a tracer of domestic wastewater. SUC has also demonstrated be persistent in groundwater systems. Elevated SUC concentrations were detected at the Long Point site, where concentrations ranged from 15-77 µg/L in the plume zone below the tile bed. However, much lower concentrations were present farther downgradient in the plume, indicating that SUC degradation or sorption reactions were active (Robertson et al., 2013). Laboratory studies have also reported degradation of SUC. For example, batch tests conducted using organic carbon-rich soil and lake bottom sediments, determined that about 50% SUC removal occurred after 30-100 days (LaBare and Alexander, 1993). However, <4% SUC removal occurred when lake water samples with lower organic carbon levels were used in similar batch tests (LaBare and Alexander, 1993).

To date, no environmental toxicological affects of artificial sweeteners have been established**.** However, other anthropogenic sources such as pharmaceuticals have also been established as tracers of domestic wastewater but have known adverse environmental affects. For instance, synthetic estrogen affects the reproductive health of wild fishes (Kidd et al., 2007). Therefore, establishing potential loss of artificial sweeteners can aid in the establishing methods of pharmaceutical breakdown in the environment. Additionally, artificial sweeteners are a more suitable conservative tracer because given the selective use of pharmaceuticals, their presence can be sporadic in wastewater. Furthermore, some of the other anthropogenic chemicals suggested as conservative tracers (i.e caffeine and cotinine) are subject to moderate to strong biological attenuiation in the environment (Sieler et al., 1999). Several pharmaceuticals and chemicals are known to sorb to solid materials. Williams et al. (2006) found significant sorption of carbamazepine to soil.

Figure 1.1: Study site locations- Provincial park septic systems.

Chapter 2:

Methods

2.1 Groundwater Sampling

Extensive groundwater sampling took place during both the on-loading and off-loading periods at the Craigleith, Six Mile Lake and Long Point sites, focusing on the proximal plume zones underlying the tile beds and also at more distal monitoring points located up to 10 m downgradient, at the Craigeith site. Sampling occurred monthly from July 2015 to August 2017 at Craigleith (NO_3-N rich) site, from October 2015 to October 2016 at Six Mile Lake (NH_4-N rich) site, and from November 2015 to December 2016 at Long Point (NO_3-N depleting) site.

Groundwater samples were obtained from multilevel bundle piezometers, consisting of from two to six sampling tubes each. Septic tank samples were obtained from dedicated polyethylene sampling tubes installed near the outlet of the tanks. Groundwater samples were collected using a peristaltic pump with silicone tubing connected to a flow through cell. Samples were obtained with a 60 cc plastic syringe, and were collected in separate polyethylene containers for sweeteners, anions, cations, NO_3^--N , NH_4^+-N, TP, and SRP. Samples were filtered with a 0.45 μm Whatman® syringe filters, excluding the TP samples which were unfiltered. SRP samples were acidified to a pH <2 with 10% HCl acid in the field. Upon returning to the lab, cation samples were acidified with OmniTrace Ultra® Nitric Acid (67-70%) to a pH <2. All other samples were left untreated. Samples were kept cold after collection and immediately transported to the laboratory where they were frozen until analysis. In addition, filtered untreated samples were collected for one sampling event at Six Mile Lake for DOC in 20 ml glass containers. Field portable meters were used to measure temperature, DO (Hach Model HQ40d), pH (Oakton ® 6+ handheld pH Meter), and EC (Oakton Cond 6+). Field analysis of dissolved Fe was determined colorimetrically using CHEMets® Visual Kits. Alkalinity was measured in the field for one sampling event at the Six Mile Lake site, using a Hach® Alkalinity test kit using a digital titrator with sulphuric acid.

2.2 Laboratory Analysis

Samples for anions (NO_3^--N, SO_4^{2-} and Cl^-), NO_2^-, NH_4^+-N, SRP and TP were analyzed at the Environmental Geochemistry Laboratory, Department of Earth and Environmental Sciences, University of Waterloo, using standard methods (APHA, 1999). SRP and TP were analyzed colourmetrically using the molybdenum blue technique with a spectrophotometer (Cary100 UV-Vis, Agilent Technologies) with an absorbance of 885 nm, which provided a detection limit of $<$ 0.05 mg/L (Murphy and Riley, 1962; APHA, 1999). For TP analyses, samples were first digested with H_2SO_4 and $(NH_4)_2S_2O_8$. DOC was measured using a Total Carbon analyzer (Model TOC-L CHP, Shimadzu Corp.), which provided a precision of ±0.3 mg/L. P samples were often diluted prior to analysis to achieve an optimum detection range of 10-150 μg/L. Anions were analyzed with ion chromatography (Model ICS-2100, Dionex Ltd.). NH_4^+ and NO_2^- were measured colourimetrically using SmartChem 200 WestCo Scientific wet chemistry analyzer (Unity Scientific).

To assess the possibility of denitrification activity at the Craigleith site, a subset of the samples (events14-30) were analyzed for the stable isotopes of NO_3^- (δ^{15}N-NO_3^- and δ^{18}O-NO_3^-). Samples were analyzed in the Environmental Isotope Laboratory (UWEIL) at the University of Waterloo using the chemical denitrification method (McIlvin and Alltabet, 2005). Samples were kept frozen prior to analysis, except for samples from sampling events 14-23, which were placed in the fridge at 4°C. Analysis of δ^{15}N-NO_3^- and δ^{18}O-NO_3^- were conducted with an Isoprime vision IRMS, trace gas, continuous flow, stable isotope ratio mass spectrometer (Thermo Finnigan/Bermen-Germany), which provided a precision of ±0.3‰. Results were reported in standard notation as indicated in E.q. 2.1, Where R is ^{15}N:^{14}N.

$$\delta^{15}N = \left(\left(\frac{R_{sample}}{R_{standard}}\right) - 1\right) x\ 10^{3}\ ‰ \qquad \text{(E.q. 2.1)}$$

Cations (Al^{3+}, Na^{+}, Fe^{2+}, Mg^{2+}, Ca^{2+},and K^{+}) were analyzed with a Perkin Elmer Optima 8000 ICP-EOS at the Centre of Cold Regions and Water Science at Wilfrid Laurier University which provided a precision of ±0.1 mg/L.

Artificial sweeteners were analyzed at the Canada Centre for Inland Waters (CCIW). Burlington, ON, by ion chromatography coupled with a tandem mass spectrometer with an electrospray ionization source in negative mode (Snider et al, 2017). The detection limits for ACE, SUC, CYC and SAC were 2, 20, 3 and 2 ng/L, respectively.

Chapter 3:

Craigleith (NO_3^- Rich) Site; Plume Characterization and Groundwater Age

3.1 Site Description

Craigleith (CR) is an overnight campground consisting of 151 campsites located near Collingwood, ON, and is open from April-November. The septic system has been in operation since 2001 and consists of a septic tank from which the wastewater is pumped to a raised tile-bed that is 1200 m^2, constructed of imported medium-coarse calcareous filter sand (Robertson et al., 2016). The filter bed is 2 m in thickness overlying fractured limestone bedrock and a thin (~0.5 m thick) sand aquifer (Robertson et al., 2016). The water table occurs at 1.5-2 m depth below the tile bed (Fig 3.1). The groundwater monitoring network consists of a previously installed network of multi-depth bundled piezometers constructed of polyethylene tubing with short (5cm long) slotted, and screened tips. It consists of 63 monitoring points in 21 multilevel piezometers (Fig 3.1a) screened below the tile-bed and up to 45 m beyond the edge of the tile bed within the sand aquifer (Robertson et al., 2016). Average wastewater loading during the summer is estimated at 17m^3/day (tile bed loading of 0.5 cm/day) based on an assumed per campsite water usage rate of 220 L/day (U.S.EPA, 2002) and a vacancy rate of 50%. The aquifer provides considerable buffering capacity (sediment Ca content 7 wt. %) such that neutral pH conditions (6.9-7.9) occur in the plume, and the wastewater is well oxidized due to the presence of a relatively thick vadose below the tile bed (Robertson et al., 2016). Sewage loading is initiated in mid- April at this site and subsides at the end of October. In the current study, sampling occurred during both the active and inactive loading periods and was specifically focused on four monitoring points as follows: the septic tank, bundle point CR1-1.9m, located in the shallow water zone below the tile bed, and two bundle points located 10 meters downgradient from the edge of the tile bed (CR12-0.7 m and CR12-1.0 m, Fig. 3.1b).

3.2 Plume Characterization

Chloride was used as the conservative tracer at the Craigleith site and concentrations in the plume monitoring points (generally 50-100 mg/L) were similar to the septic tank values during active loading and through much of the non-loading period (Table 3.1, Fig. 3.2). However, some sampling events in the late winter showed lower Cl^- values (<20 mg/L) reflecting dilution from precipitation recharge occurring during the non-loading period. Also, in the spring, some Cl^- concentrations spiked substantially higher than the septic tank values (Fig 3.2c) and it is speculated that may represent air borne fallout of Cl^- from de-icing salt applied to a highway located only 5 meters north of the tile bed. Samples that exhibited excessive dilution or possible road salt impact were generally excluded from further analysis.

Of the three septic system sites assessed in this study, the Craigleith site exhibits the highest degree of wastewater oxidation, as reflected by the nitrogen composition in the plume. Nitrogen occurs almost exclusively as NO_3^--N (9-141 mg/L, Table 3.1, Fig. 3.2) whereas NH_4^+-N values remain low (< 1mg/L, Table 3.1). The high degree of oxidation is the result of the substantial thickness of the vadose zone below the tile bed (~ 2 m, Fig. 3.1), coupled with a relatively modest wastewater loading rate of 0.5 cm/day. During the active loading period, plume NO_3^--N values tend to approach the septic tank NH_4^+-N values (64-149 mg/L, Table 3.1). However, NO_3^--N concentrations tend to decrease during the in-active loading period (Table 3.1, Fig 3.2d), which raises the possibility that nitrate attenuation reactions could be occurring.

Dissolved oxygen (DO) values in the plume zone at CR12-1.0, were generally < 1 mg/L (Table 3.1) which is sufficiently low to allow denitrification to become active. To further assess the possibility of denitrification, nitrate isotopic characterization was undertaken, the results of which are discussed in a later chapter (Chapter 7).

Figure 3.2 a-b shows ACE and SUC concentrations during both the on-loading and off-loading periods. Plume concentrations for ACE range from 1.4-37 µg/L and SUC from 3-38 µg/L, (Table 3.1, Fig. 3.2a and b). However, these values fall well below the septic tank values, which range from 37-163 µg/L for ACE and 31-126 µg/L for SUC (Table 3.1, Figs. 3.2a and b). ACE and SUC concentrations below the septic tank values suggest the possibility of sweetener degradation as the wastewater travels across the tile bed (Fig 3.2a and b; Fig 3.3 i and ii), which is further assessed in a later chapter (Chapter 6).

3.3 Groundwater Age in the Plume

Wastewater is estimated to migrate through the tile bed vadose zone at a vertical velocity of 0.5 cm/day, assuming water content in the vadose zone of 10 % (table 3.2)., velocity in the vadose zone was estimated with the values provided in table 3.2. and E.q 3.1. Groundwater age at CR1-1.9 was estimated from E.q. 3.2 with a travel distance (L) of 1.3 m (1.9-0.6). Thus, groundwater age was estimated to be 26 days old during active loading (Table 3.2). CR12 is located 10 m west of the tile bed, where flow is primarily horizontal. Seasonal breakthrough of EC was used to determine groundwater age in a manner similar to that described by Robertson et al (2012). Figure 3.4 shows EC trends at CR12 from October 2015 to October 2017. Elevated EC values are observed from May-June at depths of 0.7 m and 1m below the subsurface (Table 3.3), indicating that new wastewater from the initiation of wastewater loading has occupied the well.

3.4 Site Summary

- Highly oxidized wastewater.
- Cl^- used as the conservative tracer.
- Denitrification likely occurs during the non-loading period.
- Occasional Cl^- spikes from road salt impact require that Cl^- data be used with caution.
- Elevated ACE and SUC concentrations are present throughout the plume, but concentrations are substantially lower than the septic tank values .

$$v = \frac{q}{\theta} \qquad \text{(E.q 3.1)}$$

Where,

v (m/s) = linear vertical groundwater velocity

Q= Loading rate (m/s)

Ɵ = Water Content

$$t = \frac{L}{v} \qquad \text{(E.q 3.2)}$$

Where,

V= linear vertical groundwater velocity

L= distances below the tile line depth of 0.6 m

t= Groundwater Age

Table 3.1. Craigleith (NO_3^- rich) Site; Groundwater age, EC and concentrations of DO, Cl^-, SO_4^{2-}, Na+, NO_3-N, NH4-N, TIN, $\delta^{15}N$-NO_3^-, $\delta^{18}O$-NO_3^- SRP, ACE, SUC and rations of NO3-N/Cl, SRP/Cl, SUC/ACE, ACE/Cl and SUC/Cl in the septic tank, CR1-1.9, CR12-0.7 and CR12-1.0 during the active and inactive loading period from October 2015 to October 2017. Additional monitoring data from other monitoring points is presented in Appendix A.

Date	GW Age (mo.)	EC (µs/cm)	DO (mg/L)	Cl^- (mg/L)	$SO4^{2-}$ (mg/L)	Na (mg/L)	NO3-N (mg/L)	NH4-N (mg/L)	TIN (mg/L)	N-15 (‰)	O-18 (‰)	SRP (mg/L)	ACE (µg/L)	SUC (µg/L)	NO3-N/Cl	SRP/Cl	SUC/ACE	ACE/Cl	SUC/Cl
CR-TANK																			
27-May-16		1396		65	11		0.29	64	64			3.7	68	58	0.99	0.06	0.85	1.0	0.89
06-Jun-16		1940		99	13		0.42	131	132			10	163	117	1.3	0.10	0.71	1.6	1.2
24-Jun-16		1114		57	17		0.63	67	68			15	65	59	1.2	0.26	0.91	1.1	1.0
21-Jul-16		1577										7.8							
04-Oct-16		1447		77	6		0.2					18				0.23			
21-Oct-16		1838		78	9.3		0.22					11	66	82		0.14	1.2	0.84	1.0
04-Jun-17		1785		42	8.3		0.0	60	60			10	45	47	1.4	0.25	1.0	1.1	1.1
13-Jun-17		1484		91	13		0.0	128	128			17	99	77	1.4	0.19	0.78	1.1	0.85
20-Jun-17		1450		113	9.6		0.0	149	149			17	132	126	1.3	0.15	0.95	1.2	1.1
28-Jun-17		1302						332	332				53	68			1.3		
14-Jul-17		1727		201	25		4.0						120	99			0.83	0.60	0.49
28-Jul-17		1078		64	12		4.9	96	101			13	56	48	1.6	0.20	0.85	0.87	0.74
10-Aug-17		1103		81	8.7		0.48	118	119			18	45	47	1.5	0.22	1.1	0.55	0.58
30-Aug-17		1242		50	5.0		3.3	92	95			25	37	31	1.9	0.50	0.82	0.74	0.61
CR1-1.9																			
26-Oct-15	0.9	920	4	33	28		51					4.0	12	9.3	1.5	0.12	0.80	0.35	0.28
21-Jul-16	0.9	1248										2.9							
04-Jun-17	0.9	1176		39	13		8.5	0.07	8.6			3.5	5.7	5.6	0.22	0.09	0.99	0.14	0.14
13-Jun-17	0.9	790		68	22		29	0.27	30			5.4	18	13	0.43	0.08	0.71	0.26	0.18
20-Jun-17	0.9	914		77	31		59	0.59	59			4.6	37	22	0.77	0.06	0.58	0.49	0.29
28-Jun-17	0.9	1000		36	16		20	0.22	20				24	14	0.54		0.58	0.66	0.38
14-Jul-17	0.9	650		30	7.5		5.7	5	11				3.1	3.0	0.19		0.97	0.11	0.10
28-Jul-17	0.9	894		82	41		76	0.24	76			5	13	27	0.92	0.06	2.1	0.16	0.33
10-Aug-17	0.9	944		48	23		60	0.70	60			7	19	35	1.3	0.14	1.86	0.40	0.74
30-Aug-17	0.9	949		84	56		91	13	104			2	2.5	28	1.1	0.03	11	0.03	0.33
CR12-0.7																			
26-Oct-15	1.1	1078	0.5	37	36		45					4.9	15	13	1.2	0.13	0.88	0.39	0.35

Date	GW Age (mo.)	EC (µs/cm)	DO (mg/L)	Cl$^-$ (mg/L)	SO4^{2-} (mg/L)	Na (mg/L)	NO3-N (mg/L)	NH4-N (mg/L)	TIN (mg/L)	N-15 (‰)	O-18 (‰)	SRP (mg/L)	ACE (µg/L)	SUC (µg/L)	NO3-N/Cl	SRP/Cl	SUC/ACE	ACE/Cl	SUC/Cl
9-Dec-15	2.7	1145	0.5																
4-Jan-16	3.8	1041										2.7							
25-Jan-16	4.5	730	5	20	25		14					1.6	7.8	5.8	0.69	0.08	0.74	0.39	0.29
28-Feb-16	5.6	860	4	17	60	9	12					1.5	11	7.4	0.71	0.09	0.71	0.62	0.44
18-Apr-16	7.0	837		55	21		14					0.86	3.5	4.1	0.25	0.02	1.2	0.06	0.07
27-May-16	8.2	739			127														
6-Jun-16	8.5	660																	
24-Jun-16	2.3	693																	
21-Jul-16	2.3	1197		69	39		82					2.0			1.2	0.03			
21-Oct-16	2.6	1561		66	47	40	70					2.4	13	38	1.1	0.04	2.9	0.20	0.58
22-Feb-17	6.7	578	4	14	15		11	0.01	11	16	1.8	1.5	5.4	6.9	0.78	0.11	1.3	0.40	0.51
28-Feb-17	6.9	505		9	13		7.1	0.03	7.1	17	2.4	3.0	4.0	5.5	0.77	0.33	1.4	0.44	0.60
18-Mar-17	7.5	755		17	29		16	0.00	16	15	1.9	1.3	6.3	8.4	0.92	0.07	1.3	0.37	0.49
09-Apr-17	8.2	607		15	18		11	0.01	11	16	2.1	2.1	5.0	6.0	0.75	0.14	1.2	0.34	0.41
15-Apr-17	8.4	785		20	34		23	0.00	23	14	1.4		3.2	5.2	1.1		1.6	0.16	0.26
06-May-17	9.0	498		17	10		6.3	0.01	6.3	8.5	-2.7	1.7	1.6	3.3	0.37	0.1	2.1	0.09	0.19
18-May-17	1.1	701		115	26		21	0.02	21	8.1	-2.2	2.1	3.2	3.1	0.18	0.02	0.97	0.03	0.03
04-Jun-17	1.1	1218		126	24		18	0.02	18	9.0	-1.9	2.4	6.0	6.7	0.14	0.02	1.1	0.05	0.05
13-Jun-17	1.1	790		60	22		8.8	0.21	9.0	11	-1.1	3.3	4.5	4.7	0.15	0.06	1.1	0.07	0.08
20-Jun-17	1.1	760		66	140														
28-Jun-17	1.1	650	4	45	58		17	0.90	18				4.4	5.4	0.38		1.2	0.10	0.12
14-Jul-17	1.1	900		137	65		115	0.54	115	10	-2.5		4.3	5.7	0.84		1.3	0.03	0.04
28-Jul-17	1.1	860		39	29		34	0.27	34	13	-1.4	4	10	21	0.86	0.11	2.1	0.26	0.54
10-Aug-17	1.1	846		89	44		87	0.20	87	12	-1.9	6	8.3	29	0.98	0.06	3.5	0.09	0.33
30-Aug-17	1.1	910	4	107	58		116	3.6	120	12	-3.0	3	1.4	25	1.1	0.03	18	0.01	0.23
CR12-1.0																			
26-Oct-15	1.1	1077		35	59		36					3.7	18	16	1.0	0.11	0.9	0.51	0.45
9-Dec-15	2.7	1173	0.7	44	72		38								0.86				
4-Jan-16	3.8	1182		34	40	24	36					1.9	31	16	1.1	0.05	0.5	0.92	0.47
25-Jan-16	4.5	1190		42	121	24	30					1.1	26	15	0.71	0.03	0.6	0.61	0.35
28-Feb-16	5.6	1118		26	30	9	25					1.0	12	8.8	0.96	0.04	0.7	0.47	0.34
18-Apr-16	7.0	897		89		25	24					0.86	7.7	9.3	0.27	0.01	1.2	0.09	0.10
27-May-16	8.2	769		127	86	7	25					3.7	7.6	8.1	0.20	0.03	1.1	0.06	0.06

Date	**GW Age (mo.)**	**EC (µs/cm)**	**DO (mg/L)**	**Cl^- (mg/L)**	**$SO4^{2-}$ (mg/L)**	**Na (mg/L)**	**NO3-N (mg/L)**	**NH4-N (mg/L)**	**TIN (mg/L)**	**N-15 (‰)**	**O-18 (‰)**	**SRP (mg/L)**	**ACE (µg/L)**	**SUC (µg/L)**	**NO3-N/Cl**	**SRP/Cl**	**SUC/ACE**	**ACE/ Cl**	**SUC /Cl**
j6-Jun-16	8.5	788																	
24-Jun-16	2.3	912																	
21-Jul-16	2.3	1127		67	57		68					2.4			1.0	0.04			
21-Oct-16	2.6	1494		60	62	38	69					2.5	15	34	1.2	0.04	2.3	0.24	0.56
22-Feb-17	6.7	1123	1.5	38	88		31	0.02	31	21	4.8	1.5	17	21	0.79	0.04	1.2	0.45	0.55
28-Feb-17	6.9	1100		40	99		30	0.01	30	21	5.5	1.4	18	21	0.75	0.03	1.2	0.45	0.53
18-Mar-17	7.5	1168		30	126		20	0.02	20	23	6.3	1.1	8.7	11	0.66	0.04	1.3	0.29	0.36
09-Apr-17	8.2	939		29	75		23	0.00	23	20	4.0	0.55	15	17	0.79	0.02	1.1	0.52	0.59
15-Apr-17	8.4	1126		31	85		31	0.03	31	17	2.1	1.0	10	16	1.00	0.03	1.6	0.32	0.50
06-May-17	9.0	694		41	100		16	0.01	16	18	2.8	0.9	7.6	11	0.39	0.02	1.4	0.19	0.26
18-May-17	0.9	757		140	47		21	0.03	21	11	-1.1	1.1	6.8	8.5	0.15	0.01	1.3	0.05	0.06
04-Jun-17	0.9	672		81	49		14	0.10	14			1.8	5.5	7.8	0.17	0.02	1.4	0.07	0.10
13-Jun-17	0.9	792		85	57		18	0.34	18	13	0.1	1.4	7.3	10	0.21	0.02	1.4	0.09	0.12
20-Jun-17	1.1	779		66	83		20	0.09	20	19	4.1	1.5	7.1	9.6	0.30	0.02	1.4	0.11	0.15
28-Jun-17	1.1	888		67	8.0		0.35	0.34	0.69				8.9	7.4	0.01		0.8	0.13	0.11
14-Jul-17	1.1	888		125	59		91	0.87	92	9.2	-1.6		14	20	0.73		1.4	0.11	0.16
28-Jul-17	1.1	876		24	21		19	n.d		13	-1.0	3	9.4	20	0.80	0.12	2.1	0.39	0.84
10-Aug-17	1.1	844		106	60		97	2	99	12	1.9	3	9.2	21	0.91	0.03	2.3	0.09	0.20
30-Aug-17	1.1	912		134	82		141	1.2	143	13	-2.5	2	5.1	33	1.1	0.02	6.5	0.04	0.25

Table 3.2. Craigleith site (NO_3^- Rich); Active loading groundwater ages at CR1. Values of water content (ϴ) (assumed) and vertical velocity (V) calculated for the active loading period at CR1, using assumed sewage loading of 0.5 cm/d. Distance (L) is distance below the tile line depth of 0.6 m and flow is assumed to be dominantly vertical.

Well	ϴ	V (m/d)	L (m)	GW Age (days)
CR1-1.9	0.10	0.05	1.3	26

Table 3.3. Craigleith site (NO_3^- Rich); Seasonal breakthrough of increased electrical conductivity (EC) at CR12 observed on July 21, 2016 and 4 June, 2017. Groundwater ages were determined by the number of active loading days before EC breakthrough was observed. The park opened April 15, 2016 and April 14, 2017.

Well	Date	EC (µs/cm)	GW Age (days)
CR12-0.7	24-Jun-16	693	69
	18-May-17	701	33
CR12-1.0	24-Jun-16	912	69
	18-May-17	757	33

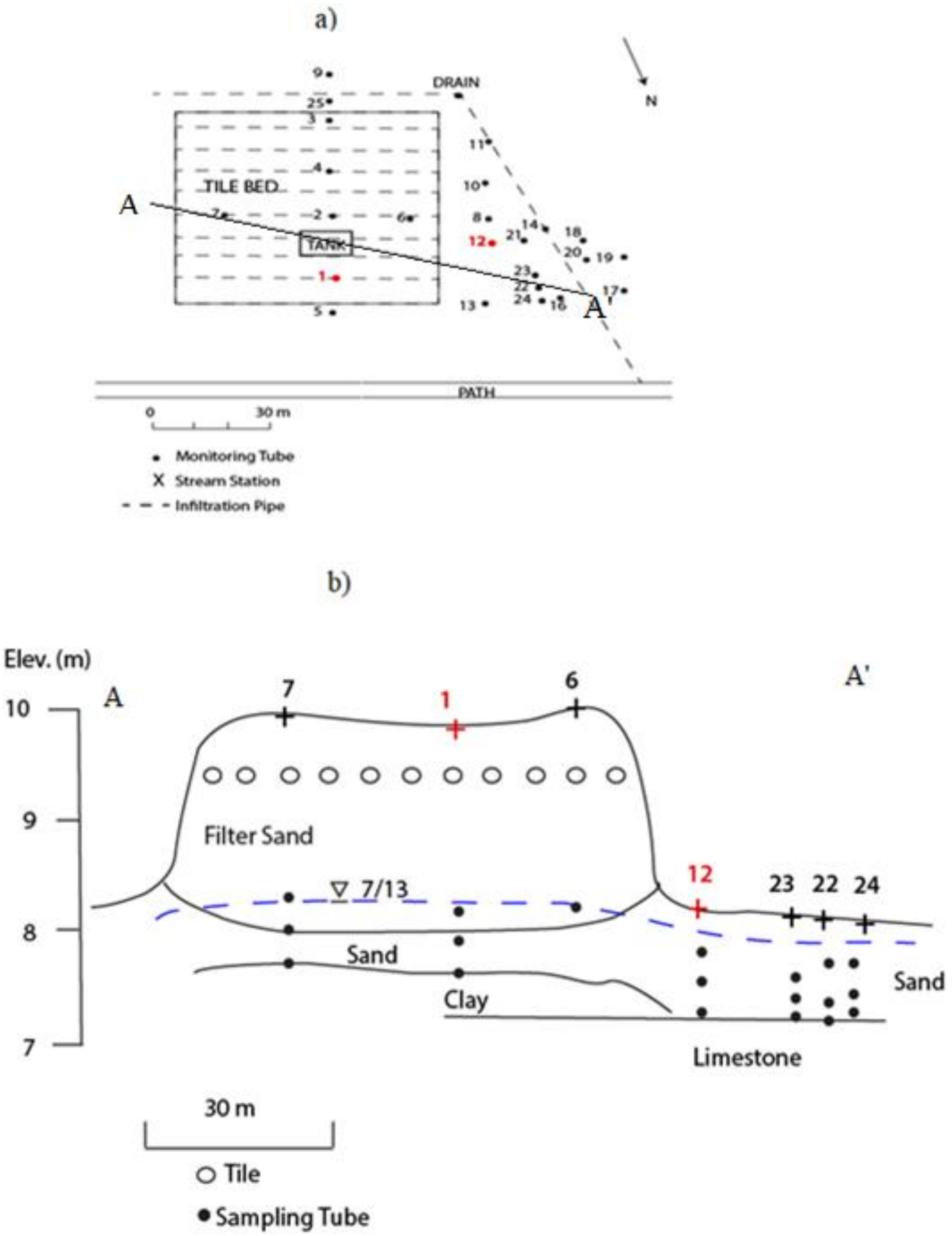

Figure 3.1 Craigleith (NO_3^- Rich) Site; (a) Plan view of the tile bed showing the tile bed and the locations of the monitoring wells. Principal wells sampled in this study are highlighted in red. (b) Cross-sectional area (A-A') of the tile bed showing the various depths each well sampled highlighted in red, water table approximation obtained in 2013.

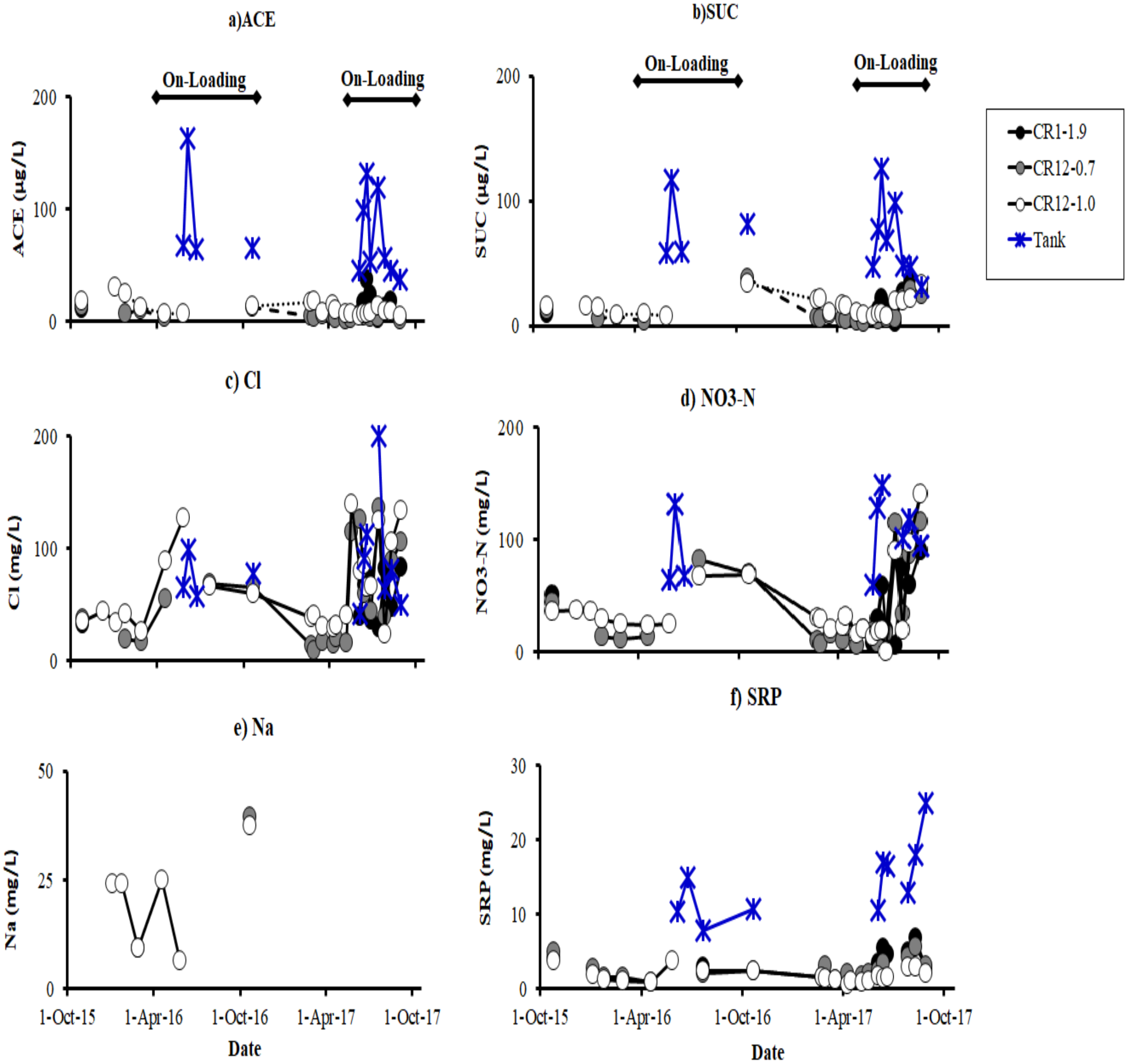

Figure 3.2. Craigleith (NO_3^- Rich) site; Trends of a) ACE, b) SUC, c) Cl^-, d) NO_3^--N, e) Na^+ and f) SRP during the on-loading and off-loading loading period from wells CR1-1.9 from beneath the tile bed and from the edge of the tile bed at well CR12-0.7, CR12-1.0 and the septic tank. Samples are from October 2015 to October 2017. Note; tank N values are primarily NH_4^+-N.

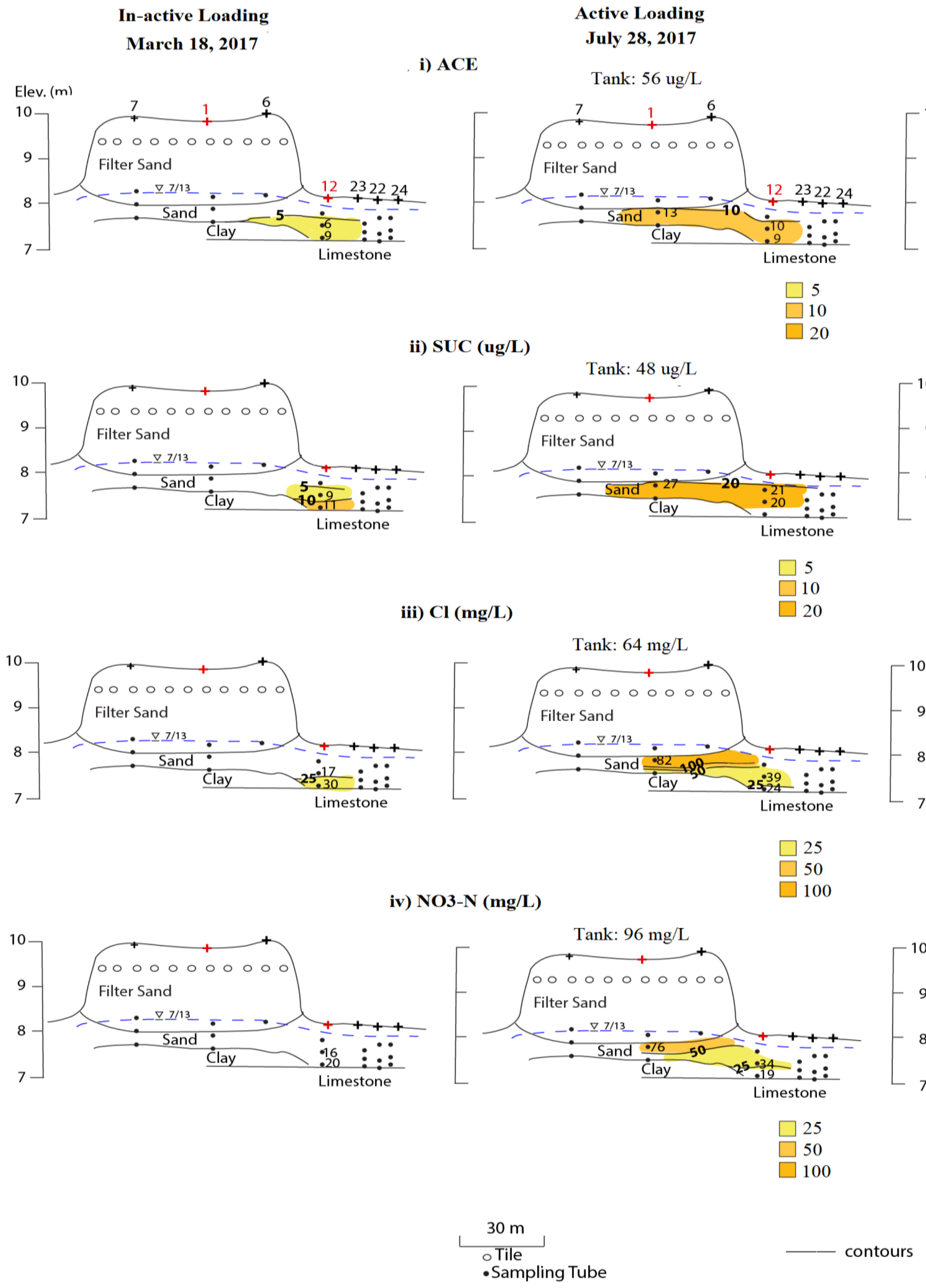

Figure 3.3. Craigleith (NO_3^- Rich) Site; Concentrations of i) ACE, ii) SUC, iii) Cl-, and iv) NO_3^--N during the a) inactive loading period on March 18, 2017 and b) active loading period on July 28, 2017. Tank value in panel vi is NH_4^+-N tank value. Note; tank N values are primarily NH_4^+-N and plume inferred to monitored wells only.

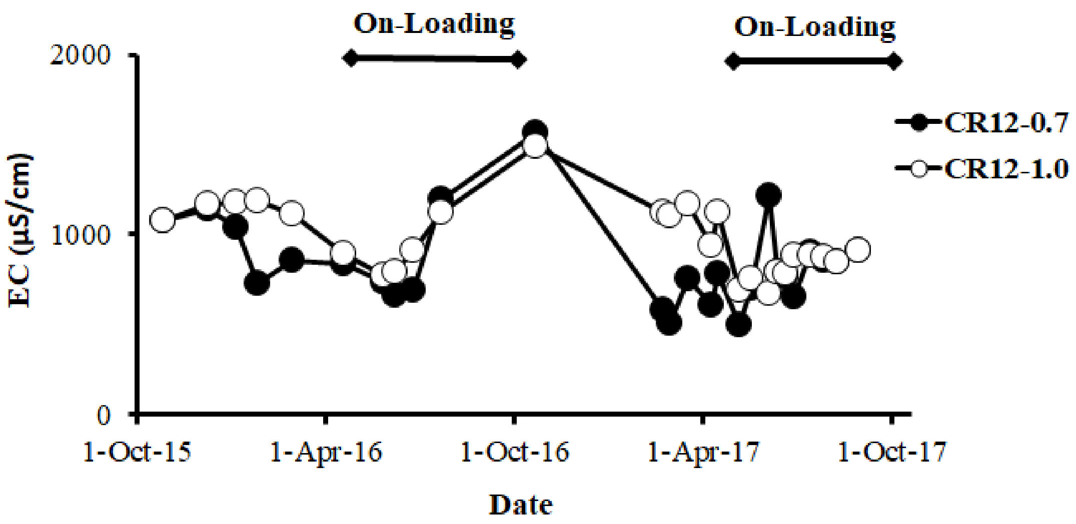

Figure 3.4. Craigleith (NO_3^- Rich) site; Trend of electrical conductivity (EC) at CR12-0.7 and CR12-1.0 from October 2015 to October 2017.

Chapter 4:

Six Mile Lake (NH$_4^+$ Rich) Site; Plume Characterization and Groundwater Age

4.1 Site Description

Six Mile Lake (SM) is an overnight campground consisting of 218 campsites located near Port Severn, ON, open from mid-May to mid-October. The septic system has been in operation for more than 10 years and, consists of a septic tank from which the wastewater is pumped to a raised tile bed 1260 m^2 in area (Fig. 4.1). Average wastewater loading is estimated at 24m^3/day (tile bed loading of 1.9 cm/day) based on an assumed per campsite water usage rate of 220L/day (U.S EPA, 2002) with an average occupancy rate of 50% (Robertson et al., 2016). It is constructed from non-calcareous (average sediment Ca 1.2 wt. %) medium-coarse, imported filter sand (Robertson et al., 2016). The filter-bed is 1.5 m thick and overlies impermeable clay (Fig 4.1). The water table is relatively shallow at this site, averaging only about 0.8 m in depth below the tile bed during active loading (Fig 4.1). The groundwater monitoring network is comprised of 27 monitoring points in 9 multilevel bundles constructed of polyethylene tubing with short (-5cm) long, slotted, and screened tips. These are located primarily below the tile bed at this site (Fig 4.1). A major highway, which receives applications of de-icing salt in the winter, is located~100 m west of the tile bed. The septic system plume maintains neutral pH, and due to the shallow water table condition, wastewater in this plume is the least well oxidized of the three sites studied. This is reflected in the dominance of NH$_4^+$-N over NO$_3^-$-N throughout most of the plume (Table 4.1).

4.2 Plume Characterization

Chloride was used as the conservative plume tracer at this site. Concentrations ranged from 49-152 mg/L during the active loading period but then slowly declined to as low as 14-23 mg/L during the inactive loading period (Table 4.1, Figs. 4.2, 4.3). In addition, elevated Na^+ concentrations are evident (Fig. 4.2) and show a positive correlation with Cl^- (R^2=0.42; Fig. 4.4), suggesting that road salt applied to the highway just 10 m west of the tile bed is likely responsible for elevated Cl^- values observed in the spring months.

The Six Mile Lake plume has high concentrations of NH_4^+-N and low concentrations of NO_3^--N reflecting incomplete nitrification. NH_4^+-N ranges from 15-105 mg/L (Table 4.1; Fig. 4.2), whereas NO_3^--N concentrations are generally much lower (0.1-1.3 mg/L (Table 4.1; Fig 4.2). However, some sampling events showed higher concentrations of NO_3^--N (up to 5-21 mg/L, Aug 4, 2016) and NH_4^+-N co-existing together (Fig. 4.3). In other septic system plumes where NO_3^--N and NH_4^+-N occurred together in similar concentrations, anammox activity has been inferred (Long Point, Robertson et al., 2012 ; Killarney, Caschetto et al., 2018). Modestly elevated SRP concentrations of up to 0.63 mg/L occur in the plume, but values are much lower than the average septic tank value of 4.4 mg/L (Table 8.1, Fig. 4.2). Elevated Fe^{2+} concentrations (Fig 4.2) exist in the plume and is suspected that P is attenuated in the form of Fe-P mineral precipitates, further discussed in chapter 8.

Elevated ACE and SUC concentrations ranging from 0.5-31 µg/L and 0.5-40 µg/L, respectively are present throughout the plume, during the both in-active and active loading periods (Table 4.1, Fig. 4.2). Concentrations in the plume core remain close to the septic tank values for both ACE (1.6-31 µg/L) and SUC (1.7-57 µg/L, Table 4.1, Figs 4.2 a-b) during the on-loading period and for much of the off-loading period, although declining concentrations are noted in the late winter early spring (Fig. 4.2) that are at least partly the result of plume dilution by precipitation recharge.

4.3 Groundwater Age in the Plume

Groundwater ages were estimated for three monitoring bundles (SM1, SM4 and SM6) that were in the central part of the tile bed (Fig. 4.1) and were of specific interest. During the active loading period, ages were estimated based on the sewage loading rate, the distance of the monitoring point from the infiltration pipes and an assumed value for tile bed water content (Table 4.2). A sandy vadose zone is present beneath the tile bed, 0.6-0.8 m in depth, and water content (ϴ) was assumed to 10% in this zone. The average velocity of groundwater in the vadose zone was estimated at 0.19 m /day based on the sewage loading rate of 1.9 cm/day. Below this zone, in the water table, a higher water content of 0.35 was assumed and slower vertical velocities of 0.05 m/day were estimated. Using this procedure, groundwater ages were estimated to range from 7 - 19 days in bundles SM1, SM4 and SM6, during the active sewage loading period (Table 4.1). The park is closed from mid October to mid-May, and no sewage loading occurs during this time. Groundwater ages for the inactive loading (Table 4.2) are estimated as length of time after park closing (~ October 15) plus the incremental age (7-19 days) accruing during active loading.

4.4 Site Summary

- Cl^- used as the conservative tracer
- Wastewater is only partially oxidized due to the shallow water table condition
- Sub oxic, Fe reducing redox conditions
- NO_3^--N and NH_4^+-N coexist; NH_4^+-N dominates
- Minimal ACE and SUC degradation
- Precipitation of Fe-P minerals

Table 4.1. Six Mile Lake (NH_4^+ rich) site; Groundwater age, EC and concentrations of Fe^{2+} (CHEM-et), Cl^-, Na^+, SO_4^{2-}, NO_3-N, NH_4-N, TIN, SRP, ACE, SUC and rations of NH4/Cl, TIN/Cl, SRP/Cl, SUC/ACE, ACE/Cl and SUC/Cl in the septic tank, SM1-1.3, SM4-1.7 and SM6-1.4 during the active and inactive loading period from October 2015 to October 2016. Note; SRP values that are bracketed (October 8, 2015 and June 17, 2016) are TP. Additional monitoring data from other monitoring points is presented in Appendix B.

Date	GW Age (mo.)	EC (µs/cm)	Fe (CHEMet)	DO (mg/L)	Cl (mg/L)	Na (mg/L)	SO4 (mg/L)	NO3-N (mg/L)	NH4-N (mg/L)	TIN (mg/L)	SRP (mg/L)	ACE (µg/L)	SUC (µg/L)	NH4-N/Cl	TIN/Cl	SRP/Cl	SUC/ACE	ACE/Cl	SUC/Cl
SM-TANK																			
08-Oct-15		1593			93		6.1	0.10	106	106	(7.6)	30	39	1.1	1.1	0.1	1.3	0.32	0.42
04-Jun-16		80		0.28	126		10	0.62	83	84	1.5			0.66	0.67	0.01			
17-Jun-16		1367	<0.05	0.32	139		7.6	0.75	59	60	(5.9)			0.43	0.43	0.00			
29-Jun-16		1377	<0.05	0.28	153		6.8	0.30	56	57	6.8			0.37	0.37	0.04			
04-Aug-16		1598	<0.05	0.3	159	81	3.8	0.06	76	76	9.0	17	34	0.48	0.48	0.01	2.0	0.11	0.21
27-Sep-16		1673	<0.05		159	124	4.7	0.21	71	71	1.9	32	57	0.45	0.45	0.01	1.8	0.20	0.36
SM1-1.3																			
07-Oct-15	0.4	1243			83		12	0.14	47	49	0.01	23	26	0.56	0.59		1.1	0.28	0.32
26-Oct-15	0.8	1229	8	10	77		8.3	0.25	29	29	0.03	5.4	7.4	0.38	0.38	4.0E-04	1.4	0.07	0.10
05-Dec-15	2.2	1133	>10	11	135		4.6	0.59	32	33	0.02	11	11	0.24	0.24	1.5E-04	1.0	0.08	0.08
07-Jan-16	3.2																		
02-Feb-16	4.0																		
29-Feb-16	4.9	115	>10		138	66	33	<0.01	8.4	8	0.02	17	15	0.06	0.06	1.2E-04	0.90	0.12	0.11
05-Apr-16	6.1	848	>10	12	61	28	16	<0.01	30	30	0.02			0.49	0.49	3.1E-04			
20-Apr-16	6.6	451	3	9.2	32		8.3	<0.01	11	11	0.02	1.6	1.7	0.34	0.34	6.4E-04	1.0	0.05	0.05
04-Jun-16	0.4																		
17-Jun-16	0.4				273														
4-Aug-16	0.4	1502	3	7.1	152	43	4.9	0.53	115	116	0.02	31	57	0.76	0.76	1.5E-04	1.8	0.20	0.38
27-Sep-16	0.4	1419	2		115	112	2.6	1.3	74	76	0.03	28	31	0.65	0.66	2.4E-04	1.1	0.24	0.27
31-Oct-16	1.0																		
SM4-1.7																			
07-Oct-15	0.4	1106	> 10	8.5	108		5.6	0.27	15	15		18	15				0.83		
26-Oct-15	0.8	1039	>10	4.6	104		2.9	0.31	14	14	0.03	13	16	0.14	0.14	3.3E-04	1.2	0.13	0.16

Date	GW Age (mo.)	EC (µs/cm)	Fe (CHEMet)	DO (mg/L)	Cl (mg/L)	Na (mg/L)	SO4 (mg/L)	NO3-N (mg/L)	NH4-N (mg/L)	TIN (mg/L)	SRP (mg/L)	ACE (µg/L)	SUC (µg/L)	NH4-N/Cl	TIN/Cl	SRP/Cl	SUC/ACE	ACE/Cl	SUC/Cl
05-Dec-15	2.2	1116	>10	9.3	134		2.4	0.38	18	18	0.01	11	15	0.13	0.14	9.0E-05	1.4	0.08	0.11
07-Jan-16	3.2	1094	>10	9.7	124		1.7	<0.01	16	16	0.02	18	24	0.13	0.13	1.4E-04	1.4	0.14	0.20
02-Feb-16	4.0																		
29-Feb-16	4.9	1025	>10		106	59	2.2	<0.01	5.5	5.5	0.02	14	19	0.05	0.05	1.5E-04	1.3	0.13	0.18
05-Apr-16	6.1	896	>10	11	94	33	2.6	<0.01	16	16	0.01			0.17	0.17	7.8E-05			
20-Apr-16	6.6	1375	>10	9.9	60		2.2	0.09	5.2	5.3	0.01	3.1	4.3	0.09	0.09	2.2E-04	1.4	0.05	0.07
04-Jun-16	0.4	788	>10	8.3	24		1.4	<0.01	12	12	0.02	3.7	6.2	0.50	0.50	7.8E-04	1.7	0.15	0.26
17-Jun-16	0.4	750	>10	7.4	77		1.9	0.41	7.7	8.1	0.00	3.9	4.8	0.10	0.11		1.2	0.05	0.06
4-Aug-16	0.4	940	>10	7.4	115	27	12	0.07	29	29	0.01	9.0	17	0.25	0.25	6.9E-05	1.9	0.08	0.15
27-Sep-16	0.4	1196	>10		138	64	2.2	0.28	17	17	0.01			0.12	0.12	6.1E-05			
31-Oct-16	1.0	1221	>10	9.9							0.01	22	31				1.4		
SM6-1.4																			
07-Oct-15	0.4	1419	5	0.23	146		6.4	0.31	59	59	0.63	23	27				1.2		
26-Oct-15	0.8	1289	4	0.81	149		14	0.23	29	30	0.05	24	24	0.20	0.20	3.1E-04	1.0	0.16	0.16
05-Dec-15	2.2	1241	5	0.34	124		18	0.61	43	44	0.10	14	17	0.35	0.36	8.0E-04	1.2	0.11	0.14
07-Jan-16	3.2	1182	8	0.30	130		45	<0.01	39	39	0.11	19	21	0.30	0.30	8.8E-04	1.1	0.15	0.16
02-Feb-16	4.0	1171	3	0.40	102		21	<0.01	41	41	0.07	12	11	0.40	0.40	6.8E-04	0.95	0.11	0.11
29-Feb-16	4.9	1027	3		93		31	<0.01	4.3	4.3	0.09	10	11	0.05	0.05	9.6E-04	1.1	0.11	0.12
05-Apr-16	6.1	760	3	0.31	45	19	22	<0.01	12	12	0.09			0.27	0.27	2.0E-03			
20-Apr-16	6.6	643	4	0.20	23		18	0.08	10	10	0.10	0.51	0.53	0.43	0.44	4.2E-03	1.0	0.02	0.02
04-Jun-16	0.4	557	3	0.23	16		3.6	0.09	31	31	0.14	1.6	2.0	1.91	1.91	8.7E-03	1.2	0.10	0.12
17-Jun-16	0.4	599	4	0.24	49		9.3	0.10	9.3	9.4	0.11	3.6	4.8	0.19	0.19	2.3E-03	1.3	0.07	0.10
4-Aug-16	0.4	1516	3	0.73	86		2	0.1	79	80	0.11	18	40	0.91	0.93	1.3E-03	2.3	0.20	0.47
27-Sep-16	0.4	1785	>DL		176	145	4.3	0.30	105	105	0.13	27	35	0.60		7.2E-04	1.3	0.15	0.20
31-Oct-16	1.0	1529	5	0.35	146		26	0.05	43	43	0.11	26	27	0.29	0.29	7.5E-04	1.0	0.18	0.19

Table 4.2. Six Mile Lake (NH_4^+ rich) site; Active loading groundwater ages at wells SM1 and SM6. Values of water content (ϴ) (assumed) and vertical velocity (V) calculated for the active loading period assuming sewage loading of 1.9 cm/d. Distances (L) assume a component of lateral flow in the unsaturated zone between the infiltration lines and the shallowest monitoring point at each nest, whereas L values reported for the deeper monitoring points are incremental and assume vertically downward flow under saturated conditions.

Well	(ϴ)	V (m/d)	L (m)	Groundwater Age (days)
SM1-0.7	0.10	0.19	1.3	7
SM1-1.0	0.35	0.05	0.3	13
SM1-1.3	0.35	0.05	0.3	19
SM4-1.1	0.10	0.19	1.7	9
SM4-1.4	0.35	0.05	0.3	16
SM4-1.7	0.35	0.05	0.3	21
SM6-0.8	0.10	0.19	1.4	7
SM6-1.1	0.35	0.05	0.3	13
SM6-1.4	0.35	0.05	0.3	19

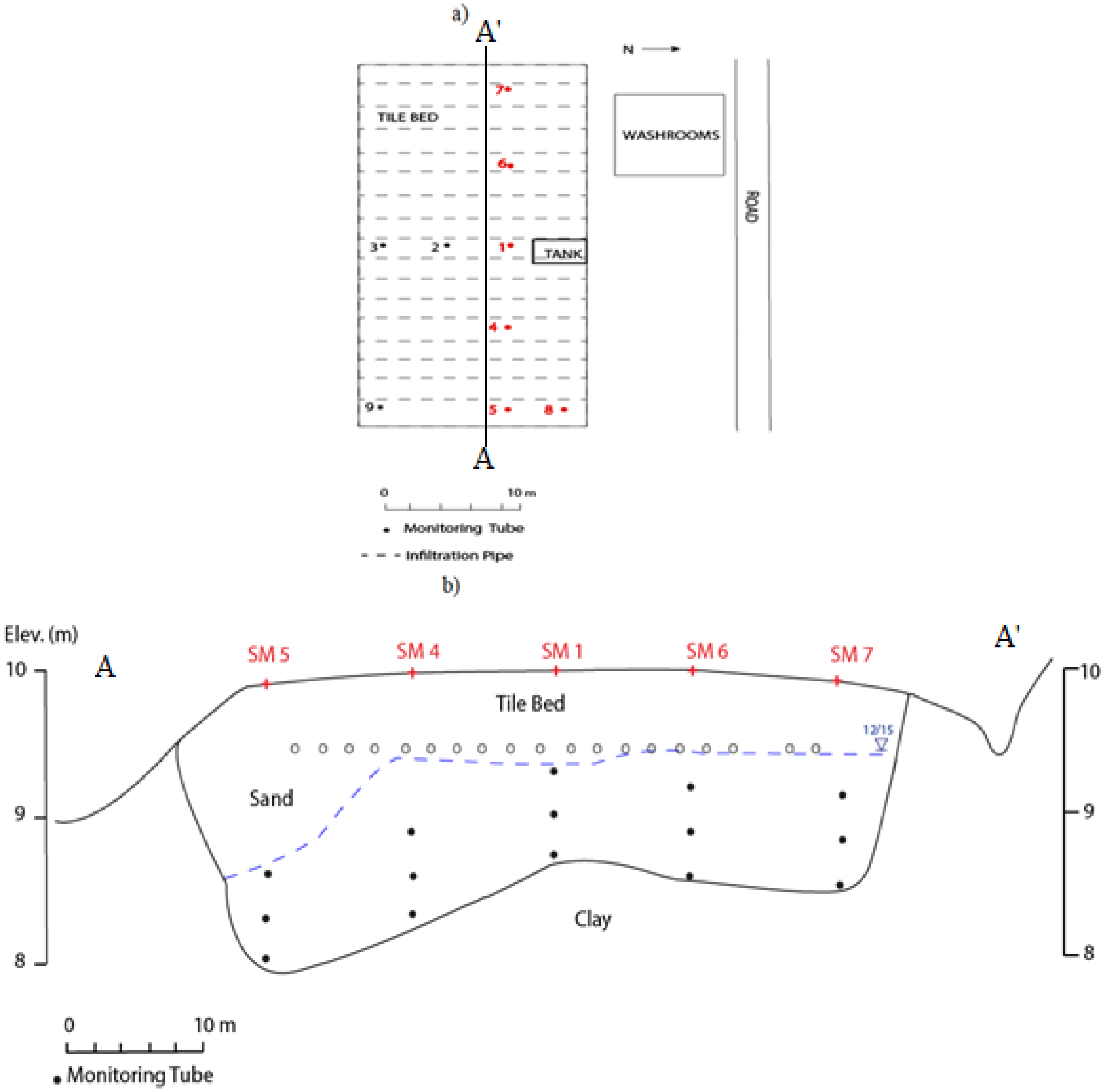

Figure 4.1 Six Mile Lake (NH_4^+ rich) site; (a) Plan view of the tile bed showing the tile bed and the locations of the monitoring bundles. Principal bundles sampled in this study are highlighted in red. (b) Cross section through the tile bed (A-A')showing the multi depth monitoring points at each location. Water table measured October 2015.

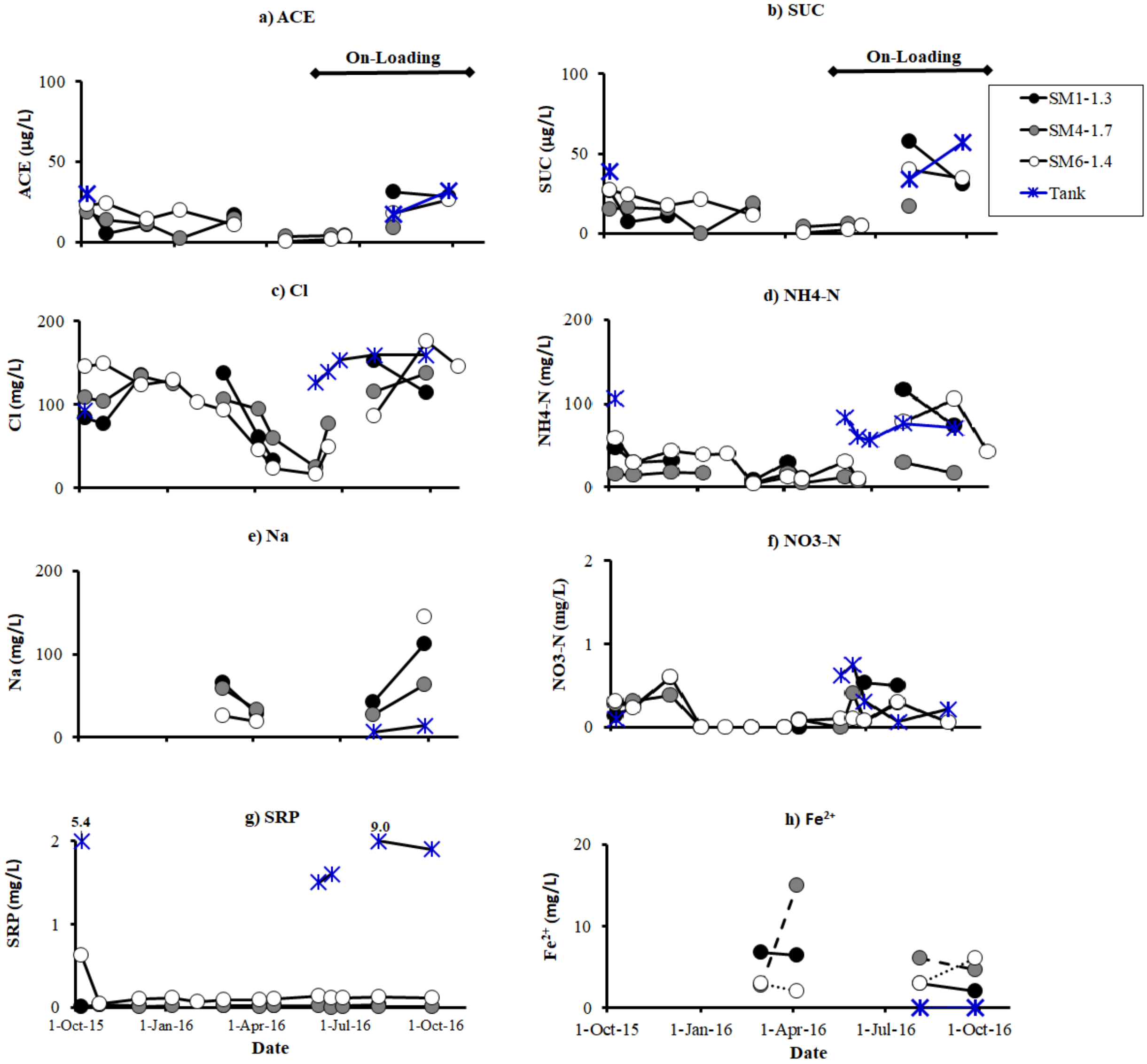

Figure 4.2 Six Mile Lake (NH_4^+ rich) site; Trends of a) ACE, b) SUC, c) Cl^-, d) NH_4-N, e) Na^+, f) NO_3-N g) SRP and h) Fe^{2+} in selected monitoring tubes (SM1-1.3, SM4-1.7 and SM6-1.4) compared to the septic tank, during both the on-loading and off-loading periods from October 2015 to October 2016.

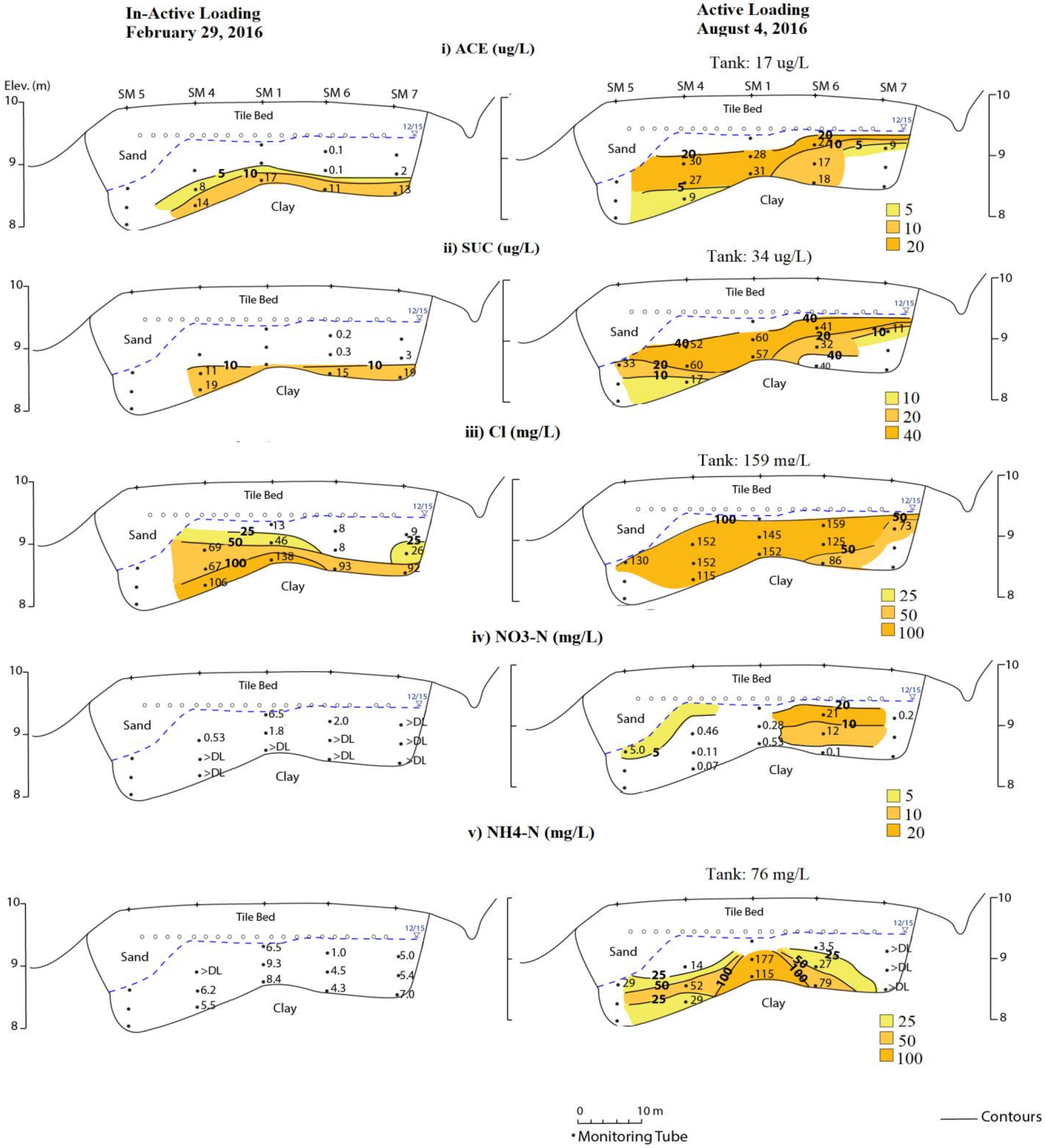

Figure 4.3. Six Mile Lake (NH$_4^+$ Rich) Site; Concentrations of i) ACE, ii) SUC, iii) Cl-, iv) NH$_4$-N and v) NO$_3$-N during the a) inactive loading period on February 29, 2016 and b) active loading period on August 4, 2016.

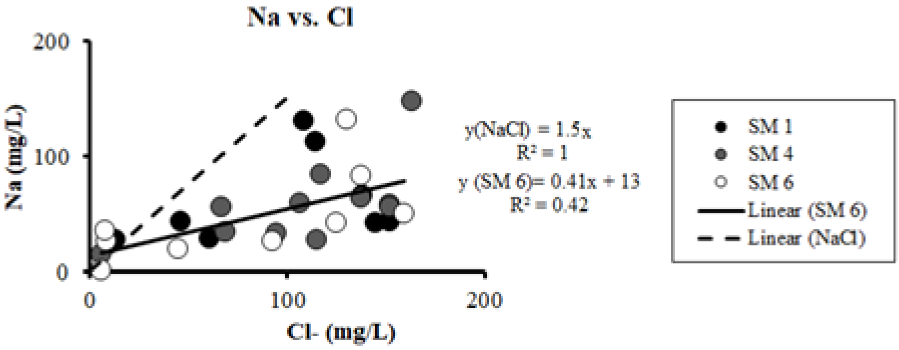

Figure 4.4. Six Mile Lake (NH_4^+ Rich) Site; Relationship between Na^+ and Cl^- from samples collected along the main transect at Six Mile Lake in February, April, August and September of 2016. Line expected for NaCl with a mass ratio of 0.66:1

Chapter 5:

Long Point (NO_3^- Depleting) Site; Plume Characterization and Groundwater Age

5.1 Site Description

Long Point is an overnight campground consisting of 266 overnight campsites located on the north shore of Lake Erie, ON, which is open seasonally, from mid-May to mid-October. Sewage from a single washroom facility is treated onsite in a septic system. The system consists a septic tank, which provides about 2 days retention during peak loading in the summer to two separate tile beds, 290 m^2 in area, which are intermittently dosed using a float-activated pump. Tile bed 2 is the focus of the current study. In 2014 a tertiary treatment module was added (Bionest^{TM}), which provided aeration of the wastewater prior to discharge to the tile beds. It was previously determined that, Cl^-, Na^+, and ACE could be used to map the wastewater plume, although high background Cl^- values in down gradient areas obscured the wastewater plume there (Robertson et al., 2016). Groundwater at the site is sub-oxic (DO < 1 mg/L; Table 5.1), both inside and outside of the wastewater plume. The groundwater plume from tile bed 2 flows southward toward the Lake Erie shoreline with a 5 m thick unconfined calcareous sand aquifer that is underlain by a clay-silt unit (Fig 5.1) (Robertson & Garda, 2018). Tile bed 2 has a monitoring network that consists of 13 multilevel bundle piezometers (Fig 5.1). Loading to the tile bed has been estimated previously at up to 10 cm/day during peak loading in the summer (Robertson et al., 2012). Thus, the wastewater loading rate at this site is much higher than at the Craigleith and Six Mile Lake sites (0.5-1.9 cm/day) due to the smaller tile bed size. The plume has a large and prominent core zone that penetrates the full thickness of the aquifer due to high loading rate and the tile bed's position near a groundwater flow divide located within 100 to 200 m north of the tile bed (Robertson et al., 2012).

5.2 Plume Characterization

Chloride concentrations remained consistent (47-81 mg/L) in bundle LP123 throughout both the active and the inactive loading periods (Fig. 5.2c). High NO_3^--N concentrations are present in the shallow zone (96-107 mg/L, LP123-2.6m) and NH_4^+-N values are low (Table 5.1), reflecting a high degree of oxidation of the wastewater. However, the septic tank samples (Table 5.2) reveal that a considerable amount of oxidation has occurred prior to the wastewater being discharged to the tile bed, presumably as a result of the installation of the tertiary aeration module in 2014. Previously, the wastewater was less well oxidized and zones of elevated NH_4^+-N were intermittently present in the plume proximal zone (Robertson et al., 2012). At greater depths (> 4 m), decreasing concentrations of NO_3^--N are observed (27-62 mg/L at LP123-5.5m Table 5.2). These declining values at depth were previously attributed to denitrification promoted by trace quantities of organic carbon and biogenic pyrite present in the aquifer sediments (Aravena and Robertson, 1998).

ACE and SUC concentrations were highly variable during this study, much more so than in previous studies. Intermittently low ACE and SUC values were measured, as low as 0.02 µg/L and 0.48 µg/L, for ACE and SUC, respectively (Fig. 5.2). Higher ACE concentrations, up to 85 µg/L were observed at a depth of 3.8 m, whereas SUC displayed an opposite trend with decreasing concentrations as low as 0.48 µg/L at a depth 5.5 m (Table 5.1, Fig 5.2). Figure 5.2 shows the trends of SUC and ACE in the shallow (2.6 m) and deep (5.5 m) wells at LP 123 during both the active and inactive periods from November 2015 to July 2016. Low ACE values, anywhere near this low, had not been observed previously in either the septic tank or plume samples at Long Point (Van Stempvoort et al., 2011; Robertson et al., 2013). However, similarly low SUC values were reported previously, in the plume during start-up in the spring of 2012 (Robertson et al., 2013) and in deeper zones, where SUC degradation in association with denitrification activity was inferred (Robertson et al., 2016).

5.3 Groundwater Age in the Plume

Groundwater ages in the Long Point plume were estimated previously from seasonal breakthrough of elevated EC values and from two sodium bromide tracer tests (Robertson et al., 2012; Fig. 5.1c). In this study, sampling was focused primarily on multilevel bundle LP123, which is located at the down gradient edge of the tile bed and has plume ages that range from 12-50 days in the shallow zone to 68-129 days at depth of 5.5 m, during active sewage loading (Fig 5.1). Groundwater ages for the inactive loading (Table 5.1) are estimated as length of time after park closing (~ October 15) plus the incremental age (12-129 days) accruing during active loading.

5.4 Site Summary

- Cl^- is used as the conservative tracer
- NH_4^+-N is absent in the shallow plume, indicating enhanced wastewater oxidation.
- Denitrification remains active below 4 m depth
- Sporadically low ACE and SUC concentrations are present in the proximal plume

Table 5.1. Long Point (NO_3^- Depleting) Site; Groundwater age, EC and concentrations of Cl^-, SO_4^{2-}, NO3-N, NH4-N, TIN, SRP, ACE, SUC and rations of NH4/Cl, TIN/Cl, SRP/Cl, SUC/ACE, ACE/Cl and SUC/Cl in the septic tank, LP123-2.6 LP123-3.8 and LP123-5.5.; TIN= NO3-N. Septic tank sample from June 2014 (Robertson et al.,2016). Tank NO3-N/Cl is TIN/Cl. Monitoring data from other well depths in bundle LP 123 is available in Appendix C (Table C.1-C.2).

Date	GW Age (months)	EC (µs/cm)	DO (mg/L)	Cl^- (mg/L)	$SO4^{2-}$ (mg/L)	NO3-N (mg/L)	NH4-N (mg/L)	TIN (mg/L)	SRP (mg/L)	ACE (µg/L)	SUC (µg/L)	NO3-N/Cl	SRP/Cl	SUC/ACE	ACE/Cl	SUC/Cl
LP-Tank																
03-Jun-16		1059		68	41	36	14	50	3	n/a	n/a	0.54	0.04			
18-Jun-16		1253		72	32	64	3	67	15	n/a	n/a	0.89	0.21			
19-Jun-16		1160		49	22	72	2	74	15	n/a	n/a	1.5	0.31			
29-Jun-16		1201		55	28	78	17	95	17	n/a	n/a	1.4	0.30			
LP123-2.6																
11-Sep-15	0.5			65	43	76				72	47	1.2		0.65	1.1	0.72
19-Nov-15	1.7	1410		80	48	107			6.0	0.84	55	1.3	0.07	65	0.01	0.68
15-Dec-15	2.6	1450		70	47	109			2.2	1.0	33	1.6	0.03	32	0.01	0.47
25-Jan-16	3	1483	0.05	69	45	111			1.8	0.72	46	1.6	0.03	64.05	0.01	0.66
23-Feb-16	4			63	61	96			1.1	43	15	1.5	0.02		0.68	0.24
19-Jun-16	0.5	1092		74	34	5			16.0				0.22			
LP123-3.8																
11-Sep-15	2.3			60	30	89				85	24	1.5		0.28	1.4	0.4
19-Nov-15	3.5	1365		58	51	79			3.4	3	54	1.4	0.06	20.3	0.05	0.93
15-Dec-15	4.4	1397		59	49	82			2.1	2	35	1.4	0.03	22.84	0.03	0.60
25-Jan-16	4.8	1430	0.05	59	48	79			1.8	0.68	37	1.3	0.03			
23-Feb-16	5.8			56	44	73			2.4	1.2	62	1.3	0.04			
19-Jun-16	2.3			53	75	95			5.9			1.8	0.11			
LP123-5.5																
11-Sep-15	4.3			51	62	40				65	5	0.78		0.01	1.3	0.01
19-Nov-15	5.5	1100		68	72	27			0.02	43	0.48	0.39	2.8E-04	0.04	0.16	0.01
15-Dec-15	6.4	1090		47	67	34			0.02	43	1.2	0.72	3.8E-04	0.05	0.52	0.03
25-Jan-16	6.8	1332	0.05	56	59	60			0.01	43	0.18	1.1	2.3E-04	0.0	0.19	0.00

Date	GW Age (months)	EC (µs/cm)	DO (mg/L)	Cl^- (mg/L)	$SO4^{2-}$ (mg/L)	NO3-N (mg/L)	NH4-N (mg/L)	TIN (mg/L)	SRP (mg/L)	ACE (µg/L)	SUC (µg/L)	NO3-N/Cl	SRP/Cl	SUC/ACE	ACE/Cl	SUC/Cl
23-Feb-16	7.8			57	58	62			0.01	43	0.22	1.1	2.6E-04		0.74	0.38
19-Jun-16	4.3	1101		56	83	32			0.05			0.57	8.9E-04			

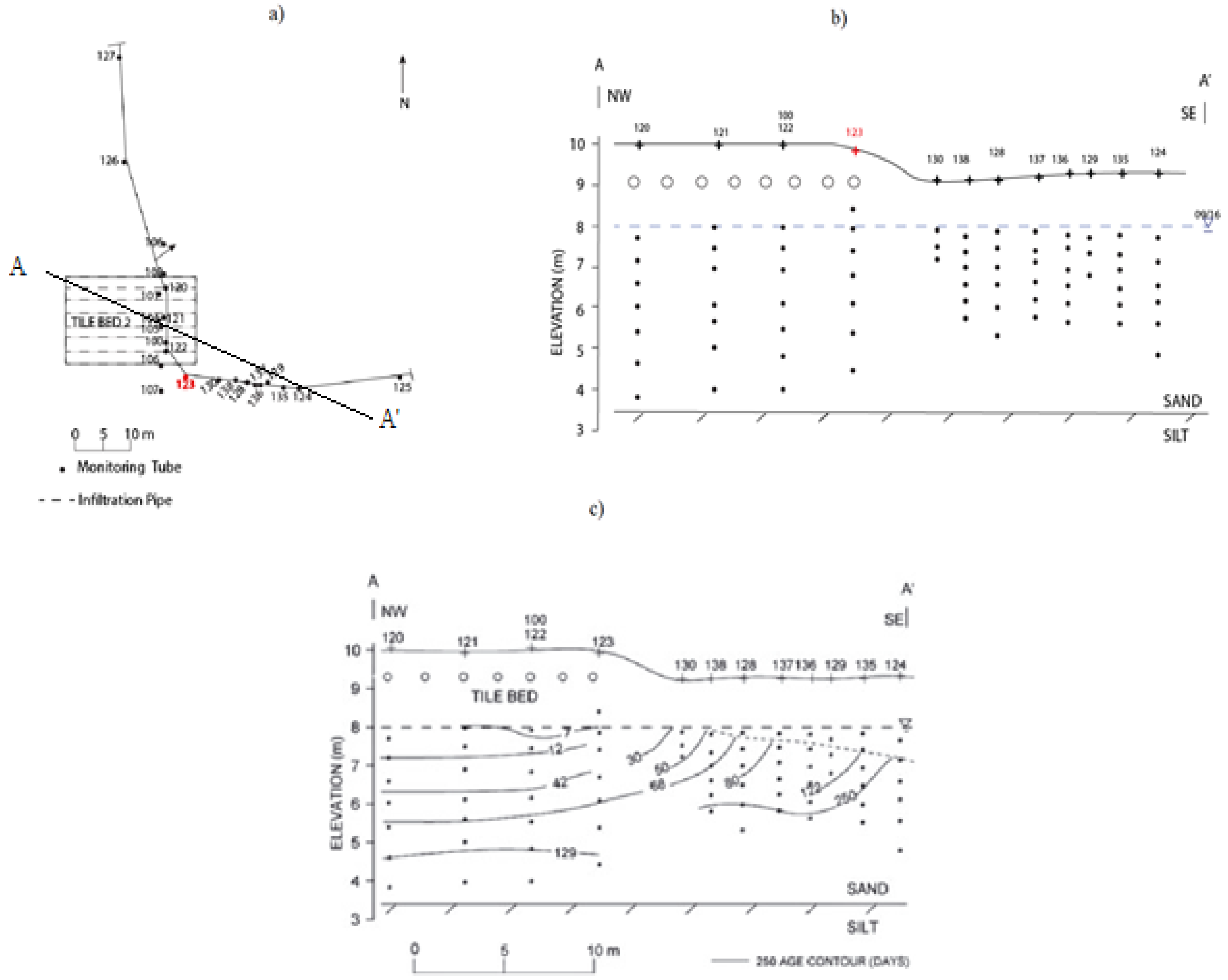

Figure 5.1 Long Point (NO$_3^-$ Depleting) Site; Plan view of Tile Bed 2 at the Long Point site adapted from Van Stempvoort et al. 2011, showing the tile bed and the locations of monitoring wells. Principal wells referenced and sampled in this study are highlighted in red. (b) Cross-sectional area of the tile bed (A-A') showing the various depths of for each well sampled, water table approximation obtained in 2016, c) Groundwater age contours (days) below tile bed 2. Piezometers used in this study are noted in red.

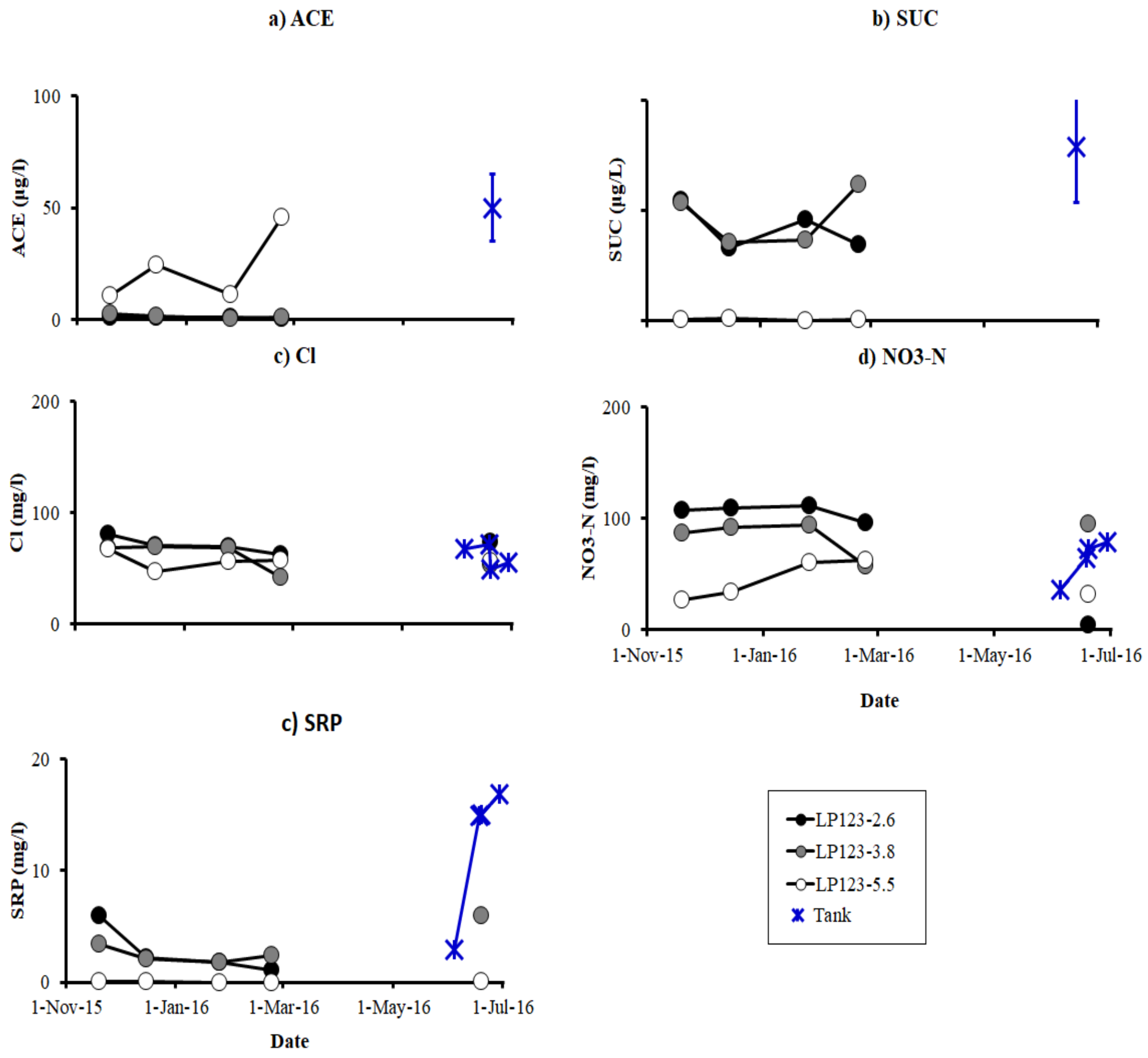

Figure 5.2. Long Point (NO_3^- Depleting) site; Trends of a) ACE, b) SUC, c) Cl^-, d) NO_3-N, and e) SRP during the on-loading and off-loading period at wells LP123- 2.6, 3.8 and 5.5 m below the subsurface and the septic tank. Note, after 2014, septic tank N is primarily NO_3^--N because of installation of a tertiary aeration module (Bionest^{TM}). Samples are from November 2016 to February 2016. Note; mean active-loading septic tank and LP123 obtained from Robertson et al (2016).

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Chapter 6:

Artificial Sweetener Persistence with Groundwater Age in Three Septic System Plumes

6.1 Results

ACE & SUC degradation at Craigleith (NO_3^- Rich) Site

Figure 6.1 and Figure 6.2 shows ACE and SUC concentrations, respectively throughout the experimental period for the distal monitoring points CR12-0.7 m and 1.0 m at the Craigleith site. These concentration trends are compared to modeled decay curves that would be expected for first order decay with half-lives of 4 and 12 months calculated using E.q. 6.1 to represent artificial sweetener loss. Half- life is the time at which concentration reaches half the initial concentration and were calculated using E.q. 6.2. Best fit, first order decay curves are also shown for the monitoring data. These trend results are further refined by providing a correction for dilution based on Cl^- concentrations (Fig. 6.1 iii, and Fig. 6.2 ii). The dilution corrected sweetener concentrations were determined by multiplying the uncorrected concentrations by the mean septic tank Cl^- concentration (85 ±42 mg/L, Table 6.1) and then dividing by the sample Cl^- concentration. For this analysis, samples that were excessively diluted ($Cl^- < 20$ mg/L, February 22-May 6, 2017 at CR12-0.7 or had elevated Cl^- that was likely the result of road salt impact (May 18-June 4, 2017 at CR12-0.7) were excluded.

Note that the decay curves shown in Figure 6.1 and Figure 6.2 are initialized to the mean values measured in the tile bed monitoring point CR1-1.9 (25±17 µg/L for ACE and 26±16 µg/L for SUC, corrected, Table 6.1). These values are much lower than the septic tank values (79 ± 40 µg/L for ACE and 72 ± 30 µg/L for SUC, Table 6.1), indicating rapid sweetener removal within the unsaturated zone. Thus, the decay rates indicated in Fig. 6.1 pertain only to loss within the groundwater flow system and exclude the unsaturated zone. The dilution corrected rates are summarized in Table 6.2 and show that ACE and SUC decay rates are very slow with half-lives of approximately 35 months. Note that the modelled decay curves for CR12-0.7 reflect primarily, only one data point (groundwater age of 6 months Fig 6.1 and Fig 6.2), and therefore the artificial sweetener removal results for this well have low significance. Much more rapid sweetener loss is indicated in the unsaturated zone with a half-life of 0.15 and 0.20 months indicated for ACE and SUC, respectively. This is based on the differences between the mean septic tank and CR1-1.9 values. (Table 6.1 and Table 6.2) and the estimated groundwater age of this well during active loading (0.9 months; Table 3.1).

ACE & SUC degradation at Six Mile Lake (NH_4^+ Rich) Site

Figure 6.3 and Figure 6.4 shows ACE and SUC concentrations, respectively throughout the experimental period for the proximal monitoring points SM1-1.3 m, SM4-1.7 m and SM6-1.4 m at the Six Mile Lake site. These concentration trends are compared to modeled decay curves that would be expected for first order decay with half-lives of 4 and 12 months calculated using Eq. 1 and Eq. 2. Best fit, first order decay curves are also shown for the monitoring data. These trend results are further refined by providing a correction for dilution based on Cl^- concentrations (Fig. 6.3 iii, and Fig. 6.4 ii). For this analysis, samples that were excessively diluted ($Cl^- < 20$ mg/L) on June 4, 2016 at SM4-1.7 and from April 20-June 4, 2016 at SM6-1.4 were excluded.

The decay curves shown in Figure 6.3 and Figure 6.4 are not initialized to the mean septic tank value (26±8 µg/L for ACE and 43±12 µg/L for SUC, corrected, Table 6.1). Thus, like Craigleith, the decay curves indicated in Figs. 6.3 and 6.4 pertain only to the sweetener loss occurring within the groundwater flow system and exclude the unsaturated zone. The dilution corrected rates are summarized in Table 6.2 and show that both ACE and SUC decay rates are very slow, with half-lives ranging from 6- 35 months. Much more rapid sweetener loss is indicated in the unsaturated zone at two of the well locations (SM4-1.7 and SM6-1.4) with a half-life in the range of 0.6- 2 months indicated for both ACE and SUC (Table 6.2), based on the differences between the mean septic tank concentrations (Table 6.1) and mean well concentrations during active loading (Table 6.2).

ACE & SUC degradation at Long Point (NO_3^- Depleting) Site

Figure 6.5 and Figure 6.6 show ACE and SUC concentrations, respectively throughout the experimental period for proximal monitoring points LP123-2.6 m and LP123-5.5 m at the Long Point site. These concentration trends are compared to modeled decay curves that would be expected for first order decay with half-lives of 4 and 12 months calculated using Eq. 6.1 and Eq. 6.2. Best fit, first order decay curves are also shown for the monitoring data. These trend results are further refined by providing a correction for dilution based on Cl^- concentrations (Fig. 6.5 iii, and Fig. 6.6 ii). Note that, the decay curves shown in Figure 6.6 and Figure 6.7 are, in this case, initialized to the mean septic tank value (47±20 µg/L for ACE and 48±40 µg/L for SUC, Table 6.1) and thus reflect sweetener loss occurring in the groundwater zone. The rates (dilution corrected) are summarized in Table 6.2 and indicate half lives ranging from 10-14 months for ACE and 5-9 month for SUC. Additionally, Figure 6.7 shows more detailed depth profiles for these sweeteners at LP123 on December 15, 2016, which reveals contrasting depth trends. ACE concentrations to 4 m depth were unusually low (< 2 ug/L) compared to values measured in previous studies (~50 ug/L, Robertson et al., 2013), whereas SUC concentrations within this depth range (15-55 ug/L) were like values measured previously (Robertson et al., 2016).

6.2 Discussion

The artificial sweeteners Acesulfame (ACE) and Sucralose (SUC) have been used previously as conservative tracers of domestic wastewater in both surface water and groundwater environments (Buerge et al., 2009; Van Stempvoort et al., 2011; Oppenheimer et al., 2011; Robertson et al., 2013; Snider et al., 2017).

At the Craigleith (NO_3^- rich) site, a large decline in the corrected ACE and SUC concentration is evident through the unsaturated zone from the septic tank to the tile bed well CR1-1.9 (79 to 25 µg/L and 72 to 26 µg/L, respectively; Fig 6.1-6.2). This decline in the unsaturated zone indicates relatively rapid sweetener loss with half lives in the range of 0.1-0.2 mo. (Table 6.2). This contrasts greatly with the groundwater zone, where much slower ACE and SUC loss (half lives of 35 months, Table 6.2) is indicated. Considering the amount of data scatter in the well samples, the groundwater rates might potentially be considered as a maximum rate, as it appears that using even slower removal rates would result in curves equally as good. The Six Mile Lake site exhibited behavior like that at Craigleith, with little to no removal observed in the saturated zone (Table 6.2), but substantially greater removal occurring in the unsaturated zone as indicated by the difference in concentrations between the mean septic tank and the tile bed values (Table 6.1). These results provide compelling evidence that sweetener loss associated with wastewater disposal in septic systems, is highly focused within the unsaturated zone, whereas these compounds become much more persistent once they enter the groundwater flow system. This is consistent however, with previous studies that indicated enhanced sweetener degradation during wastewater treatment, when oxic conditions prevail (Buerge et al., 2009 Lange et al., 2012 and Gan et al., 2013, Castrenovo et al., 2017). In the latter study, these sweeteners were reduced by 94% within 27 hrs during wastewater treatment.

When corrected for dilution, first order decay rates appear adequate for estimating constituent removal over the extended time periods investigated here. During first order decay, mass removal rates vary depending on the concentrations that are present, whereas for zero-order decay, mass removal remains constant at all concentrations. Zero-order decay (constant removal rate) can have the effect of causing complete consumption of a contaminant. This was generally not the case in this study, where detectable levels of the constituents tended to persist throughout the monitoring period, thus supporting a first-order decay model. Regnery et al., (2015) also applied the first order removal kinetics to organic contaminants under three redox conditions (suboxic with low carbon, oxic with low carbon and anoxic with high carbon) including ACE through laboratory soil experiments. Results were similar to that of the current investigation; minimal loss was observed for ACE under suboxic and anoxic conditions and greater loss was observed under aerobic, low biodegradable dissolved organic carbon (BDOC) conditions after seven days residence time, with half-life >700 days and half-life of 4.2 days were reported, respectively (Table 6.3). The oxic rate is similar to the rate observed at Craigleith in the unsaturated zone in the current investigation (half life of ~ 5 days; Table 6.2). Substantial ACE removal during sewage treatment was also established by Kahl et al (2018) where 25-75% of ACE removal occurred at the same time that biochemical oxygen demand ($CBOD_5$) was reduced by 76-98%, and redox potential and dissolved oxygen concentrations increased. This suggests that ACE removal is most efficient under conditions of low biodegradable organic carbon and high oxygen availability. Low organic carbon content is also beneficial for ammonium oxidation, suggesting a correlation between nitrification and ACE removal. ACE degradation rates observed in the unsaturated zones at Craigleith and Six Mile Lake (Table 6.2) are also consistent with results from Falas et al (2016), where ACE removal of up to 80% was observed under aerobic conditions, but no removal was observed under anaerobic conditions (iron-reducing) for more than one year. Low organic carbon content and oxic conditions also prevailed in previous laboratory experiments with successful ACE degradation (Burke et al., 2014; Regnery et al., 2015; and Burke et al., 2017.).

The effects of aeration and nitrification on ACE removal is also apparently showcased at the Long Point (NO_3^- depleting) site, where a tertiary aeration module (Bionest^{TM}) was installed in the fall of 2014. Since that time, the effluent has been substantially nitrified prior to tile-bed disposal (Robertson and Garda, 2018). The unusually low ACE concentrations (< 2 ug/L) observed intermittently in the shallow zone, in the current study, likely reflect enhanced aerobic degradation of ACE associated with this newly installed pre-treatment step. ACE has likely been degraded to varying degrees depending on the sewage loading rates; higher during low use in the spring and fall, when retention times in the Bionest^{TM} module would be much longer. In the current study, the low ACE values observed in the shallow zone throughout the late fall and winter of 2016 , likely reflect loading that occurred during the fall of 2015 when ACE degradation in the Bionest^{TM} module may have been enhanced. In contrast, at greater depths (LP123-5.5 m) where summer time loading was likely present, ACE degradation was apparently much less (Fig 6.7).

Sucralose behaviour contrasted with ACE behaviour in the current study at the Long Point Site. It remained at high concentrations (30-55 ug/L) in the shallow zone, consistent with previous studies undertaken prior to installation of the Bionest^{TM} module (Robertson et al., 2016). Also consistent with the previous study, SUC was then degraded to generally much lower values below the denitrification front present at about 4 m depth. Here it was suggested that SUC was metabolized as a carbon source in support of the denitrification reaction (Robertson et al., 2016). Thus, the consistent behaviour of SUC in the current study, compared to previous studies, in contrast to the behaviour of ACE, suggests that ACE could be more susceptible to aerobic degradation during wastewater treatment. Further investigations should be undertaken at Long Point to assess the possibility of enhanced sweetener degradation associated with the Bionest^{TM} tertiary treatment module.

Elevated SUC concentrations are also observed where elevated NO_3^--N concentrations are observed at CR (Fig 3.2), SM (Fig. 4.2) and LP (Fig. 5.2). It has been previously suggested in a series of batch tests that SUC may be used as a carbon source during denitrification (LaBrae and Alexander, 1993). Furthermore, SUC persistence under aerobic conditions has been well documented (Buerge et al., 2009; Torres et al., 2011; Table 6.3), which supports SUC persistence from CR1 to CR12 (Fig 6.1) However like ACE, SUC rapidly degraded at Craigleith from the septic tank to CR1-1.9 from 72 µg/L to 26 µg/L (Fig 6.1; Table 6.1), indicating that SUC is also able to degrade under aerobic conditions. These results coincide with findings from Buerge et al., (2011), where half-lives of up to 4 months were observed, suggesting that the degradation of SUC is variable.

Results did not indicate that seasonality may have an impact on ACE degradation due to the generally stable sweetener concentrations observed throughout the experimental period at Craigleith and Six Mile Lake (Figs 6.1-6.4). However, Kahl et al., (2018) confirmed that ACE degradation was influenced by temperature in WWTPs. Approximately 95% (Table 6.3) of ACE was removed from July to October, while less than 15% ACE was removed between January and April (Kahl et al., 2018). Burke et al., (2014) also observed in a set of column tests that ACE was removed in temperatures ranging from 20-21˚C, suggesting that ACE transforming microorganisms are present at higher temperatures, and that groundwater temperatures may have assisted ACE degradation during the active loading period.

Variability was encountered at all three sites, thus making it difficult to estimate loss precisely, over extended periods of monitoring. Lower ACE and SUC values observed during the lower-loading periods in the spring and fall may be due to loss occurring within the septic tank. It was previously suggested by Robertson et al (2016) and Snider et al (2017) that SUC is likely used as a carbon source and degraded in the tank. Additionally, elevated ACE and SUC values, observed periodically, that were higher than the septic tank values, (Fig. 3.1 and Fig 4.2), suggest that source variability was even greater than the tank data suggests. Changes in biodegradation processes can also contribute to variability and have the potential to become more active over time as bacteria populations acclimate to metabolizing specific organic compounds. Additionally, similar to the results of Snider et al (2017), sweetener concentrations at Six Mile and Craiglieth, did not always mirror Cl^- concentrations, thus imparting additional error associated with the dilution correction process. Lastly, results at Long Point are subject to a high degree of uncertainty due to the likely high variability of the tank values.

6.3 Conclusions

Redox conditions have the potential to influence degradation of ACE and SUC in subsurface environments. Microorganism are adapted to specific redox zones and microbial activity drives redox condition in the subsurface in addition to geochemical reactions. In this study it is evident that sweetener loss occurred almost exclusively in the unsaturated zone, where half-lives ranged from 0.1- 2 months at the Craigleith and Six Mile Lake sites. In contrast, minimal sweetener loss was indicated in groundwater zones at these two sites, where half-lives ranged from 6-35 months.

Sweetener behaviour was uncharacteristic at the Long Point Site. It is speculated that the Bionest^{TM} module installed in 2014 may have caused the low ACE values observed in the shallow water table zone. In contrast, SUC was persistent until encountering the denitrification zone at a depth of 4 m, where degradation presumably occurred due to the denitrification process. However, it should be noted that the currently suspected source variability at Long Point was not definitely established in this study because most of the monitoring occurred during the non-loading period in the fall and winter. Source variability would presumably seriously distort the removal rates determined in this case.

Artificial sweeteners may be an adequate conservative tracer in groundwater flow systems if chemical processes are well understood. ACE may be a suitable conservative tracer in the groundwater zone due to its displayed persistence, however has been shown to be a non-quantitative tracer of wastewater in the unsaturated zone. Also, understanding key factors affecting degradation potential, can lead to the further understanding of the degradation potential of several pharmaceuticals that bypass wastewater treatment and are otherwise more harmful to the environment and human health. It is recommended that further research be undertaken assessing the underlying processes that cause oxic/suboxic environments to contribute to ACE loss within the unsaturated zone. Its degradation by products (e.g. sulfamic acid) may also be useful as wastewater tracers (George et al., 2010).

Half life 4 mo. and 12 mo.

$$t\left(\frac{1}{2}\right) = \frac{\ln 2}{K} \qquad \text{(Eq. 6.1)}$$

Decay:

$$N(t) = N_{(0)}e^{-kt} \qquad \text{(Eq. 6.2)}$$

Where,

t= time interval (t ½ for the half life)
N(t) = quantity that remains and has not yet decayed after time (t)
$N_{(0)}$ = Initial quantity
*Craigleith; average value at CR1-1.9 (shallow water table below the tile bed; age approximately 0.3 months during active sewage loading).
* Mean value at septic tank at Six Mile Lake & Long Point;
K= decay constant ($mo.^{-1}$)

Table 6.1. Mean ± sd. septic tank and well CR1-1.9 values for Cl-, ACE, SUC, dilution corrected ACE, dilution corrected SUC and SUC/ACE at the three study sites. Six Mile Lake site sampled from October 2015- October 2016 (n=6); Craigleith sampled from May 2016 to September 2017 (n=14); Long Point sweetener values were determined in a previous study (Robertson et al., 2016, September 2008- July 2011, n=13). The mean septic tank Cl^- value at Long Point was determined in the current study (June 2016, n=4).

Study Site	Cl- (mg/L)	ACE (µg/L)	SUC (µg/L)	Corrected ACE (µg/L)	Corrected SUC (µg/L)
Six Mile Lake (n=6)	138 ± 26	26 ± 8	43 ± 12	n/a	n/a
Craigleith (n=14)	85 ± 42	79 ± 40	72 ± 30	n/a	n/a
CR1-1.9 (n=10)	47 ± 18	15 ± 11	17 ± 11	25 ± 17	26 ± 16
Long Point (n=4)	80 ± 32	47 ± 20	48 ± 40	n/a	n/a

Table 6.2. Comparison of first order decay rates for ACE and SUC at the three study sites. Values were determined from the best fit trend lines (dilution corrected) shown in Figs. 6.1-6.7 for the groundwater zone. Unsaturated zone values were determined from effluent retention times in the unsaturated zone and the difference in concentrations between the tank and tile monitoring points during active loading.

	ACE Half Life (months)		**SUC Half life (months)**	
Well	**Unsaturated Zone**	**Groundwater zone**	**Unsaturated zone**	**Groundwater zone**
Craigleith (NO_3^- rich)				
CR1-1.9	0.15	n/a	0.20	n/a
CR12-0.7	n/a	2[1]	n/a	5[1]
CR12-1.0	n/a	35	n/a	35
Six Mile Lake (NH_4^+ rich)				
SM1-1.3	No loss[2]	4	No loss[2]	2
SM4-1.7	0.6	35	0.6	35
SM6-1.4	1-2	14	1-2	6
Long Point (Denitrifying)				
LP123-2.6	n/a	10[3]	n/a	9
LP123-5.5	n/a	14	n/a	5

1) CR 12-0.7 removal rates are primarily the result of only a single data value and are therefore of limited significance.

2) No sweetener loss – slight difference between tile bed and mean septic tank value

3) LP removal rates are possibly influenced by variability in the source concentrations and therefore should be viewed with caution.

Table 6.3. ACE and SUC loss rates from WWTPs, soil and groundwater established from previous studies.

Reference	Source	Removal Rate
ACE		
Falas et al (2016)	WWTP	T(1/2)= 2-3 days; 80%(aerobic)
Kahl et al (2018)	WWTP	T(1/2)= 2-3 days; 95% (aerobic)
Regnery et al (2015)	Soil column tests	T(1/2) > 700 days (suboxic) T(1/2) = 4.2 days (aerobic)
SUC		
Torres et al (2011)	WWTP	No loss (aerobic)
Buerge et al (2001)	Soil; column tests	T(1/2) = 16 ± 9 days (suboxic)
Robertson et al (2016)	Groundwater; Long Point Plume	T(1/2) = 3 months (suboxic)

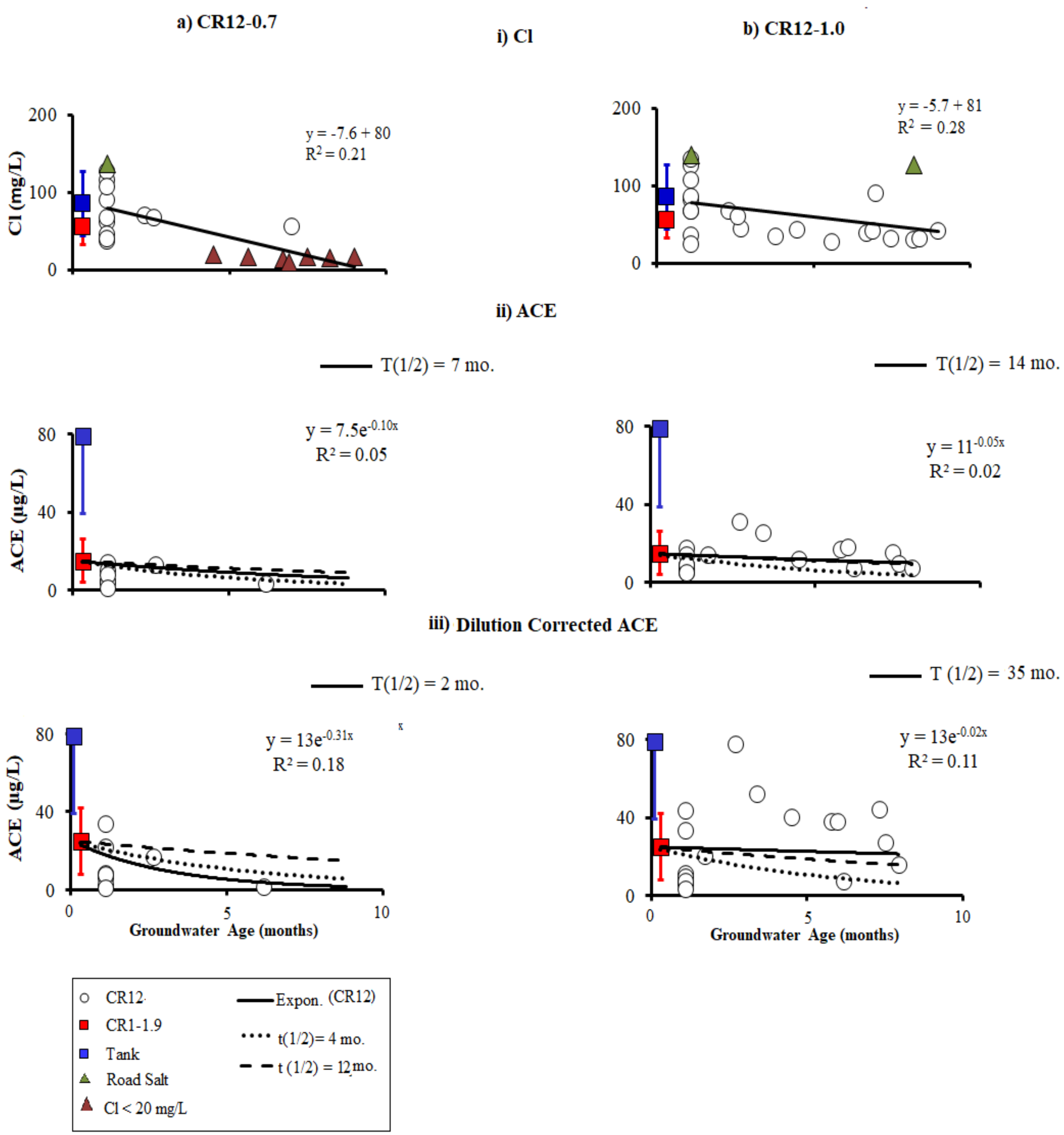


Figure 6.1. Craigleith (NO_3^- rich) site; Trends of: i) Cl^-, ii) ACE and iii) Corrected ACE with groundwater age at distal nest CR12 . Note; trend lines are initialized to the mean values at proximal well CR1-1.9 m. Samples impacted by road salt or excessive dilution (Cl < 20 mg/L) are excluded. See appendix A.2 for corrected and uncorrected ACE values.

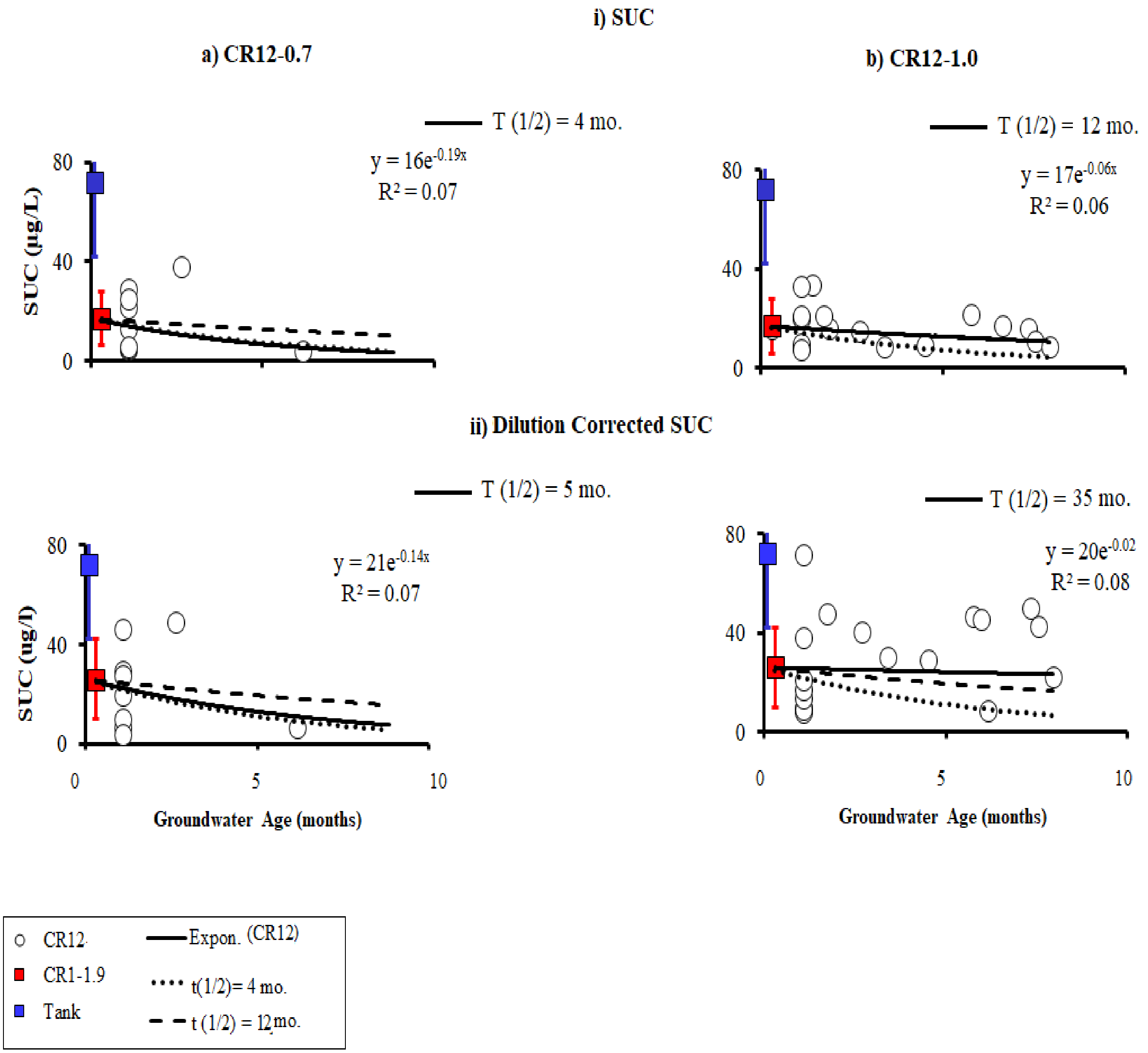


Figure 6.2. Craigleith (NO_3^- rich) site; Trends of: i) SUC and ii) corrected SUC with groundwater age at distal nest CR12 . Note; trend lines are initialized to the mean values at proximal well CR1-1.9 m. Samples impacted by road salt or excessive dilution (Cl < 20 mg/L) are excluded. See appendix A.2 for corrected and uncorrected SUC values.

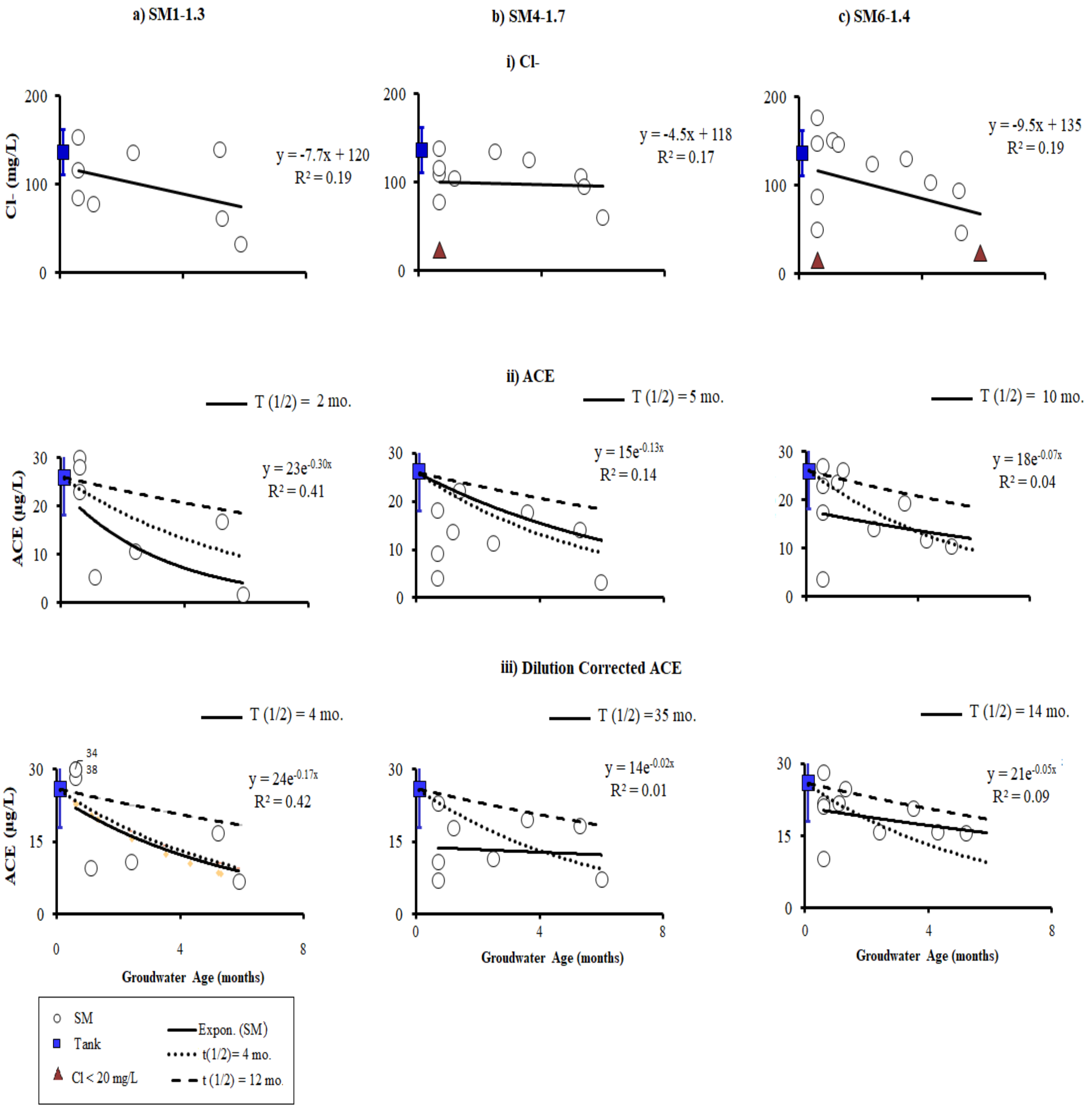


Figure 6.3 Six Mile Lake (NH_4^+ rich) site; Trends of: i) Cl^-, ii) ACE and iii) Corrected ACE with groundwater age at proximal wells SM1, SM4 and SM6 located below the tile bed. Note; trend lines for half-lives of 4 and 12 months are initialized to the mean septic tank value, whereas the trend lines for the wells are not initialized to the tank values. Samples impacted by excessive dilution (Cl < 20 mg/L) are excluded. See appendix B.2 for corrected and uncorrected ACE values.

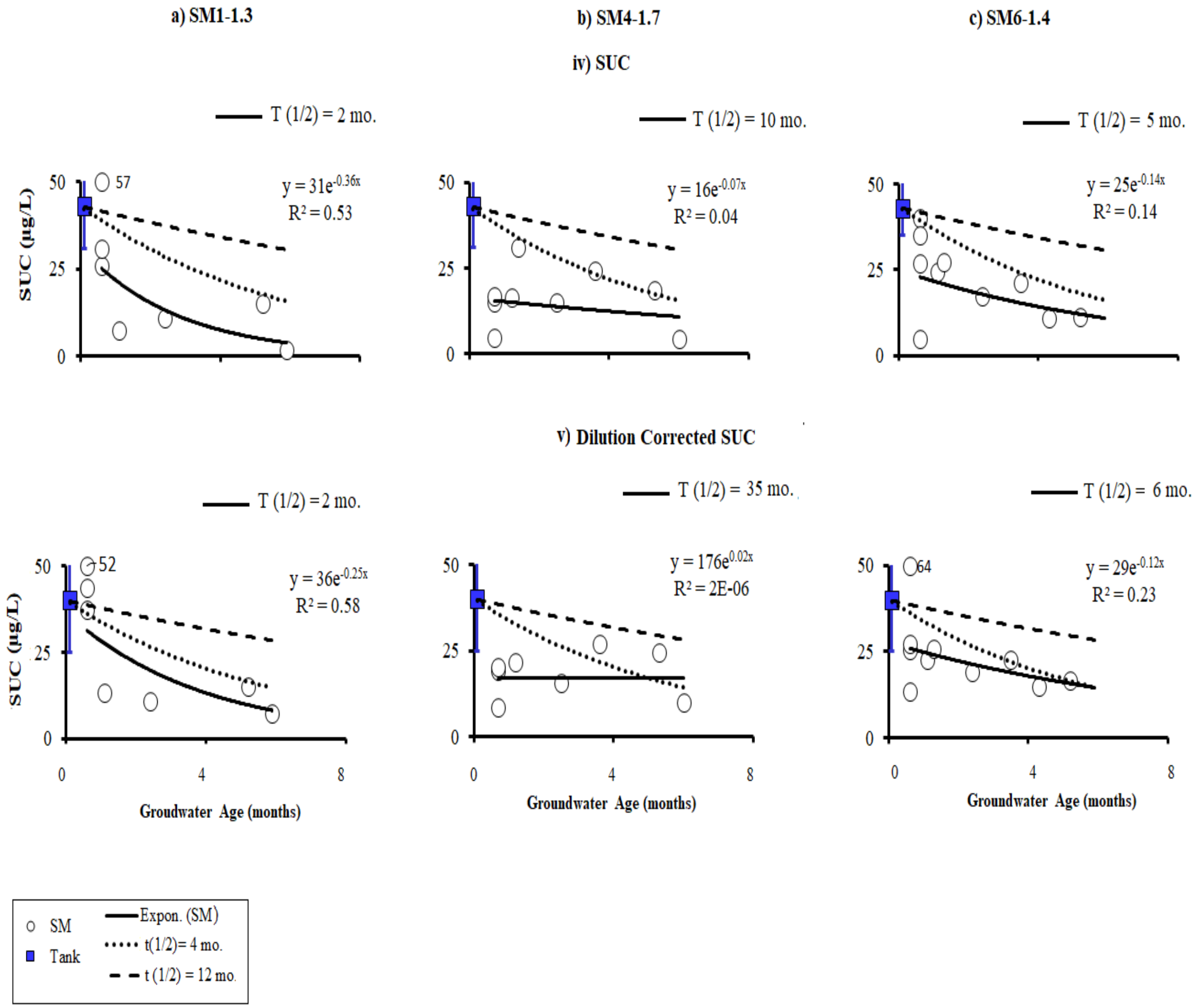


Figure 6.4. Six Mile Lake (NH_4^+ rich) site; Trends of: i) SUC and ii) corrected SUC with groundwater age at proximal wells SM1, SM4 and SM6. Note; trend lines for half-lives of 4 months and 12 months are initialized to the mean septic tank value whereas the trend lines for the wells are not initialized to the tank values. Excessively diluted samples (Cl < 20 mg/L) are excluded. See appendix B.2 for corrected and uncorrected SUC values. Dilution corrected sample from August 4, 2016 (64 ug/L) at SM6-1.4 excluded from trendline.

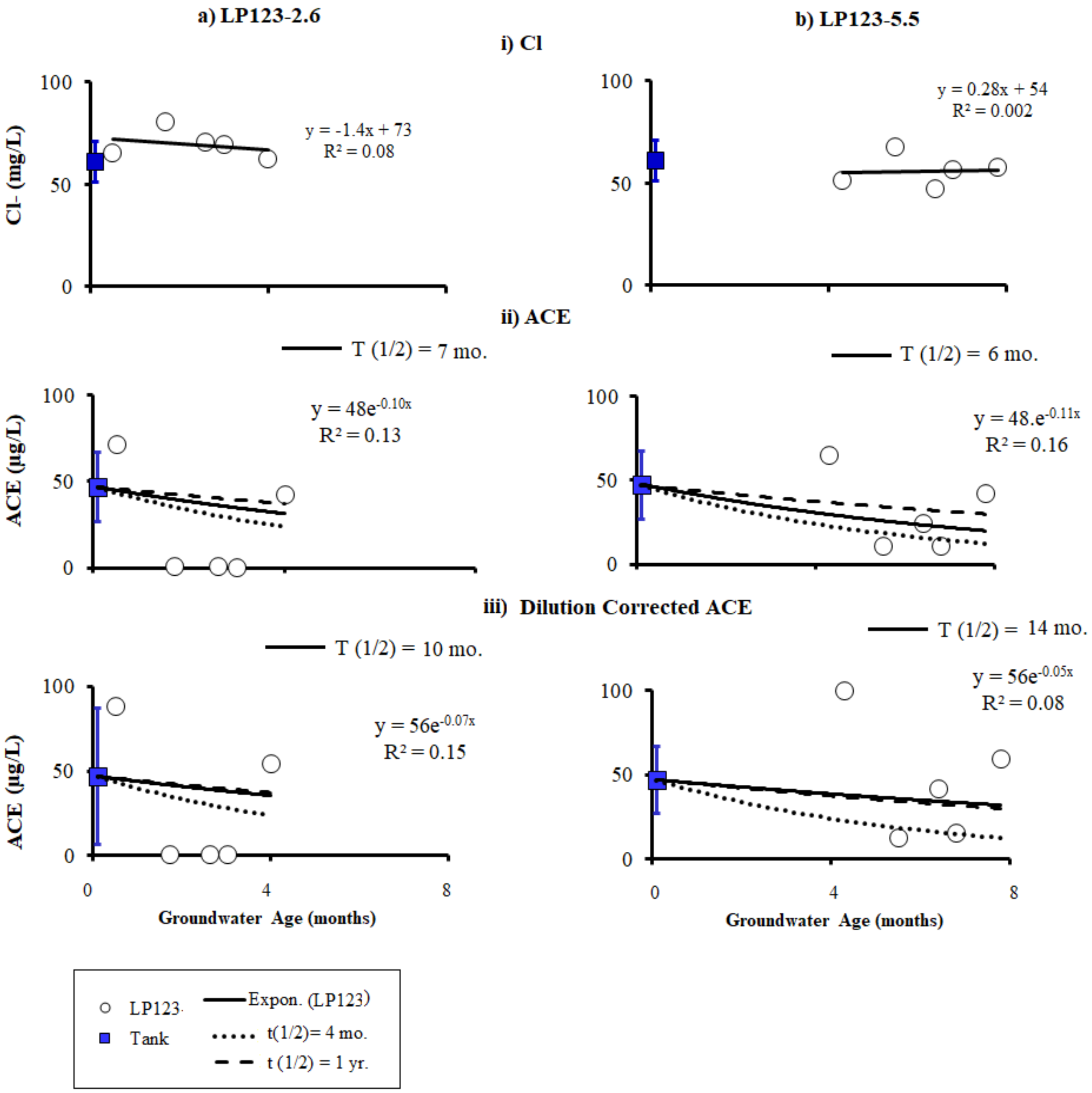
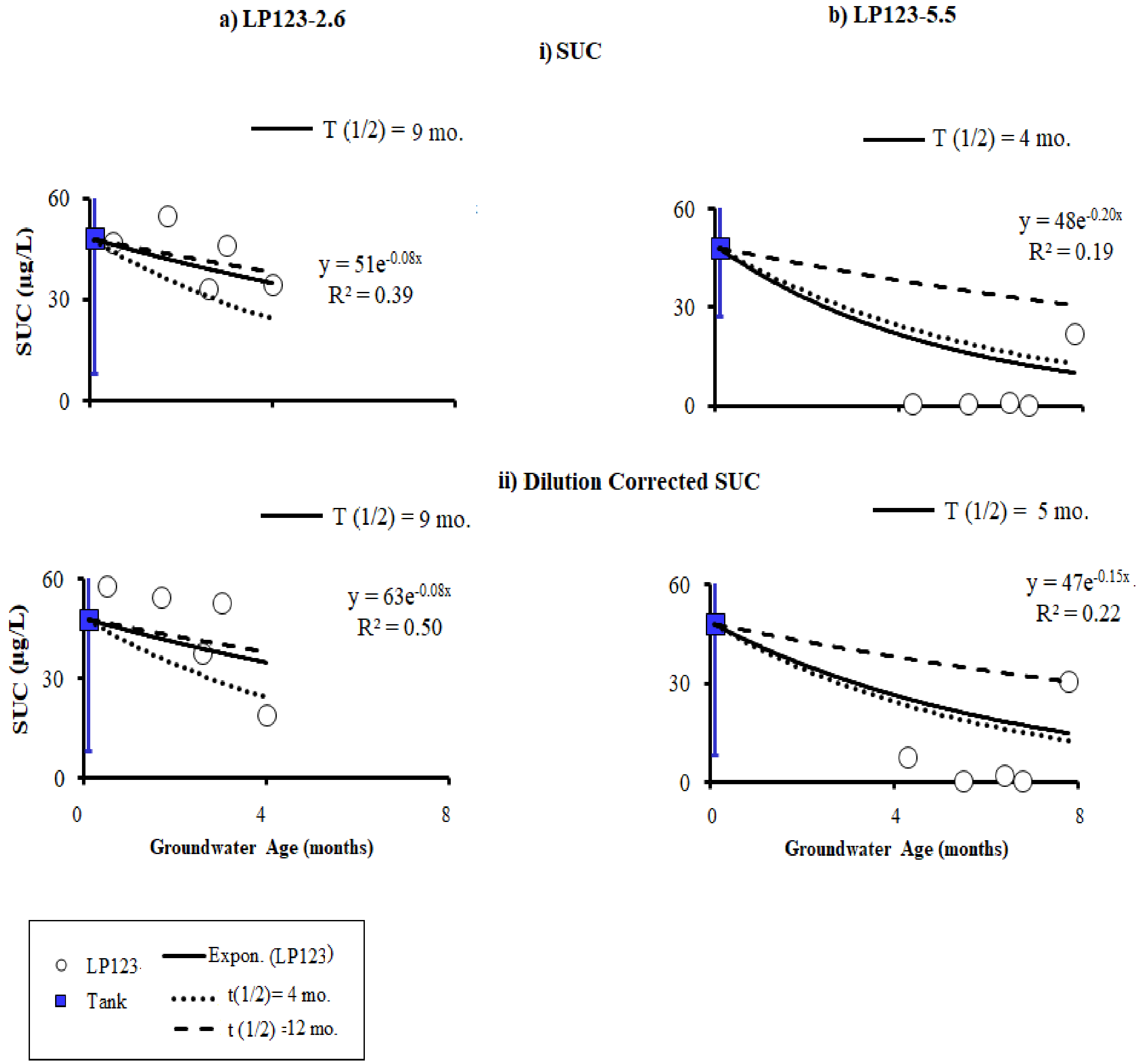


Figure 6.5. Long Point (NO_3^- depleting) site; Trends of: i) Cl^-, ii) ACE and iii) Corrected ACE with groundwater age at proximal wells LP123-2.6 m and 5.5 m located below the tile bed. Note; trend lines are initialized to the mean septic tank value. See appendix A.2 for corrected and uncorrected ACE values.


a) LP123-2.6

b) LP123-5.5

i) SUC

ii) Dilution Corrected SUC

Figure 6.6. Long Point (NO_3^- depleting) site; Trends of: i) SUC and ii) corrected SUC with groundwater age at proximal wells LP123-2.6 m and 5.5 m located below the tile bed. Note; trend lines are initialized to the mean septic tank value. See appendix A.2 for corrected and uncorrected SUC values.

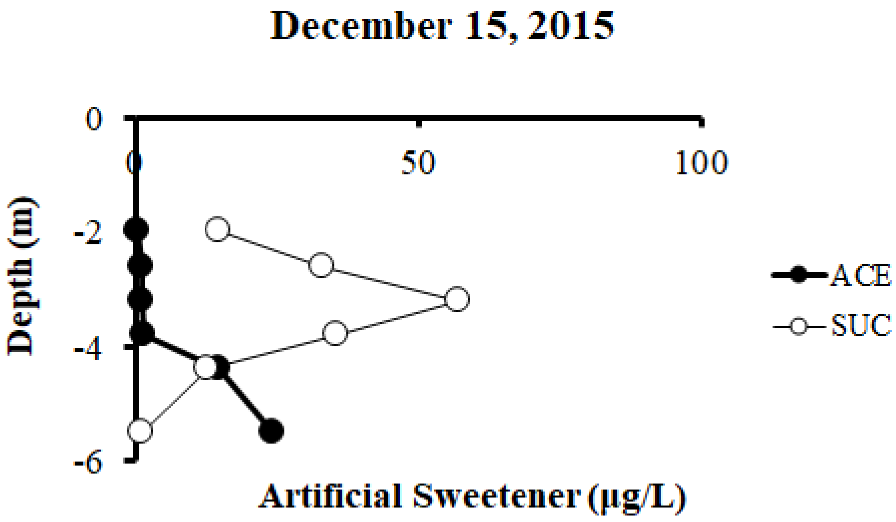


Figure 6.7. Long Point (NO_3^- Depleting) Site; concentrations of ACE and SUC with increasing depth below the subsurface at well LP123 on December 15, 2015.

Chapter 7:

Nitrogen Persistence with Groundwater Age in Three Septic System Plumes

7.1 Results

Craigleith (NO_3^- Rich) Site

Due to the relatively thick unsaturated zone present at Craigleith (~2.0 m) and the modest sewage loading rate (0.5 cm/d during active loading), the wastewater plume is well oxidized, and nitrogen occurs almost entirely as NO_3^--N. Nitrate is generally >20 mg/L whereas NH_4^+-N remains <1 mg/L (Table A.1). The nitrate isotopic values in the distal plume zone (CR12) were generally similar to values in the proximal zone (CR1) during active loading (Fig 7.1). However, during the non-loading period, as groundwater in the distal zone aged, increased values for both $\delta^{18}O$-NO_3^- (1.4-6.3‰) and $\delta^{15}N$-NO_3^- (15-23‰) were observed (Fig. 7.1, Table A.1). The slope of the enrichment lines ($\delta^{18}O$-NO_3^-: $\delta^{15}N$-NO_3^- ; 0.60-0.63; Fig 7.1c) were within the range of previous studies where denitrification was active (Long Point Provincial park; Aravena & Robertson, 1998; Killarney provincial Park; Caschetto et al., 2018; Table 7.1), providing evidence that denitrification was occurring at Craigleith. The plume core zone at CR12-1.0 m is suboxic (DO <1 mg/L, Table A.1), thus denitrification could potentially be occurring. There is a strong correlation between groundwater age and the isotopic values for both $\delta^{18}O$-NO_3^- and $\delta^{15}N$-NO_3^- (R^2=0.73-0.98; Fig 7.1). Furthermore, there is a strong relationship between $\delta^{18}O$-NO_3^- and $\delta^{15}N$-NO_3^- values (R^2=0.81-0.83; Fig 7.1), similar to other sites where denitrification is active (Table 7.1). The rate of denitrification inferred from the dilution-corrected nitrate concentrations at CR12-1.0 m, however, is extremely slow in the groundwater zone (t (1/2) = 70 months; Fig 7.2). Thus, in comparison to the other sites, it remains appropriate to refer to the Craigleith site as nitrate-persistent.

Six Mile Lake (NH_4^+ Rich) Site

Due to the shallow water table depth at Six Mile Lake (~ 1.0 m, Fig. 4.1) the wastewater is not well oxidized and nitrogen in the plume occurs predominantly as NH_4^+-N. Ammonium-N in the plume core ranges 5-105 mg/L (Table B.1) whereas NO_3^--N is generally < 1 mg/L (Table B.1) although some higher values, up to 21 mg/L are also present (Table B.1). The high NH_4^+-N values, accompanied occasionally by NO_3^--N, suggests the possibility that anaerobic ammonium oxidation (Anammox; Eq. 7.2 & 7.3) could be occurring. The trend lines of dilution-corrected TIN concentrations in the deeper monitoring points at SM1, SM4, and SM6, suggest active N attenuation with t(1/2) values ranging from 3-8 months in the groundwater zone (Table 7.3; Fig 7.4). Declining NO_3^--N values could be the result of either denitrification (E.q. 7.1) or anammox (E.q. 7.2), but the declining NH_4^+-N values, particularly at depth, where NH_4^+-N oxidation is less likely to occur, are strongly suggestive of anammox activity at this site.

Long Point (NO_3^- Depleting) Site

Elevated NO_3^--N concentrations are observed in bundle LP123 at Long Point ranging from 5-111 mg/L (Table C.1). Half-life values (8-12 months) at LP 123 suggests a slow rate of denitrification (Table 7.3; Fig. 7.5). As discussed previously in Chapter 6, the increased NO_3^--N values in the shallow depth likely reflect additional aeration provided by the Bionest^{TM} module.

7.2 Discussion

Nitrogen may be attenuated by biochemical process such as volatilization, nitrification, adsorption of NH_4^+-N, denitrification (E.q 7.1), and anaerobic oxidation of NH_4^+-N by nitrate (Anammox; E.q 7.2 and E.q 7.3) in groundwater. Anammox requires low dissolved oxygen concentrations, anammox bacteria, appropriate redox conditions and, significant ammonium and nitrate concentrations (Clark et al., 2008). In the Killarney septic system plume, which was NH_4^+-N rich, Caschetto et al (2018) observed that total inorganic nitrogen (TIN) values in deeper portions of the plume were about one third of the septic tank value due to anammox and denitrification activity (Table 7.4), suggested by isotopic enrichment of both NH_4^+-N and NO_3^--N (up to +24‰ for NH_4^+-N and +45‰ for NO_3^--N) and declining TIN concentrations. Similarly, declining NH_4^+-N and TIN values observed at the Six Mile Lake site over the inactive loading period, are also suggestive of anammox activity. Although NO_3^--N to support anammox activity was absent in many of the samples, in other samples NO_3^--N concentrations as high as 21 mg/L were present (Table B.1), indicating that partial nitrification of the wastewater was occurring. Anammox activity could potentially be occurring on August 4, 2016 when NO_3^--N and NH_4^+-N coexisted in well SM6 -1.3m at concentrations of 21 and 27 mg/L, respectively (Fig 6.2). Several sampling events also indicate that NO_3^--N and NH_4^+-N are coexisting at several of the nests up to 1 m below the subsurface (Table B.1). In some parts of the plume, it is possible that anammox activity consumed most of the available NO_3^--N shortly after nitrification occurred. This would provide an explanation for the declining NH_4^+-N values that were observed over the non-loading period, even though NO_3^--N concentrations remained low. Total Inorganic Nitrogen (TIN) loss had a half lives ranging from <0.2 months in the vadose zone to 3-7 months in the groundwater zone (Table 7.2) and likely at least partly reflect anammox activity.

Nitrogen attenuation has been previously attributed to anammox in groundwater (Robertson et al., 2012; Smith et al., 2015; Zhong et al., 2013; and Moore et al, 2011) and in landfills (Egli et al., 2001 and Liang et al., 2009). In the Long Point septic plume, NH_4+-N loss was approximately 1.2%/d, resulting in a half life value of 57 days (Table 7.4). In the groundwater plume at the Long Point Site, anammox bacteria detection belonged to the *Planctomycetalses* division of the bacteria, sequence data from molecular fingerprints have suggested bacteria from the *Can. Brocadia* and *Can. Jettenia* genera of the *Planctomycetales* as predominant community members at the Long Point Site (Robertson et al., 2012). Smith et al (2015) determined that anammox community composition was related to sampling location along the plume in Cape Cod, MA, USA plume and found that anammox bacteria *Candidatus Kuenenia* clustered in the middle of the contaminated plume in the sand aquifer. Additionally, through a series of $^{15}NO_2$ tracer tests Smith et al (2015) found that N_2 production was approximately 90% attributed to anammox at a downgradient location where NH_4^+-N values were the highest and labile organic carbon was low with an anammox rate of 9.1 nmol N L^{-1} day^{-1}.

7.3 Conclusions

The Craigleith site displayed a slow rate of denitrification as evidenced by the enrichment of both $\delta^{18}O\text{-}NO_3^-$ and $\delta^{15}N\text{-}NO_3^-$ with groundwater age. However, the removal rate was slow enough (T1/2 = 70 mo.), that the site can still be referred to as a nitrate- persistent site.

Anammox activity likely occurs at the Six Mile Lake site and is a potentially important attenuation process for nitrogen during wastewater treatment. To further enhance anammox activity, septic designs could be altered to favour the anammox activity by providing only partial nitrification of the wastewater, such that both NH_4^+-N and NO_3^--N coexist in the plume. Further investigative measures are needed to explore the N attenuation processes and biological activity at the Six Mile Lake Site by investigating microbial communities and assessing N2 production attributed by anammox and denitrification.

Denitrification

$$4NO_3^- + 5CH_2O + 4H^+ \rightarrow 2N_2 + 5CO_2 + 7H_2O \qquad \text{(Eq. 7.1)}$$

Anammox

$$NH_4^+ + NO_2^- + 4H^+ \rightarrow N_2 + 2H_2O \qquad \text{(Eq. 7.2)}$$

$$3NO_3^- + 5NH_4^+ \rightarrow 4N_2 + 9H_2O + 2H^+ \qquad \text{(Eq. 7.3)}$$

Table 7.1. Comparison of relationship between δ^{15}N-NO_3^- and δ^{18}O-NO_3^- during denitrification at Craigleith (CR12, this study) and Long Point and Killarney Park sites from previous studies.

Site	Reference	Regression Line	R^2
CR12-0.7	This Study	y= 0.63x-8.3	0.81
CR12-1.0	This Study	y= 0.60x-7.6	0.83
Killarney	Caschetto et al (2018)	y= 0.61x+1.4	0.85
Long Point	Aravena & Robertson (1998)	y= 0.46x-1.4	0.84

Table 7.2 Comparison of mean ± std. septic tank values of NH_4-N, NO_3-N and TIN at the three sites; Six Mile Lake sampled October 2015- October 2016; Craigleith sampled May 2016 to September 2017 and; Long point sampled November 2015-June 2016.

Study Site	NH4-N (mg/L)	NO3-N (mg/L)	TIN (mg/L)
Six Mile Lake (n = 6)	74 ± 18	0.24 ± 0.28	74 ± 18
Craigleith (n = 14)	108 ± 79	0.75 ± 1.9	108 ± 79
Long Point (n = 4)	6.2 ± 7.5	60 ± 19	72 ± 16

Table 7.3. Comparison of first order decay rates for TIN at the three study sites. Values were determined from the best fit trend lines (dilution corrected) shown in Figures. 7.2-7.5 for the groundwater zone. Unsaturated zone values were determined from effluent retention times in the unsaturated zone and the differences in concentrations between the tank and sub tile monitoring points during active loading.

	TIN Decay Half Life (months)	
Well	**Unsaturated Zone**	**Groundwater zone**
Craigleith[3] (NO_3^- rich)		
CR1-1.9	0.31	n/a
CR12-0.7	n/a	5[1]
CR12-1.0	n/a	70
Six Mile Lake (NH_4^+ rich)		
SM1-1.3	0.60	3
SM4-1.7	0.14	8
SM6-1.4	0.41	3
Long Point (Denitrifying)		
LP123-2.6	n/a	8[2]
LP123-5.5	n/a	12

1) CR 12-0.7 removal rates are primarily derived from a single data value and are therefore of limited significance.

2) LP removal rates are possibly influenced by variability in the source concentrations and therefore should be viewed with caution.

3) Craigleith; TIN=NO_3-N

Table 7.4. TIN removal from two septic system plumes in Ontario established from previous studies. Killarney N removal (%) reported along the flow path with respect to the septic tank effluent. Long Point N removal (t(1/2)) reported for the distal portion of the septic plume.

Reference	**Source**	**Removal**
Caschetto et al. (2018)	Killarney septic plume	60-80%
Robertson et al. (2012)	Long Point septic plume	T(1/2) = 57 days

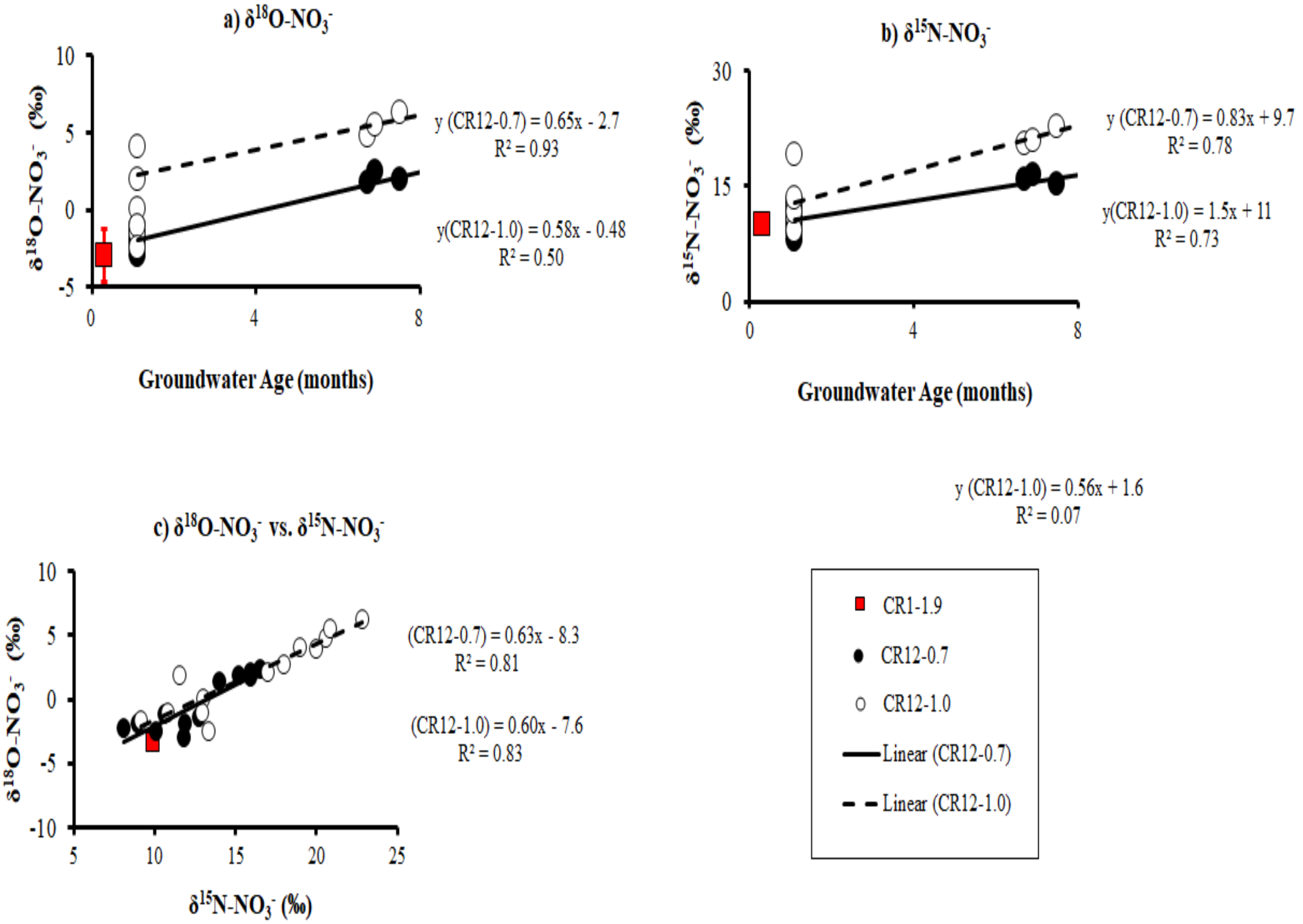
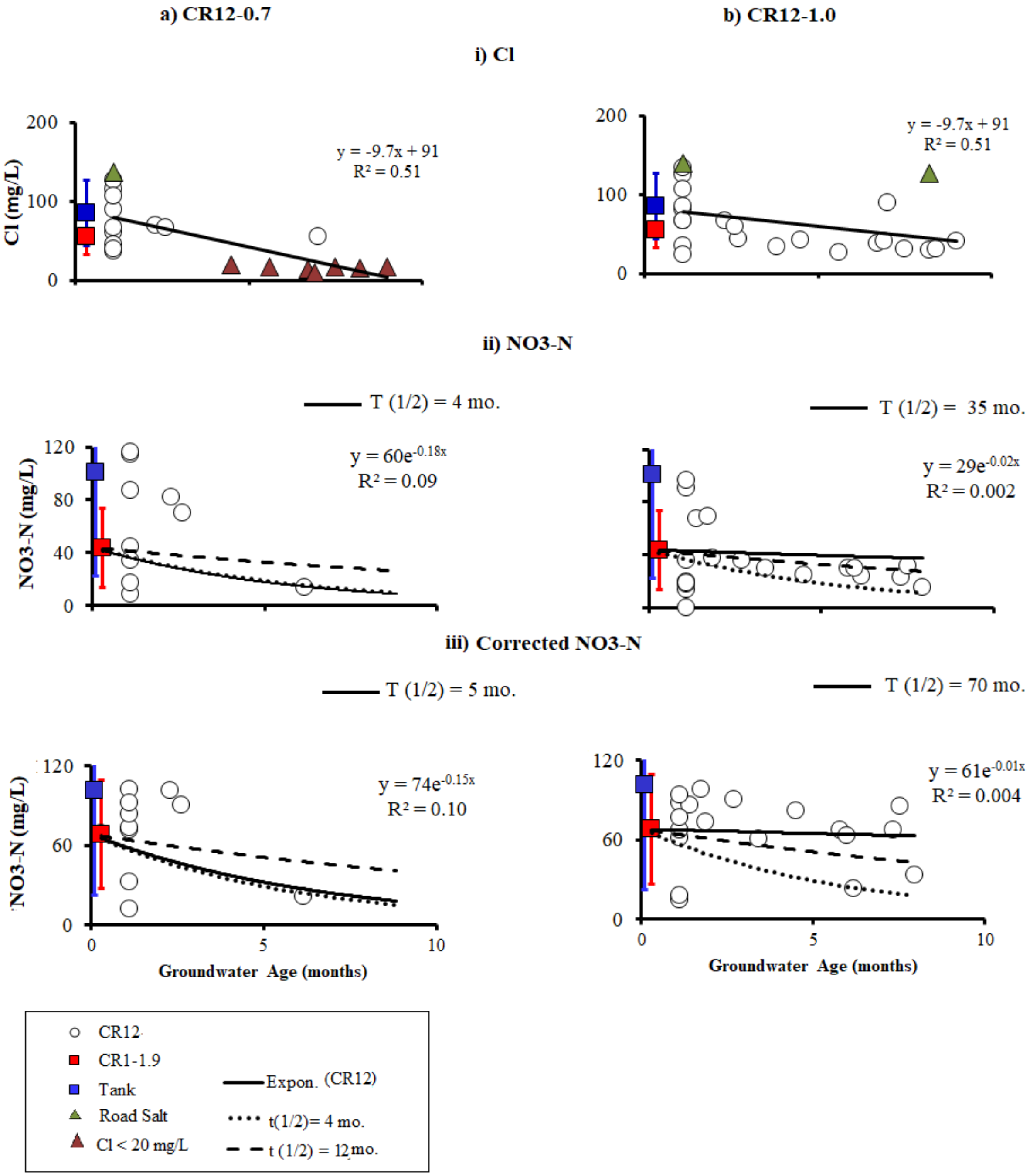


Figure 7.1. Craigleith (NO$_3^-$ rich) site; Trends of a) δ^{15}N-NO$_3^-$ b) δ^{18}O-NO$_3^-$ vs. groundwater age and, relationship between c) δ^{18}N-NO$_3^-$ vs. δ^{15}N-NO$_3^-$ at CR12. Mean ± sd CR1-1.9 values (n = 5) are also indicated. See Table A.1 for δ^{15}N-NO$_3^-$ and δ^{18}O-NO$_3$ values.



.**Figure 7.2.** Craigleith (NO_3^- rich) site; Trends of i) Cl, ii) NO_3^--N and iii) corrected NO_3-N vs. groundwater age at distal wells: a) CR12-0.7 and b) CR12-1.0. Mean septic tank values (TIN, n=14) are also shown. Note, trend lines are initialized to the mean value for the proximal tile bed monitoring point CR1-1.9. Excessively diluted samples (Cl < 20 mg/L, Table 3.1) are excluded. Samples with elevated Cl$^-$ values that were likely due to road salt impact, are also excluded (May 18- June 4, 2016 at CR12-0.7 and; May 27, 2016, May 18, 2017at CR12-1.0 (Table 3.1). See Table A.1 for corrected and uncorrected NO_3-N values.

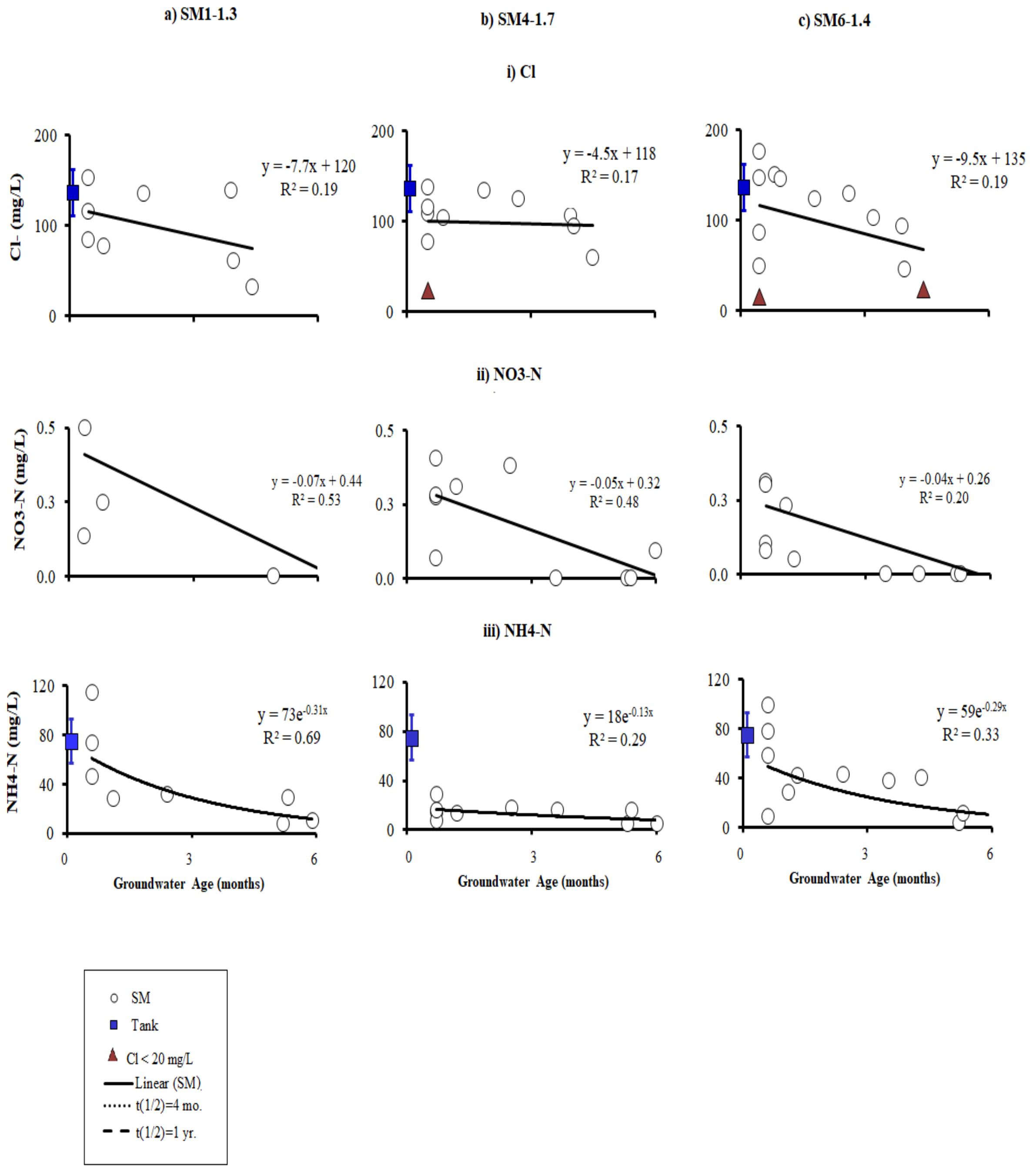


Figure 7.3 Six Mile Lake (NH_4^+ Rich) site; Trends of i) Cl-, ii) NO3-N, iii) NH4-N, at a) SM1-1.3, b) SM4-1.7 and c) SM6-1.4. Excessively diluted samples (Cl < 30 mg/L, Table 4.1) were excluded.

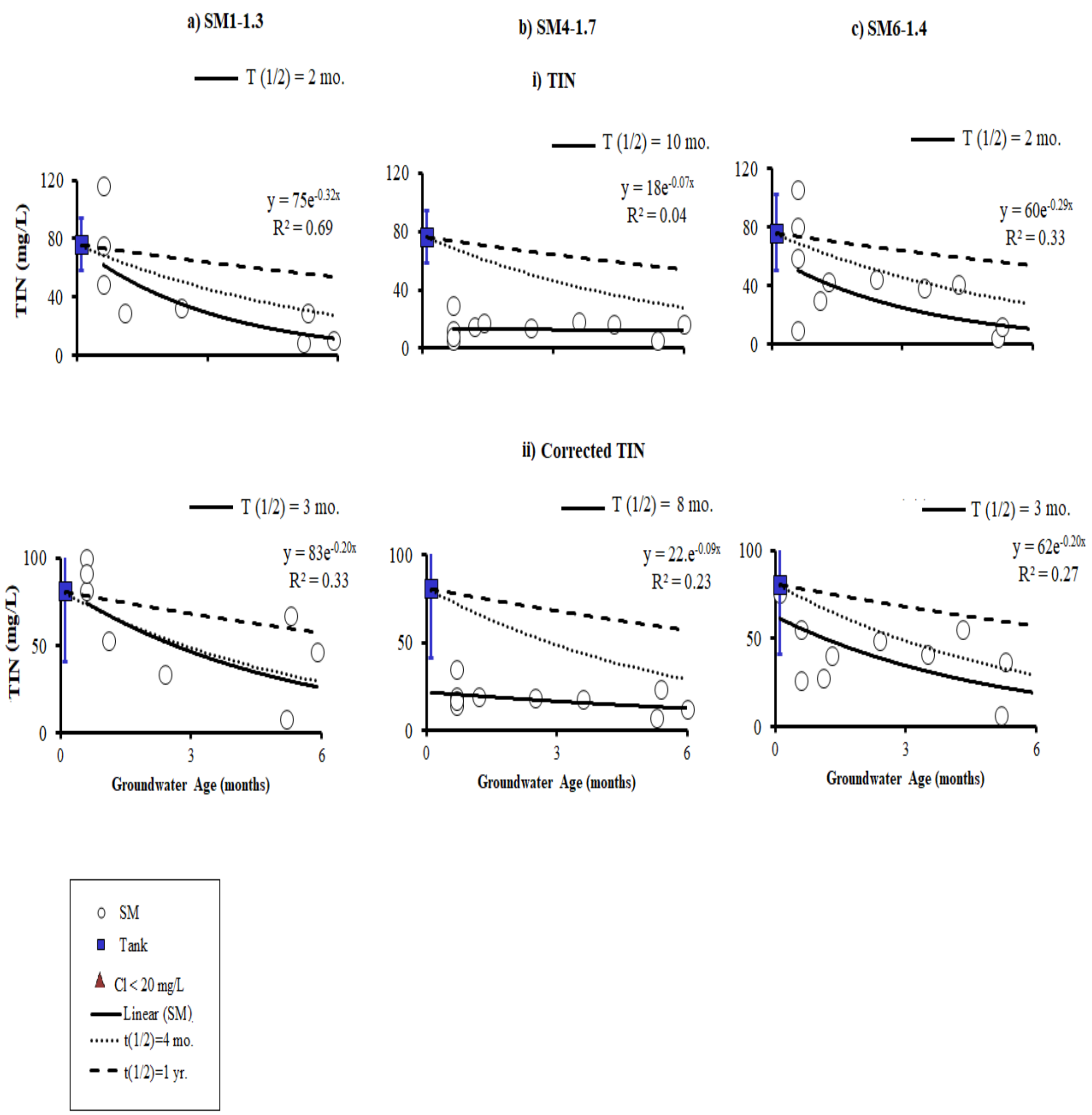


Figure 7.4 Six Mile Lake (NH_4^+ rich) site; Trends of i) TIN and ii) corrected TIN vs. groundwater age at a) SM1-1.3, b) SM4-1.7 and c) SM6-1.4. Mean ± sd. septic tank values are shown (n=6) for each parameter. Note; trend lines for half-lives of 4 months and 12 months are shown for comparison and are initialized to the mean septic tank value, whereas the trend lines for the wells are not initialized to the tank values. Excessively diluted samples (Cl < 30 mg/L, Table 4.1) were excluded. See Table B.1 for corrected and uncorrected TIN values.

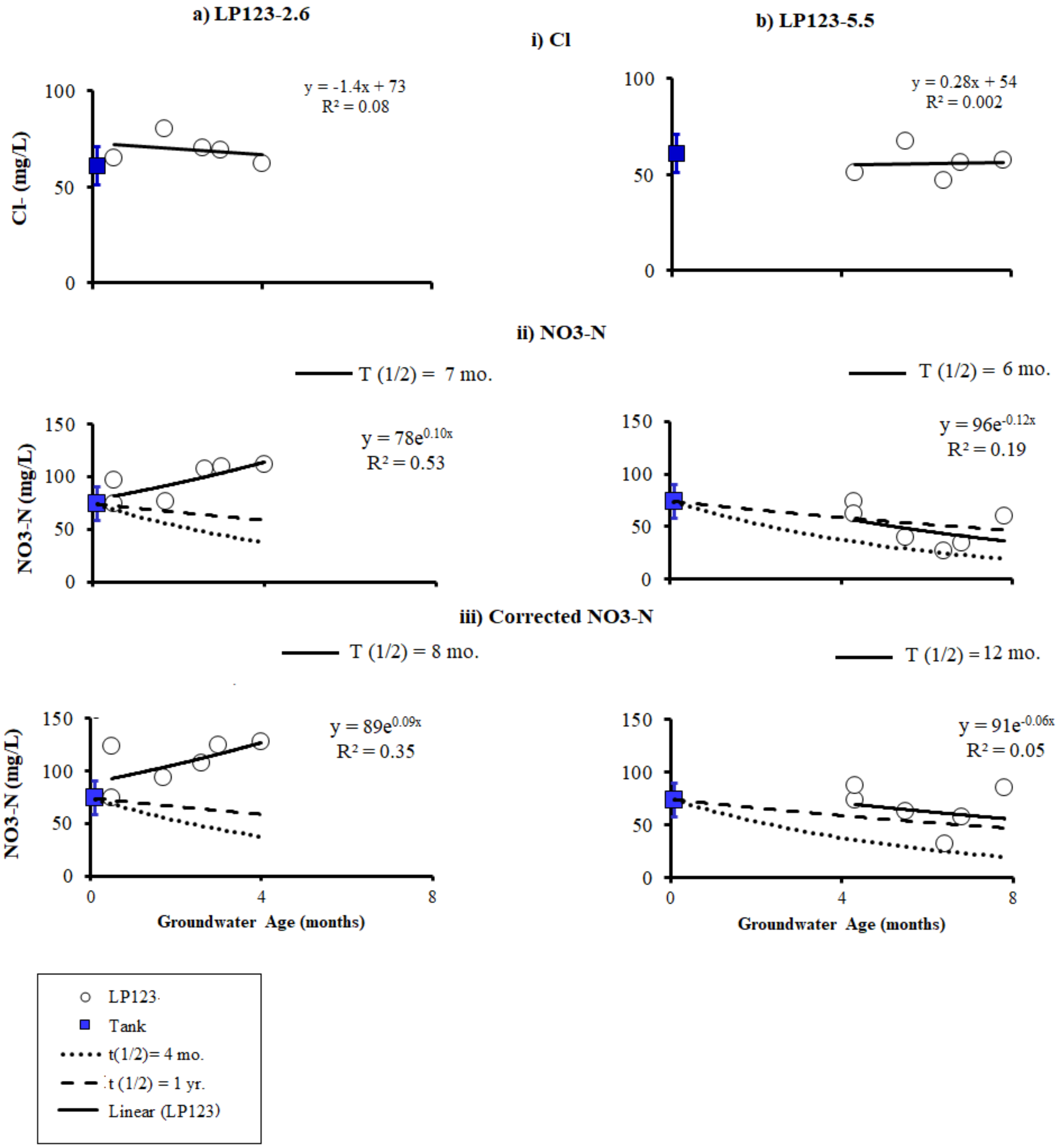


Figure 7.5. Long Pont (NO$_3^-$ depleting) site; Trends of i) Cl, ii) NO3-N and iii) corrected NO3-N vs. groundwater age at a) LP123-2.6 and b) LP123-5.5. Mean ± sd. septic tank values are shown (n=4) for each parameter. Note; trend lines for half-lives of 4 months and 12 months are shown for comparison and are initialized to the mean septic tank value, whereas the trend lines for the wells are not initialized to the tank values. See Table C.1 for corrected and uncorrected TIN values.

Chapter 8:

Phosphorus Persistence with Groundwater Age in Three Septic System Plumes

8.1 Results

Craigleith (NO_3^-rich) Site

Figure 8.1 shows that the septic tank SRP values (14 ± 4.8 mg/L) are depleted in the vadose zone (Table 8.1). However, many of the distal plume values (CR12) are close to the proximal tile bed value at CR1-1.9 (4.4 ± 1.4 mg/L; Table 8.1), indicating that SRP is not removed within the groundwater zone. Most of the phosphorus is removed in the unsaturated zone, where a half- life of only 0.21 months is indicated (Table 8.2). Figure 8.1 indicates that the rate of removal in the groundwater zone (CR12-1.0 m) is much slower, with a half life of 7 months (Table 8.2).

Six Mile Lake (NH_4^+ Rich) Site

Figure 8.2 shows that the septic tank SRP values (4.1 ± 3.1 mg/L, Table 8.1) are removed in the groundwater zone. Many of the plume values below the tile bed, are <0.1 mg/L and only a few samples exceed 1 mg/L. Thus, robust P loss in the vadose zone is indicated. Consistent with this, previous sediment coring revealed that distinct zones of elevated P accumulation were present in the filter bed sand and that these zones of P accumulation were restricted to within about 1 m below the infiltration pipes (Robertson et al., 2016). Figure 8.4 shows electron imaging of sand grains from the P enriched zone at SM1 at 0.8 m depth. Here abundant secondary coatings were present on the sand grains and these contained P (2.8-4.3 wt. %, Fig. 8.3) with Al^{3+} (17 wt. %) and Fe^{2+} (7.0-11.3 %) as the dominant cations. The substantial thicknesses of the coatings (20-

50 µm) is indicative of mineral precipitation reactions rather than sorption related processes. The groundwater plume also had elevated Fe^{2+} concentrations frequently exceeding 10 mg/L) (Table 4.1; Fig 4.1 g & h). The depth profile at nest SM1 on February 29, 2016 shows decreased porewater SRP concentrations (<0.1 mg/L) at depths below the P accumulation zone (Fig 8.5) supporting the likelihood that Fe-P mineral precipitation reactions were occurring. However, increased porewater SRP values were evident, on occasion, during the active loading period (e.g. August 4, 2016; Fig 8.5). Chemical equilibrium modelling indicated that vivianite ($Fe^{2+}_3(PO_4)_2 \cdot 8H_2O$) and hydroxyapatite ($Ca_5(PO_4)_3OH$) were generally undersaturated (SI<0; Table 8.2). Strengite ($FePO_4 \cdot 2H_2O$) was also undersaturated during the inactive loading period but exceeded saturation (SI=0.80) during active loading. However, it should be considered, that Fe^{2+}, which dominates within the plume, is likely to be oxidized to Fe^{3+} further along the plume flow path in the shallower wells where DO was frequently >5 mg/L (Table B.1). Under this scenario, strengite saturation is frequently exceeded (SI 0.81-2.9; Table 8.4). Although vivianite remains undersaturated in the plume, it is important to note that SRP concentrations would be restricted to relatively low values (0.05-0.2 mg/L) if vivianite equilibrium was achieved (Table 8.4). Thus, vivianite and strengite represent potentially important mineralogical controls on phosphorus levels in the plume. Hydroxyapatite was only oversaturated at SM6-1.4 during the active loading period (SI=0.72; Table 8.2). Of additional significance, phosphorus depletion occurred at a rapid rate in the proximal plume zone (SM1, SM4 and SM6), with a half-life of less than several weeks indicated in the unsaturated zone (Table 8.2).

Long Point (NO_3^- Depleting) Site

Figure 8.3 shows that the septic tank SRP values (12 ± 6.4, Table 8.1) are highly attenuated at LP123-5.5 m. However, some of the shallow plume values (LP12-2.6 m) are close to the septic tank tile bed indicating that most of the phosphorus is attenuated in the in the deeper groundwater zone. However, a half- life of only 1 month is indicated at LP123 (Table 8.2).

8.2 Discussion

Phosphorus behavior in this study showcases the secondary processes that can lead to immobilization of P in septic system plumes. Phosphorus attenuation, similar to that observed at the Six Mile Lake site, has been previously documented at the McRae Provincial Park Trailer Depot septic system (Robertson, 2016; Table 8.5). Here Fe^{2+} concentrations as high as 40 mg/L were observed, and electron imaging also revealed Fe-P rich secondary coatings on the sand grains. Figure 8.5 shows that when Fe^{2+} decreases during the inactive loading period and SRP also decreases. The decline in Fe^{2+} concentrations likely reflects oxidation of Fe^{2+} to Fe^{3+} during the inactive loading period. Geochemical modelling conducted at the Six Mile Lake site, further indicates the potential for mineral precipitation reactions to occur. Strengite would be supersaturated if Fe^{2+} was completely oxidized to Fe^{3+} (Table 8.4). Additionally, geochemical modelling showed that although the plume was undersaturated with respect to vivianite, saturation would occur at only slightly higher SRP concentrations of ~0.1 mg/L.

The removal of P from septic wastewater has been investigated by Chen et al (2015) via vivianite precipitation by biological iron reduction in a bench scale anaerobic sequencing batch reactor. Results indicated that the concentrations of extractable P were higher than that of aqueous P, suggesting that a certain amount of phosphorus was in the form of precipitates, where the bulk of the precipitates in reactor were mostly found to be vivianite. The lower solubility product of vivianite compared with those of other Fe-containing minerals suggests that vivianite is likely to be a more stable Fe^{2+} solid phase in some sedimentary environments when P is present and is of significance in controlling the phosphate concentrations. Chen et al (2015) demonstrated that vivianite can be the main mineral product in an Fe-amended septic system and that the strategy of P removal via iron reduction-induced vivianite precipitation in septic tanks. However, it should be noted that the chemical composition of the secondary P-containing coatings observed in this study and in previous studies (e.g. Robertson, 2008; Table 8.3), are generally highly variable and thus likely represent amorphous precursors rather than distinct mineral phases.

Phosphorus migration in the Long Point site has been extensively investigated previously over a 16-year period that detailed the advancing frontal portion of the P plume (Robertson et al., 2008). Field values indicated that first order removal rates occurred very slowly or not at all (half-life >30 years; Table 8.3), suggesting that P minerals did not precipitate in the groundwater zone. Shorter half-life values were observed at both the Craigleith and Six Mile Lake site, with half-lives ranging from 2-7 months (Table 8.2) in the groundwater zone. Thus, suggesting that P removal occurred at the Six Mile Lake and Cragleith sites at a more rapid rate than previously observed at Long Point. Note that, due to the possibility of source variability, the Long Point results could be unreliable for the determination of decay rates. Figures 8.5 and Table 8.2 indicate that the P plume remains within a single redox environment under sub oxic conditions in shallower nests, where Fe^{2+} is available. The general trend indicates that the concentrations of P and Fe^{2+} decrease with increasing depth. But Fe^{2+} increases with depth at the Long Point site (below the denitrification front) in Robertson and Garda (2018). Previous investigations in the Cambridge and Langton septic plumes indicted that although substantial P retardation is observed, the rates of P migration are nearly 1 m/a (Robertson et al., 1998). Zones of P enrichment in the Cambridge, Langton and Muskoka septic plumes were found within the vadose zone below the tile bed confined to narrow intervals 1 m below the infiltration pipes, coinciding with the position of the redoxcline where NH_4^+-N is converted to NO_3^--N (Zanini et al., 1998). Additionally, the halt of loading at two septic systems (Long Point 2 and Langton) indicated that P persisted in the vadose zone following decommissioning, and that the frontal part of the P plume continued to migrate after sewage loading had ceased (Robertson and Harman, 1999). The persistence of P after loading had ceased in the groundwater zone at the Langton and Long Point 2 sites indicated that P was being released from the sediments.

8.3 Conclusion

In summary, substantial P removal was noted in the vadose zones and proximal plume zones at these sites. However, P that is transported into the groundwater zone, will continue to be retarded by precipitation of P-minerals, but has the potential to remain mobile and ultimately to impact downgradient surface water bodies. Biochemical precipitation may be a new strategy to artificially enhance P retention in anaerobic septic systems. This may be incorporated into engineered septic tile beds.

Table 8.1. Mean ± std. septic tank SRP values at the three sites. Also included is the mean SRP value in the proximal plume zone below the tile bed at Craigleith (CR1-1.9). Six Mile Lake site sampled October 2015- October 2016 (n=6); Craigleith site sampled May 2016 to September 2017 (n=14); Long Point site sampled November 2015-June 2016 (n=4).

Site	SRP (mg/L)	Dilution Corrected SRP (mg/L)
Six Mile Lake-tank (n = 6)	4.4 ± 3.1	n/a
Craigleith-tank (n = 14)	14 ± 4.8	n/a
CR1-1.9 (n=9)	4.3 ± 1.4	6.8 ± 3.4
Long Point-tank (n = 4)	12 ± 6.4	n/a

Table 8.2. Comparison of first order decay rates for SRP at the three study sites. Values were determined from the best fit trend lines (dilution corrected) shown in Figs. 8.1-8.3 for the groundwater zone. Unsaturated zone values were determined from effluent retention times in the unsaturated zone and the difference in concentrations between the tank and sub tile monitoring points during active loading.

	SRP Half Life (months)	
Well	**Unsaturated Zone**	**Groundwater zone**
Craigleith (NO_3^- rich)		
CR1-1.9	0.21	n/a
CR12-0.7	n/a	2[1]
CR12-1.0	n/a	7
Six Mile Lake (NH_4^+ rich)		
SM1-1.3	<0.1	2
SM4-1.7	<0.1	2
SM6-1.4	<0.1	4
Long Point (Denitrifying)		
LP123-2.6	n/a	1[2]
LP123-5.5	n/a	1

1) CR 12-0.7 decay rates are primarily the result of only a single data value and are therefore of limited significance.

2) LP decay rates are possibly influenced by variability in the source concentrations and therefore should be viewed with caution.

Table 8.3. P removal established at four suboxic septic plumes in Ontario. Percent (%) removal at the Cambridge and Muskoka septic plume established from the long-term breakthrough of PO_4; the difference between the septic tank effluent and proximal plume. Removal at the Langton site pertains to the vadose zone and was established from the comparison of effluent and proximal plume core PO_4 concentrations. Half-life value at the Long Point site pertains to loss in the groundwater zone in the proximal plume.

Reference	Source	Removal Rate
Robertson (2003)	Cambridge septic plume Muskoka septic plume	11% 95%
Robertson & Harman (1999)	Langton septic plume	80%
Robertson et al (2008)	Long Point septic plume	T(1/2) >30 years

Table 8.4. Six Mile Lake (NH_4^+ rich) site; Chemical equilibrium modelling (wells SM1-1.3. SM4-1.7 and SM6-1.4) of samples collected during inactive (February 29, 2016) and active loading (August 4, 2016). Mineral saturation Indices (SI) for hydroxyapatite, strengite and vivianite are shown. Also shown are the modelled SRP values that would occur at vivianite and strengite equilibrium (SI = 0.0) and strengite SI values for the case where all Fe has been oxidized to Fe $^{3+}$.. SI values calculated using the geochemical modelling program PHREEQC (Parkhurst & Appelo, 2013).

Parameter	In-active loading			Active loading		
	SM1-1.3	**SM4-1.7**	**SM6-1.4**	**SM1-1.3**	**SM4-1.7**	***SM6-1.1**
pH	6.2	6.1	6.1	7.8	7.4	7.5
[1]pe	5.1	5.5	5.2	n/a	n/a	n/a
Temperature (˚C)	1.0	2.2	3.0	32	24	27
DO (mg/L)	0.29	0.35	0.31	0.53	0.41	0.78
[2]Alkalinity (mg/L as $CaCO_3$)	254	272	234	n/a	n/a	n/a
Fe^{2+} (mg/L)	7	3	0.8	<0.1	6	0.1
Mg^+ (mg/L)	27	28	11	12	13	15
Ca^{2+} (mg/L)	93	79	40	43	43	44
Na^+ (mg/L)	66	59	26	43	27	42
K+ (mg/L)	4	9	8	5	9	17
Al^{3+} (mg/L)	0.3	0.1	0.9	<0.1	<0.1	<0.1
Cl^- (mg/L)	135	106	93	152	115	125
[3]SO_4^{2-} (mg/L)	11	0.73	10	1.6	3.8	5
NH4-N (mg/L)	8.4	5.5	4.3	115	29	27
SRP (mg/L)	0.02	0.02	0.09	0.02	0.01	0.16
[4]SRP_{viv} (mg/L)	0.1	0.2	0.2	0.06	0.05	0.05
[5]SRP_{streng} (mg/L)	5.5	4.2	2.7	76	4.5	18
Hydroxyapatite SI	-10	-11	-10	-0.43	-3.6	0.72
Strengite SI	-0.21	-0.26	-0.03	-1.7	0.80	-0.07
[6]$Strengite_{Fe3+}$ SI	2.9	-0.03	2.6	-1.7	0.81	-0.07
Vivianite SI	-4	-5.4	-5.6	-14	-6.3	-9.6

*Active-loading SM6-1.4 cation data unavailable.
[1]pe calculated from Eh (mV) using Eq. 8.1
[2]Alkalinity and Eh values obtained during the inactive loading period. Values additionally used in the geochemical model for the active loading period.
[3]Value recalculated for PHREEQC; SO_4^{2-} as S(6)
[4]SRP concentrations if vivianite SI=0
[5]SRP concentrations if strengite SI=0
[6]Strengite SI if all Fe is oxidized to Fe^{3+}

Table 8.5. Six Mile Lake (NH_4^+ Rich) Site; Eh value used to calculate redox potential (pe) at SM1-1.3, SM4-1.7 and SM6-1.4 and used in the geochemical modelling program PHREEQC to determine SI of minerals in table 8.2. Eh values are field values obtained during inactive loading (February 29, 2016).

	SM1-1.3	SM4-1.7	SM6-1.4
Eh (mV)	284	308	290

$$pe = \frac{Eh\ x\ F}{2.303RT} \qquad \text{(Eq. 8.1)}$$

pe= Redox Potential (suboxic)
Eh (mV)= Redox Potential
F= Faradays Constant (cal/V)
R= 8.314 cal/K
T= Temperature; 283K

Vivianite

$$3Fe^{2+} + 2H_3PO_4 \leftrightarrow Fe_3(PO_4)_2 + 6H^+ \qquad \text{(Eq. 8.2)}$$

Strengite

$$Fe^{3+} + H_3PO_4 \leftrightarrow FePO_4 + 3H^+ \qquad \text{(Eq. 8.3)}$$

Hydroxyapatite

$$5Ca^{2+} + 3H_3PO_4 + e^- \leftrightarrow Ca_5(PO_4)_3 + 9H^+ \qquad \text{(Eq. 8.4)}$$

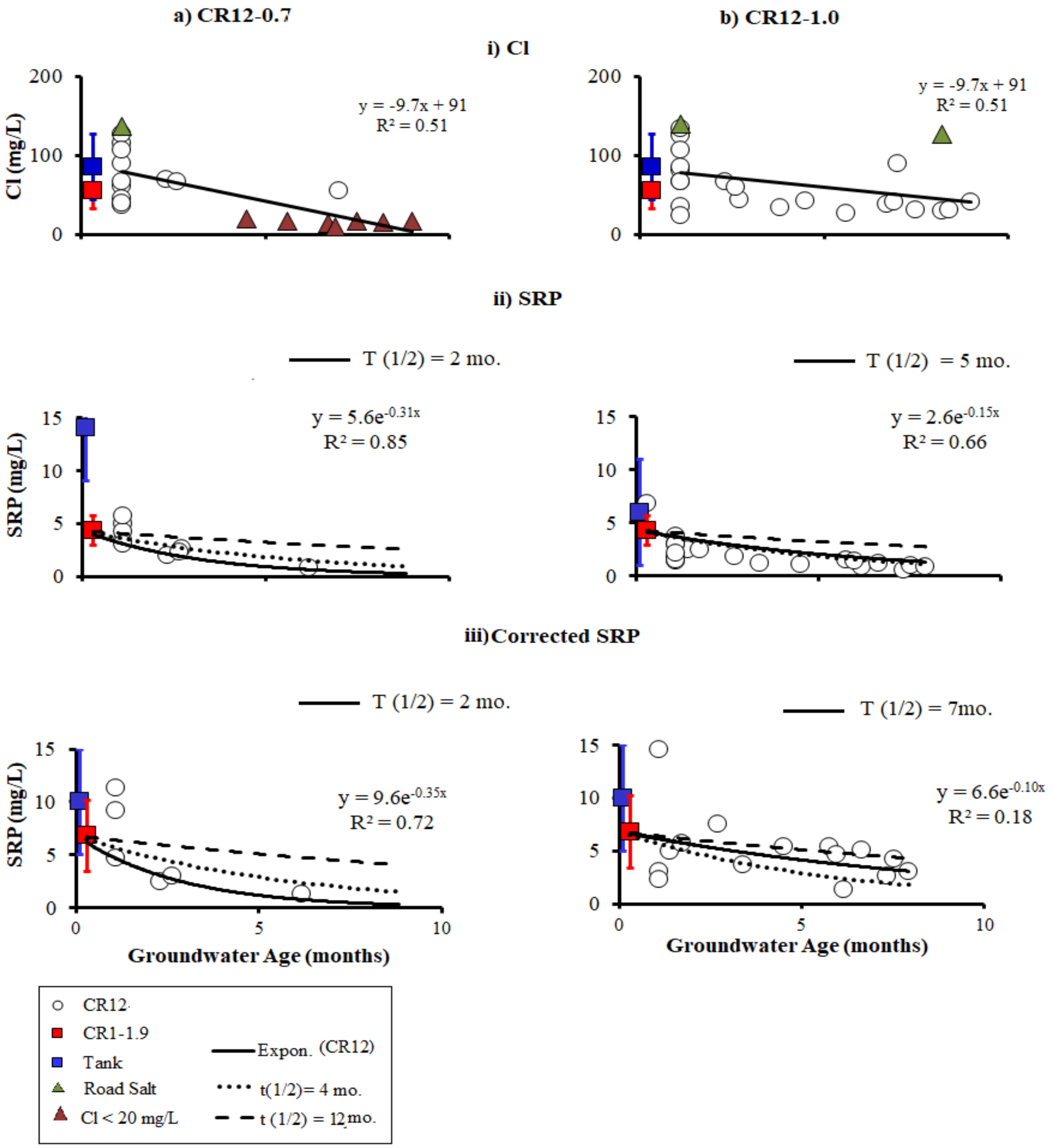


Figure 8.1. Craigleith (NO$_3^-$ Rich) site; Trends of i) Cl, ii) SRP and iii) Dilution Corrected SRP vs. groundwater age at a) CR12-0.7 and b) CR12-1.0. Mean SRP septic tank ± sd. values are shown (n=14). Trend lines are compared to modelled decay curves with a half life values of 4 months and 12 months respectively. CR1-1.9 mean (n = 10) as the initial value where the groundwater age is approximately 0.3 months. Excessively diluted samples (Cl < 20 mg/L, Table 3.1) were excluded from panels ii-iii; February 28-January 25, 2016 and from February 22-May 18, 2017 at CR12-0.7 (Table 3.1). Sampling events with high Cl- values due to suspected road salt intrusion were also excluded; May 18- June 4, 2016 at CR12-0.7 and; May 27, 2016, May 18, at CR12-1.0 (Table 3.1). See Table A.1 for uncorrected and corrected SRP values.

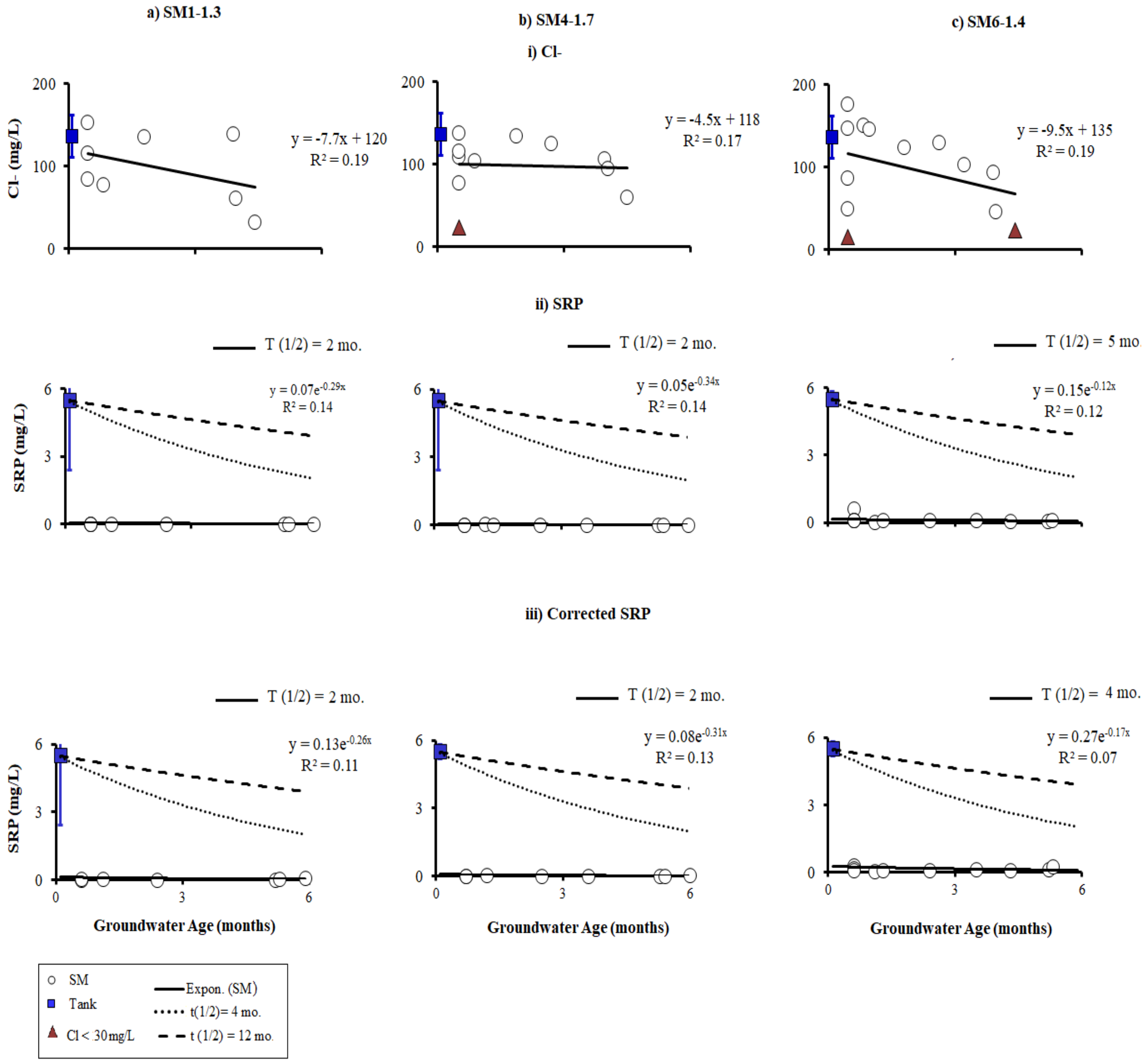


Figure 8.2 Six Mile Lake (NH_4^+ Rich) site; Trends of i) Cl, ii) SRP and iii) Dilution Corrected SRP at a) SM1-1.3, b) SM4-1.7 and c) SM6-1.4. Mean ± sd. septic tank values are shown (n=6) for each parameter. Modelled decay curves shown for half lives of 4 and 12 months are also shown. Diluted Cl values (< 30 mg/L) are excluded from panel ii (Table 4.2). See Table B.2 for uncorrected and corrected SRP values.

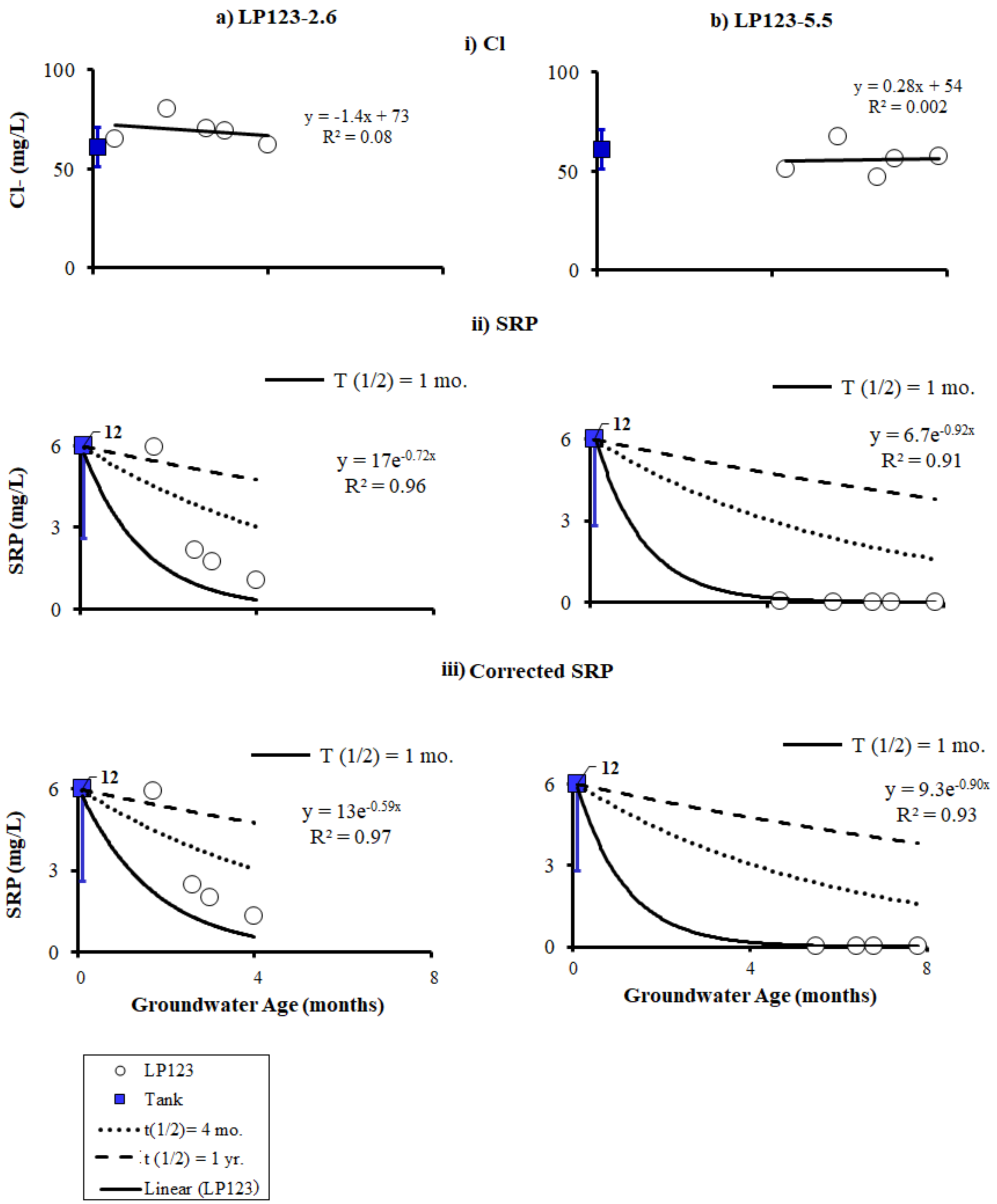
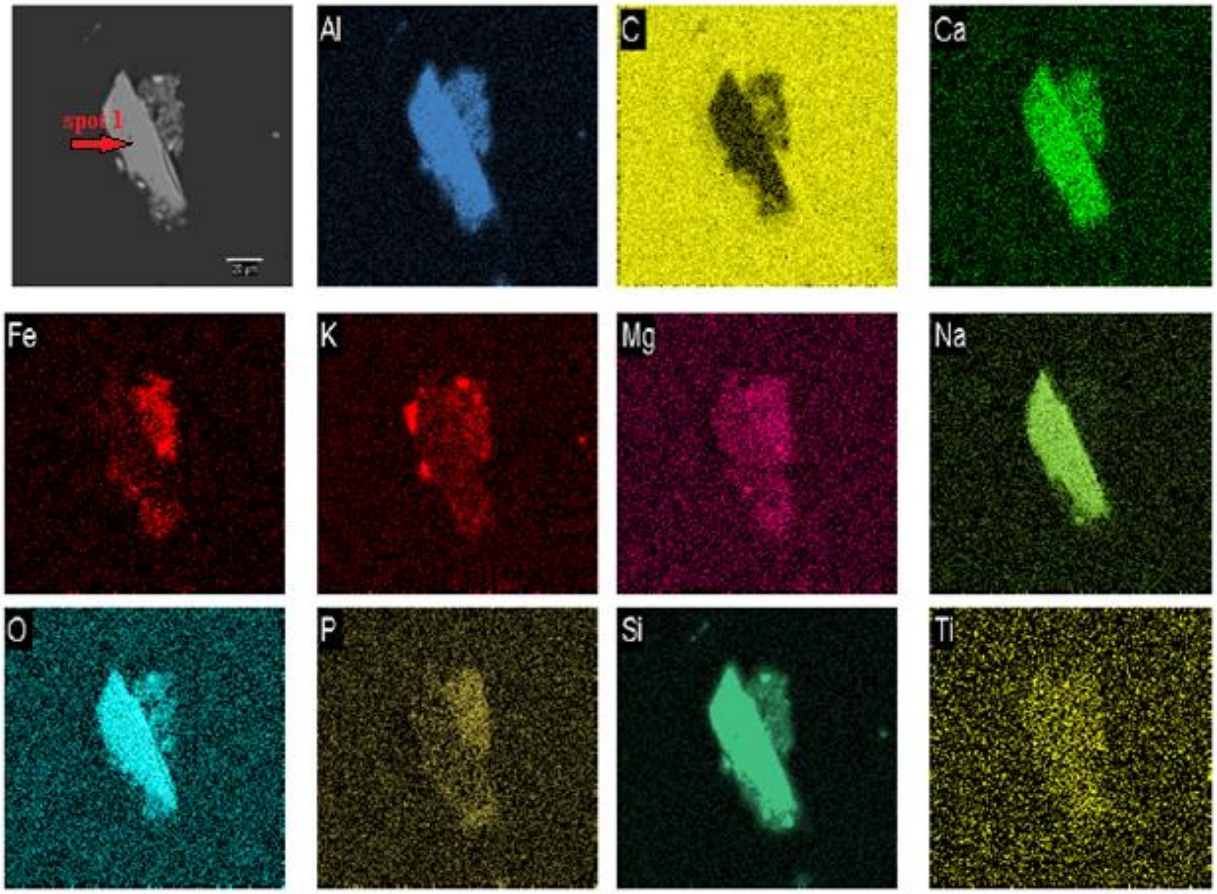
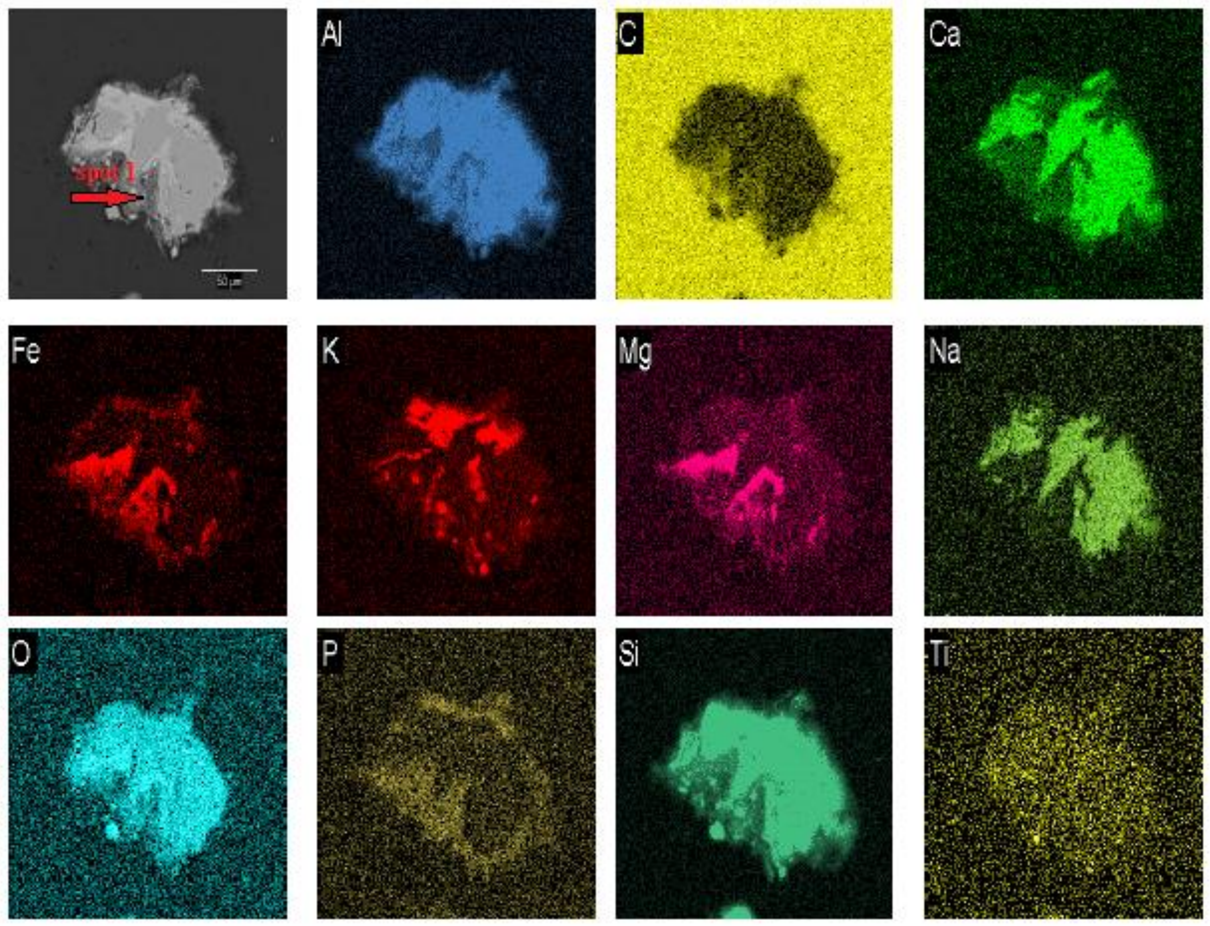


Figure 8.3. Long Point (NO_3^- Depleting) site; Trends of i) Cl, ii) SRP and iii) Dilution corrected SRP vs. groundwater age at a) LP123-2.6 and b) LP123-5.5. Mean ± sd. septic tank values are also shown (n=4) for each parameter. Also shown are modelled decay curves half lives of 4 and 12 months. See Appendix C.1 for uncorrected and corrected SRP values.



Area 1	O	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe
Spot 1	35.6	1.8	17.6	25.4	4.3	0.8	1.0	2.4	3.5	0.7	7.0



Area 2	O	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe
Spot 1	34.9	3.8	17.2	24.1	2.8	0.8	0.5	2.0	2.1	0.4	11.3

Figure 8.4. Back scattered electron images and X-ray elemental compositions of two sand grains from core sample SM1-0.8m depth. Both panels show secondary Fe-Al-P coatings of considerable thickness (~20-50 µm) on primary plagioclase grains. (adapted from Robertson et al,,2016).

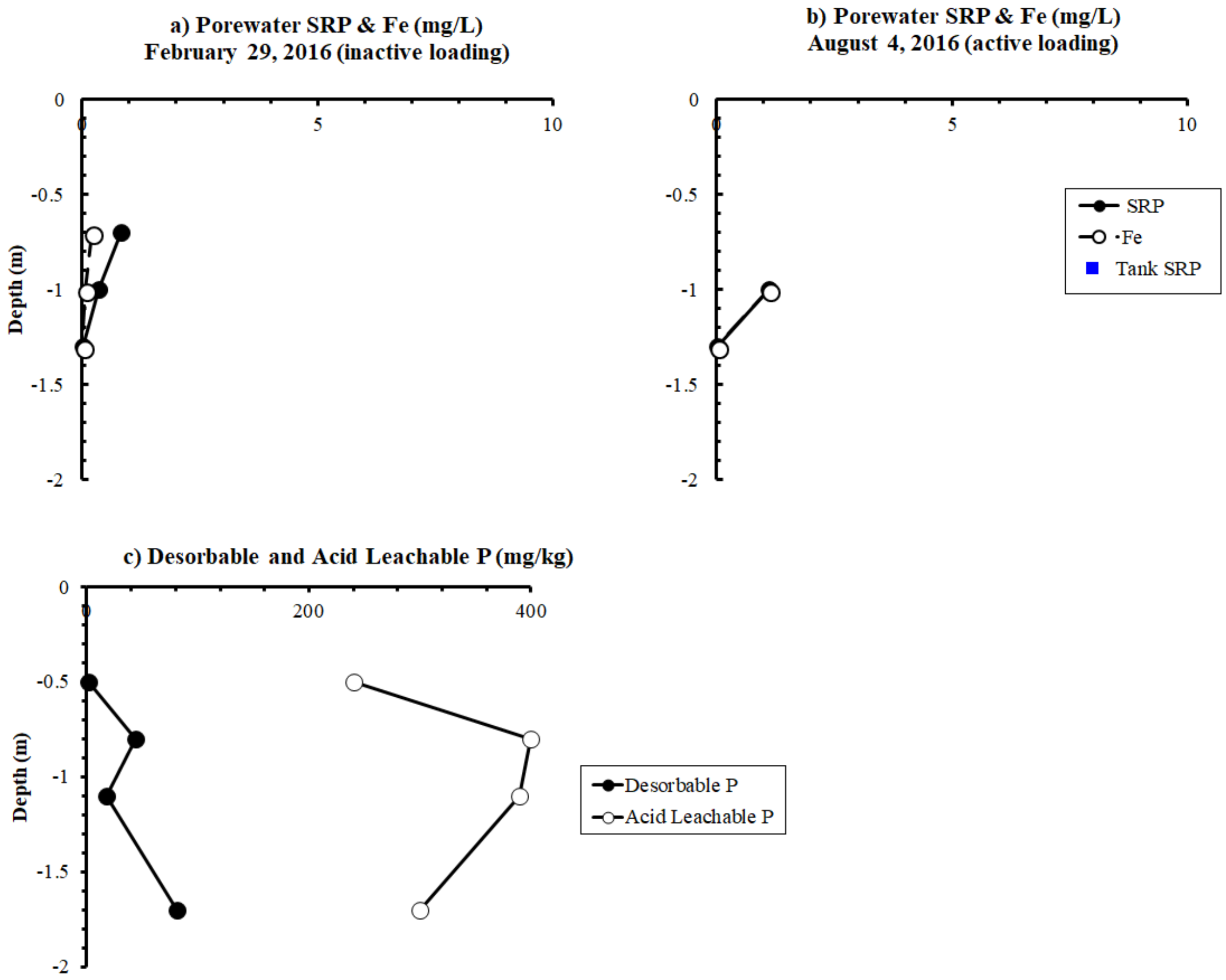


Figure 8.5. Six Mile Lake (NH_4^+ rich) site; Depth profiles of SRP and Fe at bundle SM1 during : a) Inactive-loading (February 29, 2016) and b) Active-loading (August 4, 2016). Also shown are sediment profiles of: c) sediment desorbable and acid leachable P at SM1 (data from Robertson et al., 2016).

Chapter 9:

Summary and Conclusions

The current investigation was to determine decay rates and monitor the behaviour of N, P and artificial sweeteners in three septic system plumes that offered differing redox conditions, with particular attention given to their behaviour during the non-loading period. The plume zones of interest were located directly below the infiltration beds and directly down gradient. The sites were selected to represent the range of redox condition: Craigleith; NO_3^- rich, Six Mile Lake; NH_4^+-rich, Fe reducing, and Long Point; NO_3^- depleting. This study provided a novel investigative approach for assessing contaminant degradation in septic plumes and has provided new insight into N, P and artificial sweetener persistence and degradation in the groundwater zone.

Groundwater sampling for cations, anions, TP, SRP, NH_4^+-N, NO_3^--N, and artificial sweeteners took place during the on-loading and off-loading periods at the three sites. Monthly sampling occurred from July 2015 to August 2017 at Craigleith, from October 2015 to October 2016 at Six Mile Lake and, from November 2015 to December 2016 at Long Point. Groundwater samples were obtained from multilevel bundle piezometers, and septic tank samples were obtained during the on-loading periods.

Groundwater ages during active loading were estimated at each of the three sites (E.q 3.1 and E.q. 3.2), where vertical velocities were estimated from the average sewage loading rate and an assumed water content of 10% in the vadose zone and 35% in the groundwater zone. Groundwater age was estimated from projected velocities and travel distances in the unsaturated zone. In the deeper monitoring points, downward flow under saturated conditions was assumed. Groundwater ages during inactive loading were estimated by adding the number of in-active loading days to the active loading groundwater age. At Craigleith, groundwater ages at nests CR12 located 10 m beyond the edge of the tile bed were also estimated using seasonal breakthrough of EC, where increasing EC values in the spring/summer indicated the arrival of wastewater from the new loading season.

Chloride (Cl^-) was used as the conservative tracer at all three sites including during the non-loading period. Some sampling events, particularly near the end of the winter period, exhibited low Cl^- values indicating dilution and these samples were excluded from rate calculations. Measured concentrations of ACE, SUC, NO_3^--N, TIN and SRP were further refined to correct for dilution by multiplying the uncorrected concentrations by the mean septic tank Cl^- concentration and then dividing by sample Cl^- concentration.

Important findings are summarized below;

Artificial Sweeteners

- Sweetener decay rates (monitored and corrected for dilution concentrations) were compared to best fit first-order decay rates of 4 and 12 months.
- Sweetener loss occurs almost exclusively in the unsaturated zone ($t1/2 < 2$ months) but was relatively persistent in the groundwater zones at both the Craigleith and Six Mile Lake sites, where $t1/2 > 35$ months occurs.
- ACE degradation appears most active under nitrification and high oxygen availability as showcased particularly at the Craigleith site, consistent with some wastewater treatment plant studies.

- Persistence of SUC are well documented in saturated zones (Buerge et al., 2009; Torres et al., 2011).
- Uncharacteristically low ACE values in the shallow water table zone observed at the Long Point site are likely due to newly installed pre-treatment module (Bionest^{TM}).
- SUC was persistent at the Long Point site until the denitrification zone was encountered at approximately 4 m depth and was then subsequently degraded.

Nitrogen

- N removal rates (monitored and corrected for dilution concentrations) were compared to best fit first-order decay rates of 4 and 12 months.
- The wastewater plume is well oxidized, and nitrogen occurs almost entirely as NO_3^--N at Craigleith.
- Increases of both $\delta^{18}O$-NO_3^- (1.4-6.3‰) and $\delta^{15}N$-NO_3^- (15-23‰) during non-loading and the relationship between $\delta^{18}O$-NO_3^- and $\delta^{15}N$-NO_3^- ($R^2 = 0.81$-0.83) indicated that denitrification was active, although at a slow rate.
- Slow rate of denitrification is inferred at Craigleith (t(1/2)= 70 months). Therefore, Craigleith was referred to as nitrate-persistent.
- At Six Mile Lake the wastewater plume is not well oxidized, and nitrogen occurs mostly as NH_4^+-N.
- NH_4^+-N depletion accompanied by NO_3^--N removal, suggested that anammox activity may be occurring.
- Declining NH_4^+-N values are strong evidence of anammox activity at Six Mile Lake

Phosphorus

- SRP decay rates (monitored and corrected for dilution concentrations) were compared to best fit first-order decay rates of 4 and 12 months.
- Most of the SRP is attenuated in the unsaturated zone at all three sites.
- SRP is highly attenuated in the groundwater plume particularly at the Six Mile Lake site, where concentrations are generally below 1 mg/L.
- Sediment coring at Six Mile Lake revealed distinct zones of elevated P accumulation and secondary mineral coatings with Al^{3+} and Fe-P composition, indicative of attenuation by mineral precipitation. .
- Fe^{2+} was also prominent in the plume at Six Mile Lake (> 10 mg/L)
- Chemical Equilibrium modelling suggests that when the Fe^{2+} is eventually oxidized to Fe^{3+} , almost complete P attenuation is likely to occur in the form of Fe-P mineral precipitates.
- Consistent with mineral precipitation, rapid SRP depletion in the proximal plume zone is noted at Six Mile Lake, with half-lives less than several weeks indicated.

Chapter 10:

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Appendix A

Craigleith Tile Bed- Geochemical, Field and Artificial Sweetener Data

Table A.1. Craigleith (NO_3^- Rich) Site; Detailed concentrations of Electrical Conductivity (EC), Dissolved Oxygen (DO), Cl^-, $SO4^{2-}$, Fe^{2+}, Na^+, Mg^{2+} Al^{3+}, K^+, Ca^{2+}, NO3-N, NO3/Cl, Corrected for dilution NO3-N, NH4-N, N-15, O-18, soluble reactive phosphorus (SRP), Corrected for dilution SRP, and total phosphorus (TP) throughout the experimental period from July 2015 to September 2017.

Well	EC (μs/cm)	DO (mg/L)	Cl (mg/L)	SO_4^{2-} (mg/L)	Fe^{2+} (mg/L)	Na^+ (mg/L)	Mg^{2+} (mg/L)	Al^{3+} (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	NO_3-N(mg/L)	NO3/Cl	Corrected NO3 (mg/L)	NH_4-N (mg/L)	N-15 (‰)	O-18 (‰)	SRP (mg/L)	SRP/Cl	Corrected SRP (mg/L)	TP (mg/L)
1-Jul-15, event 1																				
CR-22-0.8			17	83							0.18	0.01	0.93				1.3	0.08	6.5	
-1			22	113							0.13	0.01	0.50				1.0	0.05	3.9	
CR-23-0.8			14	74							0.26	0.02	1.6				1.2	0.08	7.2	
-1			23	39							0.05	<0.01	0.19				1.2	0.05	4.5	
CR-24-0.6			13	56							0.30	0.02	1.9				0.15	0.01	0.92	
-0.8			20	99							0.34	0.02	1.5				1.3	0.07	5.6	
CR-CK5													<0.01				0.35			
CR-21-1.2			28	141							0.07	<0.01					0.7	0.02	2.1	
CR-22-0.8			16	92							0.05	<0.01					0.8	0.05	4.3	
-1			18	104							0.10	0.01	0.48				0.5	0.03	2.5	
CR-23-0.8			13	75							0.06	<0.01					1.0	0.08	6.5	
-1			24	126							0.10	<0.01					1.0	0.04	3.5	
CR-24-0.6																	0.2			
-0.8			18	101							0.10	0.01	0.50				0.7	0.04	3.3	
26-Oct-15, event 2																				
CR-1-1.9	920	4	33	28							51	1.5	129				4.0	0.12	10.2	
-2.2	887		40	24							16	0.4	35				1.0	0.03	2.2	
CR-8-0.6	832		24	22							25	1.0	88				3.3	0.14	11.7	
-0.9	1160		45	52							51	1.1	97				2.5	0.06	4.8	
CR-12-0.7	1078	<0.5	37	36							45	1.2	103				4.9	0.13	11.4	
-1	1077		35	59							36	1.0	87				3.7	0.11	8.9	
CR-16-0.9	1126		45	77							15	0.34	29				0.04	<0.01	0.08	
CR-21-0.9	1139	0.5	40	34							51	1.3	109				2.1	0.05	4.4	
-1.2	1155		43	68							42	1.0	83				0.52	0.01	1.0	
CR-22-0.8	1172		38	39							44	1.2	99				1.1	0.03	2.5	
-1	1155		45	80							42	0.95	81				1.1	0.02	2.0	

Well	EC (µs/cm)	DO (mg/L)	Cl (mg/L)	SO_4^{2-} (mg/L)	Fe^{2+} (mg/L)	Na^+ (mg/L)	Mg^{2+} (mg/L)	Al^{3+} (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	NO_3-N(mg/L)	NO3/Cl	Corrected NO3 (mg/L)	NH_4-N (mg/L)	N-15 (‰)	O-18 (‰)	SRP (mg/L)	SRP/Cl	Corrected SRP (mg/L)	TP (mg/L)
CR-23-0.8	1170		23	22							28	1.2	105				1.9	0.08	7.2	
-1	1129		40	48							47	1.2	100				1.0	0.03	2.2	
CR-24-0.6	1220		45	35							49	1.1	91				0.29	0.01	0.54	
-0.8	1178		30	36							33	1.1	94				0.87	0.03	2.5	
CR-CK5	1047		40	133							17	0.43	36				0.85	0.02	1.8	
9-Dec-15, event 3																				
CR-12-0.7	1145	0.5																		
-1	1173	0.7	44	72							38	0.9	73							
4-Jan-16, event 4																				
CR-12-0.7	1041																2.7			
-1	1182		34	40	<0.1	24	13	0.9	13	112	36	1.1	92				1.9	0.06	4.7	
24-Jan-16, event 5																				
CR-12-0.7	730	5	20	25							14	0.70	60				1.6	0.08	6.9	
-1	1190		42	121	<0.1	24	15	0.9	14	121	30	0.72	61				1.1	0.03	2.3	
28-Feb-16, event 6																				
CR-12-0.7	860	4	17	60	<0.1	9	5	0.9	7	51	12	0.71	60				1.5	0.09	7.5	
-1	1118		26	30	<0.1	9	5	0.9	5	60	25	1.0	82				1.0	0.04	3.3	
CR-CK5																	0.44			
18-Apr-16, event 7																				
CR-12-0.7	837		55	21							14	0.25	22				0.86	0.02	1.33	
-1	897		89		<0.1	25	16	0.9	16	85	24	0.27	23				0.86	0.01	0.82	
CR-CK5	710																0.26			
27-May-16, event 8																				
CR-12-0.7	739																			
-1	769		127	86	<0.1	7	3	0.9	5	43	25	0.20	17				3.7	0.03	2.5	
CR-CK	760																0.01			
6-Jun-16, event 9																				
CR-12-0.7	660																			
-1	788																			
CR-CK																	0.46			

Well	EC (µs/cm)	DO (mg/L)	Cl (mg/L)	SO_4^{2-} (mg/L)	Fe^{2+} (mg/L)	Na^{+} (mg/L)	Mg^{2+} (mg/L)	Al^{3+} (mg/L)	K^{+} (mg/L)	Ca^{2+} (mg/L)	NO_3- N(mg/L)	NO3/Cl	Corrected NO3 (mg/L)	NH_4-N (mg/L)	N-15 (‰)	O-18 (‰)	SRP (mg/L)	SRP/Cl	Corrected SRP (mg/L)	TP (mg/L)
24-Jun-16, event 10																				
CR-12-0.7	693																			
-1	912																			
21-Jul-16, event 11																				
CR-1-1.9	1248																0.48			
CR-12-0.7	1197		69	39							82	1.2	101				0.37	0.01	0.45	
-1	1127		67	57							68	1.0	86				0.33	<0.01	0.41	
21-Oct-16, event 13																				
CR-12-0.7	1561		66	47	>DL	40	20	0.8		211	70	1.1	90			26	2.4	0.04	3.0	
-1	1494		60	62	>DL	38	19	0.9		178	69	1.2	98			25	2.5	0.04	3.5	
22-Feb-17, event 14																				
CR-12-0.7	578	4	14	15							11	0.78	67	0.01	16	1.8	1.5	0.11	9.3	
-1	1123	1.5	38	88							31	0.79	67	0.02	21	4.8	1.5	0.04	3.3	
28-Feb-17, event 15																				
CR-12-0.7	505		9.2	13							7.1	0.77	66	0.03	17	2.4	3.0	0.33	28	
-1	1100		40	99							30	0.75	63	0.01	21	5.5	1.4	0.03	2.9	
18-Mar-17, event 16																				
CR-12-0.7	755		17	29							16	0.92	78	<0.01	15	1.9	1.3	0.07	6.3	
-1	1168		30	126							20	0.66	56	0.02	23	6.3	1.1	0.04	3.1	
9-Apr-17, event 17																				
CR-12-0.7	607		15	18							11	0.75	64	0.01	20	2.1	2.1	0.14	12	
-1	939		29	75							23	0.79	67	<0.01	16	4.0	0.55	0.02	1.6	
15-Apr-17, event 18																				
CR-12-0.7	785		20	34							23	1.1	98	<0.01	14	1.4		<0.01	<0.01	
-1	1126		31	85							31	1.0	85	0.03	17	2.1	1.0	0.03	2.6	
6-May-17, event 19																				
CR-12-0.7	498		17	10							6.3	0.38	32	0.01		-2.7	1.7	0.10	8.5	
-1	694		41	100							16	0.39	33	0.01	18	2.8	0.9	0.02	1.8	
18-May-17, event 20																				
CR-12-0.7	701		115	26							21	0.18	15	0.02		-2.2	2.1	0.02	1.5	
-1	757		140	47							21	0.15	13	0.03		-1.1	1.1	0.01	0.67	

Well	**EC (µs/cm)**	**DO (mg/L)**	**Cl (mg/L)**	**SO_4^{2-} (mg/L)**	**Fe^{2+} (mg/L)**	**Na^+ (mg/L)**	**Mg^{2+} (mg/L)**	**Al^{3+} (mg/L)**	**K^+ (mg/L)**	**Ca^{2+} (mg/L)**	**NO_3-N(mg/L)**	**NO3/Cl**	**Corrected NO3 (mg/L)**	**NH_4-N (mg/L)**	**N-15 (‰)**	**O-18 (‰)**	**SRP (mg/L)**	**SRP/Cl**	**Corrected SRP (mg/L)**	**TP (mg/L)**
4-Jun-17, event 21																				
CR-1-1.9	1176		39	13							8.5	0.22	18	0.07	6.6		3.5	0.09	7.5	
-2.2	1190												0							
CR-12-0.7	1218		126	24							18	0.14	12	0.02		-1.9	2.4	0.02	1.6	
-1	1411		81	49							14	0.17	14	0.10			1.8	0.02	1.9	
13-Jun-17, event 22																				
CR-1-1.9	790		68	22							29	0.43	37	0.27	7.4		5.4	0.08	6.7	
-2.2	701										18									
CR-12-0.7	790		60	22							8.8	0.15	12	0.21		-1.1	3.3	0.06	4.7	
-1	792		85	57							18	0.21	18	0.34	15	0.10	1.4	0.02	1.4	
20-Jun-17, event 23																				
CR-1-1.9	914		77	31							59	0.77	65	0.59	9.5	-2.0	4.6	0.06	5.1	
-2.2																				
CR-12-0.7	760																			
-1	779		66	83							20	0.30	26	0.09	19	4.1	1.5	0.02	1.9	
28-Jun-17, event 24																				
CR-1-1.9	1000		36	16							20	0.54	46	0.22						
-2.2			58	27							14	0.24	21							
CR-12-0.7	650		45	58							17	0.38	32	0.90						
-1	888		67	8.0							0.35	0.01	0	0.34						
14-Jul-17, event 25																				
CR-1-1.9	650		30	7.5							5.7	0.19	16	5	11	-1.5				
CR-12-0.7	900		137	65							115	0.84	71	0.54	10	-2.5				
-1	888		125	59							91	0.73	62	0.87	9.2	-1.6				
28-Jul-17, event 26																				
CR-1-1.9	894	4	82	41							76	0.92	78	0.24	10	-2.9	5.0	0.06	5.1	2.8
CR-12-0.7	860	0.5	39	29							34	0.86	73	0.27	13	-1.4	4.3	0.11	9.2	
-1	876		24	21							19	0.79	67	n.d	13	-1.0	3.0	0.12	11	
10-Aug-17, event 27																				
CR-1-1.9	944		48	23							60	1.3	107	0.70	9.9	-4.5	6.8	0.14	12	3.1
CR-12-0.7	846		89	44							87	1.0	83	0.20	12	-1.9	5.7	0.06	5.4	

Well	**EC** (µs/cm)	**DO** (mg/L)	**Cl** (mg/L)	**SO_4^{2-}** (mg/L)	**Fe^{2+}** (mg/L)	**Na^+** (mg/L)	**Mg^{2+}** (mg/L)	**Al^{3+}** (mg/L)	**K^+** (mg/L)	**Ca^{2+}** (mg/L)	**NO_3-N**(mg/L)	**NO3/Cl**	**Corrected NO3** (mg/L)	**NH_4-N** (mg/L)	**N-15** (‰)	**O-18** (‰)	**SRP** (mg/L)	**SRP/Cl**	**Corrected SRP** (mg/L)	**TP** (mg/L)
-1	844		106	60							97	0.91	78	2	12	1.9	2.9	0.03	2.4	
30-Aug-17, event 28																				
CR-1-1.9	949	4	84	56							91	1.1	92	13	9.4	-5.6	2.5	0.03	2.5	6.4
CR-12-0.7	910	0.5	107	58							116	1.1	93	3.6	12	-3.0	3.0	0.03	2.4	7.3
-1	912		134	82							141	1.1	90	1.2	13	-2.5	2.1	0.02	1.3	4.4

Table A.2. Craigleith (NO$_3^-$ Rich) Site; Detailed concentrations of Cl$^-$, artificial sweeteners Acesulfame (ACE), ACE/Cl, corrected for dilution ACE, Sucralose (SUC), SUC/Cl, Corrected for dilution SUC, SUC/ACE, Saccharin (SAC), Cyclamate (CYC) and Sulfamic acid (H$_3$NO$_3$) from October 2015 to September 2017.

Well	Cl (mg/L)	ACE (µg/L)	ACE/Cl	Corrected ACE (mg/L)	SUC (µg/L)	SUC/Cl	Corrected SUC (mg/L)	SUC/ACE	SAC (µg/L)	CYC (µg/L)	H$_3$NO$_3$ (µg/L)
26-Oct-15, event 2											
CR-1-1.9	33	12	0.35	30	9.3	0.28	24	0.80	0.08	<0.01	
-2.2	40	28	0.69	59	15	0.37	31	0.53	0.04	<0.01	
CR-8-0.6	24	12	0.50	43	12	0.50	43	1.0	0.02	<0.01	
-0.9	45	25	0.55	46	18	0.41	35	0.74	0.02	<0.01	
CR-12-0.7	37	15	0.40	34	13	0.35	30	0.88	0.05	<0.01	
-1	35	18	0.53	45	16	0.45	38	0.85	0.03	<0.01	
CR-CK5	40	10	0.26	0.22	9.9	0.25	21	0.97	0.03	<0.01	
4-Jan-16, event 4											
CR12-1	34	31	0.93	79	16	0.48	41	0.52			14
24-Jan-16, event 5											
CR-12-0.7	20	7.8	0.40	34	5.8	0.29	25	0.74	0.14	0.01	
-1	42	26	0.62	52	15	0.35	30	0.58	0.11	0.17	11
28-Feb-16, event 6											
CR-12-0.7	17	11	0.62	53	7.4	0.44	37	0.71	0.02	<0.01	4
-1	26	12	0.47	40	8.8	0.34	29	0.71	0.02	0.03	2
CR-CK5		1.9			1.4			0.74	<0.01	<0.01	
18-Apr-16, event 7											
CR-12-0.7	55	7.7	0.14	12	9.3	0.17	14	1.2	0.49	<0.01	
-1	89	3.5	0.04	3.4	4.1	0.05	3.9	1.2	0.18	<0.01	14
27-May-16, event 8											
CR-12-0.7		7.6			8.1			1.1			
-1	127	3.0	0.02	2.0	2.1	0.02	1.4	0.72	0.16	<0.01	2
CR-CK		3.0			2.1			0.70	0	0.13	
21-Oct-16, event 13											
CR-12-0.7	66	13	0.20	17	38	0.57	49	2.9	0.02	<0.01	48
-1	60	15	0.24	21	34	0.56	48	2.3	0.06	<0.01	31
22-Feb-17, event 14											
CR-12-0.7	14	5.4	0.40	34	6.9	0.51	43	1.3	0.01		

Well	Cl (mg/L)	ACE (µg/L)	ACE/Cl	Corrected ACE (mg/L)	SUC (µg/L)	SUC/Cl	Corrected SUC (mg/L)	SUC/ACE	SAC (µg/L)	CYC (µg/L)	H_3NO_3 (µg/L)
-1	38	17	0.45	38	21	0.55	47	1.2	0.01		
28-Feb-17, event 15											
CR-12-0.7	9.2	4.0	0.44	37	5.5	0.60	51	1.4	<0.01		
-1	40	18	0.45	38	21	0.53	45	1.2	<0.01		
18-Mar-17, event 16											
CR-12-0.7	17	6.3	0.37	31	8.4	0.49	42	1.3	<0.01		
-1	30	8.7	0.29	24	11	0.36	31	1.3	0.01		
9-Apr-17, event 17											
CR-12-0.7	15	5.0	0.34	29	6.0	0.41	35	1.2	<0.01		
-1	29	15	0.52	44	17	0.59	50	1.1	0.01		
15-Apr-17, event 18											
CR-12-0.7	20	3.2	0.16	14	5.2	0.26	22	1.6	0.04		
-1	31	10	0.32	27	16	0.50	43	1.6	0.03		
6-May-17, event 19											
CR-12-0.7	17	1.6	0.10	8.1	3.3	0.20	17	2.0	0.05		
-1	41	7.6	0.19	16	11	0.26	22	1.4	0.06		
18-May-17, event 20											
CR-12-0.7	115	3.2	0.03	2.4	3.1	0.03	2.3	0.98	0.03		
-1	140	6.8	0.05	4.1	8.5	0.06	5.2	1.3	0.03		
4-Jun-17, event 21											
CR-1-1.9	39	5.7	0.14	12	5.6	0.14	12	0.99	0.01		
-2.2											
CR-12-0.7	126	6.0	0.05	4.1	6.7	0.05	4.5	1.1	0.01		
-1	81	5.5	0.07	5.8	7.8	0.10	8.2	1.4	0.01		
13-Jun-17, event 22											
CR-1-1.9	68	18	0.26	22	13	0.18	16	0.71	0.03		
CR-12-0.7	60	4.5	0.07	6.3	4.7	0.08	6.7	1.1	0.02		
-1	85	7.3	0.09	7.3	10	0.12	10	1.4	0.02		
20-Jun-17, event 23											
CR-1-1.9	77	37	0.49	42	22	0.29	24	0.58	0.08		
CR12-1	66	7.1	0.11	9.1	9.6	0.14	12	1.4	0.16		
28-Jun-17, event 24											

Well	Cl (mg/L)	ACE (µg/L)	ACE/Cl	Corrected ACE (mg/L)	SUC (µg/L)	SUC/Cl	Corrected SUC (mg/L)	SUC/ACE	SAC (µg/L)	CYC (µg/L)	H_3NO_3 (µg/L)
CR-1-1.9	36	24	0.66	56	14	0.38	32	0.58	0.01		
CR-12-0.7	45	4.4	0.10	8.4	5.4	0.12	10	1.2	0.02		
-1	67	8.9	0.13	11	7.4	0.11	9.4	0.83	0.01		
14-Jul-17, event 25											
CR-1-1.9	30	3.1	0.11	8.9	3.0	0.10	8.6	0.97	0.03		
CR-12-0.7	137	4.3	0.03	2.7	5.7	0.04	3.5	1.3	0.19		
-1	125	14	0.11	10	20	0.16	14	1.4	0.16		
28-Jul-17, event 26											
CR-1-1.9	82	13	0.16	13	27	0.33	28	2.1	0.04		
CR-12-0.7	39	10	0.26	22	21	0.54	46	2.1	0.96	0.38	
-1	24	9.4	0.39	33	20	0.84	72	2.1	0.88	0.33	
10-Aug-17, event 27											
CR-1-1.9	48	19	0.40	34	35	0.74	63	1.9	0		
CR-12-0.7	89	8.3	0.09	7.9	29	0.32	28	3.5	0.04	0.86	
-1	106	9.2	0.09	7.4	21	0.20	17	2.3	0.11	0.75	
30-Aug-17, event 28											
CR-1-1.9	84	2.5	0.03	2.6	28	0.34	29	11	0.02		
CR-12-0.7	107	1.4	0.01	1.1	25	0.23	20	18	0.01	0.10	
-1	134	5.1	0.04	3.2	33	0.25	21	6.5	0.03	0.36	

Appendix B

Six Mile Lake Tile Bed -Geochemical, Field and Artificial Sweetener Data

Table B.1. Six Mile Lake (NH$_4^+$ Rich) Site; Detailed concentrations of Electrical Conductivity (EC), Dissolved Oxygen (DO), Cl$^-$, SO4^{2-}, Fe^{2+} (CHEMet) Fe^{2+}, Na$^+$, Mg^{2+} Al^{3+}, K$^+$, Ca^{2+}, NO$_3$-N, NO$_2$-N, NO$_3$-N, NH$_4$-N, Total Inorganic Carbon (TIN), TIN/Cl, Corrected for dilution TIN, Soluble Reactive Phosphorus (SRP), SRP/Cl, Corrected for dilution SRP, Total Phosphorus (TP), Dissolved Organic Carbon (DOC), Reduction Potential (Eh) and Alkalinity (CaCO$_3$) throughout the experimental period from October 2015 to September 2016.

Well	EC (μs/cm)	DO (mg/L)	Cl (mg/L)	SO$_4^{2-}$ (mg/L)	Fe^{2+} CHEMet)	Fe^{2+} (mg/L)	Na$^+$ (mg/L)	Mg^{2+} (mg/L)	Al^{3+} (mg/L)	K$^+$ (mg/L)	Ca^{2+} (mg/L)	NO$_3$-N (mg/L)	NO$_2$-N (mg/L)	NH$_4$-N (mg/L)	TIN (mg/L)	TIN/Cl	Corrected TIN (mg/L)	SRP (mg/L)	SRP/Cl	Corrected SRP (mg/L)	TP (mg/L)	DOC (mg/L)	Eh (mV)	Alk (mg/L) as CaCO3
7/8-Oct-15																								
SM 1-0.7																								
-1	1628	5.4			2													<0.01			1.6			
-1.3	1243		83	12								0.14	2.0	47	49	0.59	81	0.01	<0.01	0.01	0.03			
SM 2-1.1	1450	5.3	135	8.1	5							0.18	2.0	20	22	0.16	23	0.28	<0.01	0.29				
-1.4	1310	9.0	132	8.5	> 10							0.38	<0.01	24	24	0.19	26	0.10	<0.01	0.11				
-1.7	1030	9.0	85	7.2	> 10							0.51	<0.01	5.8	6.3	0.07	10	0.05	<0.01	0.08				
SM 3-0.9	1331	5.1	80	11	5							0.60	<0.01	7.7	8.3	0.10	14	0.25	<0.01	0.44				
-1.2	1153	0.25	132	15	> 10							0.56	<0.01	13	14	0.10	14	0.03	<0.01	0.03				
-1.5	951	8.6	81	6.0								0.37	<0.01	8.1	8.5	0.10	14	0.09	<0.011	0.15				
SM 4-1.1	1028	3.0	129	15	5							0.50	<0.01	10	10	0.08	11	0.34	<0.01	0.37	0.02			
-1.4	1071	0.21	115	2.9	8							0.15	<0.01	6.8	7.0	0.06	8.4	0.03			0.03			
-1.7	1106	8.5	108	5.6	> 10							0.27	<0.01	15	15	0.14	20	<0.01						
SM 5-1.3	990	0.23	59	3.4	> 10							0.19	<0.01	6.7	6.9	0.12	16	<0.01			0.01			
-1.6	954	0.65	68	4.7	> 10							0.35	<0.01	7.5	7.8	0.11	16	0.03	<0.01	0.07	0.03			
1.9																								
SM 6-0.8	1434	7.9	124	33	0.6							37	<0.01	20	57	0.46	64	0.03	<0.01	0.04	0.03			
-1.1	1318	0.28	153	15	10							0.43	<0.01	45	45	0.30	41	0.24	<0.01	0.22	0.16			
-1.4	1419	0.23	146	6.4	5							0.31	<0.01	59	59	0.40	56	0.63	<0.01	0.59	0.37			
SM 7-0.8	986	2.5	108	10	5							0.24	<0.01	16	17	0.15	21	0.13	<0.01	0.16	0.08			
-1.1	1174	0.31	87	7.7	> 10							0.55	<0.01	14	15	0.17	23	0.01	<0.01	0.01	0.01			
SM 8-1.6	1098	0.30			n.d													0.02			0.02			
-1.9	1142	9.4	149	15	n.d							17	<0.01	0.42	17	0.12	16	0.03	<0.01	0.03				
-1	741	0.22	102	14	10							0.55	<0.01	1.0	1.6	0.02	2	0.01	<0.01	0.01				

Well	**EC (µs/cm)**	**DO (mg/L)**	**Cl (mg/L)**	**SO_4^{2-} (mg/L)**	**Fe^{2+} CHEMet)**	**Fe^{2+} (mg/L)**	**Na^+ (mg/L)**	**Mg^{2+} (mg/L)**	**Al^{3+} (mg/L)**	**K^+ (mg/L)**	**Ca^{2+} (mg/L)**	**NO_3-N (mg/L)**	**NO_2-N (mg/L)**	**NH_4-N (mg/L)**	**TIN (mg/L)**	**TIN/Cl**	**Corrected TIN (mg/L)**	**SRP (mg/L)**	**SRP/Cl**	**Corrected SRP (mg/L)**	**TP (mg/L)**	**DOC (mg/L)**	**Eh (mV)**	**Alk (mg/L) as CaCO3**
26-Oct-15																								
SM 1-0.7																								
-1	1188	1.5	85	14	0.6							3.0	<0.01	13	16	0.19	26	0.50	<0.01	0.81				
-1.3	1229	10	77	8.3	8							0.25	<0.01	29	29	0.38	53	0.03	<0.01	0.05				
SM 4-1.1																								
-1.4	862	0.56	132	2.4	>10							0.19	<0.01	6.2	6.4	0.05	6.7	0.02	<0.01	0.03	0.23			
-1.7	1039	4.6	104	2.9	>10							0.31	<0.01	14	14.4	0.14	19	0.03	<0.01	0.04	0.18			
SM 5-1.3	957	9.1	137	23	>10							0.29	<0.01	9.5	9.8	0.07	10	0.03	<0.01	0.03				
-1.6	958	0.48	106	2.2	>10							0.25	<0.01	8.7	8.9	0.08	12	0.04	<0.01	0.05				
-1.9	862	9.9	90	4.6	>10							0.39	<0.01	7.9	8.3	0.09	13	0.02	<0.01	0.03				
SM 6-0.8																								
-1.1	1343	0.56	142	32	7							0.15	<0.01	23	23	0.16	22	0.55	<0.01	0.54	0.60			
-1.4	1289	0.81	149	14	4							0.23	<0.01	29	30	0.20	27	0.05	<0.01	0.04	0.16			
SM 7-0.8	989	0.50	94	6.7	6							0.16	<0.01	0.29	0.45	<0.01	0.65	0.01	<0.01	0.02	0.04			
-1.1	1135	0.63	122	2.2	>10							0.21	<0.01	13	13	0.11	15	0.02	<0.01	0.02	0.15			
-1.4																								
05-Dec-15																								
SM 1-0.7	521	10	37	12	n.d							10	<0.01	<0.01	10	0.27	37	0.71	0.02	2.67	0.54	8		
-1.3	1133	11	135	4.6	>10							0.59	<0.01	32	33	0.24	33	0.02	<0.01	0.02	0.16	12		
SM 4-1.1	579	0.36	45	18	0							3.0	<0.01	0.13	3.1	0.07	10	0.01	<0.01	0.03	0.07	5		
-1.4	1121	0.35	122	3.2	9							0.30	<0.01	22	22	0.18	25	0.02	<0.01	0.02	0.06	10		
-1.7	1116	9.3	134	2.4	>10							0.38	<0.01	18	18	0.14	19	0.01	<0.01	0.01	0.18	17		
SM 5-1.3	997	0.31	74	3.2	>10							0.37	<0.01	12	13	0.17	24	0.01	<0.01	0.01	0.22	8		
-1.6	1029	0.28	115	2.1	>10							0.31	<0.01	12	13	0.11	15	0.01	<0.01	0.02	0.02	10		
-1.9																								
SM 6-0.8	739	0.46	41	43	n.d							15	<0.01	2.1	18	0.42	59	0.18	<0.01	0.61	0.22	8		
-1.1	1118	0.34	88	60	2							3.1	<0.01	54	58	0.65	90	0.51	<0.01	0.80	0.51	10		
-1.4	1241	0.34	124	18	5							0.61	<0.01	43	44	0.36	49	0.10	<0.01	0.11	0.06	11		
SM 7-0.8	819	0.36	32	3.8	3							0.24	<0.01	<0.01		<0.01		<0.01			0.05	5		
-1.1	975	0.31	95	1.6	>10							0.29	<0.01	17	17	0.18	25	<0.01			0.03	8		

Well	EC (μs/cm)	DO (mg/L)	Cl (mg/L)	SO_4^{2-} (mg/L)	Fe^{2+} CHEMet	Fe^{2+} (mg/L)	Na^{+} (mg/L)	Mg^{2+} (mg/L)	Al $^{3+}$ (mg/L)	K^{+} (mg/L)	Ca^{2+} (mg/L)	NO_3-N (mg/L)	NO_2-N (mg/L)	NH_4-N (mg/L)	TIN (mg/L)	TIN/Cl	Corrected TIN (mg/L)	SRP (mg/L)	SRP/Cl	Corrected SRP (mg/L)	TP (mg/L)	DOC (mg/L)	Eh (mV)	Alk (mg/L) as CaCO3
-1.4	1055	10	60	1.9	>10							0.29	<0.01	21	21	0.35	49	0.01	<0.01	0.02	0.04	15		
07-Jan-16																								
SM 1-0.7																								
-1	641	0.32	57	26	n.d							2.2	<0.01	2.9	5.1	0.09	12	0.21	<0.01	0.51	0.23			
SM 4-1.1	425	0.29	20	11	n.d							<0.01	<0.01	<0.01		<0.01		0.01	<0.01	0.08	0.03			
-1.4	745	0.27	45	6.1	5							<0.01	<0.01	9.4	9.4	0.21	29	0.02	<0.01	0.05	0.03			
-1.7	1094	9.7	124	1.7	>10							<0.01	<0.01	16	16	0.13	18	0.02	<0.01	0.02	0.08			
SM 5-1.3																								
-1.6	995	9.0	103	3.0	>10							<0.01	<0.01	11	11	0.11	15	0.01	<0.01	0.02	0.03			
-1.9																								
SM 6-0.8	401	0.40	13	11	n.d							<0.01	<0.01	1.1	1.1	0.08	11	0.26	0.02	2.64	0.27			
-1.1	819	0.34	55	82	5							<0.01				<0.01	<0.01	0.69	0.01	1.74	0.67			
-1.4	1182	0.30	130	45	8							<0.01	<0.01	39	39	0.30	42	0.11	<0.01	0.12	0.05			
SM 7-0.8	562	0.34	22	7.9	2							<0.01	<0.01	<0.01		<0.01	<0.01	0.01	<0.01	0.03	0.06			
-1.1	929	0.29	97	2.3	>10							<0.01	<0.01	13	13	0.13	19	0.01	<0.01	0.01	0.04			
-1.4																								
02-Feb-16																								
SM 1-0.7																								
-1	765	0.38	101	35	n.d							3.3	<0.01	2.8	6.1	0.06	8.4	0.32	<0.01	0.44				
-1.3																								
SM 4-1.1	548	0.34	52	8.2	n.d							<0.01	<0.01	0.52	0.52	0.01	1.4	0.01	<0.01	0.02	0.04			
-1.4	925	0.30	88	10	>10							<0.01	<0.01	13	13	0.15	20	0.01	<0.01	0.02	0.04			
-1.7																								
SM 5-1.3	781	0.33	84	3.5	>10							<0.01	<0.01	11	11	0.13	18	<0.01						
-1.6	880	0.29	92	2.9	>10							<0.01	<0.01	11	11	0.12	17	0.01	<0.01	0.02				
-1.9																								
SM 6-0.8	367	0.32	9	15	0							<0.01	<0.01	<0.01				0.22	0.02	3.24				
-1.1	637	0.30	19	28	5							<0.01	<0.01	29	29	1.57	216	0.73	0.04	5.45				
-1.4	1171	0.40	102	21	3							<0.01	<0.01	41	41	0.40	55	0.07	<0.01	0.09				
SM 7-0.8	540	0.45	22	7.3	2							<0.01	<0.01	0.84	0.84	0.04	5.2	0.01	<0.01	0.03	0.07			

Well	**EC (µs/cm)**	**DO (mg/L)**	**Cl (mg/L)**	**SO_4^{2-} (mg/L)**	**Fe^{2+} CHE Met)**	**Fe^{2+} (mg/L)**	**Na^+ (mg/L)**	**Mg^{2+} (mg/L)**	**Al^{3+} (mg/L)**	**K^+ (mg/L)**	**Ca^{2+} (mg/L)**	**NO_3-N (mg/L)**	**NO_2-N (mg/L)**	**NH_4-N (mg/L)**	**TIN (mg/L)**	**TIN/Cl**	**Corrected TIN (mg/L)**	**SRP (mg/L)**	**SRP/Cl**	**Corrected SRP (mg/L)**	**TP (mg/L)**	**DOC (mg/L)**	**Eh (mV)**	**Alk (mg/L) as CaCO3**
-1.1	792	0.35	65	2.4	>10							<0.01	<0.01	10	10	0.15	21	0.01	<0.01	0.02	0.05			
15-Feb-16																								
SM 1-1.3																		0.10						
SM 4-1.7																		0.02						
SM 5-1.9																		0.01						
SM 7-1.4																		0.03						
29-Feb-16																								
SM 1-0.7	424		13	11	n.d	0.20	27	12	<0.01	30	34	6.5	<0.01	6.5	13	1.00	138	0.82	0.06	8.8				
-1	667		46	19	n.d	0.06	43	21	0.62	32	68	1.8	<0.01	9.3	11	0.24	33	0.36	0.01	1.08				
-1.3	115		138	33	>10	6.8	66	27	0.34	36	93	<0.01	<0.01	8.4	8.4	0.06	8.4	0.02	<0.01	0.02			284	254
SM 4-1.1	528		69	14	n.d	<0.01	34	19	0.31	31	67	0.53	<0.01	<0.01	0.53	0.01	1.1	0.01	<0.01	0.01	0.02			
-1.4	835		67	13	4	1.0	56	22	0.18	34	90	<0.01	<0.01	6.2	6.2	0.09	13	0.01	<0.01	0.02	0.02			
-1.7	1025		106	2.2	>10	2.7	59	28	0.09	34	79	<0.01	<0.01	5.5	5.5	0.05	7.2	0.02	<0.01	0.02	0.01		308	272
SM 6-0.8	355		8	10	n.d	2.0	26	15	<0.01	31	45	2.0	<0.01	1.0	3.0	0.36	50	0.25	0.03	4.1				
-1.1	528		8	13	6	4.7	35	22	<0.01	33	53	<0.01	<0.01	4.5	4.5	0.59	81	0.75	0.10	14				
-1.4	1027		93	31	3	0.8	26	11	0.93	7.8	40	<0.01	<0.01	4.3	4.3	0.05	6.4	0.09	<0.01	0.13			290	234
SM 7-0.8	456		9	7.6	3	0.52	33	14	<0.01	31	65	<0.01	<0.01	5.0	5.0	0.56	77							
-1.1	675		26	1.9	>10	1.9	44	21	<0.01	33	68	<0.01	<0.01	5.4	5.4	0.21	29				0.02			
-1.4	999		92	2.8	>10	17	51	25	<0.01	34	104	<0.01	<0.01	7.0	7.0	0.08	11				0.01		296	222
05-Apr-16																								
SM 1-0.7	247	4.1	2	1.9	n.d	<0.01	<0.01	4	<0.01	3	14	<0.01	<0.01	<0.01		<0.01	<0.01	0.89	0.52	72				
-1	291	0.29	5	5.2	n.d	<0.01	<0.01	5	<0.01	3	16	<0.01	<0.01	6.5	6.5	1.24	171	0.48	0.09	13				
-1.3	848	12	61	16	>10	6	28	15	<0.01	24	43	<0.01	<0.01	30	30	0.49	67	0.02	<0.01	0.04			3382	173
SM 4-1.1	295	1.1	6	4.4	0	<0.01	<0.01	3	<0.01	3	14	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01					
-1.4	395	0.35	6	4.3	3	1	14	8	<0.01	5	32	<0.01	<0.01	5.5	5.5	0.95	132	0.01	<0.01	0.17				
-1.7	896	11	94	2.6	>10	15	33	19	<0.01	6	60	<0.01	<0.01	16	16	0.17	24	0.01	<0.01	0.01			3070	219
SM 5-1.3	267	1.3	16	4.0	2	0.25	<0.01	3	<0.01	2	16	0.50	<0.01	1.4	1.9	0.12	16	<0.01						
-1.6	395	7.7	20	3.5		4	5	7	<0.01	3	30	0.0	<0.01	3.3	3.3	0.16	22	<0.01						
-1.9	271	12	15	3.3	3	1	<0.01	5	<0.01	3	20	0.0	<0.01	2.5	2.5	0.17	23						1184	191

Well	EC (µs/cm)	DO (mg/L)	Cl (mg/L)	SO_4^{2-} (mg/L)	Fe^{2+} CHEMet)	Fe^{2+} (mg/L)	Na^+ (mg/L)	Mg^{2+} (mg/L)	Al^{3+} (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	NO_3-N (mg/L)	NO_2-N (mg/L)	NH_4-N (mg/L)	TIN (mg/L)	TIN/Cl	Corrected TIN (mg/L)	SRP (mg/L)	SRP/Cl	Corrected SRP (mg/L)	TP (mg/L)	DOC (mg/L)	Eh (mV)	Alk (mg/L) as CaCO3
SM 6-0.8	340	1.3	8	6.8	<0.01	<0.01	<0.01	6	<0.01	4	25	1.8	<0.01	<0.01	1.8	0.24	33	0.26	0.03	4.9				
-1.1	429	0.32	6	9.4	5	2	1	9	<0.01	3	19	<0.01	<0.01	6.9	6.9	1.17	161	0.80	0.13	19				
-1.4	760	0.31	45	22	3	2	19	14	<0.01	8	40	<0.01	<0.01	12	12	0.27	37	0.09	<0.01	0.28			3422	203
SM 7-0.8	299	0.58	4	3.3	1	<0.01	<0.01	5	<0.01	3	30	<0.01	<0.01	<0.01		<0.01		<0.01						
-1.1	301	0.35	6	1.4	3	1	<0.01	3	<0.01	4	13	<0.01	<0.01	3.8	3.8	0.65	90	0.01	<0.01	0.13				
-1.4	662	12	45	1.5	>10	10	20	13	<0.01	11	44	<0.01	<0.01	11	11	0.24	33	0.01	<0.01	0.02			3094	183
SM 8-1.6	244	8.4	4	3.2	<0.01	<0.01	<0.01	4	<0.01	4	23	0.83	<0.01	<0.01		<0.01		0.63	0.15	20.				
-1.9	230	11	8	2.8	<0.01	<0.01	<0.01	3	<0.01	3	19	0.59	<0.01	<0.01		<0.01		0.61	0.08	11				
-2.2	266	12	9	1.9	0.2	<0.01	<0.01	6	<0.01	18	27	<0.01	<0.01	0.78	0.78	0.09	12	0.03	<0.01	0.45				
20-Apr-16																								
SM 1-0.7	279	9.7	3	5.3	<0.01							0.51	0.02	<0.01	0.5	0.17	23	0.86	0.28	38				
-1	285	0.28	6	4.6								0.1	0.02	0.55	0.64	0.10	14	0.42	0.07	9.4				
-1.3	451	9.2	32	8.3	3							<0.01	<0.01	11	11	0.34	47	0.02	<0.01	0.09	0.03			
SM 4-1.1	282	0.69	5	4.1	<0.01							0.27	0.02	<0.01	0.29	0.06	7.9		<0.01					
-1.4	321	0.29	6	2.5	2							<0.01	<0.01	1.8	1.8	0.31	43	0.01	<0.01	0.22				
-1.7	1375	9.9	60	2.2	>10							0.09	<0.01	5.2	5.3	0.09	12	0.01	<0.01	0.03	0.04			
SM 5-1.3	690	0.36	14	3.4	2							0.15	<0.01	0.82	1.0	0.07	10	<0.01						
-1.6	911	9.2	28	3.0	7							0.18	<0.01	2.6	2.8	0.10	13	<0.01						
-1.9	755	9.2	19	2.6	1							0.15	<0.01	2.2	2.3	0.12	17	<0.01			0.02			
SM 6-0.8	307	0.64	3	2.5	0							0.13	<0.01	0	0.13	0.05	7.0	0.29	0.12	16				
-1.1	405	0.26	6	5.8	6							0.0	<0.01	4.3	4.3	0.70	96	0.66	0.12	15				
-1.4	643	0.20	23	18	4							0.08	<0.01	10	10	0.44	60	0.10	<0.01	0.58	0.04			
SM 7-0.8	308	0.33	4	3.2	1							0.13	<0.01	<0.01	0.13	0.03	4.6	0.01	<0.01	0.20				
-1.1	283	0.26	5	0.69	1							0.06	<0.01	2.8	2.8	0.59	82	<0.01	<0.01	0.13				
-1.4	588	9.9	23	1.7	>10							0.06	<0.01	9.3	9.4	0.42	57	0.02	<0.01	0.10	0.14			
SM 8-1.6	750	5.1	6	3.8	0.6							0.67	<0.01	<0.01	0.67	0.11	16		<0.01					
-1.9	609	4.8	5	3.6	<0.01							1.1	<0.01	<0.01	1.1	0.21	29		<0.01					
-2.2	843	9.1	18	2.9	1							0.70	<0.01	<0.01	0.70	0.04	5.2	0.02	<0.01	0.11	0.04			

Well	**EC (µs/cm)**	**DO (mg/L)**	**Cl (mg/L)**	**SO_4^{2-} (mg/L)**	**Fe^{2+} CHE Met)**	**Fe^{2+} (mg/L)**	**Na^+ (mg/L)**	**Mg^{2+} (mg/L)**	**Al^{3+} (mg/L)**	**K^+ (mg/L)**	**Ca^{2+} (mg/L)**	**NO_3-N (mg/L)**	**NO_2-N (mg/L)**	**NH_4-N (mg/L)**	**TIN (mg/L)**	**TIN/Cl**	**Corrected TIN (mg/L)**	**SRP (mg/L)**	**SRP/Cl**	**Corrected SRP (mg/L)**	**TP (mg/L)**	**DOC (mg/L)**	**Eh (mV)**	**Alk (mg/L) as CaCO3**
04-Jun-16																								
SM 1-0.7																								
-1	627	8.0	48	13	0.2							1.1	<0.01	1.4	2.6	0.05	7.4	0.28	0.01	0.81				
-1.3																								
SM 4-1.1	570	7.3	24	3.7	<0.01							0.27	<0.01	<0.01	0.27	0.01	1.6	0.01	<0.01	0.04				
-1.4	769	0.14	43	1.2	5							0.09	<0.01	25	26	0.60	83	0.01	<0.01	0.02				
-1.7	788	8.3	24	1.4	>10							0.0	<0.01	12	12	0.50	69	0.02	<0.01	0.11	0.03			
SM 5-1.3	417	4.9	10	2.1	8							0.09	<0.01	4.7	4.8	0.46	64	0.01	<0.01	0.09				
-1.6	497	7.2	22	1.7	>10							0.07	<0.01	6.2	6.3	0.29	40	0.01	<0.01	0.08				
-1.9																								
SM 6-0.8	360	6.8	3	12	0.4							0.28	<0.01	<0.01	0.3	0.08	12	0.40	0.12	16				
-1.1	424	8.4	4	7.7	5							0.09	<0.01	4.9	5.0	1.3	183	0.38	0.10	14				
-1.4	557	0.23	16	3.6	3							0.09	<0.01	31	31	1.9	264	0.14	0.01	1.2	0.08			
SM 7-0.8	336	6.9	2	2.6	2							0.0	<0.01	0.55	0.5	0.24	33	<0.01						
-1.1																								
-1.4	706	7.3	51	1.7	4							0.13	<0.01	12	12	0.24	32	<0.01			0.12			
SM 8-1.6																								
-1.9	349	1.0	5	1.2	<0.01							1.4	<0.01	<0.01	1.4	0.29	40	0.48	0.10	14	0.34			
-2.2																								
17-Jun-16																								
SM 1-0.7																								
-1	692	6.9	273	29	>10							18	<0.01	0.60	19	0.07	10	0.20	<0.01	0.10				
-1.3																								
SM 4-1.1																								
-1.4	337	0.20	43	1.5	>10							0.15	<0.01	6.5	6.6	0.15	21	0.01	<0.01	0.04				
-1.7	750	7.4	77	1.9	>10							0.41	<0.01	7.7	8.1	0.11	15	<0.01			0.08			
SM 5-1.3	397	7.7	14	1.9	>10							0.19	<0.01	3.3	3.5	0.24	33	<0.01						
-1.6	493	7.3	23	2.2	>10							0.0	<0.01	4.7	4.7	0.20	28	0.02	<0.01	0.09				

Well	EC (µs/cm)	DO (mg/L)	Cl (mg/L)	SO_4^{2-} (mg/L)	Fe^{2+} CHEMet	Fe^{2+} (mg/L)	Na^+ (mg/L)	Mg^{2+} (mg/L)	Al^{3+} (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	NO_3-N (mg/L)	NO_2-N (mg/L)	NH_4-N (mg/L)	TIN (mg/L)	TIN/Cl	Corrected TIN (mg/L)	SRP (mg/L)	SRP/Cl	Corrected SRP (mg/L)	TP (mg/L)	DOC (mg/L)	Eh (mV)	Alk (mg/L) as CaCO3
-1.1	609	0.24	28	6.7	5							0.09	<0.01	3.9	4.0	0.14	20	0.35	<0.01	1.7				
-1.4	599	0.24	49	9.3	4							0.10	<0.01	9.3	9.5	0.19	27	0.11	<0.01	0.32				
SM 7-0.8																								
-1.1																								
-1.4	692	6.9			>10								<0.01	5.2	5.2			0.01			0.04			
04-Aug-16																								
SM 1-0.7																								
-1	1498	0.53	145	5.0	4	1.1	42	12	<0.01	19	31	0.28	0.02	177	177	1.22	169	1.1	0.01	1.0				
-1.3	1502	7.1	152	4.9	3	<0.01	43	12	<0.01	23	43	0.53	0.02	115	116	0.76	105	0.02	<0.01	0.02				
SM 4-1.1	1315	1.1	152	4.5	n.d	<0.01	58	16	<0.01	16	89	0.46	0.02	14	14	0.09	13	0.01	<0.01	0.01				
-1.4	1540	0.41	152	2.1	>10	6.0	55	15	<0.01	24	61	0.11	<0.01	52	52	0.34	47	0.01	<0.01	0.01				
-1.7	940	7.4	115	12	>10	6.0	27	13	<0.01	8.0	43	0.07	<0.01	29	29	0.25	35	0.01	<0.01	0.01				
SM 5-1.3	1118	0.38	130	17	6	3.0	58	10	<0.01	30	56	5.0	0.04	29	34	0.26	37	0.02	<0.01	0.02				
-1.6	1002	2.9			5	6.6	71	23	<0.01	19	121		<0.01											
-1.9																								
SM 6-0.8	1164	0.62	159	18	n.d	<0.01	50	15	<0.01	11	54	21	0.02	3.5	25	0.15	21	0.41	<0.01	0.35				
-1.1	1237	0.78	125	15	0.1	<0.01	42	15	<0.01	18	44	12	0.04	27	39	0.32	44	0.16	<0.01	0.18				
-1.4	1516	0.73	86	2	3							0.1	<0.01	79	79	0.92	126	0.11	<0.01	0.18				
SM 7-0.8	888	6.7	73	2	n.d	<0.01	35	9.3	<0.01	7.2	70	0.2	0.04	<0.01	0.21	<0.01	<0.01	<0.01						
-1.1																								
-1.4																								
SM 8-1.6																								
-1.9	1051	1.6	70	5	n.d	<0.01	16	12	<0.01	7.8	53	13	<0.01	<0.01	13	0.19	26	0.42	<0.01	0.83				
-2.2	891	7.4	55	3	0.4	<0.01	15	17	<0.01	5.1	103	1.3	1.3	<0.01	2.6	0.05	6.5	0.04	<0.01	0.09				
27-Sep-16																								
SM 1-0.7		probe broken																						
-1	1454		108	21	4	4.9	131	33	<0.01	55	106	3.1	<0.01	77	80	0.74	102	1.3	0.01	1.6	0.34			
-1.3	1419		115	2.6	2	0.35	112	34	<0.01	52	117	1.3	0.11	74	76	0.66	91	0.03	<0.01	0.03	0.01			
SM 4-1.1	1632		163	35	0.1	0.04	148	59	<0.01	48	247	0.0	1.0	8.6	10	0.06	8.2	0.01	<0.01	0.01	0.04			
-1.4	1170		117	15	>10	6.4	85	28	<0.01	43	156	0.15	<0.01	23	23	0.20	28	0.01	<0.01	0.01	0.06			

Well	EC (µs/cm)		Cl (mg/L)	SO_4^{2-} (mg/L)	Fe^{2+} CHE Met)	Fe^{2+} (mg/L)	Na^+ (mg/L)	Mg^{2+} (mg/L)	Al^{3+} (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	NO_3-N (mg/L)	NO_2-N (mg/L)	NH_4-N (mg/L)	TIN (mg/L)	TIN/Cl	Corrected TIN (mg/L)	SRP (mg/L)	SRP/Cl	Corrected SRP (mg/L)	TP (mg/L)	DOC (mg/L)	Eh (mV)	Alk (mg/L) as CaCO3
-1.7	1196		138	2.2	>10	4.6	64	23	<0.01	36	89	0.28	<0.01	17	17	0.12	17	0.01	<0.01	0.01	0.03			
SM 5-1.3	777		37	2.4	>10	18	72	27	<0.01	38	137	0.54	<0.01	14	15	0.39	54	0.01	<0.01	0.02	0.07			
-1.6	786		55	2.0	>10	16	59	23	<0.01	36	118	0.0	<0.01	12	12	0.21	29	0.02	<0.01	0.04	0.04			
-1.9	774		56	2.9	3							0.31	<0.01	10	11	0.19	26	<0.01	<0.01	<0.01	0.02			
SM 6-0.8	1370		130	38	n.d	0.02	132	40	<0.01	46	187	33	<0.01	2.6	35	0.27	38	0.37	<0.01	0.39	0.41			
-1.1	1402		137	30	n.d	0.02	83	24	<0.01	40	88	20	<0.01	30	50	0.36	50	0.10	<0.01	0.11	0.17			
-1.4	1785		176	4.3	n.d	6.0	145	42	<0.01	62	145	0.30	<0.01	105	105	0.60	83	0.13	<0.01	0.10	0.14			
SM 7-0.8	1164		140	7.8	1	1.1	91	28	<0.01	38	216	2.1	<0.01	0.6	2.7	0.02	2.7	<0.01			0.03			
-1.4	1067		98	2.0	>10	<0.01	22	5.3	<0.01	30	0.9	0.22	0.03	13	13	0.14	19	0.01	<0.01	0.01	0.05			
31-Oct-16																								
SM 1-0.7																								
-1	1120	3.7	161	13	2.5							7.3	<0.01	13	20	0.13	17	0.83	<0.01	0.71	0.60			
-1.3																								
SM 4-1.1	1177	3.7	136	23	n.d							1.1	<0.01	1.5	2.6	0.02	2.6	0.01	<0.01	0.01	0.05			
-1.4	1196	0.35	138	12	8							0.07	<0.01	5.1	5.2	0.04	5.2	0.01	<0.01	0.01	0.01			
-1.7	1221	9.9			>10								<0.01					0.01			0.02			
SM 5-1.3	980	0.36	63	1.3	>10							0.05	<0.01	11	11	0.18	25	0.01	<0.01	0.02	0.03			
-1.6	1042	6.7	70	1.8								<0.01	<0.01	11	11	0.16	22	0.01	<0.01	0.03	0.02			
-1.9																								
SM 6-0.8	1701	1.6	178	116	n.d							30	<0.01	14	44	0.25	35	0.55	<0.01	0.43	0.52			
-1.1	1529	0.32	142	30	2							0.06	<0.01	53	54	0.38	52	0.22	<0.01	0.21	0.18			
-1.4	1529	0.35	146	26	5							0.05	<0.01	43	43	0.29	40	0.11	<0.01	0.10	0.12			
SM 7-0.8	1116	0.30	139	2.9	1							<0.01	<0.01	0.52	0.52	<0.01	0.52	<0.01	<0.01	<0.01	0.02			
-1.1																								
-1.4	1116	10	102	1.8	>10							0.18	<0.01	15	15	0.15	20	0.03	<0.01	0.04	0.04			

Table B.2. Six Mile Lake (NH_4^+ Rich) Site; Detailed concentrations of Cl^-, artificial sweeteners Acesulfame (ACE), ACE/Cl, corrected for dilution ACE, Sucralose (SUC), SUC/Cl, Corrected for dilution SUC, SUC/ACE, Saccharin (SAC) and Cyclamate (CYC) from October 2015 to September 2016.

Well	Cl (mg/L)	ACE (µg/L)	ACE/Cl	Corrected ACE (mg/L)	SUC (µg/L)	SUC/Cl	Corrected SUC (mg/L)	SUC/ACE	SAC (µg/L)	CYC (µg/L)
7/8-Oct-15										
SM1-1.3	83	23	0.28	38	26	0.32	44	1.1	6.3	0.65
SM4-1.4	115	19	0.17	23	18	0.16	22	0.94	7.8	<0.01
-1.7	108	18	0.17	23	15	0.14	19	0.83	9.1	<0.01
SM 5-1.3	59									
-1.6	68	14	0.20	27	15	0.21	30	1.1	6.3	0.06
SM 6-0.8	124	25	0.20	28	30	0.24	34	1.2	7.0	1.3
-1.1	153	24	0.16	22	37	0.24	33	1.5	11	0.98
-1.4	146	23	0.16	22	27	0.19	26	1.2	12	<0.01
SM 7-0.8	108	13	0.12	17	6.3	0.06	8	0.49	3.6	6.0
-1.1	87	21	0.24	34	30	0.35	48	1.4	13	5.2
SM8-1.9	149	19	0.12	17	20	0.13	19	1.1	0.16	<0.01
26-Oct-15										
SM1-1.3	77	5	0.07	10	7.4	0.10	13	1.4	1.5	0.16
SM4-1.4	132	25	0.19	26	26	0.20	28	1.0	11	
-1.7	104	13	0.13	18	16	0.16	22	1.2	6.6	
SM 5-1.3	137	6	0.05	6	9.2	0.07	9	1.5	2.9	0.08
-1.6	106	10	0.09	13	14	0.14	19	1.5	4.3	0.08
SM6-1.1	142	28	0.19	27	37	0.26	35	1.3	9.9	1.2
-1.4	149	24	0.16	22	24	0.16	23	1.0	7.7	0.05
SM 7-0.8	94									
-1.1	122	18	0.14	20	29	0.24	33	1.6	11	1.6
05-Dec-15										
SM1-1.3	135	11	0.08	11	11	0.08	11	1.0	4.0	0.39
SM 4-1.1	45									
-1.4	122	7.4	0.06	8	9.8	0.08	11	1.3	2.9	<0.01
-1.7	134	11	0.08	11	15	0.11	16	1.4	4.8	<0.01
SM 5-1.3	74									
-1.6	115	9.3	0.08	11	15	0.13	18	1.7	4.4	<0.01

Well	Cl (mg/L)	ACE (µg/L)	ACE/Cl	Corrected ACE (mg/L)	SUC (µg/L)	SUC/Cl	Corrected SUC (mg/L)	SUC/ACE	SAC (µg/L)	CYC (µg/L)
SM 6-0.8	41	1.0	0.02	3	1.5	0.04	5	1.5	0.38	<0.01
-1.1	88	8.7	0.10	14	12	0.14	20	1.4	1.0	0.10
-1.4	124	14	0.11	16	17	0.14	19	1.2	4.9	0.41
SM7-1.1	95	8.7	0.09	13	11	0.12	16	1.3	3.8	1.0
-1.4	60	6.0	0.10	14	8.8	0.15	20	1.5	2.9	<0.01
07-Jan-16										
SM 1-0.7										
-1	57									
SM 4-1.1	20	0.75	0.04	5	2	0.08	11	2.2	0.13	<0.01
-1.4	45	4.8	0.11	15	7	0.16	22	1.5	1.6	<0.01
-1.7	124	18	0.14	20	24	0.20	27	1.4	6.4	<0.01
SM 5-1.3										
-1.6	103	13	0.13	18	20	0.19	26	1.5	5.2	<0.01
-1.9										
SM 6-0.8	13	0.44	0.03	5	1	0.04	6	1.2	0.06	<0.01
-1.1	55									
-1.4	130	19	0.15	21	21	0.16	23	1.1	6.8	<0.01
SM 7-0.8	22									
-1.1	97	8.7	0.09	12	12	0.13	18	1.4	4.4	2.1
-1.4										
02-Feb-16										
SM4-1.4	88	6.4	0.07	10	10	0.11	16	1.6	1.8	<0.01
-1.6	92	7.1	0.08	11	15	0.17	23	2.2	2.9	<0.01
SM 6-0.8	9	0.08	0.01	1	0.21	0.02	3	2.6	0.01	<0.01
-1.1	19	0.28	0.02	2	0.48	0.03	4	1.7	0.02	<0.01
-1.4	102	12	0.11	16	11	0.11	15	0.95	4.7	0.12
SM7-1.1	65	3.3	0.05	7	6.7	0.10	14	2.0	1.6	0.27
15-Feb-16										
SM 1-1.3		17			15			0.89	5.5	0.13
SM 4-1.7		16			21			1.3	5.9	<0.01
SM 5-1.9		11			15			1.4	4.6	<0.01
SM 7-1.4		9.9			20			2.0	3.9	<0.01

Well	Cl (mg/L)	ACE (µg/L)	ACE/Cl	Corrected ACE (mg/L)	SUC (µg/L)	SUC/Cl	Corrected SUC (mg/L)	SUC/ACE	SAC (µg/L)	CYC (µg/L)
29-Feb-16										
SM1-1.3	138	17	0.12	17	15	0.11	15	0.90	6.0	<0.01
SM4-1.4	67	7.4	0.11	15	10	0.16	22	1.4	2.1	<0.01
-1.7	106	14	0.13	18	19	0.18	24	1.3	5.8	<0.01
SM 6-0.8	8	0.10	0.01	2	0.16	0.02	3	1.6	0.02	<0.01
-1.1	8	0.10	0.01	2	0.26	0.03	5	2.5	0.01	<0.01
-1.4	93	10	0.11	16	11	0.12	17	1.1	3.8	<0.01
SM7-1.1	26	1.8	0.07	9	3.3	0.13	18	1.9	0.84	<0.01
-1.4	92	13	0.15	20	19	0.21	29	1.4	6.2	<0.01
20-Apr-16										
SM 1-0.7	3	0.03	0.01	1	<0.01				0.01	<0.01
-1	6	0.15	0.02	3	0.14	0.02	3	0.93	0.02	<0.01
-1.3	32	1.6	0.05	7	1.7	0.05	7	1.0	0.7	<0.01
SM 4-1.1	5	0.21	0.04	6	0.35	0.07	10	1.7	<0.01	<0.01
-1.4	6	0.28	0.05	7	0.49	0.08	12	1.7	0.02	<0.01
-1.7	60	3.1	0.05	7	4.3	0.07	10	1.4	1.2	<0.01
SM 5-1.3	14	1.0	0.07	10	1.5	0.11	15	1.4	0.36	<0.01
-1.6	28	1.7	0.06	8	2.4	0.09	12	1.5	0.70	<0.01
-1.9	19	1.6	0.08	12	2.3	0.12	17	1.5	0.65	<0.01
SM 6-0.8	3	0.16	0.06	9	0.13	0.05	7	0.79	0.02	<0.01
-1.1	6	0.31	0.05	7	0.26	0.04	6	0.84	0.02	<0.01
-1.4	23	0.51	0.02	3	0.53	0.02	3	1.0	0.17	<0.01
SM 7-0.8	4	0.14	0.04	5	0.31	0.08	11	2.2	0.02	<0.01
-1.1	5	0.06	0.01	2	0.09	0.02	3	1.6	0.03	<0.01
-1.4	23	0.58	0.03	4	1.1	0.05	7	1.9	0.40	<0.01
SM 8-1.6	6	0.24	0.04	6	0.22	0.04	5	0.92	0.01	<0.01
-1.9	5	0.32	0.06	9	0.33	0.06	9	1.0	0.05	<0.01
-2.2	18	0.20	0.01	2	0.19	0.01	1	1.0	0.07	<0.01
04-Jun-16										
SM1-1	48	5.3	0.11	15	1.9	0.04	5	0.36	1.1	0.19
SM 4-1.1	24	4.5	0.19	27	4.3	0.18	25	0.95	1.4	<0.01
-1.4	43	4.1	0.10	13	6.5	0.15	21	1.6	2.3	<0.01

Well	Cl (mg/L)	ACE (µg/L)	ACE/Cl	Corrected ACE (mg/L)	SUC (µg/L)	SUC/Cl	Corrected SUC (mg/L)	SUC/ACE	SAC (µg/L)	CYC (µg/L)
-1.7	24	3.7	0.15	21	6.2	0.26	35	1.7	1.9	<0.01
SM 5-1.3	10	1.3	0.13	18	2.2	0.21	29	1.6	0.66	<0.01
-1.6	22	2.3	0.10	14	3.3	0.15	21	1.5	1.2	<0.01
SM 6-0.8	3	0.11	0.03	5	0.17	0.05	7	1.5	0.05	<0.01
-1.1	4	0.12	0.03	4	0.21	0.06	8	1.7	0.07	<0.01
-1.4	16	1.6	0.10	14	2.0	0.12	17	1.2	0.78	<0.01
SM 7-0.8	2	0.17	0.08	10	0.24	0.10	14	1.4	0.12	<0.01
-1.4	51	2.4	0.05	6	3.3	0.06	9	1.4	1.1	<0.01
SM8-1.9	5	0.34	0.07	10	0.43	0.09	12	1.3	0.01	<0.01
17-Jun-16										
SM1-1	273	28	0.10	14	35	0.13	17	1.3	3.2	6.9
SM4-1.4	43	2.7	0.06	9	3.1	0.07	10	1.1	1.1	<0.01
-1.7	77	3.9	0.05	7	4.8	0.06	9	1.2	1.6	<0.01
SM 5-1.3	14	0.70	0.05	7	1.2	0.08	12	1.7	0.40	<0.01
-1.6	23	2.1	0.09	12	3.4	0.15	20	1.7	1.1	<0.01
SM6-1.1	28	4.7	0.17	23	5.9	0.21	29	1.3	2.0	6.5
-1.4	49	3.6	0.07	10	4.8	0.10	14	1.3	1.2	2.4
SM7-1.4		2.3			2.8			1.2	1.2	<0.01
04-Aug-16										
SM1-1	145	28	0.19	27	60	0.42	57	2.1	17	2.1
-1.3	152	31	0.20	28	57	0.38	52	1.8	20	1.7
SM 4-1.1	152	30	0.20	28	52	0.34	47	1.7	4.2	0.31
-1.4	152	27	0.18	25	60	0.39	54	2.2	15	2.2
-1.7	115	9.0	0.08	11	17	0.15	20	1.9	1.3	<0.01
SM 5-1.3	130	17	0.13	18	33	0.25	35	1.9	5.1	2.2
SM 6-0.8	159	27	0.17	23	41	0.26	35	1.5	2.5	0.15
-1.1	125	17	0.14	19	32	0.25	35	1.8	4.7	2.1
-1.4	86	18	0.20	28	40	0.47	64	2.3	12.5	<0.01
SM 7-0.8	73	9.1	0.13	17	11	0.15	21	1.2	0.65	0.92
SM8-1.9	70	18	0.25	35	44	0.63	88	2.5	0.11	<0.01
-2.2	55	7.5	0.14	19	6.2	0.11	16	0.83	1.3	<0.01

Well	Cl (mg/L)	ACE (µg/L)	ACE/Cl	Corrected ACE (mg/L)	SUC (µg/L)	SUC/Cl	Corrected SUC (mg/L)	SUC/ACE	SAC (µg/L)	CYC (µg/L)
27-Sep-16										
SM1-1	108	23	0.22	30	35	0.33	45	1.5	2.0	<0.01
-1.3	115	28	0.24	34	31	0.27	37	1.1	10	<0.01
SM 5-1.3	37	6.8	0.18	25	9.6	0.26	35	1.4	1.8	<0.01
-1.6	55	7.9	0.14	20	10	0.18	25	1.3	2.0	<0.01
-1.9	56	6.9	0.12	17	9.7	0.17	24	1.4	1.6	<0.01
SM 6-0.8	130	26	0.20	27	33	0.25	35	1.3	1.5	<0.01
-1.1	137	18	0.13	18	29	0.21	29	1.6	2.5	<0.01
-1.4	176	27	0.15	21	35	0.20	27	1.3	12	<0.01
SM 7-0.8	140	15	0.10	14	28	0.20	27	1.9	1.1	0.77
-1.4	98	10	0.11	15	14	0.14	19	1.3	4.6	<0.01
31-Oct-16										
SM1-1	161	12	0.07	10	11	0.07	10	1.0	1.7	<0.01
SM 4-1.1	136	8.9	0.07	9	13	0.10	13	1.5	0.02	<0.01
-1.7		22			31			1.4	7.0	<0.01
SM 5-1.3	63	12	0.19	26	26	0.42	57	2.2	5.5	<0.01
-1.6	70	15	0.21	30	29	0.42	58	2.0	6.9	<0.01
SM 6-0.8	178	27	0.15	21	43	0.24	33	1.6	6.9	10
-1.1	142	30	0.21	29	35	0.25	34	1.2	12	18
-1.4	146	26	0.18	25	27	0.19	26	1.0	6.5	<0.01
SM 7-0.8	139	16	0.11	16	25	0.18	25	1.6	2.0	2.0
-1.4	102	7.0	0.07	10	10	0.10	14	1.4	2.7	<0.01

Appendix C

Long Point Tile Bed Geochemical, Field and Artificial Sweetener Data

Table C.1. Long Point (NO3- Depleting) Site; Detailed concentrations of Electrical Conductivity (EC), Dissolved Oxygen(DO), Cl-, SO42-, NO3-N, NO_3^-/Cl, corrected for dilution NO3-N, NO2-N, NH4-N, Soluble Reactive Phosphorus (SRP), SRP/Cl, corrected for dilution SRP, Total Phosphorus (TP), and Dissolved Organic Carbon (DOC) from November 2015-January 2017.

Well	EC (µs/cm)	DO (mg/L)	Cl $^{-}$ (mg/L)	SO4 $^{2-}$ (mg/L)	NO_3-N (mg/L)	NO_3/Cl	Corrected NO_3-N (mg/L)	NO_2-N (mg/L)	NH_4-N (mg/L)	SRP (mg/L)	SRP/Cl	Corrected SRP (mg/L)	TP (mg/L)	DOC (mg/L)
19-Nov-15														
LP 121-3.8	1280		66	49	80	1.2	98	0.04	<0.01	1.5	0.02	1.8		
-4.4	1320		75	50	84	1.1	89	0.02	<0.01	0.43	0.01	0.41		
-5	1160		52	63	35	0.7	55	0.08	<0.01	0.01	<0.01	0.02		
-6	1004		45	87	1	<0.01	2	0.01	<0.01	0.3	0.01	0.46		
LP 123-2	1518		80	49	48	0.6	48	0.05	<0.01	5.6	0.07	5.6		
-2.6	1410		80	48	107	1.3	107	0.30	<0.01	6.0	0.07	5.9		
-3.2	1444		81	46	107	1.3	106	0.15	<0.01	5.3	0.07	5.3		
-3.8	1348		69	51	86	1.3	100	0.19	<0.01	3.4	0.05	3.9		
-4.4	1365		58	53	79	1.4	109	0.06	<0.01	0.03	<0.01	0.04		
-5.5	1100		68	72	27	0.4	31	0.12	<0.01	0.02	<0.01	0.02		
LP 124-3.1	1441		73	61	45	0.6	49	0.02	<0.01	0.01	<0.01	0.01		
-3.6	1295		44	64	62	1.4	113	0.06	<0.01	0.01	<0.01	0.02		
-4.5	1338		57	66	47	0.8	66	0.04	<0.01	0.02	<0.01	0.03		
LP 135-2.7	1245		54	55	71	1.3	106	0.01	0.63	1.5	0.03	2.2		
-31	1409		65	64	93	1.4	115	0.01	2	0.01	<0.01	0.01		
-3.5	1399		64	61	92	1.4	114	0.04	0.94	0.02	<0.01	0.02		
LP 136-1.9	1184		47	38	72	1.5	123	0.25	<0.01	1.1	0.02	1.8		
-2.3	895		40	62	43	1.1	86	0.28	<0.01	2.5	0.06	5.0		
-2.7	1034		40	59	49	1.2	97	0.03	<0.01	2.3	0.06	4.6		
-3.1	1283		57	51	76	1.3	108	0.09	<0.01	2.2	0.04	3.1		
PVC	1340		63	53	83	1.3	105	0.09	<0.01	1.9	0.03	2.4		
15-Dec-15														
LP 121-3.8										0.92				
-4.4										0.24				
-5										0.01				
-6										0.1				

Well	EC (µs/cm)	DO (mg/L)	Cl $^-$ (mg/L)	SO4 $^{2-}$ (mg/L)	NO$_3$-N (mg/L)	NO$_3$/Cl	Corrected NO$_3$-N (mg/L)	NO$_2$-N (mg/L)	NH$_4$-N (mg/L)	SRP (mg/L)	SRP/Cl	Corrected SRP (mg/L)	TP (mg/L)	DOC (mg/L)
LP 123-2	1520		76	51	121	1.6	127	0.04	<0.01	2.4	0.03	2.5		171
-2.6	1450		70	47	109	1.5	124	0.34	<0.01	2.2	0.03	2.5		154
-3.2	1461		72	45	107	1.5	119	0.18	<0.01	1.6	0.02	1.8		150
-3.8	1388		69	49	92	1.3	106	0.21	0.02	2.1	0.03	2.4		101
-4.4	1397		59	53	82	1.4	111	0.06	0.02	0.01	<0.01	0.02		114
-5.5	1090		47	67	34	0.72	58	0.06	0.02	0.02	<0.01	0.03		
LP 124-2.1	745		17	31	17	1.0	79			0.01	<0.01	0.04		
-2.6	1173		44	50	64	1.5	117			0.01	<0.01	0.02		
-4.5										0.02				
LP 135-1.9	71		20	21	26	1.3	104							
-2.3	841		24	33	27	1.1	90							
-2.7										1.1				
-3.1										0.10				
-3.5										0.20				
LP 136-1.9										0.08				
-2.3														
-2.7														
-3.1										0.08				
-3.5										0.06				
LP 138-1.9	1416		74	48	99									
-2.3	1314		68	42	83									
-2.7	1396		64	41	97									
-3.1	1316		57	51	34									
-3.4	1356		60	54	82									
25-Jan-16														
LP 123-2	1469	< 0.5	73	50	108	1.5	118			2.0	0.03	2.2		
-2.6	1483	< 0.5	69	45	111	1.6	128			1.8	0.03	2.0		
-3.2	1480	< 0.5	71	45	107	1.5	120			1.8	0.03	2.1		
-3.8	1385	< 0.5	69	48	94	1.4	109			1.8	0.03	2.1		
-4.4	1430	< 0.5	59	56	79	1.3	108			0.01	<0.01	0.01		
-5.5	1332	< 0.5	56	59	60	1.1	86			0.01	<0.01	0.02		

Well	EC (µs/cm)	DO (mg/L)	Cl^- (mg/L)	SO4 $^{2-}$ $^($mg/L)	NO_3-N (mg/L)	NO_3/Cl	Corrected NO_3-N (mg/L)	NO_2-N (mg/L)	NH_4-N (mg/L)	SRP (mg/L)	SRP/Cl	Corrected SRP (mg/L)	TP (mg/L)	DOC (mg/L)
23-Feb-16														
LP 123-2										1.0				
-2.6			63	61	96	1.5	123			1.1	0.02	1.3		
-3.2			59	52	90	1.5	123			1.9	0.03	2.6		
-3.8			42	44	57	1.4	108			2.4	0.06	4.6		
-4.4			56	62	73	1.3	104			<0.01				
-5.5			57	58	62	1.1	87			0.01	<0.01	0.02		
LP 124-1.6										0.02				
-2.1										0.01				
LP 135-1.9										0.8				
-2.3										0.5				
LP 138-1.9										1.6				
-2.3										2.1				
-2.7										1.9				
-3.1										1.2				
19-Jun-16, event 9														
LP 4-2.1	601		2.7	11	0.14	0.05	4.0			0.01	0.17	14		
-2.8	603		1.5	7	0.08	0.05	4.0			0.01	0.27	21		
-3.6	673		16	55	4.6	0.30	24			<0.01				
-4.4	1201		52	63	42	0.81	65						0.02	
-5.1	1236									0.01				
-5.8	1082		49	90	0.14	<0.01	0.23							
LP 123-2	1092									3.2				
-2.6	968									7.8				
-3.2	1073									8.1				
-3.8	1264									2.3				
-4.4	1196									1.2				
-5.5	1101									0.01				
LP 124-1.6	670									0.01				
-1.9													1.6	
-2.1	625									0.01				

Well	EC (µs/cm)	DO (mg/L)	Cl $^-$ (mg/L)	SO4 $^{2-}$ (mg/L)	NO_3-N (mg/L)	NO_3/Cl	Corrected NO_3-N (mg/L)	NO_2-N (mg/L)	NH_4-N (mg/L)	SRP (mg/L)	SRP/Cl	Corrected SRP (mg/L)	TP (mg/L)	DOC (mg/L)
-2.6										1.5				
-3.1	1124									0.02				
-3.6	1147									0.01				
-4.5	1203									1.4				
LP 135-1.5	603									0.03				
-2.3	842												0.61	
-3.1	1032									0.12				
-3.5	1095									0.01				
LP 136-1.5	420												0.07	
-1.9	581									0.83				
-2.3	1058									5.1				
-2.7	137												1.3	
-3.1	960									0.39				
-3.6	1160									2.4				
LP 138-2.3	1126									3.0				
-2.7	1229									1.1				
-3.1	1221									0.61				
-3.9													0.77	
11-Oct-16, event 12														
LP 4-2.8	447		2	9.0	0.12	0.1	6.0							
-3.6	646		13	34	4.6	0.34	27							
-4.4	1209		51	88	31.8	0.62	50							
-5.1			58	126	9.9	0.17	14							
LP 7-4.4	467		46	78	0.13	<0.01	0.23							
-5.1	1125		45	104	3.2	0.07	5.8							
-5.8	1038		45	74	0.02	<0.01	0.04							
-6.4	1020		28.8	50	0.34	0.01	0.94							
LP 124-2.1	553		3.0	6.9	0.12	0.04	3.1							
-2.6	705		13	19	11	0.85	68							
-3.1	1049		25	32	31	1.3	100							
-3.6	1200		37	50	49	1.3	106							

Well	**EC (µs/cm)**	**DO (mg/L)**	**Cl $^{-}$ (mg/L)**	**SO4 $^{2-}$ (mg/L)**	**NO_3-N (mg/L)**	**NO_3/Cl**	**Corrected NO_3-N (mg/L)**	**NO_2-N (mg/L)**	**NH_4-N (mg/L)**	**SRP (mg/L)**	**SRP/Cl**	**Corrected SRP (mg/L)**	**TP (mg/L)**	**DOC (mg/L)**
-4.5	1242		54	82	48	0.89	71							
LP 135-1.5	553		3	7.6	0.18	0.07	5.8							
-1.9	527		6	11	6.5	1.1	90							
-2.3	638		13	26	11	0.87	70							
-3.1	910		29	47	34	1.2	94							
-3.5	1162		41	52	48	1.2	94							
LP 136-1.5	431		1	5.5	0.11	0.10	8.1							
-1.9	430		3	8.6	1.9	0.76	61							
-2.3	864		34	27	42	1.3	101							
-2.7	1185		36	35	47	1.3	106							
-3.1	1120		52	50	71	1.4	111							
-3.5	1162		32	37	30	0.9	75							
LP 138-1.9	433		2	6.2	1.4	0.8	61							
-2.3	701		20	17	23	1.2	95							
-2.7	1270		56	42	27	0.5	39							
-3.1	1244		63	50	76	1.2	97							
-3.5	1179		58	57	70	1.2	96							
28-Dec-16, event 13														
LP 4-2.8										0.02				
-3.6										0.02				
-4.4										0.01				
-5.1										0.01				
LP 7-4.4										0.05				
-5.1										0.01				
-5.8										0.09				
-6.4										0.08				
LP 124-2.1										0.04				
-2.6										0.05				
-3.1										0.05				
-3.6										0.03				
-4.5										0.05				

Well	EC (µs/cm)	DO (mg/L)	Cl $^-$ (mg/L)	SO4 $^{2-}$ (mg/L)	NO_3-N (mg/L)	NO_3/Cl	Corrected NO_3-N (mg/L)	NO_2-N (mg/L)	NH_4-N (mg/L)	SRP (mg/L)	SRP/Cl	Corrected SRP (mg/L)	TP (mg/L)	DOC (mg/L)
LP 135-1.5										0.02				
-1.9										1.1				
-2.3										0.71				
-3.1										0.19				
-3.5										0.03				
LP 136-1.5										0.04				
-1.9										1.0				
-2.3										3.3				
-2.7										3.8				
-3.1										2.2				
-3.5										1.4				
LP 138-1.9										2.0				
-2.3										10				
-2.7										2.8				
-3.1										0.85				
-3.5										0.89				

Table C.2. Long Point (NO_3^- Depleting) Site; Detailed concentrations of Cl^-, artificial sweeteners Acesulfame (ACE), ACE/Cl, corrected for dilution ACE, Sucralose (SUC), SUC/Cl, Corrected for dilution SUC, SUC/ACE, Saccharin (SAC), Cyclamate (CYC) and Sulfamic acid from November 2015 to January 2017.

Well	Cl (mg/L)	ACE (µg/L)	ACE/Cl	Corrected ACE (µg/L)	SUC (µg/L)	SUC/Cl	Corrected SUC (µg/L)	SUC/ACE	SAC (µg/L)	CYC (µg/L)	H_3NO_3 (µg/L)
19-Nov-15											
LP 123-2	80	0.35	<0.01	0.35	7.6	0.09	7.6	22	0.03	<0.01	
-2.6	80	0.84	0.01	0.83	55	0.68	55	65	0.03	<0.01	
-3.2	81	0.43	0.01	0.42	27	0.34	27	64	0.04	<0.01	
-3.8	69	2.6	0.04	3.1	54	0.78	62	20	0.11	<0.01	
-4.4	58	17	0.29	23	22	0.38	31	1.3	0.02	0.05	
-5.5	68	11	0.16	13	0.48	0.01	0.56	0.04	0.04	0.22	
15-Dec-15											
LP 123-2	76	0.62	0.01	0.65	15	0.20	16	24	0.01	<0.01	9
-2.6	70	1.0	0.01	1.2	33	0.47	38	32	0.04	<0.01	24
-3.2	72	1.1	0.01	1.2	57	0.79	63	53	0.02	<0.01	
-3.8	69	1.6	0.02	1.8	35	0.51	41	23	0.02	<0.01	
-4.4	59	15	0.25	20	13	0.22	17	0.87	0.03	0.02	
-5.5	47	25	0.52	42	1.2	0.03	2.0	0.05	0.02	0.08	
LP 124-2.1	17	5.4	0.32	25	6.6	0.38	30	1.2	0.02	<0.01	
-2.6	44	31	0.71	57	29	0.65	52	0.92	0.04	<0.01	
LP 135-1.9	20	6.6	0.33	26	17	0.86	69	2.6	0.02	<0.01	3
-2.3	24	6.7	0.28	23	18	0.75	60	2.6	0.01	<0.01	1
LP 138-1.9	74	0.81	0.01	0.87	64	0.87	69	80	0.04	<0.01	22
-2.3	68	1.8	0.03	2.2	72	1.06	85	39	0.02	<0.01	49
-2.7	64	38	0.60	48	65	1.02	81	1.7	0.03	<0.01	25
-3.1	57	26	0.46	37	34	0.60	48	1.3	0.01	<0.01	24
-3.4	60	30	0.50	40	40	0.68	54	1.4	0.03	0.09	15
25-Jan-16											
LP 123-2	73	0.30	<0.01	<0.01	5.1	0.07	6	17.4	0.01	n.d	
-2.6	69	0.72	0.01	0.83	46	0.66	53	64.0	0.04	n.d	
-3.2	71	1.0	0.01	1.1	21	0.30	24	21.0	0.02	n.d	
-3.8	59	0.68	0.01	0.93	37	0.62	50	53.7	0.02	n.d	
-4.4	59	13	0.22	18	5.2	0.09	7	0.4	0.03	0.02	

Well	Cl (mg/L)	ACE (µg/L)	ACE/Cl	Corrected ACE (µg/L)	SUC (µg/L)	SUC/Cl	Corrected SUC (µg/L)	SUC/ACE	SAC (µg/L)	CYC (µg/L)	H_3NO_3 (µg/L)
-5.5	56	11	0.19	16	0.18	0.00	0.25	0.02	0.02	0.08	
23-Feb-16											
LP 123-2		43			20			0.46	0.04	<0.01	
-2.6	63	43	0.68	55	15	0.24	19	0.35	0.00	0.41	
-3.2	59	43	0.73	58	9	0.15	12	0.21	0.00	<0.01	
-3.8	42	43	1.01	81	12	0.28	22	0.28	0.00	<0.02	
-4.4	56								0.01	<0.03	
-5.5	57	43	0.74	59	22	0.38	31	0.52	0.01	0.13	

Appendix D

Craigleith, Six Mile Lake & Long Point Septic Tank Geochemical, Field and Artificial Sweetener Data

Table D.1. Craigleith (CR; NO3- Rich) site, Six Mile Lake (SM; NH4+ Rich) site, and Long Point (LP; NO3- Depleting) site septic tank geochemistry; Detailed concentrations of Electrical Conductivity (EC), Dissolved Oxygen (DO), Cl-, SO42-, NO2-N, NO3-N, NH4-N, Total Inorganic Nitrogen (TIN), TIN/Cl, Soluble Reactive Phosphorus (SRP), Total Phosphorus (TP); and artificial sweeteners Acesulfame (ACE), ACE/Cl, Sucralose (SUC), SUC/Cl, SUC/ACE, Saccharin (SAC) and Cyclamate (CYC). Sampled during the active loading period from May 2016-September 2017 at CR, October 2015-October 2016 at SM, and June 2016 at LP.

Date	EC (µs/cm)	DO (mg/L)	Cl^- (mg/L)	$SO4^{2-}$ (mg/L)	NO_3-N (mg/L)	NO2-N (mg/L)	NH_4N(mg/L)	TIN (mg/L)	TIN/Cl	SRP (mg/L)	TP (mg/L)	ACE (µg/L)	ACE/Cl	SUC (µg/L)	SUC/Cl	SUC/ACE	SAC (µg/L)	CYC (µg/L)
CR; NO_3^- Rich																		
27-May-16	1396		65	11	0.29		64	64	1.0	3.7	9.0	68	1.0	58	0.89	0.85	26	9.5
06-Jun-16	1940		99	13	0.42		131	132	1.3	10	15	163	1.6	117	1.2	0.71	67	7.9
24-Jun-16	1114		57	17	0.63		67	68	1.2	15	8.0	65	1.1	59	1.0	0.91	21	9.1
21-Jul-16	1577									7.8								
04-Oct-16	1447		77	6	0.2					18								
21-Oct-16	1838		78	9.3	0.22					11	1.9	66	0.84	82	1.0	1.2		
04-Jun-17	1785		42	8.3	0.0		60	60	1.4	10		45	1.1	47	1.1	1.0	15	13
13-Jun-17	1484		91	13	0.0		128	128	1.4	17		99	1.1	77	0.85	0.8	33	48
20-Jun-17	1450		113	9.6	0.0		149	149	1.3	17		132	1.2	126	1.1	1.0	52	13
28-Jun-17	1302						332	332				53		68		1.3	28	19
14-Jul-17	1727		201	25	4.0			4.0	0.02			120	0.60	99	0.49	0.83	68	18
28-Jul-17	1078		64	12	4.9		96	101	1.6	13	8.7	56	0.87	48	0.74	0.85	26	17
10-Aug-17	1103		81	8.7	0.48		118	119	1.5	18	10	45	0.55	47	0.58	1.1	21	9.0
30-Aug-17	1242		50	5.0	3.3		92	95	1.9	25	16	37	0.74	31	0.61	0.82	20	2.2
SM; NH_4^+ Rich																		
08-Oct-15	1593		93	6.1	0.10	< DL	106	106	1.1	5.4	7.6	30	0.32	39	0.42	1.3	17	2.0
04-Jun-16	80	0.28	126	10	0.62	<DL	83	84	0.67	1.5	1.1							
17-Jun-16	1367	0.32	139	7.6	0.75	0.02	59	60	0.43	1.6	5.9							
29-Jun-16	1377	0.28	153	6.8	0.30	0.04	56	57	0.37	6.8								

04-Aug-16	1598	0.3	159	3.8	0.06	0.02	76	76	0.48	9.0		17	0.11	34	0.21	2.0	11	6.8
27-Sep-16	1673		159	4.7	0.21	0.05	71	71	0.45	1.9	1.8	32	0.20	57	0.36	1.8	16	14
Date	**EC (µs/cm)**	**DO (mg/L)**	**Cl^- (mg/L)**	**$SO4^{2-}$ (mg/L)**	**NO_3-N (mg/L)**	**NO2-N (mg/L)**	**NH_4N(mg/L)**	**TIN (mg/L)**	**TIN/ Cl**	**SRP (mg/L)**	**TP (mg/L)**	**ACE (µg/L)**	**ACE/ Cl**	**SUC (µg/L)**	**SUC/ Cl**	**SUC/ACE**	**SAC (µg/L)**	**CYC (µg/L)**
LP; NO_3^- Depleting																		
03-Jun-16	1059		68	41	36	7.0	14	57	0.84	3	9							
18-Jun-16	1253		72	32	64	>DL	3.0	67	0.94	15	13							
19-Jun-16	1160		49	22	72	>DL	2.0	74	1.5	15	13							
29-Jun-16	1201		55	28	78	0.32	17	96	1.7	17	20							