Investigating the Role of Water Quality on the Galvanic Corrosion of Lead in Hard Drinking Water with a Focus on NOM

by

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AUTHOR'S DECLARATION

This thesis consists of material all of which I authored or coauthored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

Statement of Contributions

Patrick King was the sole author for Chapters 1, 2, and 5, which were written under the supervision of Dr. Peter M. Huck and Dr. Sigrid Peldszus and were not written for publication.

Chapters 3 and 4 were written for publication in the future, and the exceptions to sole authorship of the material are as follows:

Research Presented in Chapters 3 and 4:
Patrick King designed and managed the experiments, and completed the majority of the experimental work, data analysis, and data interpretation at the University of Waterloo under the supervision of Dr. Peter M. Huck and Dr. Sigrid Peldszus**.** Several individuals at the University of Waterloo assisted with the experimental work. Lin Shen and Kirti Nemani performed the liquid chromatography with organic carbon detection (LC-OCD) analysis for Patrick King's samples and provided the raw data. The LC-OCD chromatograms were then integrated and evaluated by Patrick King. Mark Merlau performed the ion chromatography for the chloride, sulfate, and nitrate concentrations. Fariba Amiri completed the dissolved organic carbon (DOC) and total organic carbon (TOC) analyses in Chapter 3. As well, several co-op students and undergraduate research assistants, namely Patrick Beaulieu, Aleksandar Jakovljevic, Sam Sherlock, Nancy Zhou, Yolanda Fang, and Jayesh Boily, provided support in the lab under the supervision of Patrick King. These tasks included assisting with the construction of the test pieces, cleaning glassware, preparing synthetic waters, sampling, measuring water quality parameters (e.g. pH, alkalinity, specific conductance, turbidity, fluorescence excitation emission matrix) and sample preparation for other analyses such as LC-OCD and inductively coupled plasma-mass spectrometry (ICP-MS).

Patrick King prepared samples for ICP-MS and field flow fractionation (FFF). The ICP-MS analysis for measuring the total and dissolved lead and copper concentrations was completed at Dalhousie University by Heather Daurie. Dr. Benjamin Trueman completed the FFF coupled with ICP-MS and ultraviolet absorption at 254 nm analyses at Dalhousie University. Dr. Trueman also completed the solubility modelling for lead in the various waters using tidyphreeqc. Anushka Mishrra completed the scale analysis, which included imaging with a scanning electron microscope, energy dispersive X-ray spectroscopy, X-ray powder diffraction, and ICP-MS, under the supervision of Dr. Daniel Giammar. ALS Environmental (Waterloo Ontario) completed the collision reaction cell ICP-MS analysis for total metals, and the TOC and DOC analyses in Chapter 4.

As the first author, Patrick King was responsible for designing and managing the experimental work, carrying out data collection and analysis, and drafting and preparing Chapters 3 and 4 for future submission as manuscripts. Dr. Sigrid Peldszus, Kimia Aghasadeghi, Dr. Peter M. Huck, Dr. Graham Gagnon, and Dr. Benjamin Trueman contributed to the study design and interpretation of the results. Anushka Mishrra and Dr. Daniel Giammar also provided guidance with interpretation of the results, in particular for the scale analysis. At the time of thesis submission, Dr. Peter M. Huck and Dr. Sigrid Peldszus were the only coauthors that had reviewed Chapters 3 and 4.

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Abstract

Although the use of lead in water distribution systems is currently prohibited in Canada, old lead service lines, lead solder, and lead containing plumbing fixtures continue to be sources of lead in the tap water of many households. Due to the potential health impacts associated with the exposure to lead, it is a regulated contaminant. As the regulations regarding lead in drinking water are becoming more stringent, many municipalities not currently implementing corrosion control measures may be required to do so in the near future. Water quality plays an important role with regards to the corrosion and subsequent release of lead into drinking water. The impacts of many water quality parameters on the release of lead have been well studied, however the impact of some parameters such as hardness and natural organic matter (NOM), require further examination. In particular, the majority of lead corrosion research has focused on soft waters and not on hard waters, which have much higher concentrations of dissolved inorganic carbon (DIC) and hardness. To address literature gaps this study had two major goals; the first goal was to determine if hard waters could be aggressive to lead and the second goal was to evaluate if NOM could be a water quality factor of concern for lead release in real drinking water in Southern Ontario.

To achieve these objectives the study was conducted in two phases. The first phase (Phase I) involved assessing the impact of pH, DIC, hardness, and NOM on the galvanic corrosion of lead using synthetic waters. The test pieces consisted of lead and copper pipes with an external galvanic connection. This experiment involved 20 weeks of "dump and fill" events where the test pieces were manually emptied and then refilled with water of the same chemistry. The pH had a potentially significant impact on the release of total lead from the test pieces, with an increase in the pH from 7 to 8.5 resulting in a decrease in the release of total lead by an average of 4,390 µg/L. DIC did not have a significant impact on the release of lead, but did potentially significantly increase the galvanic current. To be precise, an increase in the DIC concentration from 10 mg/L to 80 mg/L increased the galvanic current by an average of 28.4 µA. NOM dosed at a relatively high concentration of 7 mg DOC/L of Suwannee River NOM (SR NOM) had a potentially significant impact on the release of dissolved lead from the test pieces, increasing it by an average of 2,320 µg/L. Using fluorescence excitation emission matrix (FEEM), it was

identified that there was a correlation between the release of dissolved lead and a decrease in the humic and fulvic acid intensities during stagnation. This provided indirect evidence that the formation of lead-NOM complexes were at least partially responsible for the increase in dissolved lead. Interestingly, hardness did not have a significant effect on the galvanic current or lead release, and oversaturating the waters with calcium carbonate did not mitigate lead release.

As SR NOM at a relatively high concentration of 7 mg DOC/L was found to greatly increase the release of dissolved lead in a variety of synthetic waters in Phase I, the second phase of this study (Phase II) focused on assessing if NOM could be a water quality factor of interest in real drinking water in Southern Ontario. This involved comparing lead release from test pieces exposed to raw groundwater from a municipal well in Cambridge, Ontario, treated but unchlorinated water from the Mannheim Water Treatment Plant which receives water from the Grand River in Southern Ontario, and four synthetic waters that modelled the real waters. Two of the synthetic waters modelled each of the real waters; one with SR NOM at a similar DOC concentration as in the real waters and another without any NOM. Phase II utilized test pieces of the same design as in Phase I and involved 21 weeks of "dump and fill" experiments. As expected, the dissolved lead release varied significantly between the different water types. Interestingly, the real waters released less dissolved lead than the synthetic waters with SR NOM but more dissolved lead than the synthetic waters without NOM. Using field flow fractionation with inductively coupled plasma mass spectrometry and ultraviolet absorption at 254 nm, it was determined that both the complexation of lead with NOM and colloidal dispersion caused by NOM could be attributed to elevated dissolved lead release in the presence of SR NOM and to a lesser extent the NOM in the real waters. Based on testing of the NOM using FEEM and liquid chromatography with organic carbon detection, it appeared that humic and to a lesser extent fulvic acids formed soluble complexes with oxidized lead.

The results suggest that hard waters could be aggressive towards lead, as lead release was relatively high in many of the hard waters. Additionally, hardness was not found to have a significant impact on lead release in Phase I and hardness films were not detected on any of the lead pipes in Phase I or II. Furthermore, DIC was found to increase the galvanic current between the lead and copper pipes, indicating that hard waters may be particularly susceptible to galvanic corrosion. As well, NOM may be a water quality factor of interest in a variety of real waters in Southern Ontario, including hard waters. Optimization of the treatment or removal of NOM is recommended for utilities that are attempting to decrease lead concentrations in consumers' taps.

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ADHD: Attention Deficit Hyperactivity Disorder
AL: Action Level
ANOVA: Analysis of Variance
ANSI: American National Standards Institute
AwwaRF: American Water Works Association Research Foundation
BLL: Blood Lead Level
CDOC: Hydrophilic Dissolved Organic Carbon
CRC: Collision Reaction Cell
CSMR: Chloride to Sulfate Mass Ratio
DIC: Dissolved Inorganic Carbon
DOC: Dissolved Organic Carbon
EDS: Energy Dispersive X-ray Spectroscopy
Em: Emission
Ex: Excitation
FEEM: Fluorescence Excitation Emission Matrix
FFF: Field Flow Fractionation
HOC: Hydrophobic Dissolved Organic Carbon
IC: Ion Chromatography
ICP-MS: Inductively Coupled Plasma Mass Spectrometry
IHSS: International Humic Substances Society
IQ: Intelligence Quotient
LC-OCD: Liquid Chromatography with Organic Carbon Detection
LCR: Lead and Copper Rule
LDPE: Low-Density Polyethylene
LMW: Low Molecular Weight
LSI: Langelier Saturation Index
MAC: Maximum Acceptable Concentration
MECP: Ministry of Environment, Conservation, and Parks
NOM: Natural Organic Matter

NSERC: Natural Sciences and Engineering Research Council of Canada
NSF: National Sanitation Foundation
PACl: Polyaluminum Chloride
PLSLR: Partial Lead Service Line Replacement
PVC: Polyvinylchloride
SEC: Size Exclusion Chromatography
SEM: Scanning Electron Microscope
SR NOM: Suwannee River Natural Organic Matter
SUVA: Specific Ultraviolet Absorption
TIC: Total Inorganic Carbon
TOC: Total Organic Carbon
US EPA: United States Environmental Protection Agency
UV: Ultraviolet
UV_{254}: Ultraviolet Absorption at 254 nm
WHO: World Health Organization
XRD: X-ray Powder Diffraction

Note

Chapter 1

Introduction

1.1 Problem Statement

Lead is a bluish grey heavy metal that is naturally present in the Earth's crust and has been used as a material in a variety of items including pipes, batteries, weights, ammunition, cable covers, and sheets for radiation protection (Agency for Toxic Substances and Disease Registry [ATSDR], 2019). Due to the reduction of lead in gasoline and paint, food and drinking water are now the largest sources of lead for the majority of the population in Canada (Health Canada, 2017). The use of lead service lines was allowed in Canada until 1975, and lead solder was allowed in water distribution systems and plumbing fixtures until 1990 (Health Canada, 2009). In addition, a variety of plumbing fixtures can contain significant quantities of lead. In fact, until 2014 the National Sanitation Foundation (NSF)/American National Standards Institute (ANSI) Standard 61 permitted "lead free" plumbing fixtures to contain up to 8% lead by weight. However, the NSF/ANSI Standard 61 now allows for only 0.25% lead by weight in the wetted surface of water system and plumbing products (Latham et al., 2015). As well, galvanized steel pipes can be a source of lead by either releasing lead directly from lead-containing zinc coatings on the surface of the pipe or indirectly by releasing lead that was seeded on the surface from upstream lead sources (Clark et al., 2015).

The release of lead into drinking water is of concern as it can enter the body and cause elevated blood lead levels (BLLs) which are linked to a variety of health impacts (Edwards et al., 2009; Hanna-Attisha et al., 2016; Triantafyllidou & Edwards, 2012). Perhaps the most significant impact of lead is on the neurodevelopment of children, with lead exposure being correlated to decreased intelligence quotient (IQ), and attention deficit hyperactivity disorder (ADHD) (Evens et al., 2015; Goodlad et al., 2013; Shadbegian et al., 2019). In fact, no safe BLL has been identified in children, indicating that the exposure to even small amounts of lead can cause negative health impacts (ATSDR, 2019). There is also evidence that *in utero* exposure to lead can affect the neurodevelopment of children (Emory et al., 2003; Jedrychowski et al., 2009; Parajuli et al., 2013). As well, chronic exposure to lead has been linked to neurological disorders in adults (Bleecker et al., 2005; Hänninen et al., 1998). Chronic exposure to lead has also been linked to hypertension, renal dysfunction, and cancer (Ekong et al., 2006; Fu & Boffetta, 1995; Navas-Acien et al., 2007).

Due to the health impacts associated with lead in drinking water, various agencies have set drinking water standards for it. Health Canada has set a maximum acceptable concentration (MAC) guideline of 5 μg/L for lead in drinking water (Health Canada, 2019). This was lowered in 2019 from 10 μg/L due to recent toxicological research and improvements in analytical methods for measuring lead in drinking water (Health Canada, 2017). This regulation is more stringent than in most other jurisdictions and may pose a challenge for many utilities. Currently, in Ontario, the enforceable MAC for lead regulated by the Ministry of Environment, Conservation, and Parks (MECP) is 10 μg/L (Government of Ontario, 2020). However, as the Health Canada guideline was recently lowered from 10 μg/L to 5 μg/L, it is likely that the enforceable MAC in Ontario will be lowered to 5 μg/L in the near future (Health Canada, 2017). The United States Environmental Protection Agency (US EPA) Lead and Copper Rule (LCR) requires municipalities to implement additional corrosion control measures if more than 10% of consumers' taps that are sampled exceed the action level (AL) of 15 μg/L for lead (Lead and Copper Rule, 2019; United States Environmental Protection Agency [US EPA], 1991). In addition, the World Health Organization (WHO) has set a maximum contaminant level for lead in drinking water of 10 μg/L (World Health Organization [WHO], 2011a).

Corrosion and the release of lead into drinking water is a research area of high importance for the water treatment industry due to the necessity of protecting public health. For starters, the issue has received more publicity in recent years as a result of the Flint Water Crisis, when a switch in the drinking water source from finished water from the City of Detroit to the Flint River resulted in an increase in the concentration of lead and other metals in the tap water of about 40% of the households that were using city water (Del Toral, 2015; Flint Water Crisis Fast Facts, 2019). The difference in the aggressiveness of the waters was primarily due to the fact that orthophosphate was added to the City of Detroit water, while no corrosion inhibitor was added to the Flint River water (Del Toral, 2015). In addition, ferric chloride was added as a coagulant to the Flint River water, which resulted in a higher chloride to sulfate mass ratio (CSMR), which also would have increased its aggressiveness towards lead and other metals (Del Toral, 2015). Although the probability of such a situation occurring in Canada is low, it is not impossible as lead service lines still serve some older buildings in most municipalities in Canada. For example, in 2016 it was estimated that about 1,500 homes in the City of Waterloo had lead service lines (Thompson, 2016). In addition, lead in excess of the Health Canada guideline of 5 µg/L has been widely reported in Canada. For instance, an investigation by nine universities and 10 media organizations conducted 12,000 tests to measure lead exposure in 11 Canadian cities, and found that one third of the samples exceeded the Health Canada guideline of 5 µg/L (Cribb et al., 2019). However, it was not stated in Cribb et al. (2019) how many samples exceeded 10 µg/L which is the MAC in Ontario and in many other provinces, and was the Health Canada guideline for much of the study period from 2014-2019. Thus, it is possible that this article overstated the severity of the issue in Canada. Nonetheless, these results are alarming and emphasize the need for swift action to address this issue. Due to increasingly stringent regulations and increased public awareness, it is likely that several municipalities in Ontario that are not currently implementing corrosion control measures may be required to do so in the near future.

The most effective means of reducing lead in a consumer's tap is to perform a lead service line replacement, however this is difficult and time consuming due to both legal and logistical constraints (Sandvig et al., 2008; Triantafyllidou & Edwards, 2010). As the utility only owns the portion of the service line up to the property line, in many cases only that portion of the lead pipe is replaced, referred to as a partial lead service line replacement (PLSLR) (Triantafyllidou & Edwards, 2010). However, PLSLRs are not recommended due to the potential for increased lead release following the replacement. In the short term, lead release can be increased due to the disruption of lead corrosion scales, which can be released as particulate lead into the water (Boyd et al., 2004; Sandvig et al., 2008; Schock et al., 1996; Triantafyllidou & Edwards, 2010). In the long term, lead release can be accelerated due to galvanic corrosion if part of the lead service line is replaced with copper or another metal (Brown et al., 2013; Clark et al., 2013; Kogo et al., 2017; Triantafyllidou & Edwards, 2010), and this effect can last for at least several months following a PLSLR (Cartier et al., 2012). Due to the difficulties with removing lead service lines and plumbing fixtures, the chemistry of drinking water is often altered to decrease the solubility of lead. A common means of doing this is by adjusting the pH and dissolved inorganic carbon (DIC) concentration to minimize the solubility of lead (Schock & Gardels, 1983; American

Water Works Association Research Foundation [AwwaRF], 1990) or by adding corrosion inhibitors such as orthophosphate (Cartier et al., 2013; Colling et al., 1992; Edwards et al., 2001a; Edwards & McNeill, 2002).

Many utilities in Southern Ontario use drinking water that is high in both alkalinity and hardness, which is commonly referred to as "hard water". Historically, it was thought that calcium carbonate scales that formed on pipes in distribution systems that use hard water would protect lead pipes against corrosion (Merrill & Sanks, 1977). However, it has been shown that corrosion and lead release can still be an issue even in municipalities that use hard water (Colling et al., 1987; Colling et al., 1992; Richards et al., 2018). Therefore, there is a need to investigate if DIC and hardness can form protective calcium carbonate scales on lead pipes. There is also a need to evaluate the impact of different water quality factors, such as pH and natural organic matter (NOM), in hard water on corrosion and lead release to evaluate which hard waters are likely to be the most aggressive towards lead. The pH is known to have a large impact on the solubility of lead, with an optimal pH being around 9.6 according to modelling by Schock and Gardels (1983). Furthermore, a study by the American Water Works Association Research Foundation (AwwaRF) (1990) suggested that an increase in the pH by 1 unit when it is in the range of 6 to 8, can decrease lead solubility by a factor of between five and ten. NOM has been found to greatly increase the release of dissolved lead (Dryer & Korshin, 2007; Korshin et al., 1999; Korshin et al., 2005; Korshin & Liu, 2019; Lin & Valentine, 2008a; Lin & Valentine, 2009; Valentine & Lin, 2009), and Colling et al. (1992) determined it has an effect even in hard water. However, the mechanisms of how NOM increases lead release require further study. As well, the impact of different types of NOM on lead corrosion needs to be compared to determine which components are the most important. The interplay of these factors along with DIC and hardness are likely to have a large impact on how aggressive a certain hard water is towards lead, and how likely high lead concentrations in consumers' taps will be for a given utility. This information will be valuable to many utilities that use hard water and are concerned about the possibility of having to implement corrosion control measures due to tightening regulations.

1.2 Objectives

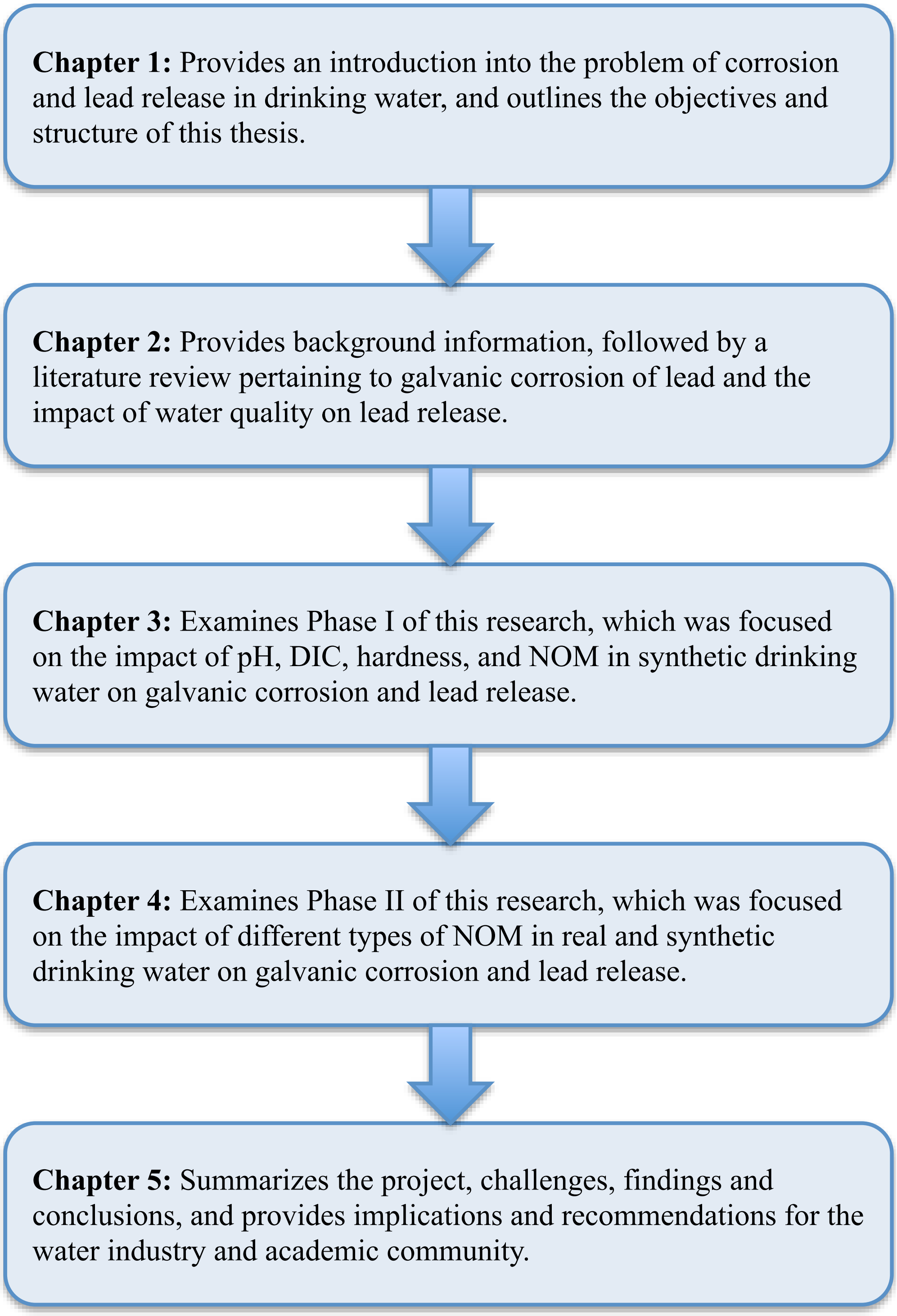
The major goals of this study were to determine if hard drinking water could be aggressive to lead and to determine if NOM is a water quality factor of concern with regards to lead release in Southern Ontario drinking water. To achieve these goals, this study was conducted in two phases. The first phase (Phase I) was focused on evaluating the impact of pH, DIC, hardness, and NOM on the galvanic corrosion of lead using synthetic drinking waters. The second phase (Phase II) focused on evaluating the impact of different types of NOM on the galvanic corrosion of lead using both real and synthetic drinking waters. Both of these phases were bench scale and followed a “dump and fill” protocol similar to that outlined in Triantafyllidou and Edwards (2010).

The specific objectives of this research study were to:

1. Evaluate the impact of pH, DIC, hardness, and NOM on galvanic corrosion and lead release using synthetic drinking waters (Phase I);
2. Compare the aggressiveness of real raw groundwater, treated river water, and synthetic drinking waters to lead (Phase II);
3. Investigate the impact of different types and concentrations of NOM on galvanic corrosion and lead release, in order to determine if NOM could be a significant water quality factor influencing lead release in real Southern Ontario drinking water (Phase II);
4. Using field flow fractionation (FFF) combined with inductively coupled plasma mass spectrometry (ICP-MS) and ultraviolet absorption at 254 nm (UV_{254}) detection, investigate the impact of different types and concentrations of NOM on the characteristics of dissolved lead (Phase II);
5. Explore changes to the characteristics of NOM upon stagnation in lead and copper test pieces using fluorescence excitation emission matrix (FEEM) and liquid chromatography with organic carbon detection (LC-OCD; Phases I and II);
6. Investigate the impact of water quality, in particular hardness and NOM, on the formation of corrosion scales on lead pipes (Phases I and II);
7. Assess the applicability of tidyphreeqc modelling software to predict lead release by comparing lead solubility predicted by the model and measured dissolved lead concentrations (Phases I and II).

1.3 Thesis Structure

This thesis is composed of three main chapters along with an introduction and conclusion. Chapters 3 and 4 were written in journal article format and were being prepared for submission at the time of writing. The structure of this thesis along with a brief description of the chapters is displayed in Figure 1.1.



Chapter 1: Provides an introduction into the problem of corrosion and lead release in drinking water, and outlines the objectives and structure of this thesis.

Chapter 2: Provides background information, followed by a literature review pertaining to galvanic corrosion of lead and the impact of water quality on lead release.

Chapter 3: Examines Phase I of this research, which was focused on the impact of pH, DIC, hardness, and NOM in synthetic drinking water on galvanic corrosion and lead release.

Chapter 4: Examines Phase II of this research, which was focused on the impact of different types of NOM in real and synthetic drinking water on galvanic corrosion and lead release.

Chapter 5: Summarizes the project, challenges, findings and conclusions, and provides implications and recommendations for the water industry and academic community.

Figure 1.1 Thesis structure.

Chapter 2

Literature Review

2.1 Background on Corrosion and Lead Release into Drinking Water

The corrosion of metallic pipes and fixtures is an issue for many drinking water utilities in Canada. It is a process that involves the deterioration of a material due to an interaction with its environment. For the corrosion of metallic materials to occur the four components of an electrochemical cell need to be present and these components include an anode, a cathode, a connection between the anode and the cathode to transfer electrons between them, and an electrolyte solution to conduct ions between the anode and cathode. In a water distribution system, the anode and cathode are sites of different electrochemical potential on the surface of the metal, the metal provides an electrochemical connection, and the water is the electrolyte solution. The reaction results in the oxidation of the metal and the reduction of an electron acceptor, usually oxygen or aqueous chlorine species (Health Canada, 2009; Triantafyllidou & Edwards, 2010). The concentration of metals such as lead, copper and iron in the water at a consumer's tap is often used to determine if corrosion has occurred (Health Canada, 2009). Lead can be released into drinking water from a variety of sources including lead service lines, lead solder, plumbing fixtures containing lead such as brass, and galvanized steel pipes (Clark et al., 2015; Giammar et al., 2010; Health Canada, 2009; Latham et al., 2015). As an example, corroded lead pipes and a corroded galvanized pipe are shown in Figure 2.1 (Wasserstrom et al., 2017).

Figure 2.1 Internal corrosion scales of pipe samples that have been cut in half lengthwise. Pb (lead) segments Pb-A and Pb-B contain a fully uniform scale coating, while galvanized pipe G is tuberculated. Reprinted with permission from *Scale Formation Under Blended Phosphate Treatment for a Utility With Lead Pipes* (E467), by Wasserstrom, Miller, Triantafyllidou, DeSantis, and Schock, 2017. Journal – American Water Works Association. © 2017 American Water Works Association.

The thermodynamically favorable lead containing species is dependent on the water quality. A predominance diagram for a system with a lead concentration of $1x10^{-6}$ M and a carbonate concentration of 0.001 M is displayed in Figure 2.2 (Huang, 2016). At a low redox potential in the orange coloured area, elemental lead is favoured and no corrosion occurs. At an intermediate redox potential (approximately -0.3 V to 1 V) lead (II) species are favoured. At a high redox potential (greater than approximately 1 V) lead (IV) species are favoured. Dissolved lead species predominate in the aqua coloured area and solid lead species predominate in the baby blue coloured area (Huang, 2016). In the lead (II) region, dissolved lead is favoured at a pH lower than approximately 6 and higher than approximately 11. Meanwhile, the solid lead species cerussite ($PbCO_3$) or hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) are favoured in the pH range of approximately 6 to 11. In the lead (IV) region, plattnerite (β-PbO_2) or scrutinyite (α-PbO_2) are favoured regardless of the pH, however the redox potential required to oxidize lead to lead (IV) is inversely related to the pH (Huang, 2016).

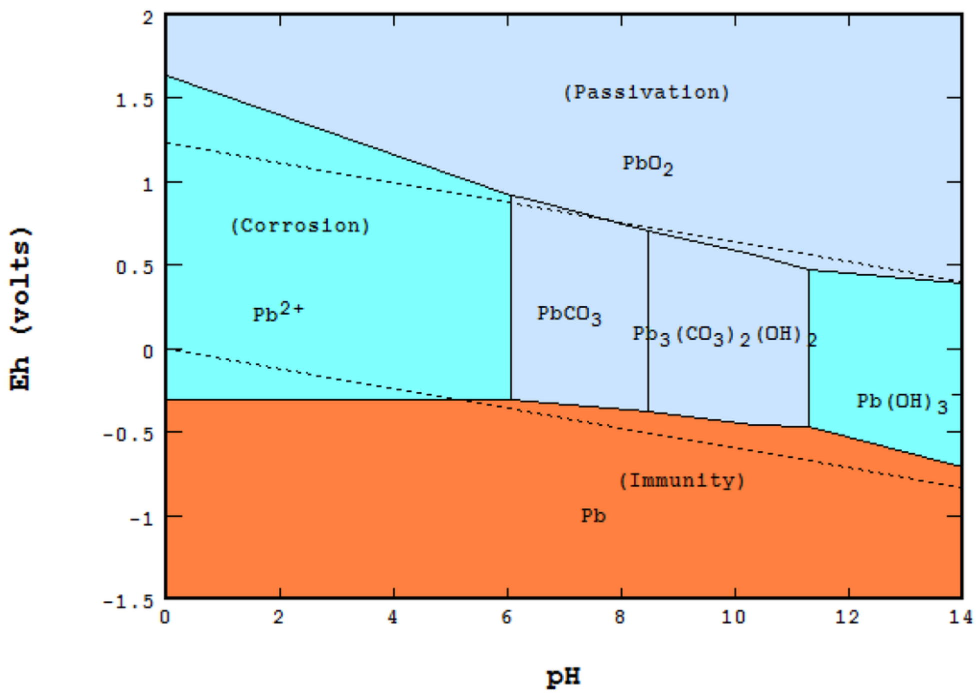


Figure 2.2 Predominance diagram for a lead carbonate system with a lead concentration of $1x10^{-6}$ M and a carbonate concentration of 0.001 M. Reprinted from *The Eh-pH Diagram and Its Advances* (https://www.mdpi.com/2075-4701/6/1/23) (6) by, H. Huang, 2016. Metals, used under CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/).

In order to predict the solubility and dissolution of lead from lead corrosion scales it is important to know which lead containing solids are present. Historically, it was believed that lead (II) solids controlled the solubility of lead in drinking water, but it is now known that lead (IV) solids can also be important (Boyd et al., 2008). The most commonly detected lead scales are cerussite, hydrocerussite, and plattnerite, as these are the predominant solid lead species in a lead carbonate system (Giammar et al., 2010; Huang, 2016). Lead (II) scales are usually white in color while lead (IV) scales are typically brownish-red in color (Xie & Giammar, 2011). However, if other dissolved species are present in the water different corrosion scales can form, such as lead hydroxyapatite ($Pb_5(PO_4)_3OH$), hydroxylpyromorphite ($Pb_5(PO_4)_3OH$), and phosphohedyphane ($Ca_2Pb_3(PO_4)_3Cl$) (Bae et al., 2019; Giammar et al., 2010; Noel et al., 2014; Peters et al., 1999). In real waters, scales also tend to be heterogeneous, contain a variety of different layers, and are more complex than predicted by solubility models (Cantor, 2017; Tully et al., 2019; Schock et al., 2014). For example, a study by Schock et al. (2014) found that harvested lead service lines from Madison Wisconsin had three distinct layers of corrosion scales. The outer layer interacted with the flowing water; the intermediate layer interacted with the water at a slower rate limited by diffusion, while the inner layer was isolated from recent contact with the water (Schock et al., 2014). The water in the pipes is often not in equilibrium with the corrosion scales and a change in water quality can lead to dissolution of the scales and an increase in lead release (Noel et al., 2014).

Lead in water is often differentiated into the dissolved and particulate fractions. Dissolved lead is defined as the fraction of lead that is able to pass through a 0.4 μm or 0.45 μm filter, while particulate lead is the fraction that is retained on the filter (AwwaRF, 1990). Particulate lead is the result of the abrasion, dislodgement, and transport of pieces of scale or lead fixtures, or due to the sorption of lead with other particulates that often contain iron, manganese, and aluminum (Brown et al., 2013; Cantor, 2017). Additionally, particulate lead can be more significant if a galvanic connection is present (Cartier et al., 2013). Particulate lead can increase lead concentrations above the theoretical solubility, can accumulate downstream from lead fixtures, and provide a source of lead even after the lead fixtures are removed (Bisogni et al., 2000; Schock et al., 2014). In summary, corrosion and the release of lead in water distribution systems is complex and is dependent on several factors including the source of the lead, galvanic connections, the water quality, and the flow regime.

2.2 Galvanic Corrosion of Lead

Corrosion and the release of lead is often more severe if lead is galvanically connected to a more noble metal, such as copper or brass (Brown et al., 2013; Kogo et al., 2017). This is referred to as galvanic corrosion and can occur if there has been a PLSLR, where part of a lead service line is replaced with a copper pipe (Triantafyllidou & Edwards, 2010). As shown in Figure 2.3, in this situation near the galvanic connection lead acts as the anode and is preferentially sacrificed, while copper acts as the cathode and is protected against corrosion (Brown et al., 2013; Triantafyllidou & Edwards, 2010). In addition, because lead (II) is a Lewis acid, a local drop in pH can occur near the surface of the lead pipe. Thus, galvanic corrosion can accelerate lead release by increasing the corrosion rate or by lowering the pH at the surface of the lead (Ma et al., 2016; Triantafyllidou & Edwards, 2010). Copper can also accelerate the corrosion of lead through deposition corrosion, where copper is deposited directly on the surface of the lead pipe (Hu et al., 2012).

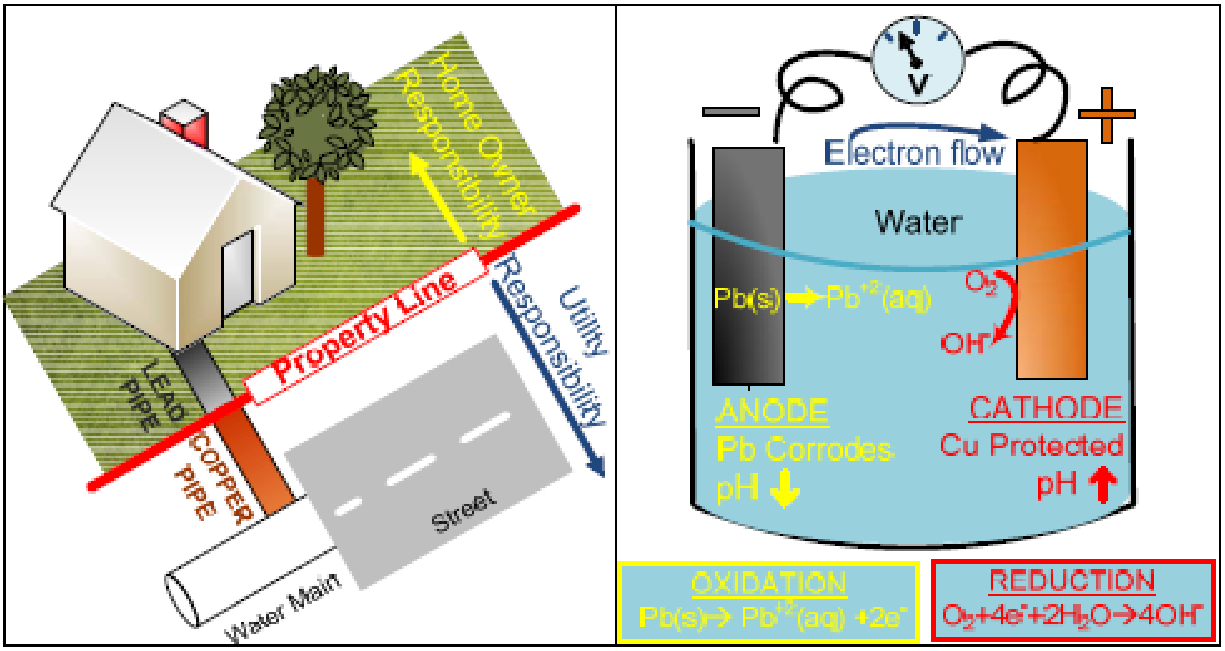


Figure 2.3 Conceptualized PLSLR (left). Galvanic cell with electrons being transferred from a lead coupon to a copper coupon (right). From *Contribution of Galvanic Corrosion to Lead in Water After Partial Lead Service Line Replacements* (3). Triantafyllidou and Edwards 2010. Reprinted with permission. © Water Research Foundation.

The impact of a galvanic connection on corrosion and lead release can vary from case to case. For instance, Arnold and Edwards (2012a) found that lower flow situations with longer stagnation periods made galvanic corrosion more severe and suggested that this was due to the formation of enhanced microcorrosive environments during stagnation. The manner in which the lead is connected to the other metal can impact galvanic corrosion as well. Connectors with crevices that allow the outside of the lead pipe to be in contact with water can greatly increase lead release (Clark et al., 2013). Additionally, the use of dielectrics can decrease lead release and the use of brass connectors can have slight benefits when compared to a direct connection to copper (Clark et al., 2013). As well, increasing the distance between the lead and the other metal can decrease lead release from a galvanic connection (Clark et al., 2013). Some studies have found that the increase in lead release due to galvanic corrosion may be temporary and only for the portion of the lead pipe that is in close proximity to the less noble metal (Boyd et al., 2012; Clark et al., 2013). However, Cartier et al. (2012) found that the galvanic current did not decrease even after seven months of experimentation and therefore proposed that the impacts could be relatively long lived.

2.3 Impact of Water Quality on Lead Release

2.3.1 pH

As evidenced in Figure 2.2 in section 2.1, common lead corrosion scales expected at pH values and redox potentials in drinking water include the lead carbonate solids cerussite and hydrocerussite (Huang, 2016). Using LEADSOL equilibrium modeling, Schock and Gardels (1983) determined that in a strictly lead carbonate system, the minimum solubility of lead at 25^0C occurs at a pH of 9.8 with a total inorganic carbon (TIC) concentration of 40 mg $CaCO_3$/L. To validate their results, they found that increasing the pH of water from 8.5 to 9.5 resulted in an immediate and substantial decrease in the rate of lead release from lead pipes in a pilot loop study (Schock & Gardels, 1983). Furthermore, a study by the AwwaRF (1990) suggested that in the pH range of 6 to 8, an increase in the pH by 1 unit could decrease lead solubility by a factor of between five and ten. According to Health Canada, pH adjustment is the most common method for reducing corrosion in drinking water systems and utility experience indicates that adjusting the pH from 7.9 to 9.5 is effective for reducing corrosion (2009). For example, the city of San Francisco reduced 90th percentile lead concentrations in consumers' taps from 30.9 µg/L to 1.0 µg/L in the Moccasin Water System by raising the median pH of the water from 6.8 to 8.7. The utility's findings also suggested that pH adjustment was more effective than raising the alkalinity (Wilzcak et al., 2010).

Kim et al., (2011) investigated the relationship between pH and lead release in a study that included a batch dissolution test, a pipe loop study, and household sampling in London Ontario. In the dissolution test, it was found that both hydrocerussite and a lead scale extracted from a harvested lead service line composed of mainly hydrocerussite with lesser amounts of cerussite and minium (Pb_3O_4), had a minimum solubility at a pH of 8 (Kim et al., 2011). The pipe loop study utilized harvested lead service lines from the City of London. In this study, raising the pH from 7.1 to 7.8 significantly decreased total lead release, but a further raise in the pH had no significant impact on lead release (Kim et al., 2011). Similarly, the results from the household sampling suggested that raising the pH of the treated water in London from 7.1 to 7.6 significantly decreased lead concentrations in half of the households that were being monitored, but a further raise in the pH to 8.1 did not impact total lead concentrations (Kim et al., 2011).

However, some studies have found that in certain situations raising the pH did not lower lead release (Brown et al., 2013; Churchill et al., 2000; Kim et al. 2011; Tang et al., 2006). Kim et al. (2011) found that increasing the pH above 8 did not have a significant effect on lead release. Furthermore, Churchill et al. (2000) found that raising the pH from 8 to 9 increased lead release in a pipe loop that included both lead solder and brass plumbing fixtures, and suggested that lead release might be more related to the variability in pH than the pH value itself. As well, adjusting the pH to an optimal value may not be sufficient to lower lead concentrations below the MAC and therefore may not be an effective corrosion control strategy in some cases (Brown et al., 2013; Schock, 1980).

As both the water quality and stagnation periods are variable in premise plumbing, both the dissolution rates and equilibrium solubility of corrosion scales can control the release of lead into drinking water. Therefore, to more thoroughly understand the impact of pH on the release of lead, it is important to know the dissolution rates and equilibrium solubility of different corrosion scales at different pH values. Giammar et al. (2010) found that in bench scale continuous flow stirred tank reactor experiments, the dissolution rate of hydrocerussite decreased with increasing pH, in the range of 7.5 to 10. Furthermore, Noel et al. (2014) determined that the equilibrium solubility of hydrocerussite decreased with increasing pH, also in the pH range of 7.5 to 10. Plattnerite dissolution rates are the lowest at a pH of approximately 8.5 and have been found to increase if the pH is decreased to 7 or increased to 10 (Giammar et al., 2010; Xie & Giammar, 2011). Based on equilibrium chemistry in a system where lead (IV) is favoured, the solubility of plattnerite would be expected to increase with increasing pH (Giammar et al., 2010). However, in a system where lead (II) is favoured, plattnerite would be reduced to lead (II) and the lowest concentration of dissolved lead would be expected at a pH of between approximately 10 and 11 (Giammar et al., 2010). In summary, the literature suggests an optimal pH value for minimizing lead concentrations in water is between about 8 and 10, with the exact value depending on the type of corrosion scales that are present and other water quality parameters.

2.3.2 Dissolved Inorganic Carbon and Alkalinity

The carbonate system is widely regarded to be the most important acid-base system in natural waters. This system consists of gaseous carbon dioxide ($CO_{2(g)}$), dissolved carbon dioxide

($CO_{2(aq)}$), carbonic acid (H_2CO_3), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}) and carbonate containing solids (Snoeyink & Jenkins, 1980). TIC is the sum of species containing inorganic carbon in a solution, while the DIC is the fraction of TIC that is dissolved (< 0.45 μm). In most natural waters with a low ionic strength, the DIC concentration can be calculated as

$$DIC = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \tag{1}$$

where $[HCO_3^-]$ is the concentration of bicarbonate in M, $[CO_3^{2-}]$ is the concentration of carbonate in M, and $[H_2CO_3^*]$ is the concentration of effective carbonic acid in M, where

$$[H_2CO_3^*] = [H_2CO_3] + [CO_{2(aq)}] \tag{2}$$

where $[H_2CO_3]$ is the concentration of carbonic acid in M and $[CO_{2(aq)}]$ is the concentration of dissolved carbon dioxide in M (Snoeyink & Jenkins, 1980).

Alkalinity is defined as "a measure of the capacity of a water to neutralize strong acid" (Snoeyink & Jenkins, 1980). The ability to neutralize strong acids comes from species such as bicarbonate, carbonate, hydroxide, silicates, borates, ammonia, phosphates, and organic basis (Snoeyink & Jenkins, 1980). In the majority of natural waters, the concentration of bicarbonate, carbonate, and hydroxide are much higher than the concentration of the other aforementioned bases. Therefore, the alkalinity is commonly estimated as

$$Alk = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \tag{3}$$

where Alk is the alkalinity in M, $[OH^-]$ is the concentration of hydroxide in M, and $[H^+]$ is the concentration of hydrogen ions in M (Snoeyink & Jenkins, 1980). Furthermore, in most natural waters with a near neutral pH this can be further simplified to

$$Alk = [HCO_3^-] + 2[CO_3^{2-}] \tag{4}$$

As common lead (II) corrosion scales include the lead carbonate solids cerussite and hydrocerussite, the alkalinity and DIC concentration are expected to have an effect on lead release (Giammar et al., 2010; Huang, 2016).

Historically, corrosion control consisted of oversaturating drinking water with calcium carbonate so that it would precipitate out of the water and form a protective film on pipes (Merrill & Sanks, 1977; Richards et al., 2018; Wilczak et al., 2010). This popularized the use of corrosion indices such as the Langelier Saturation Index (LSI) and the Ryznar Stability Index. However, research has proven that corrosion has little to do with calcium carbonate precipitation and limited research has been conducted to prove that precipitating calcium carbonate actually mitigates lead release (AwwaRF, 1990; Richards et al., 2018; Schock, 1989; Wilczak et al., 2010). Furthermore, based on the simulation shown in Figure 2.4, it is apparent that lead is still soluble even in water with a high TIC concentration, with the optimal value depending on the pH of the water (Brown et al., 2013; Schock & Gardels, 1983).

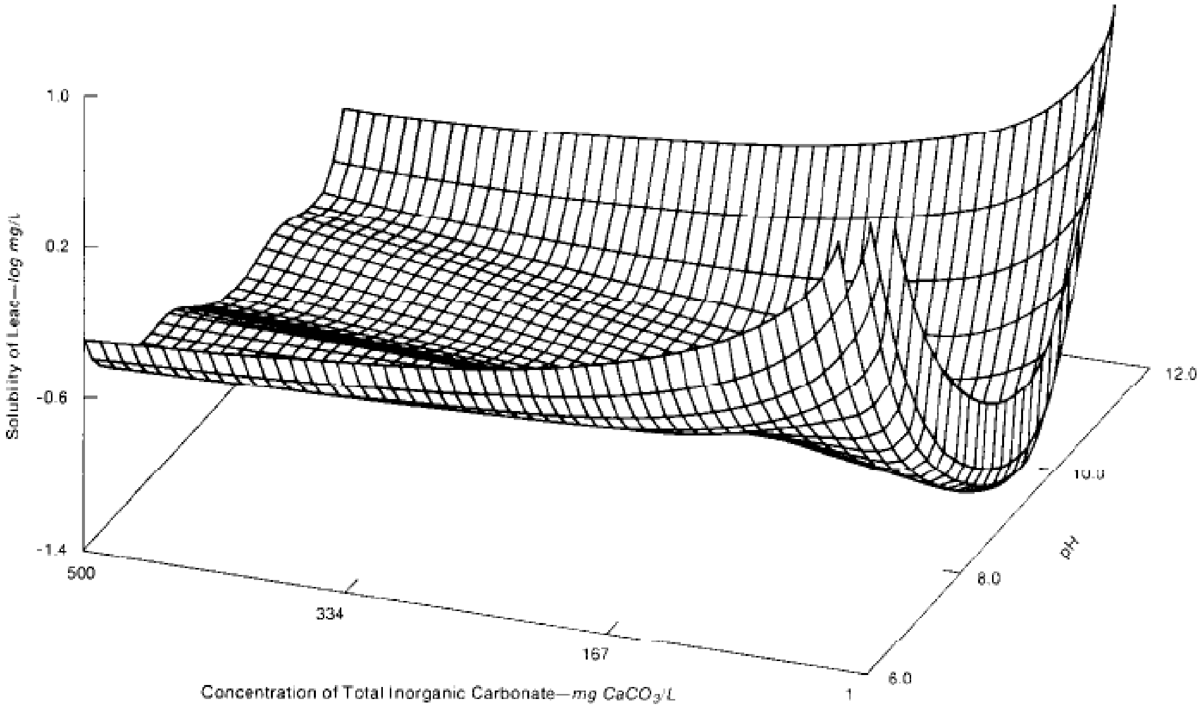


Figure 2.4 Three-dimensional plot of the relationship of lead solubility in log mg/L to pH and TIC concentration in mg $CaCO_3$/L. This figure was generated with LEADSOL computer software using theoretical chemical equilibrium relationships. Reprinted with permission from *Plumbosolvency Reduction by High pH and Low Carbonate – Solubility Relationships* (88), by Schock and Gardels, 1983. Journal – American Water Works Association. © 1983 American Water Works Association.

As previously mentioned, using LEADSOL computer software with chemical equilibrium relationships, Schock and Gardels (1983) determined that in a strictly lead carbonate system at 25^0C, the minimum solubility of lead occurs at a pH of 9.8 and a TIC concentration of approximately 40 mg $CaCO_3$/L. In fact, a study by Dodrill and Edwards (1995) that included the 90th percentile lead concentration data from 365 utilities in the US, found that most utilities that exceeded the LCR AL of 15 µg/L had drinking water with a very low alkalinity (< 30 mg $CaCO_3$/L). They also found that the average 90th percentile lead concentrations dropped significantly if the alkalinity was over 30 mg $CaCO_3$/L (Dodrill & Edwards, 1995).

The impact of DIC on the release of lead is complex and dependent on the source of the lead, the corrosion scales that are present, and other water quality parameters (Brown et al., 2013; Churchill et al., 2000; Giammar et al., 2010; Nguyen et al., 2011a; Noel et al., 2014; Tam & Elefsiniotis, 2009; Tang et al., 2006; Xie et al., 2010; Xie & Giammar, 2011). For example, a higher DIC concentration tends to increase the dissolution rates of the relatively insoluble lead (IV) corrosion scale plattnerite, into more soluble lead (II) (Giammar et al., 2010; Valentine & Lin, 2009). In general, the literature suggests that an alkalinity of 30-75 mg $CaCO_3$/L is optimal for minimizing lead concentrations (Dodrill & Edwards, 1995; Edwards et al., 2001a; Edwards & McNeill, 2002; Health Canada, 2009; Schock, 1980). Summaries of select studies that have investigated the impact of DIC or alkalinity on the release of lead are included in Table A.1 in Appendix A.

Interestingly, many studies have suggested that increasing the alkalinity above the range of 30-75 mg $CaCO_3$/L provides no additional benefit for reducing lead release in water and may even cause an increase due to complexation with carbonate (Edwards et al., 2001a; Nguyen et al., 2011a; Tam & Elefsiniotis, 2009). Colling et al. (1987) found that water with a high alkalinity (150-300 mg $CaCO_3$/L) could either be aggressive to lead (high propensity) or relatively non-aggressive to lead (low propensity) depending on the type of corrosion scale that formed. Evidently, the role of DIC and the release of lead are complex and in real situations can be difficult to predict. Although waters with high concentrations of DIC are typically less aggressive towards lead than waters with low concentrations of DIC, they can still be of concern.

2.3.3 Hardness

Water hardness is caused by polyvalent metallic ions, mainly calcium and magnesium, and is often expressed as milligrams of calcium carbonate per litre (mg $CaCO_3$/L). Water can be classified as soft, moderately hard, hard, or very hard, as indicated in Table 2.1 (World Health Organization [WHO], 2011b).

Table 2.1 Classification of Water Based on Hardness

Hardness (mg $CaCO_3$/L)	Water Type
<60	Soft
60-120	Moderately Hard
120-180	Hard
>180	Very Hard

*Data from (WHO, 2011b)

There have been a limited number of research studies that have investigated the impact of hardness on corrosion and lead release, and this may be due to the historical belief that calcium carbonate films could protect pipes from corrosion (Colling et al, 1992; Merrill & Sanks, 1977; Richards et al., 2018; Wilczak et al., 2010). However, more recent studies have suggested that the precipitation of calcium carbonate has little to do with the corrosion process and limited research has been conducted to prove that calcium carbonate films can actually seal and protect lead pipes from corrosion (AwwaRF, 1990; Richards et al., 2018; Schock, 1989; Wilczak et al., 2010). If hardness films such as calcium carbonate can form on lead pipes, it could potentially take several years before enough scaling would occur to significantly reduce the release of lead. This may be why no study has definitively proven that hardness films can protect lead pipes from corrosion.

There have been a few studies that have found that hardness can play a role with regards to what type of corrosion scales form (Colling et al., 1987; Colling et al., 1992; DeSantis et al., 2018; Edwards et al., 2001a; Wasserstrom et al., 2017). Colling et al. (1992) determined that the aggressiveness of hard water was dependent on what type of corrosion scale formed. Aggressive hard water (total lead release greater than 100 µg/L following a 30 min stagnation period) formed scales composed of thin hexagonal plates while less aggressive hard water (total lead release less than 30 µg/L following a 30 min stagnation period) formed scales with smooth solid surfaces (Colling et al., 1987; Colling et al., 1992). Furthermore, Colling et al. (1987) suggested that the hardness to alkalinity ratio might effect the formation of corrosion scales and how aggressive the water is towards lead. Water with a high hardness to alkalinity ratio (greater than 1.7) was more aggressive to lead than water with a low hardness to alkalinity ratio (lower than 1.7) (Colling et al., 1987). Similarly, Kim et al. (2011) found that there was a positive relationship between lead release and hardness in eight households in London Ontario.

There is evidence that calcium can be incorporated into corrosion scales when phosphate based corrosion inhibitors are added, with previous studies identifying brushite ($CaHPO_4 \cdot 2H_2O$), amorphous calcium aluminum phosphate ($CaAl_3(PO_4)(PO_3OH)(OH)_6$), and phosphohedyphane corrosion scales (Bae et al., 2019; Edwards et al., 2001a, Wasserstrom et al., 2017). Even when phosphate is not added, calcium and magnesium can be incorporated into lead corrosion scales, in particular the outer layer that is in direct contact with the water (Schock et al., 2014). For instance, Schock et al. (2014) conducted scale analysis using Inductively Coupled Plasma Atomic Emission Spectroscopy on corrosion scales from harvested lead service lines from Madison Wisconsin and found that the outer scale layer contained 0.5-1.4% calcium and 0.1-0.2% magnesium. The calcium concentration in the water varied from 65-95 mg/L and the magnesium concentration varied from 34-50 mg/L, indicating that the hardness varied from 302-443 mg $CaCO_3$/L (Schock et al., 2014). Although these studies identified that calcium and magnesium can be incorporated into corrosion scales, they do not prove that hardness films mitigated lead release.

A few studies have investigated the effects specifically of calcium on lead release and the results have been inconsistent (Bisogni et al., 2000; Dodrill & Edwards, 1995; Tang et al., 2006). Tang et al. (2006) found that an increase in the concentration of calcium at a pH greater than 7.9 reduced the release of lead from lead coupons, suggesting that calcium precipitation might have mitigated lead release. However, the calcium concentration was positively correlated with alkalinity, so it is unclear whether or not this was due to the calcium or the DIC concentration (Tang et al., 2006). Bisogni et al. (2000) suggested that the presence of calcium in water could reduce the zeta potential and precipitate lead containing colloids out of suspension, thus reducing the concentration of particulate lead. Conversely, Dodrill and Edwards (1995) found that the concentration of calcium had little or no impact on the 90th percentile lead concentrations of 365 utilities. Overall, the effect of hardness on the corrosion and release of lead has not been thoroughly studied and there is a need for more research investigating if hardness films such as calcium carbonate can provide protection against corrosion.

2.3.4 Natural Organic Matter

A common constituent in drinking water is NOM and it is composed of a mixture of organic compounds, which have diverse molecular sizes, aromaticities, and chemical compositions. NOM can increase lead release by taking part in redox reactions, inhibiting the formation of corrosion scales, forming soluble lead-NOM complexes, and inducing colloidal dispersion by adsorbing to corrosion scales (Dryer & Korshin, 2007; Korshin et al., 1999; Korshin et al., 2005; Korshin & Liu, 2019; Lin & Valentine, 2008a; Lin & Valentine, 2009; Valentine & Lin, 2009). A summary of studies that have looked into the impact of NOM on lead release can be found in Table A.2 in Appendix A. Several studies have identified that NOM can act as a reductant and accelerate the reduction of relatively insoluble lead (IV) into more soluble lead (II) (Dryer & Korshin, 2007; Korshin & Liu, 2019; Lin & Valentine, 2008a; Lin & Valentine, 2009; Valentine & Lin, 2009; Winning et al., 2017). It is unclear which fraction of NOM is responsible for the reductive capacity, but Winning et al. (2017) suggested that it is not aquatic humic substances. Aromatic groups in NOM do appear to play a role, as there is a relationship between lead release from the reduction of solid lead (IV) into dissolved lead (II) and a decrease in UV_{254} (Dryer & Korshin, 2007; Lin & Valentine, 2009; Valentine & Lin, 2009). Similarly, a decrease in the specific ultraviolet absorption (SUVA) is linked to the reduction of lead (IV) into lead (II), where the SUVA is defined as

$$SUVA = UV_{254}/DOC*100 \qquad (5)$$

where the SUVA is in L-mg/C-m, the UV_{254} is in cm^{-1}, and the dissolved organic carbon (DOC) concentration is in mg/L (Lin & Valentine, 2008a; Valentine & Lin, 2009).

Additionally, NOM can adsorb to corrosion scales which can prevent the formation of cerussite, hinder the growth of hydrocerussite crystals, and form a thin amorphous film on the surface of the metal (Korshin et al., 1999; Korshin et al., 2000; Korshin et al., 2005; Liu et al., 2010; Trueman et al., 2017; Valentine & Lin, 2009). NOM can also act as a complexing agent for metals such as lead, increasing the solubility (Korshin et al., 1999; Korshin et al., 2000; Trueman & Gagnon, 2016a; Trueman et al., 2017; Trueman et al., 2018; Trueman et al., 2019a; Willison & Boyer, 2012). More recent studies have also noted that colloidal dispersion caused by NOM adsorbing to lead corrosion scales may be a driving mechanism for an increase in dissolved lead (Korshin et al., 2005, Korshin & Liu, 2019; Trueman et al., 2018; Willison & Boyer, 2012). For example, Korshin and Liu (2019) found that the presence of Suwannee River standard fulvic acid greatly increased the concentration of colloidal lead, which was defined as being between 0.1 μm and 0.45 μm in size, and would usually be incorporated into the dissolved lead fraction (< 0.45 μm). This may be due to a negative shift in the zeta potential of nanoparticles, inducing colloidal dispersion (Korshin et al., 2005; Korshin & Liu, 2019; Liu et al., 2010). A few studies have utilized an innovative technique with either size exclusion chromatography (SEC) or FFF combined with ICP-MS and UV_{254} detection to investigate the properties of metal and NOM containing colloidal particles. These studies have found that both the formation of lead-NOM complexes and colloidal dispersion can be responsible for an increase in colloidal lead due to the presence of NOM (Trueman & Gagnon, 2016a; Trueman et al., 2017; Trueman et al., 2018; Trueman et al., 2019a). For these reasons, NOM can increase the concentration of dissolved lead above the theoretical solubility predicted by solubility models (Dryer & Korshin, 2007; Korshin et al., 1999; Lin & Valentine, 2008a).

In contrast, some studies have found that low concentrations of NOM (DOC ≤ 1 mg/L) did not increase lead release (Arnold, 2011; Triantafyllidou & Edwards, 2007). Arnold (2011) found that water with a DOC concentration of 1 mg/L had lower lead release from a lead pipe connected to a polyvinylchloride (PVC) pipe than water with no NOM and suggested that low concentrations of NOM could stabilize the release of particulate lead. This study also found that NOM was less important when lead was connected galvanically to copper compared to when there was no galvanic connection, when the DOC concentration was 4 mg/L (Arnold, 2011). In addition, NOM can stabilize lead release in a shorter time period, although lead concentrations may remain high even after stabilizing (Korshin et al., 1999).

As NOM is made up of a diverse collection of organic compounds, different types and components of NOM are likely to have different impacts on lead release. For instance, Willison and Boyer (2012) found that Suwannee River NOM (SR NOM) was significantly more aggressive towards lead than either salicylic acid or tryptophan, which were used as model compounds for NOM. The authors suggested that NOM adsorbing to the lead surface was a more important mechanism than the formation of lead-NOM complexes, but further research is required to confirm this finding (Willison & Boyer, 2012). Additionally, the impacts of NOM on lead corrosion are less substantial if the water has been coagulated, chlorinated or ozonated (Korshin et al., 2005; Lin & Valentine, 2009; Trueman et al., 2018; Valentine & Lin, 2009). This may be due to the removal or alteration of aromatic groups in the NOM, which are thought to be responsible for the reductive properties of the NOM (Lin & Valentine, 2009; Valentine & Lin, 2009). It is likely that improved removal or treatment of NOM will help to reduce lead release, which is in line with multi-barrier treatment decision making.

Although NOM has been found to have the largest impact on lead release in aggressive waters with a low pH and low DIC concentration (Korshin et al., 1999; Lin & Valentine, 2008a), it has been proven to increase lead release in waters with a high DIC concentration as well (Colling et al., 1992). Colling et al. (1992), found that adding peat slurry to water with a high concentration of DIC that was relatively non-aggressive to lead would make it more aggressive. They also found that removing NOM from water with a high DIC concentration that was relatively aggressive to lead using a granular activated carbon column would make it less aggressive (Colling et al., 1992).

2.3.5 Disinfectant Residual/Redox Potential

As shown in Figure 2.2 in section 2.1, maintaining a high redox potential can minimize lead release by facilitating the formation of low solubility lead (IV) corrosion scales (Brown et al., 2013; Huang, 2016). Several studies have found that free chlorine can maintain a high enough redox potential to oxidize lead (0) to lead (IV), while in most situations monochloramine can only maintain a redox potential high enough to oxidize lead (0) to lead (II) (Brown et al., 2013; Edwards & Dudi, 2004; Rajasekharan et al., 2007; Switzer et al., 2006). Figure 2.5 displays redox potentials measured by Rajasekharan et al. (2007) superimposed on a predominance diagram. The results suggested that under the conditions investigated, lead (0) could be oxidized to lead (IV) at a pH greater than approximately 1.7 if free chlorine was used as a disinfectant and at a pH greater than approximately 9.5 if monochloramine was used as a disinfectant (Rajasekharan et al., 2007).

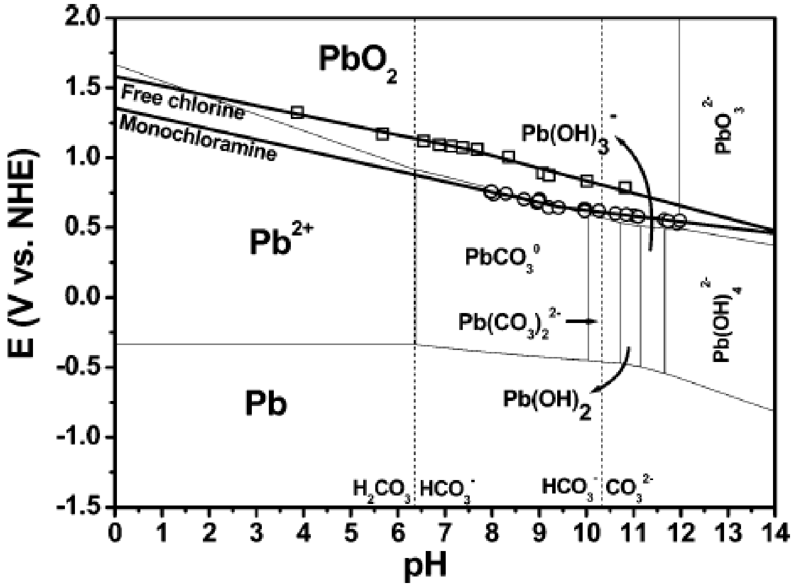


Figure 2.5 Predominance diagram for a lead carbonate system with the concentration of dissolved lead species equal to 7.25×10^{-8} M (15 μg/L) and the concentration of DIC equal to 1.5×10^{-3} M (18 mg/L) at 25 °C. Measured equilibrium potentials are shown as open squares for free chlorine, and as open circles for monochloramine. Reprinted with permission from *Electrochemistry of Free Chlorine and Monochloramine and its Relevance to the Presence of Pb in Drinking Water* (4255), by Rajasekharan, Clark, Boonsalee, & Switzer, 2007. Environmental Science & Technology. Copyright (2007) American Chemical Society.

Not only does monochloramine maintain a lower redox potential than free chlorine, it has also been found to facilitate the reduction of lead (IV) to lead (II), which can cause a large increase in lead release if chlorine is replaced with chloramine as a disinfectant (Edwards & Dudi, 2004; Giammar et al., 2010; Lin & Valentine, 2008b; Lin & Valentine, 2009; Xie & Giammar, 2011). In fact, this was observed in Washington D.C., when large increases in lead concentrations were measured in consumers' taps when the utility switched disinfectants from free chlorine to chloramine in the year 2000 (Edwards & Dudi, 2004). Interestingly, several studies have found that monochloramine can increase the reduction rate of lead (IV) to lead (II) compared to control water without any disinfectant (Lin & Valentine, 2008b; Lin & Valentine, 2009; Xie & Giammar, 2011). Lin and Valentine (2009) proposed that this may be due to the formation of an intermediate species in the monochloramine decay chain that reacts with lead (IV) oxide. As discussed in section 2.3.8, the nitrate and ammonia produced from the use of chloramines can also attack lead and increase lead release (Edwards & Dudi, 2004). Overall, free chlorine maintains a higher redox potential than chloramine and therefore its use as a disinfectant can help minimize lead concentrations in drinking water by forming and stabilizing lead (IV) corrosion scales.

2.3.6 Chloride to Sulfate Mass Ratio

The CSMR is defined as

$$CSMR = C_{Cl}/C_{SO4} \tag{6}$$

where C_{Cl} is the concentration of chloride in mg/L and C_{SO4} is the concentration of sulfate in mg/L. According to ionic transport theory, if a lead-copper galvanic connection is present then water with a CSMR greater than 0.77 should be significantly more aggressive to lead than water with a CSMR less than 0.77 (Nguyen et al., 2011a). However, several studies have found that in practice this threshold is closer to 0.5 (Edwards & Triantafyllidou, 2007; Nguyen et al., 2010; Triantafyllidou & Edwards, 2010). Without a galvanic connection, the CSMR has not been found to have a large impact on lead release (Hu et al., 2012; Nguyen et al., 2010; Triantafyllidou & Edwards, 2010).

Hu et al. (2012), found that the CSMR had a large impact on lead release when lead was galvanically connected to copper. When compared to water with a CSMR of 0.2, water with a CSMR of 16.2 released six times more lead when free chlorine was used as a disinfectant and eight times more lead when chloramine was used as a disinfectant. Additionally, water with a CSMR of 16.2 had a higher galvanic current and resulted in a more substantial drop in pH near the junction compared to water with a CSMR of only 0.2 (Hu et al., 2012). Sulfate can create a protective layer on the lead surface by creating low solubility lead sulfate corrosion scales, even in water with a pH as low as 3 (Nguyen et al., 2011a). In contrast, chloride can form soluble complexes with lead, which can increase the concentration of lead in the water (Tang et al., 2006). Using a scanning electron microscope (SEM), it was observed by Tang et al. (2006) that water with a relatively high sulfate concentration formed smooth corrosion scales while water with a relatively high chloride concentration formed flaky scales. The difference in solubility and structure of these corrosion scales provides a mechanistic explanation for the CSMR threshold for lead corrosion (Tang et al., 2006).

A few recent studies have found that using the CSMR as a parameter to evaluate the aggressiveness of water towards lead when a galvanic connection is present is not as useful as originally thought. For instance, Kogo et al. (2017) found that in the range of 0.2 to 1, the CSMR had little impact on lead release when lead was galvanically connected to copper. The authors suggested that this might have been due to a high bicarbonate concentration and the use of orthophosphate as a corrosion inhibitor (Kogo et al., 2017). Additionally, it has been suggested that increasing the concentration of both chloride and sulfate while maintaining a constant CSMR increases the aggressiveness of the water to lead (Ng & Lin, 2016; Willison & Boyer, 2012). For example, Ng and Lin (2016) found that increasing the sulfate concentration increased lead release from a lead wire galvanically connected to a copper wire. In fact, sulfate at the same molar concentration as chloride was found to have a similar effect on lead release as chloride (Ng & Lin, 2016). Therefore, it is important to monitor the chloride and sulfate concentrations in addition to the CSMR when studying galvanic corrosion, as all three parameters play a role with regards to corrosion and lead release.

2.3.7 Corrosion Inhibitors

The most commonly used corrosion inhibitors include orthophosphate, polyphosphates, and silicates, all of which can be added with or without zinc (Health Canada, 2009). In some cases, including galvanic corrosion, zinc can offer cathodic protection, but it has been shown that in most circumstances zinc orthophosphate is not more effective than orthophosphate without zinc (Schneider, et al., 2007; Schneider et al., 2011). It has been proven that orthophosphate is an effective corrosion inhibitor for lead and is usually dosed at a concentration around 3 mg PO_4/L (Cantor et al., 2000; Cantor, 2017; Cartier et al., 2013; Colling et al., 1992; Edwards et al., 2001a; Edwards & McNeill, 2002; Hayes et al., 2014; Tam & Elefsiniotis, 2009). An optimal pH when orthophosphate is added as a corrosion inhibitor is 7.4, but it has proven to be effective in a range of at least 7.2 to 7.8 (Brown et al., 2013). The reduction in lead release is largely attributed to the formation of low solubility lead phosphate corrosion scales, with some identified species including lead hydroxyapatite, hydroxylpyromorphite, and phosphohedyphane (Bae et al., 2019; Giammar et al., 2010; Noel et al., 2014; Peters et al., 1999). In addition to forming lead phosphate scales, orthophosphate has been found to decrease the dissolution rates of hydrocerussite and plattnerite corrosion scales (Giammar et al., 2010; Noel et al., 2014). However, orthophosphate addition increases the concentration of phosphate in wastewater, which is undesirable as it can cause eutrophication in receiving water bodies and can require removal at the wastewater treatment plant to meet regulations, which increases the cost of treatment (Cantor et al., 2000; Cantor, 2017; Schock et al., 2014). It has also been suggested that orthophosphate can increase the release of particulate lead in some situations (Xie & Giammar, 2011).

The reversion of polyphosphates to orthophosphate is believed to be the mechanism for corrosion control using polyphosphates (Edwards et al., 2001a; Edwards & McNeill, 2002). However, polyphosphates are known to sequester metals and are often added to drinking water to sequester iron to prevent red water issues (Brown et al., 2013; Cantor et al., 2000; Edwards et al., 2001a; Edwards & McNeill, 2002; Trueman et al., 2018). For this reason, polyphosphates have been found to increase lead release in many situations and therefore they are not recommended for lead corrosion control (Cantor et al., 2000; Edwards et al., 2001a; Edwards & McNeill, 2002; Schock et al., 2005; Trueman et al., 2018).

Silicate based corrosion inhibitors offer an alternative to phosphate based corrosion inhibitors but have not been studied as thoroughly (Health Canada, 2009). As sodium silicate is a basic compound, it is difficult to determine if its use as a corrosion inhibitor reduces lead release by forming a protective scale or by increasing the pH (Health Canada, 2009; LaRosa Thompson et al., 1997; Lintereur et al., 2010; Woszczynski et al., 2015). An increase in the pH does appear to be responsible for much of the reduction in lead release attributed to silicate (Lintereur et al., 2010; Woszczynski et al., 2015). However, it has been found that the decrease in lead release is more than what would be predicted from the increase in the pH alone (LaRosa Thompson et al., 1997). Although silicates do not appear to form lead-silicate solids, it has been suggested that silicates can form a protective film on pre-existing lead corrosion scales (LaRosa Thompson et al., 1997). At a minimum, silicate based corrosion inhibitors can effectively sequester metals like iron without increasing lead release, which is an advantage over polyphosphate (LaRosa Thompson et al., 1997; Schock et al., 2005). For example, a switch from polyphosphate to sodium silicate dosed at 25-30 mg/L as SiO_2 in Hopkinton Massachusetts, reduced 90th percentile lead concentrations in consumers' taps from 77 µg/L to 2 µg/L, while maintaining a low turbidity (Schock et al., 2005). Despite the potential benefits of silicate based corrosion inhibitors, they have not been found to be as effective as orthophosphate for reducing lead release (Kogo et al., 2017; LaRosa Thompson et al., 1997; Woszczynski et al., 2015). More research is needed to determine the mechanisms of how silicates inhibit corrosion and lead release, and how their performance can be optimized.

2.3.8 Other

Several other water quality factors in addition to those previously discussed can impact corrosion and lead release, such as metals, nitrate and temperature. For instance, elevated concentrations of iron have been associated with high concentrations of lead in drinking water. Knowles et al. (2015), found that the use of ferric sulfate as a coagulant resulted in twice as much lead release from lead solder compared to the use of polyaluminum chloride (PACl) and alum. Potential reasons for increased lead release include; the incorporation of iron into lead corrosion scales, the adsorption of lead to iron particles, and the galvanic corrosion of lead due to iron particles (Knowles et al., 2015; Trueman & Gagnon, 2016b). Other metals such as manganese and aluminum can also increase the release of lead into drinking water in a similar fashion (Knowles et al., 2015; Schock et al., 2014; Trueman et al., 2019b).

In addition, nitrate has been found to increase lead release from lead and brass at concentrations as low as 10 mg NO_3-N/L (Edwards & Dudi, 2004; Nguyen et al., 2011b). Nguyen et al. (2011b), determined that nitrate can increase the galvanic current between lead and other metals, decrease the stability of corrosion scales, and make corrosion less uniform.

Several studies have found that the concentration of lead measured in water sampled from household taps varies seasonally, with the highest lead concentrations occurring in the summer (Del Toral et al., 2013; Health Canada, 2017; Karalekas et al., 1983; Masters et al., 2016; Ngueta et al., 2014). Although several water quality parameters vary seasonally, temperature has been identified as an important factor that influences the release of lead into water from lead service lines and fixtures (Lintereur et al., 2010; Masters et al., 2016; Ngueta et al., 2014; Tang et al., 2006). For this reason, Health Canada (2017) recommends that lead monitoring in drinking water should be conducted at the same time each year between June and October. However, there is not a clear relationship between temperature and lead release, as the impact of temperature varies depending on the corrosion scales that are present (Colling et al., 1992; Masters et al., 2016; Schock, 1980). Masters et al. (2016) found that the dissolution of lead from lead (IV) oxide (PbO_2) and plumbonacrite ($Pb_{10}(CO_3)_6O(OH)_6$) was higher when the temperature was 20^0C compared to 4^0C. Conversely, they found that there was no difference in the dissolution of cerussite and hydrocerussite at 4^0C and 20^0C (Masters et al., 2016). In all, several different water quality factors impact the severity of corrosion and lead release. Therefore, it is crucial to monitor lead concentrations in susceptible household taps, especially after there has been a change in the chemistry of the water in the distribution system.

2.4 Knowledge Gaps and Research Needs

Upon reviewing the literature, it is evident that corrosion and lead release is a complex issue and is dependent on several different factors including the water quality, the source of the lead, corrosion scales, the presence of galvanic connections, and the flow regime. Compared to many other water quality factors, the impacts of hardness and NOM have not been studied as thoroughly. This section will discuss knowledge gaps and research needs with regards to these water quality factors to provide justification for the experimental work.

2.4.1 Corrosion and Lead Release in Hard Drinking Water

In general, studies have found that water with a low alkalinity (< 30 mg $CaCO_3$/L) is more aggressive to lead than water with a moderate or high alkalinity (> 30 mg $CaCO_3$/L), particularly when the pH is relatively low (Dodrill & Edwards, 1995; Edwards et al., 2001a; Edwards & McNeill, 2002; Health Canada, 2009; Schock, 1980). Although soft water is generally more aggressive towards lead than hard water, it has been suggested that hard water can still be aggressive depending on other water quality factors like pH and NOM (Colling et al., 1987; Colling et al., 1992). As calcium and magnesium can be incorporated into corrosion scales and the calcium concentration has been found to impact lead release, it is possible that hardness could have a significant impact on corrosion and lead release (Bae et al., 2019; Bisogni et al., 2000; Edwards et al., 2001a; Schock et al., 2014; Tang et al., 2006; Wasserstrom et al., 2017). This suggests that there is a need to investigate the impact of hardness separately from DIC on corrosion and lead release in a controlled laboratory experiment.

Additionally, no research study has definitively proven that water with a positive LSI, that is oversaturated with calcium carbonate, can actually form protective calcium carbonate films (AwwaRF, 1990; Richards et al., 2018; Schock, 1989; Wilczak et al., 2010). As well, it has been suggested that the ratio between hardness and alkalinity can impact the structure of corrosion scales (Colling et al., 1992). Therefore, there is a need to determine if there is an interaction effect between DIC and hardness on lead release. This is crucial for assessing if certain hard waters could be more aggressive to lead than others. As many utilities in Southern Ontario use hard water, such as the Region of Waterloo where the hardness can be over 500 mg $CaCO_3$/L (Region of Waterloo & City of Guelph, n.d.), it is important to evaluate if hard waters can be aggressive to lead, which hard waters are the most aggressive, and what can be done from a water treatment standpoint to minimize lead release in the distribution system.

2.4.2 Role of NOM with Regards to Corrosion and Lead Release

NOM can greatly increase the release of dissolved lead (< 0.45 μm) by forming lead-NOM complexes or through colloidal dispersion (Korshin et al., 1999; Korshin et al., 2000; Korshin et al., 2005; Korshin & Liu, 2019; Willison & Boyer, 2012). However, it is not well understood which components of NOM are responsible for complexing with lead and inducing colloidal dispersion (Gao et al., 2018; Korshin et al., 2005; Korshin & Liu, 2019; Winning et al., 2017). Evaluating the impact of different types and concentrations of NOM on corrosion and lead release can provide insight into which components of NOM are primarily responsible for increasing the release of dissolved lead. In particular, a comparison between synthetic NOM and real NOM would be useful, as most studies have focused on one or the other and it appears that NOM in treated drinking water does not behave the same as NOM added to synthetic water (Korshin et al., 2005; Lin & Valentine, 2009; Trueman et al., 2018; Valentine & Lin, 2009). As well, characterizing the NOM both before and after contact with lead using advanced equipment such as LC-OCD and FEEM is required, in order to evaluate how the interaction with lead can impact the characteristics of the NOM. The use of either SEC coupled with ICP-MS and UV_{254} detection (SEC/ICP-MS; SEC/UV_{254}) or FFF coupled with ICP-MS and UV_{254} detection (FFF/ICP-MS; FFF/UV_{254}) would complement the aforementioned analyses by providing a comparison between the size of colloidal particles containing lead and NOM, to determine if there is a correlation between the two.

The impact of NOM in hard water has rarely been studied, but it has been suggested that groundwater with relatively high concentrations of NOM are more aggressive towards lead than groundwater with lower concentrations of NOM (Colling et al., 1992). This is of particular interest in Southern Ontario, as many utilities use hard water that can have measurable quantities of NOM. For instance, the Mannheim water treatment plant in the Region of Waterloo can have treated water with relatively high hardness and a DOC concentration of approximately 3.4 mg/L (Chapter 4). Also, as the characteristics of NOM varies depending on the source, it is important to understand if NOM in Southern Ontario drinking water can be of potential concern with regards to corrosion and lead release.

Chapter 3

Impact of pH, DIC, Hardness, and NOM on the Galvanic Corrosion of Lead

This chapter is based on an article that at the time of thesis submission was being prepared for submittal to Environmental Science & Technology tentatively titled “Impact of pH, DIC, Hardness, and NOM on the Galvanic Corrosion of Lead”. The cited references in this chapter are included in the list of references at the end of the thesis.

This article focuses on the results of a bench scale “dump and fill” experiment to assess the role of pH, DIC, hardness, and NOM on galvanic corrosion and lead release (Phase I). As identified in Chapter 2, the DIC concentration and hardness were controlled separately in order to analyze their effects on corrosion and lead release separately. NOM was also included as a factor in this experiment in order to study its effect on corrosion and lead release in synthetic drinking waters with different chemistry. A conclusion section (section 3.4) was added for the thesis submission, however it will not be included in the journal article, as Environmental Science and Technology does not allow a conclusion section. Appendix B contains supplemental information referenced in this chapter, while Appendix C contains the raw data that was collected.

The author would like to acknowledge the contributions of the individuals who will be coauthors of the journal article that will be submitted: Dr. Sigrid Peldszus, Anushka Mishrra, Dr. Benjamin Trueman, Kimia Aghasadeghi, Dr. Graham Gagnon, Dr. Daniel Giammar, and Dr. Peter M. Huck. Please refer to the Statement of Contributions in the front matter of the thesis for a detailed description of the work that was completed by the coauthors and lab assistants.

Summary

A two-level fractional factorial design was utilized to investigate the impact of pH, DIC, hardness, and NOM on the galvanic corrosion of lead using a variety of synthetic drinking waters. A “dump and fill” protocol was followed, with test pieces consisting of lead and copper pipes with an external galvanic connection**.** Increasing the pH from 7 to 8.5 decreased the release of total lead by an average of 4,390 µg/L (Figure 3.1)**.** Increasing the DIC concentration from 10

mg/L to 80 mg/L increased the galvanic current by an average of 28.4 µA, but did not significantly impact lead release. The hardness did not impact lead release and there was no evidence that the precipitation of calcium carbonate protected lead pipes against corrosion. The addition of SR NOM at a concentration of 7 mg DOC/L increased the concentration of dissolved lead (< 0.45 µm) by an average of 2,320 µg/L. The increase in dissolved lead release may have been caused by complexation, as strong correlations were identified between dissolved lead release and the decrease in humic ($R^2 = 0.88$; $p < 0.001$) and fulvic acid ($R^2 = 0.78$; $p < 0.001$) intensities measured by FEEM.

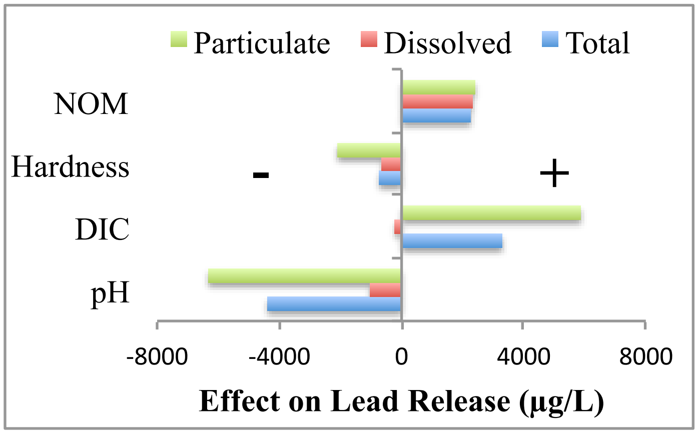


Figure 3.1 Effects of water quality factors on lead release.

3.1 Introduction

The exposure to lead in drinking water is a known cause of elevated BLLs, which has been linked to neurological and neurodevelopmental disorders such as decreased IQ in children (Edwards et al., 2009; Evens et al., 2015; Hanna-Attisha et al., 2016; Shadbegian et al., 2019; Triantafyllidou & Edwards, 2012). Due to the health impacts associated with lead exposure, it is a regulated contaminant in drinking water in North America. Health Canada has set a MAC guideline of 5 µg/L, which was lowered from 10 µg/L in 2019 due to recent toxicological research and improvements in analytical methods for lead (Health Canada, 2019). Meanwhile, the US EPA has set an AL of 15 µg/L (US EPA, 1991). The most common sources of lead in drinking water include lead service lines, lead solder, lead containing plumbing fixtures, and galvanized pipes (Clark et al., 2015; Giammar et al., 2010; Latham et al., 2015).

Corrosion and the subsequent release of lead are often accelerated if there is a galvanic connection between lead and another metal, such as copper or brass (Brown et al., 2013; Kogo et al. 2017; Triantafyllidou & Edwards, 2010). Galvanic corrosion can accelerate lead release by either increasing the corrosion rate or causing a local drop in the pH near the surface of the lead (Ma et al., 2016; Triantafyllidou & Edwards, 2010). This can occur if there has been a PLSLR where part of the lead service line is replaced with copper (Triantafyllidou & Edwards, 2010). It has been suggested that the impacts of a PLSLR can be relatively long-lived (Cartier et al., 2012; Triantafyllidou & Edwards, 2010). Copper can also accelerate the corrosion of lead through deposition corrosion, when copper is deposited directly on the surface of the lead pipe (Hu et al., 2012).

Water quality plays an important role with regards to corrosion and lead release. The impacts of pH and DIC/alkalinity on lead release have been well studied and play an important role with regards to the solubility of lead carbonate corrosion scales (AwwaRF, 1990; Giammar et al., 2010; Noel et al., 2014; Schock, 1980; Schock & Gardels, 1983). Although an optimal pH for minimizing lead release is case-specific, previous research has suggested that an optimal pH for minimizing lead release is in the range of 8 to 10 (Giammar et al., 2010; Kim et al., 2011; Noel et al., 2014; Schock & Gardels, 1983, Wilzcak et al., 2010). Waters with an alkalinity less than about 30 mg $CaCO_3$/L have been found to be the most aggressive towards lead and previous research suggests that an alkalinity of approximately 30-75 mg $CaCO_3$/L is optimal for minimizing lead release (Dodrill & Edwards, 1995; Edwards et al., 2001a; Edwards & McNeill, 2002; Schock, 1980; Tam & Elefsiniotis, 2009). The literature is inconsistent with regards to whether or not increasing the alkalinity above this range (> 75 mg $CaCO_3$/L) can decrease lead release any further (Arnold, 2011; Edwards & McNeill, 2002; Liu et al., 2010; Nguyen et al., 2010; Nguyen et al., 2011a; Noel et al., 2014; Tam & Elefsiniotis, 2009; Triantafyllidou & Edwards, 2011; Zhou et al., 2015). Therefore, it is likely that the impact of DIC at high concentrations is dependent on the experimental conditions. In particular, the impact of DIC specifically on galvanic corrosion can be difficult to predict, as it can buffer against pH changes near the surface of the lead but can increase the galvanic current and the corrosion rate (Arnold, 2011; Nguyen et al., 2011a; Triantafyllidou & Edwards, 2010; Triantafyllidou & Edwards, 2011; Zhou et al., 2015).

In the past, adjusting the pH and alkalinity of water to be oversaturated with calcium carbonate was a common corrosion control method. It was thought that a protective calcium carbonate film could form on lead pipes, which would prevent the direct contact of the water with the metal, thus preventing corrosion (Merrill & Sanks, 1977). However, limited research has been conducted to prove that precipitating calcium carbonate actually mitigates lead release and more recent literature has suggested that corrosion has little to do with calcium carbonate precipitation (AwwaRF, 1990; Richards et al., 2018; Schock, 1989; Wilczak et al., 2010). Although hard waters are typically less aggressive to lead than soft waters, corrosion and lead release have nonetheless been found to occur in hard waters (Colling et al., 1987; Colling et al., 1992). In addition, a few studies have found that hardness can play a role with regards to what type of corrosion scales form (Colling et al., 1987; Colling et al., 1992; DeSantis et al., 2018; Edwards et al., 2001a; Wasserstrom et al., 2017). Furthermore, Bisogni et al. (2000) found that calcium, a component of hardness, can increase the zeta potential of colloidal particles, leading to their destabilization. Hence, it is possible that in certain situations hardness could destabilize colloidal lead, and therefore decrease the concentration of lead in the water (Bisogni et al., 2000). However, the impact of hardness under controlled conditions and in a variety of different water types has not been studied, making it difficult to definitively say if hardness can mitigate corrosion and lead release. In particular, as a given utility can have multiple source waters with varying concentrations of DIC and hardness, there is a need to research the impact of these water quality factors separately and to investigate if there is an interaction between these two factors. To the author's knowledge, the impact of DIC and hardness on lead release has not been evaluated separately under controlled conditions.

In a variety of waters, Korshin et al. (1999) identified that NOM greatly increased the release of dissolved lead (< 0.45 μm) and the proportion of the total lead that is dissolved by adding concentrated NOM from a natural source and Aldrich Humic Acid. Through the use of anodic stripping voltammetry, they identified the potential of NOM to form complexes with lead (Korshin et al., 1999). As well, Korshin et al. (1999) identified that NOM could alter the structure of corrosion scales and the zeta potential, which could cause colloidal dispersion and this was confirmed in subsequent research studies (Korshin et al., 2005; Korshin & Liu, 2019;

Valentine & Lin, 2009). In particular, using SEM imaging, it has been identified that NOM can block the formation of cerussite, hinder the formation of hydrocerussite, and form a NOM-containing amorphous layer (Korshin et al., 1999; Korshin et al., 2000; Korshin et al., 2005). Both the formation of lead-NOM complexes and colloidal dispersion have been identified using SEC coupled with ICP-MS and UV_{254} detection (Trueman & Gagnon, 2016a; Trueman et al., 2017; Trueman et al., 2018), and FFF coupled with ICP-MS and UV_{254} detection (Trueman et al., 2019a). However, which components are responsible for complexing with lead and causing colloidal dispersion have not been well studied. Additionally, NOM can act as a reductant and reduce less soluble lead (IV) to more soluble lead (II) (Dryer & Korshin, 2007; Korshin & Liu, 2019; Lin & Valentine, 2008a; Lin & Valentine, 2009; Valentine & Lin, 2009; Winning et al., 2017). There is a need to characterize NOM both before and after stagnation in a lead pipe or fixture to gain a more thorough understanding of the mechanisms of how NOM increases the release of dissolved lead. There is also a need to evaluate the impact of NOM in hard waters, with differing amounts of DIC and hardness, as this has not been studied under controlled conditions to the author's knowledge.

This study employed a two-level fractional factorial design to systematically investigate the impact of pH, DIC, hardness, and NOM on galvanic corrosion, lead release and scale formation. Other goals of this study were to explore changes in the characteristics of NOM upon stagnation in lead and copper test pieces using FEEM and LC-OCD, and to compare measured dissolved lead concentrations to the theoretical solubility calculated by tidyphreeqc software. This study followed a "dump and fill" protocol consisting of water replacement three times a week over a period of 20 weeks. Synthetic waters were utilized in order to control the different water quality factors. Following completion of the 20-week experiment, scale analysis was conducted, and consisted of imaging using a SEM, energy dispersive X-ray spectroscopy (EDS), X-ray powder diffraction (XRD), and ICP-MS.

3.2 Materials and Methods

3.2.1 Test Pieces

The test pieces were based on a design by Parks et al. (2014) and consisted of new lead and copper pipes with an external galvanic connection. The lead pipes were manufactured by Canada

Metal North America and were 50 cm in length with an outer diameter of 1” (2.54 cm) and an inner diameter of ¾’’ (1.91 cm). The copper pipes were Cerro type M pipes and were 50 cm in length with a nominal diameter of ¾’’ (1.91 cm). The pipes were connected with flexible PVC tubing and separated using a rubber Danco 36333W 5/8’’ (1.59 cm) hose washer. The galvanic connection was provided with bronze ground clamps and copper ground wire attached to the lead and copper pipes at a distance of 10 cm from the junction. Finally, the test pieces were plugged using size three rubber stoppers and plumbers tape, as shown in Figure 3.2.

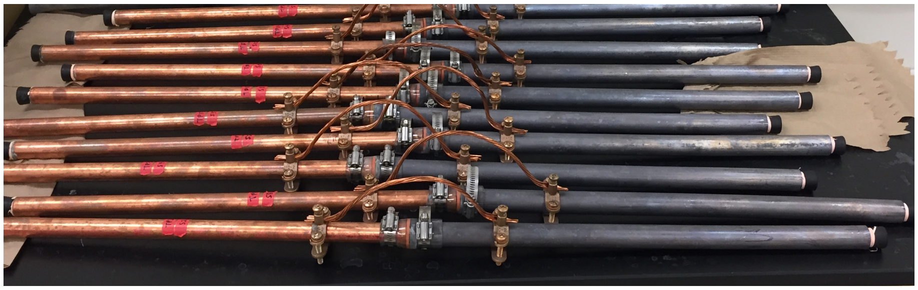


Figure 3.2 Lead and copper test pieces utilized in the experiment. The lead and copper pipes were attached using flexible PVC tubing and separated using a rubber hose washer. The galvanic connection was provided through the use of bronze ground clamps and copper ground wire.

Cleaning and pretesting of the test pieces was completed using a similar protocol as Parks et al. (2014). After the test pieces were assembled, they were flushed with tap water then rinsed three times with ultrapure MilliQ Water (18.2 MΩ/cm, 5 µg/L or less Total Organic Carbon [TOC]) and three times with NSF extraction water (pH = 8.0 +/- 0.5, DIC = 122 +/- 5 mg/L, free chlorine = 2 +/- 0.5 mg/L), as outlined in NSF/ANSI Standard 61 Section B.9.1 (2016). Afterwards, the test pieces were stagnated with NSF extraction water for a period of 24 hours, followed by three subsequent 12-hour stagnations with fresh NSF extraction water. The stagnated water from the three 12 hour stagnations was combined to form a composite sample that was analyzed for total lead and copper using ICP-MS. In total, 14 test pieces were constructed and the 10 test pieces that had the most consistent total lead release were used in the subsequent experimental work.

3.2.2 Experimental Design

The impact of four water quality factors on the release of lead was investigated; pH, DIC, hardness and NOM, using a 2^{4-1} fractional factorial design with two mid-point replicates as outlined in Table 3.1. A fractional factorial design was utilized in order to study the factors with a reasonable number of synthetic waters and test pieces, while ensuring that the main effects were not confounded with two-factor interaction effects. The mid-point replicates (TP9 and TP10) were included to provide an estimate of the pure error in the experiment, in order to calculate the significance of the effects. The targets for pH, DIC, and hardness were selected based on looking at a range of values typical in drinking water in Southern Ontario, as well as determining what would be practical to achieve in the synthetic water (City of Guelph, 2018; City of Ottawa, 2018; Oxford County, 2018; Region of Waterloo & City of Guelph, n.d; Woolwich Township, 2018). The DIC concentration was controlled instead of alkalinity because it is insensitive to pH. The NOM levels were selected as 0 mg DOC/L and 7 mg DOC/L, to be consistent with a similar study conducted by Zhou et al. (2015). Average measured values were within 0.1 units for pH, 12.3% for DIC, 20.3% for hardness, and 15.6% for DOC.

Table 3.1 Target Chemistry of the Synthetic Waters Prior to Stagnation in the Test Pieces

Test Piece	pH	DIC	Hardness	NOM
TP1	-	-	-	-
TP2	+	-	-	+
TP3	-	+	-	+
TP4	+	+	-	-
TP5	-	-	+	+
TP6	+	-	+	-
TP7	-	+	+	-
TP8	+	+	+	+
TP9	0	0	0	0
TP10	0	0	0	0

Level	pH	DIC mg/L	Hardness mg $CaCO_3$/L	NOM mg DOC/L
-	7	10	50	0
0	7.75	45	250	3.5
+	8.5	80	450	7

3.2.3 Synthetic Waters

Ultrapure MilliQ water was used as a starting matrix for all 10 of the synthetic drinking waters. The pH was controlled by adding either sodium hydroxide (Sigma-Aldrich) from a 0.1 M stock solution or sulfuric acid (Sigma-Aldrich) from a 0.1 M stock solution. The DIC was added as sodium bicarbonate (BDH) from a 0.4 M stock solution. 70% of the hardness was added from calcium chloride dihydrate (EMD Millipore) from a 0.2 M stock solution and 30% of the hardness was added from magnesium sulfate heptahydrate (EMD) from a 0.1 M stock solution. Both calcium and magnesium were added in order to better simulate real drinking waters in

Southern Ontario (City of Guelph, 2018; City of Ottawa, 2018; City of Toronto, 2018; City of Waterloo, 2018). Sodium chloride (Sigma-Aldrich) was added from a 0.3 M stock solution and sodium sulfate (EMD) was added from a 0.1 M stock solution in order to maintain a consistent CSMR of 1.25 (measured range: 1.17–1.29), a chloride concentration of 223 mg/L (measured range: 233-239 mg/L), and a sulfate concentration of 186 mg/L (measured range: 182-200 mg/L). The dose of the chemicals added to the synthetic waters is listed in Table B.1.

NOM was added as reference SR NOM (International Humic Substances Society [IHSS], 2R101N) from a stock solution with a DOC concentration of approximately 165 mg/L (Zhou et al., 2015). The SR NOM was composed of 50.70 wt% carbon, 3.97 wt% hydrogen, 41.48 wt% oxygen, 1.27 wt% nitrogen, 1.78 wt% sulfur, and an ash content of 4.01 wt% (International Humic Substances Society [IHSS], n.d.a). The SR NOM stock solution was prepared by dissolving 200 mg of SR NOM in a 500 mL solution with 20 mL of 0.1 M sodium hydroxide to neutralize the pH (Zhou et al., 2015). The sodium hydroxide, sulfuric acid, and SR NOM were prepared on an as needed basis while the other stock solutions were prepared fresh weekly. 2 L of each synthetic water type was prepared weekly in plastic Nalgene® bottles and was transferred headspace free to 500 mL high-density polyethylene or low-density polyethylene (LDPE) bottles until use in the test pieces.

3.2.4 Sample Collection

The experiment was conducted over a period of 20 weeks and followed a "dump and fill" protocol similar to the method outlined in Triantafyllidou and Edwards (2010), with water replacement on Mondays, Wednesdays and Fridays. Each week of the "dump and fill" experiments ran from Wednesday to the subsequent Wednesday, and therefore the synthetic waters were stagnated in the test pieces following a weekly pattern of 48, 72, and 48 hours. The synthetic waters were prepared on Tuesday for the subsequent week's "dump and fill" events in order to minimize the water age prior to stagnation. This was acceptable as the synthetic water quality was found to be stable for a period of at least one week and no precipitation was observed. All of the experimental work was completed in a laboratory at room temperature (approximately 20^0C). Water quality parameters were routinely analyzed in the unstagnated synthetic waters to ensure that they were close to the target values (Tables B.2, B.9, B.12,

Appendix C). The pH of the synthetic waters was measured and adjusted if necessary to within 0.2 pH units of the target value prior to stagnation in the test pieces. Prior to sample collection on Wednesdays, the galvanic current between the lead and copper pipes was measured (end of the final 48-hour stagnation period of the week, Table B.2).

Samples from the test pieces were collected in 500 mL LDPE bottles that were pre-washed in a 7% nitric acid bath (Fisher Scientific trace-metal grade) for a minimum of 16 hours. Samples were taken periodically for a variety of water quality analyses (Tables B.10-12, Appendix C) including total and dissolved lead and copper using ICP-MS following the final 48-hour stagnation event of the week (Monday to Wednesday). The total and dissolved lead and copper samples from the 48-hour stagnation events were measured on a biweekly basis, while the other water quality parameters were measured on a monthly basis (Table B.2). Samples for dissolved lead and copper analysis were filtered through a 0.45 μm cellulose nitrate membrane filter (General Electric Healthcare Life Sciences Whatman™) prior to acidification in polypropylene (Caplug) vials with 7% nitric acid to pH 2 or less (Fisher Scientific trace-metal grade). Additionally, a composite sample was taken weekly, that combined 3.5 mL of acidified effluent from the week's three "dump and fill" events for total lead and copper analysis using ICP-MS (Table B.2). Samples for total lead and copper analysis were acidified with 70% nitric acid (Fisher Scientific trace-metal grade) to pH 2 or less and were held for a minimum of 16 hours before being transferred to polypropylene vials (Caplug). The acidification for collection of samples for total lead and copper analysis was completed immediately after samples were collected for other water quality analyses, if any. The dissolved and particulate lead concentrations that are reported were from the select individual 48-hour stagnation events while the total lead and copper concentrations that are reported were from the weekly composite samples. Therefore, the total lead and copper concentrations reported are not equal to the sum of the dissolved and particulate lead and copper concentrations.

3.2.5 Analytical Methods

The galvanic current between the lead and copper pipes was measured using a multimeter with a 400 Ω resistance (Klein Tools® MM400). Measurements were taken after the reading had stabilized (~ 10 seconds at the same reading). Lead and copper analysis was conducted using

ICP-MS (Thermofisher X series II; *Standard Method 3125*) at Dalhousie University (American Public Health Association [APHA] et al., 2005). The detection limits for lead and copper were 0.4 μg/L and 0.7 μg/L respectively.

LC-OCD, FEEM, and DOC analyses were conducted on samples that were filtered through a sterile 0.45 μm polyethersulfone membrane filter (Pall Corporation Supor®) and were stored at 4^0C prior to analysis. Samples for LC-OCD, FEEM, and DOC were stored in glass vials that were pre-baked at 450^0C for a minimum of one hour. Samples for FEEM were analyzed within 48 hours of collection on a Cary Eclipse Fluorescence Spectrophotometer in a quartz cuvette (Agilent Technologies). The split widths of the emission (Em) wavelengths were set at 1 nm and varied from 300 to 600 nm. The split widths of the excitation (Ex) wavelengths were set at 10 nm and varied from 250 to 380 nm. The FEEM spectra for MilliQ water was subtracted from the sample measurements in order to remove Raman scattering regions. Peak picking was used to estimate three NOM fractions, humic acids (Ex/Em = 270 nm/460 nm), fulvic acids (Ex/Em = 320 nm/415 nm), and protein-like materials (Ex/Em = 280 nm/330 nm) (Peiris et al., 2008). Samples for LC-OCD were normally analyzed within one week of collection (DOC-Labour Dr. Huber). A 28 mM phosphate buffer was used in the mobile column at a flow rate of 1 mL/min with a resin separation range of 0.1 to 18 kDa. The eluent passed through three separate detectors to measure organic carbon, organic nitrogen, and UV_{254}. The organic carbon was measured after oxidation to carbon dioxide in a Gräentzel thin film reactor and the organic nitrogen was measured after transformation to nitrate (Huber et al., 2011). ChromCALC software (DOC-Labor Dr. Huber) was used to integrate the chromatograms generated by the LC-OCD. TOC and DOC were measured during the final week (week 20) using a TOC analyzer (Shimadzu TOC-V_{CPH}, *Standard Method 5310 B)* (APHA et al., 2005). Samples were acidified to a pH of approximately 2 with hydrochloric acid prior to analysis on the TOC analyzer. Unless otherwise stated, the DOC measurements that are reported were measured on the LC-OCD and not from the TOC analyzer.

The pH was measured using a pH probe (Thermo Scientific Orion 9106BNWP, *Standard Method 4500-*H^+ *B*) (APHA et al., 2005) and alkalinity was measured using titration (*Standard Method 2320 B*) (APHA et al., 2005). The DIC concentration was then estimated using chemical equilibrium relationships based on the pH and alkalinity. A variety of metals including calcium, magnesium, and sodium, were measured using collision reaction cell (CRC) ICP-MS (measured by ALS Environmental, *modified from EPA 6020 B*) (United States Environmental Protection Agency [US EPA], 2014). Hardness was then estimated based on the calcium and magnesium concentrations from the CRC ICP-MS results (*Standard Method 2340 B*) (APHA et al., 2005). The specific conductance was measured using a conductivity probe (YSI Professional Plus, *Standard Method 2510 B*) (APHA et al., 2005). Turbidity was measured using a nephelometer (HACH® 2100Q Portable Turbidimeter, *Standard Method 2130 B*) (APHA et al., 2005). Chloride and sulfate were measured using ion chromatography (IC) (Thermo Scientific Dionex™ ICS-1100, *Standard Method 4110 C*) (APHA et al., 2005).

The scale analysis was completed at the end of the 20-week long "dump and fill" experiment at Washington University in St. Louis and involved the examination of cross sections and transverse sections of the pipe. To prepare a cross section, one end of the pipe was carefully filled with a 0.5" (1.27 cm) deep mixture of hardener and epoxy resin (18 wt%). Once the epoxy had cured, this section was cut from the rest of the segment and polished using sandpapers of increasingly fine grit (up to 1200 grit). The polishing was done with mineral oil on the sandpaper to minimize the generation of airborne particles. The polished sample was sonicated in ethanol to remove residual mineral oil and pipe particles prior to analysis. The cross sections of the test pieces were analyzed using a SEM (Thermofisher Quattro S E-SEM). EDS (Oxford AzTec Energy Dispersive X-ray Spectrometer) with the SEM was used to semi-quantitatively determine the elemental composition of the pipe scales. The remaining length of the pipe was cut lengthwise to yield two half cylinders (transverse sections) from which scales were collected by scraping them off with a metal spatula or with 1200 grit sandpaper. Portions of the ground up scale were analyzed by XRD (Bruker d8 Advance X-ray diffractometer with Cu Kα radiation). A 1" (2.54 cm) low background silicon crystal (MTI) sample holder was utilized. The powdered scales collected were weighed and digested in concentrated hydrochloric and nitric acid (3:1 by volume) at 75°C for one hour in preparation for quantitative analysis of their elemental composition using ICP-MS (PerkinElmer Elan DRCII).

3.2.6 Data Analysis

Since this was a two-level factorial experiment, the main effects of each factor for galvanic current, lead release, and copper release were calculated as the difference in the average response at the high level of the factor subtracted by the average response at the low level of the factor. The two factor interaction effects were calculated as the difference in the average response when both the factors were at the same level subtracted by the average response when the factors were at different levels. Analysis of variance (ANOVA) was used to determine the significance of the effects. The weekly measurements were treated as repeat measurements and therefore the ANOVA was completed on average values from the test pieces. The mid-point replicates were used to determine the pure error, in order to assess significance using an F-test. Upon analysis, it was determined that the galvanic current and lead data did not require a transformation but the copper data did. The copper data was transformed using the Box Cox method, which involves a power transformation in order to improve the normality of the data. A λ value of 0.5 was utilized for the copper transformation, which is the equivalent to a square root transformation (Montgomery, 2013). The ANOVA analysis was completed using MATLAB®.

Faraday's Law was used to estimate the amount of lead that was oxidized throughout the 20-week experiment using the galvanic current measurements (Cartier et al., 2012; Dudi, 2004). According to Faraday's Law, one coulomb of charge is equal to one mole of electrons, and therefore the amount of lead that was oxidized could be calculated by assuming that two moles of electrons were required to oxidize one mole of lead (0) to lead (II). It was also assumed that the galvanic current was constant throughout the entire week and equal to the galvanic current measured at the end of the final 48-hour stagnation event. The fraction of total lead that was stored as a corrosion scale and the fraction of lead that was released into the water were then approximated by comparing the mass of lead (II) expected to be produced and the mass of lead that was actually released.

Dr. Benjamin Trueman at Dalhousie University completed solubility modelling for lead in the synthetic waters using tidyphreeqc, which is an R package for solubility modelling in PHREEQC (Dunnington, 2019; Garnier, 2018; Parkhurst & Appelo, 2013; Wickham, 2017; Wickham & Bryan, 2019). The equilibrium constants available in the "minteq" database in PHREEQC were modified to be in accordance with the values in Table 4-14 in Schock et al. (1996). This model incorporated the pH, DIC, sulfate, and chloride concentrations but did not incorporate the sodium, calcium, magnesium, or DOC concentrations.

A two-tailed paired sample t-test was conducted to compare the NOM fractions from FEEM and LC-OCD analyses before and after stagnation to determine if there were significant changes ($p < 0.05$). R^2 values were also calculated between dissolved lead release and the change in humic and fulvic acids measured by FEEM, and SUVA and humics measured by LC-OCD. Statistical calculations for FEEM and LC-OCD were completed using Excel.

3.3 Results and Discussion

3.3.1 Impact of Water Quality Factors on Galvanic Corrosion

3.3.1.1 Effects of Water Quality Factors

The effects of the water quality factors and their significance on the galvanic current, lead release, and copper release are displayed in Table 3.2. Additionally, the average galvanic current, lead release, and copper release from the individual test pieces are tabulated in Table 3.3, and more detailed summary statistics are listed in Table B.7. As is evident from Table 3.3, there were large differences among the test pieces for various parameters (galvanic current, lead, copper etc.), and in many cases the coefficient of variation was relatively modest. Thus, an initial look at the data shows that different conditions (combinations of independent variables) had a very substantial effect. As discussed below, there were challenges associated with demonstrating, with statistical significance, the effects of the different experimental variables on observed results.

Table 3.2 Effects and Significance of Water Quality Factors Determined Using ANOVA

Parameter		pH (A)	DIC (B)	Hardness (C)	NOM (D)	AB+ CD	AC+ BD	AD+ BC
Galvanic Current	Effect	-9.2	**28.4**	-0.9	11.8	-8.2	9.4	1.6
	p-value	0.154	**0.051**	0.761	0.121	0.171	0.151	0.613
Total Lead	Effect	**-4,390**	3,290	-731	2,260	-3,290	-1,840	-3,040
	p-value	**0.089**	0.118	0.447	0.170	0.119	0.206	0.128
Dissolved Lead	Effect	-1,030	-225	-654	**2,320**	-636	-217	-1,000
	p-value	0.135	0.493	0.207	**0.060**	0.212	0.505	0.138
Particulate Lead	Effect	**-6,320**	**5,870**	-2,100	2,400	**-5,420**	102	**-4,000**
	p-value	**0.053**	**0.057**	0.157	0.139	**0.062**	0.879	**0.084**
Total Copper	Effect	**-90.3**	**107**	-81.0	***152***	**-93.9**	75.3	-73.9
	p-value	**0.076**	**0.054**	0.108	***0.034***	**0.080**	0.164	0.129
Dissolved Copper	Effect	**-66.4**	***92.2***	-61.4	***105***	**-74.5**	68.4	-51.8
	p-value	**0.083**	***0.045***	0.108	***0.036***	**0.071**	0.129	0.190
Particulate Copper	Effect	**-20.4**	**9.3**	-1.3	***26.7***	-13.4	-3.3	-10.4
	p-value	**0.056**	**0.096**	0.346	***0.042***	0.122	0.310	0.105

*Effects are in µA for galvanic current and µg/L for lead and copper

**Bolded values were found to be significant at 10% based on ANOVA, and bolded and italicized values were found to be significant at 5% based on ANOVA

***Effects were calculated from untransformed data while significance was calculated based on untransformed data for galvanic current and lead release and Box Cox transformed data with $\lambda = 0.5$ for copper.

Table 3.3 Galvanic Current, Lead Release, and Copper Release in the Test Pieces

Parameter		TP1	TP2	TP3	TP4	TP5	TP6	TP7	TP8	TP9	TP10
Galvanic Current (µA)	Mean	25.0	26.5	71.9	33.2	25.0	21.6	51.4	55.2	45.8	41.3
	SD	4.4	1.4	7.0	3.8	3.5	4.9	4.3	3.1	4.7	3.6
	CV	17.5	5.2	9.8	11.4	14.2	22.7	8.4	5.5	10.1	8.8
Total Lead (µg/L)	Mean	693	3,700	12,600	4,480	7,110	1,900	8,390	1,130	2,620	1,380
	SD	343	569	9,060	5,500	3,690	1,330	6,530	386	925	126
	CV	49.4	15.4	72.0	123	51.9	69.8	77.9	34.3	35.3	9.1
Dissolved Lead (µg/L)	Mean	166	2,310	3,890	132	3,050	122	140	578	1,580	1,140
	SD	42.0	230	503	28.9	620	30.0	48.1	145	319	81.6
	CV	25.3	10.0	12.9	21.9	20.4	24.6	34.4	25.2	20.2	7.1
Particulate Lead (µg/L)	Mean	399	1,800	18,100	3,840	4,590	1,400	9,490	250	1,320	260
	SD	244	1,290	22,200	4,680	2,470	1,280	9,940	171	718	100
	CV	61.3	71.4	123	122	53.8	91.3	105	68.5	54.4	38.6
Total Copper (µg/L)	Mean	10.9	91.4	438	25.8	80.7	7.5	55.1	98.4	84.5	69.7
	SD	5.5	75.9	152	8.4	24.1	5.5	32.4	23.0	26.6	16.7
	CV	50.1	83.0	34.7	32.7	29.9	72.7	58.8	23.3	31.5	24.0
Dissolved Copper (µg/L)	Mean	2.9	47.2	326	12.1	29.5	1.4	39.8	71.8	55.4	44.9
	SD	2.6	9.1	89.3	3.4	6.0	1.2	16.4	16.2	7.8	5.3
	CV	88.5	19.2	27.4	27.9	20.4	84.9	41.3	22.6	14.1	11.8
Particulate Copper (µg/L)	Mean	6.9	29.9	66.7	9.5	46.0	9.0	31.7	21.2	20.9	17.4
	SD	6.6	53.4	25.8	5.1	20.3	9.1	34.3	8.9	10.1	4.0
	CV	95.5	178	38.7	53.6	44.2	101	108	42.1	48.3	22.9

*SD = standard deviation, CV = coefficient of variation

**Galvanic current was measured between the lead and copper pipes at the end of the final 48-hour stagnation event of the week

***Total lead and copper were measured in the weekly composite samples

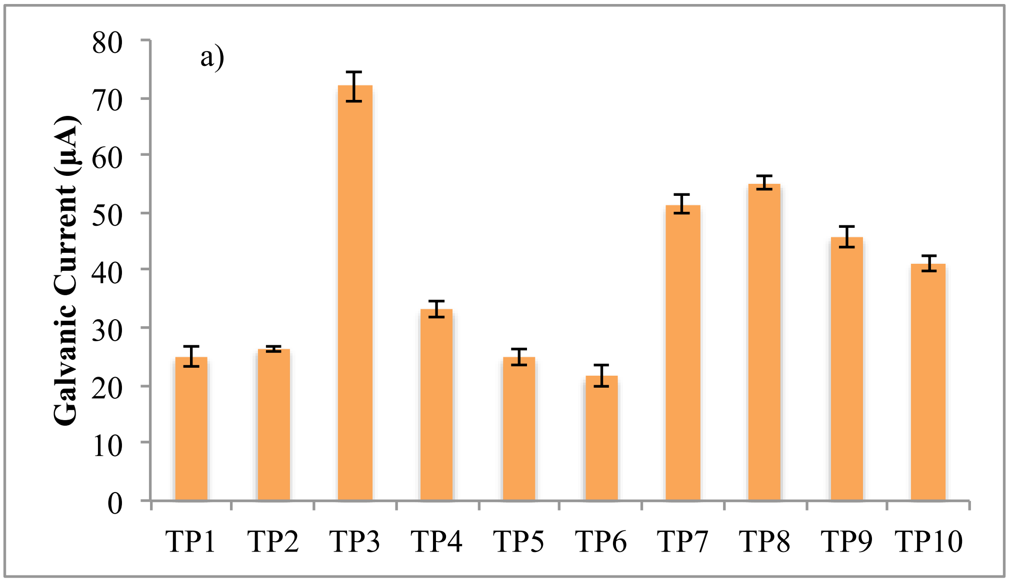
****Dissolved and particulate lead and copper were measured from the samples collected following the final 48-hour stagnation event on weeks 4,8,10,12,14,16,19, and 20

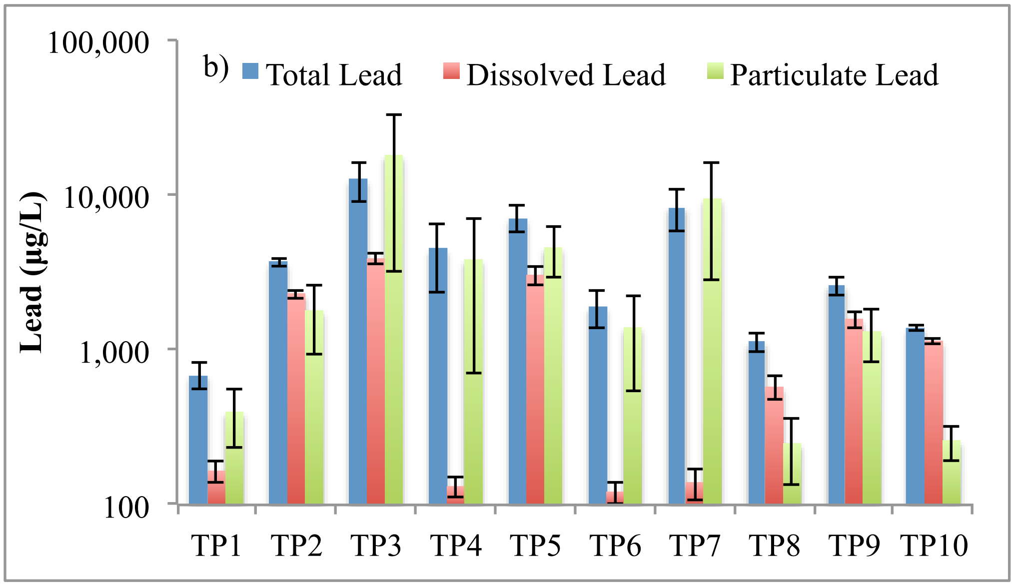
Due to the high amount of variability in this experiment, in particular large differences in lead release between the mid-point replicates (TP9 and TP10), which were used for determining the standard error, significance at 10% was reported in addition to the standard 5%. This was deemed to be appropriate as many of the effects had significance that were close to 5%, there was limited replication in the fractional factorial design, and a few other corrosion studies have reported significance at 10% (Dodrill & Edwards, 1995; Doré et al., 2019; Tam & Elefsiniotis, 2009). It is noted that using a significance of 10% carries the increased risk of finding an effect to be significant when it was actually not. Effects with significance less than 5% ($p < 0.05$) were considered to be significant and effects between 5% and 10% ($0.05 < p < 0.1$) were designated as potentially significant. However, it was assumed that none of the effects for particulate lead were significant as the ANOVA analysis for particulate lead identified a potentially significant lack of fit error (p = 0.089).

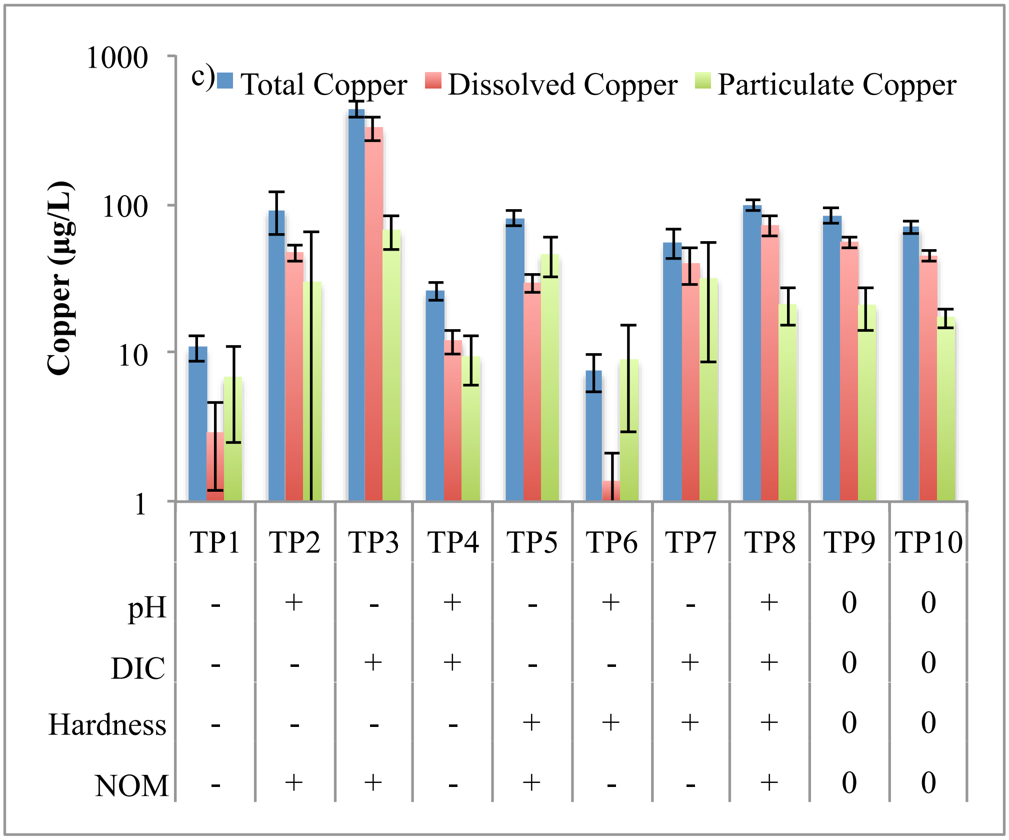
The pH was found to have a potentially significant effect on total lead release, total copper release, dissolved copper release, and particulate copper release. DIC was found to have a potentially significant effect on the galvanic current, total copper release, and particulate copper release, and a significant effect on dissolved copper release. Hardness was not found to have a significant effect on any of the response variables**.** SR NOM was found to have a potentially significant effect on dissolved lead release and a significant effect on total copper release, dissolved copper release, and particulate copper release**.** As well, a few confounded two-factor interaction effects were found to be potentially significant for total copper release and dissolved copper release. The effects are discussed in more detail in the subsequent sections.

3.3.1.2 Galvanic Current

The galvanic current measured between the lead and copper pipes of the test pieces is shown in Figure 3.3a, summary statistics for the galvanic current in the test pieces are provided in Table 3.3**,** and a time series panel plot for the galvanic current over 20 weeks is displayed in Figure B.1. TP3 measured the highest galvanic current during every single week of measurements with an overall average of 71.9 µA. This was mostly attributed to having a high DIC concentration of 80 mg/L, since this factor was a very close to being significant (p = 0.051) and no other factors or interactions came close to this level of significance**.** In fact, the three test pieces with the highest average galvanic current were TP3, TP8, and TP7, all of which had a high DIC concentration of 80 mg/L. The four test pieces with a low DIC concentration of 10 mg/L, TP6, TP1, TP5, and TP2 had the lowest average galvanic current. Thus, it is not surprising that DIC had a potentially significant effect on the galvanic current, with the galvanic current being on average 28.4 µA higher when the DIC concentration was 80 mg/L compared to 10 mg/L (Table 3.2).


a)
Galvanic Current (µA)
0
10
20
30
40
50
60
70
80
TP1
TP2
TP3
TP4
TP5
TP6
TP7
TP8
TP9
TP10


b)
Total Lead
Dissolved Lead
Particulate Lead
Lead (µg/L)
100
1,000
10,000
100,000
TP1
TP2
TP3
TP4
TP5
TP6
TP7
TP8
TP9
TP10



	TP1	TP2	TP3	TP4	TP5	TP6	TP7	TP8	TP9	TP10
pH	-	+	-	+	-	+	-	+	0	0
DIC	-	-	+	+	-	-	+	+	0	0
Hardness	-	-	-	-	+	+	+	+	0	0
NOM	-	+	+	-	+	-	-	+	0	0

Figure 3.3 a) Galvanic current measured between lead and copper pipes of the test pieces. b) Lead release from the test pieces. c) Copper release from the test pieces. The galvanic current was measured at the end of the final 48-hour stagnation event of the week. Total lead and copper were measured from the weekly composite samples over the entire 20-week study. The dissolved and particulate lead and copper were measured from samples collected after the final 48-hour stagnation event on weeks 4, 8, 10, 12, 14, 16, 19, and 20. Thus, the sum of the dissolved and particulate metals is not equal to the total metals. Bars represent average values and error bars represent the 90% confidence interval.

The increase in galvanic current associated with an increase in the DIC concentration was in accordance with previous studies and was likely due to an increase in the conductivity of the water (Nguyen et al., 2011a; Triantafyllidou & Edwards, 2010; Zhou et al., 2015). Zhou et al. (2015) investigated the impact of water quality on the performance of a sodium silicate corrosion inhibitor (24 mg SiO_2/L) using a “dump and fill” protocol and test pieces similar to those used in this study. They found that increasing the alkalinity from 15 to 250 mg $CaCO_3$/L (DIC from 7.6 mg/L to 62.6 mg/L) increased the galvanic current by 18.2 µA and suggested that this was due to an increase in conductivity (Zhou et al., 2015). This is similar to the 28.4 µA increase in galvanic current when the DIC concentration was increased from 10 mg/L to 80 mg/L in the current study.

Zhou et al. (2015) also found that increasing the concentration of SR NOM from 1 mg DOC/L to 7 mg DOC/L significantly increased the galvanic current and identified a significant interaction between alkalinity and SR NOM. In the current study, adding 7 mg DOC/L of SR NOM did not significantly increase the galvanic current, but there was some indication that at a high DIC concentration of 80 mg/L the SR NOM may have increased galvanic current (Table 3.2). At a high DIC concentration of 80 mg/L, the addition of 7 mg DOC/L of SR NOM increased the galvanic current by an average of 21.3 μA**.** Further research investigating the effect of NOM on galvanic current is needed to better understand the role of NOM with respect to galvanic corrosion.

3.3.1.3 Total Lead

The total lead measured in the weekly composite samples is shown in Figure 3.3b, summary statistics for the total lead released from the test pieces are provided in Table 3.3**,** and a time series panel plot for the total lead release over 20 weeks is displayed in Figure B.2. The total lead release from the test pieces was quite high, varying from an average of 693 μg/L (TP1) to 12,600 μg/L (TP3)**.** Total lead release was also highly variable week to week, with coefficient of variations ranging from 9.1% (TP10) to 122.6% (TP4). Much of this variability was due to high amounts of particulate lead, which is discussed in section 3.3.1.5. Examining the time series plots in Figure B.2, it is evident that there was a period of increased variability from weeks 7 to 12 compared to both before (weeks 1 to 6) and after (weeks 13 to 20). This is attributed to having different people performing the “dump and fill” events during weeks 7 to 12. This finding stresses the importance of having a very consistent “dump and fill” procedure when high amounts of particulate lead are expected.

The pure error in the experiment was relatively high, with TP9 releasing almost twice as much lead on average compared to TP10 despite having identical water quality entering the mid-point replicate test pieces. It is possible that slight differences in the test pieces, especially near the junction of the lead and copper pipes, could have resulted in large differences in lead release. Two possible reasons include particulate lead being trapped at the junction or differences in the size of the crevices near the outer surface of the lead pipe (Clark et al., 2013). In fact, Clark et al.

(2013) found that lead concentrations near the outer wall of a lead pipe during galvanic corrosion can be as high as 9.4 x 10^6 µg/L. The high amount of variability made it difficult to determine the significance of the effects of the water quality factors on total lead release.

The pH had a potentially significant effect on total lead release with an increase in pH from 7 to 8.5 decreasing lead release by an average of 4,390 µg/L (Table 3.2). This result was expected, as a general pH range for minimizing lead solubility has been suggested to be around 8-10 (Giammar et al., 2010; Kim et al., 2011; Noel et al., 2014; Schock & Gardels, 1983; Wilzcak et al., 2010). Unlike for galvanic current, the DIC did not have a significant effect on total lead release (Table 3.2). This is in accordance with previous studies, where an increase in the DIC concentration increased the galvanic current but did not increase lead release (Nguyen et al., 2011a; Triantafyllidou & Edwards, 2010; Zhou et al., 2015).

The hardness had a negligible impact on total lead release, indicating that calcium carbonate did not precipitate and form a protective film in this study (Table 3.2). This is in accordance with literature that has suggested that calcium carbonate precipitation has little to do with corrosion (AwwaRF, 1990; Dodrill & Edwards, 1995; Richards et al., 2018; Schock, 1989; Wilczak et al., 2010). However, this finding is not in accordance with some studies that have suggested that calcium and hardness can have an impact on lead release (Bisogni et al., 2000; Colling et al., 1987; Colling et al., 1992; Tang et al., 2006). Colling et al., (1987) found that the hardness to alkalinity ratio could play a role with lead release by altering the structure of corrosion scales. They found that waters with hardness to alkalinity ratio greater than 1.7 released more lead than waters with a ratio less than 1.7 (Colling et al., 1987). This relationship was not found in the current study and this may be due to the large range of hardness to alkalinity ratios in the synthetic waters. As well, it is possible that this threshold is only of importance in certain water types and not in the synthetic waters used in the current study. Bisogni et al. (2000) found that at a concentration of 5 mg/L, calcium destabilized colloidal lead particles by altering the zeta potential. However, increasing the calcium concentration from 5 mg/L to 40 mg/L did not provide any additional benefit (Bisogni et al., 2000). In this study, even at the low hardness level the calcium concentration was at least 12 mg/L (Table B.12); so increasing the hardness further did not likely have much of an impact on the zeta potential of colloids. It is also possible that the high variability of total lead release would render any small effect of hardness insignificant. Like hardness, SR NOM was not found to have a significant impact on total lead release, but it did have a larger effect than the hardness did (Table 3.2).

3.3.1.4 Dissolved Lead

The dissolved lead release following select individual 48-hour stagnation events is shown in Figure 3.3b, summary statistics for the dissolved lead release from the test pieces are provided in Table 3.3, and a time series panel plot for the dissolved lead release over 20 weeks is displayed in Figure B.3. As evidenced in Figure B.3, the results for the dissolved lead release were more consistent than total lead release (which included particulate lead) and appeared to be relatively stable throughout the 20 weeks of experimentation. The coefficient of variation for dissolved lead ranged from 7.1% in TP10 to 34.4% in TP7. The SR NOM was found to have a potentially significant impact on dissolved lead release; with the addition of 7 mg DOC/L of SR NOM increasing dissolved lead release by an average of 2,320 µg/L (Table 3.2). Average dissolved lead release in the test pieces exposed to water with a SR NOM concentration of 7 mg DOC/L was extremely high, and ranged from 578 µg/L (TP8) to 3,890 µg/L (TP3), compared to only 122 µg/L (TP6) to 166 µg/L (TP1) in the test pieces with synthetic water with no SR NOM. Even the mid-point replicates with a SR NOM concentration of 3.5 mg DOC/L had high average dissolved lead concentrations of 1,580 µg/L in TP9 and 1,140 µg/L in TP10. Thus, it seems that even at a concentration of 3.5 mg DOC/L, the SR NOM was able to greatly increase the release of dissolved lead. The impact of SR NOM on the release of dissolved lead and the fractionation of the total lead is highlighted in Figure 3.4.

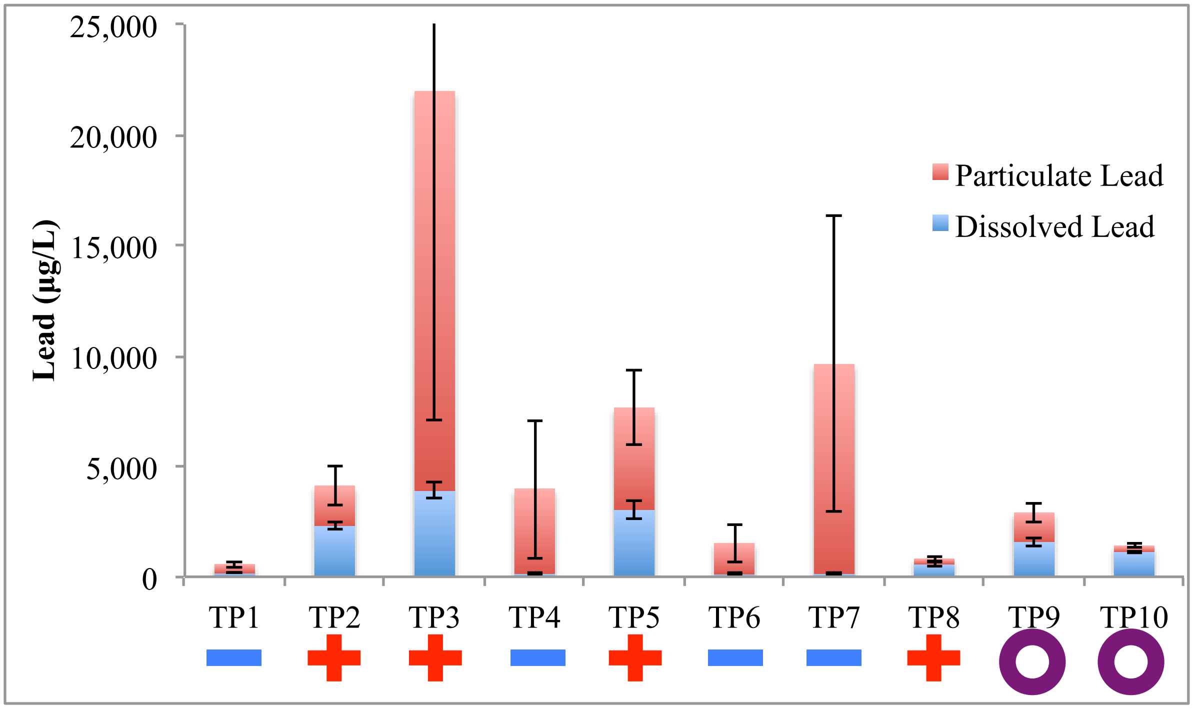


Figure 3.4 Lead release during the final 48-hour stagnation event on weeks 4, 8, 10, 12, 14, 16, 19, and 20. Blue bars represent average dissolved lead release and the difference between the top and bottom of the red bars represent average particulate lead release. The top of the red bar indicates average total lead release. The error bars represent the 90% confidence interval. Red "+" sign indicates a SR NOM concentration of 7 mg DOC/L, blue "-" sign indicates no NOM, and a purple "O" indicates a SR NOM concentration of 3.5 mg DOC/L.

The order of magnitude increase in dissolved lead release from adding SR NOM is consistent with the literature (Willison & Boyer, 2012; Zhou et al., 2015). However, the dissolved lead concentrations in the present study were an order of magnitude higher than in previous work by Zhou et al. (2015), which used similar test pieces and synthetic water also dosed with a SR NOM concentration of 7 mg DOC/L (average of 2,460 µg/L vs 273 µg/L). Possible explanations for this difference include, in the present study, a lack of disinfectant, more aggressive water, and the use of new lead pipes instead of harvested lead pipes. It is believed that complexation or colloidal dispersion were primarily responsible for the drastic increase in dissolved lead that was observed when the SR NOM was added to the synthetic waters, as previous research by Trueman and colleagues that has included either SEC or FFF with ICP-MS and UV_{254} detection has suggested that these are important mechanisms (Trueman & Gagnon, 2016a; Trueman et al., 2017; Trueman et al., 2018; Trueman et al., 2019a).

The pH was not found to have a significant impact on dissolved lead release and this was likely due to the dominant effect that the SR NOM had (Table 3.2). However, the two test pieces with the highest dissolved lead release, TP3 (3,890 µg/L) and TP5 (3,050 µg/L), both had 7 mg DOC/L of SR NOM and a low pH of 7. In comparison, the test pieces that had 7 mg DOC/L of SR NOM and a high pH of 8.5, TP2 (2,310 µg/L) and TP8 (578 µg/L), released much less dissolved lead. This is in accordance with studies that have suggested that more aggressive waters with a low pH are more susceptible to the negative impacts of NOM (Korshin et al., 1999; Lin & Valentine, 2008a). Neither, the DIC or hardness had a significant impact on dissolved lead release (Table 3.2). This provides further evidence that calcium carbonate precipitation was not an important mechanism with regards to lead release in this study.

3.3.1.5 Particulate Lead

The particulate lead release following the select 48-hour stagnation events is shown in Figure 3.3b and summary statistics for the particulate lead release from the test pieces are provided in Table 3.3. Average particulate lead release was the lowest in TP8 and the highest in TP3. The release of particulate lead was sporadic and highly variable, with coefficient of variations ranging from 39% (TP10) to 123% (TP3). As discussed in section 3.3.2, this may have been due to the relatively large amount of oxidized lead that was stored in the corrosion scales. Due to a high degree of variability, the lack of fit error from ANOVA was found to be significant at 10% ($p = 0.0893$). However, it was determined that a Box Cox transformation would not significantly improve the normality of the data. The magnitude of the lack of fit error indicates that there was a high likelihood of an effect being deemed significant for particulate lead using ANOVA, when in reality it was not. For this reason, the particulate lead data was interpreted with a high degree of caution and it was assumed that none of the effects were statistically significant even though ANOVA suggested that some of them were.

The pH, DIC, and their interaction effects on the release of particulate lead were relatively large (Table 3.2). It was interesting that the DIC was found to potentially increase the release of particulate lead, but not surprising. The DIC significantly increased the galvanic current and the amount of oxidized lead. Thus, the DIC would be expected to also increase the production of lead corrosion scales and particulate lead (Cartier et al., 2012; Doré et al., 2019; Zhou et al., 2015). It is recommended that further research investigating the relationship between DIC and particulate lead be pursued.

3.3.1.6 Copper

Average total, dissolved, and particulate copper release from the test pieces are displayed in Figure 3.3c and summary statistics are provided in Table 3.3. As with lead, the total copper concentrations were measured from the weekly composite samples, and the dissolved and particulate copper concentrations were measured from samples collected after select 48-hour stagnation events. As expected based on the galvanic series, the release of total copper was much lower than total lead and ranged from 7.5 µg/L (TP6) to 438 µg/L (TP3). In addition, the total copper release was not as variable as the total lead release with the coefficient of variation ranging from 23% (TP8) to 83% (TP2). Due to more consistent data, the effects of the water quality factors were more significant for copper than for lead (Table 3.2).

An increase in the pH from 7 to 8.5 decreased the release of total copper by 90.3 µg/L, dissolved copper by 66.4 µg/L, and particulate copper by 20.4 µg/L (Table 3.2). An increase in the DIC concentration from 10 mg/L to 80 mg/L increased the release of total copper by 107 µg/L, dissolved copper by 92.2 µg/L, and particulate copper by 9.3 µg/L (Table 3.2). The sum of the pH/DIC interaction and the hardness/NOM interaction was found to have a potentially significant effect on both total copper release and dissolved copper release (Table 3.2). As both the pH and DIC had significant effects on total and dissolved copper release, it is more likely that the pH/DIC interaction was the potentially significant interaction effect. When the pH was low at 7, an increase in the DIC concentration from 10 mg/L to 80 mg/L increased total copper release by 200 µg/L, while at a high pH of 8.5, an increase in the DIC concentration only increased total copper release by 12.7 µg/L. This is in accordance with previous studies that have suggested that waters with a high DIC concentration and low pH are the most aggressive to copper, with the DIC having a larger effect when the pH is lower (Dodrill & Edwards, 1995; Edwards et al., 1996; Xiao et al., 2007). This is likely due to the solubility of copper hydroxides and the formation of soluble copper carbonates (Dodrill & Edwards, 1995; Edwards et al., 1996).

SR NOM at a concentration of 7 mg DOC/L significantly increased total copper release by 152 µg/L, dissolved copper release by 105 µg/L, and particulate copper release by 26.7 µg/L (Table 3.3). As is the case with lead, NOM has been linked to increased dissolved copper concentrations in drinking water (Arnold et al., 2012b; Boulay & Edwards, 2001; Edwards & Sprague, 2001b; Korshin et al., 1996). Edwards and Sprague (2001b) suggested that NOM could increase the release of dissolved copper by forming soluble copper-NOM complexes or through colloidal dispersion. NOM can also impact the natural aging process of copper pipes and influence the type of corrosion scales that form (Arnold et al., 2012b; Korshin et al., 1996). These findings indicate that waters with a low pH, high DIC concentration, and a high concentration of NOM are particularly aggressive towards copper and could potentially be of concern for utilities.

3.3.2 Measured Lead Release Versus Predicted Lead Release with Faraday's Law

Faraday's Law can be used to predict the amount of oxidized lead from galvanic corrosion using the galvanic current (Cartier et al., 2012; Dudi, 2004). A comparison of the total lead release predicted by Faraday's Law and the actual total lead release is shown in Figure B.4. Over the 20 week long experiment, between only 2.7% (TP8) and 37.3% (TP5) of the total lead release predicted by Faraday's Law was actually released into the water (Table B.3). It is presumed that the remainder of the oxidized lead was stored in the corrosion scales (62.7% - 97.3%). This is consistent with previous studies that have found that the majority of lead oxidized due to galvanic corrosion was stored as a corrosion scale (Cartier et al., 2012; Zhou et al., 2015). It is presumed that some of the corrosion scales that formed were dislodged on a sporadic basis, which would explain why particulate lead concentrations (section 3.3.1.5) were high and variable throughout the experimental work.

3.3.3 Solubility Modelling with Tidyphreeqc

Tidyphreeqc was utilized to approximate the theoretical solubility of lead for the different synthetic waters. The lead solubility determined by the software was largely dependent on the pH and DIC concentration, as this model assumed that the lead solids that could form were either cerussite or hydrocerussite. Complexation between lead (II) and the other dissolved species mentioned in section 3.2.6 were also incorporated. However, this model did not incorporate complexation between lead and NOM or any lead in colloidal species. The tidyphreeqc modelling software predicted that hydrocerussite would form in TP2 and TP6, while cerussite would form in all of the other test pieces. The dissolved lead concentration predicted by the model ranged from 157 μg/L (TP2 and TP6) to 393 μg/L (TP1 and TP5). Figure B.5 shows a comparison between the dissolved lead release predicted by tidyphreeqc and the dissolved lead concentrations that were actually measured. Overall, the model did not accurately predict dissolved lead concentrations in any of the synthetic waters. The concentration of dissolved lead was overestimated in the absence of NOM, yet was greatly underestimated in the presence of SR NOM. The model may have overestimated dissolved lead in the synthetic waters without NOM as the corrosion scales that formed were more complex than predicted (section 3.3.5) and the system may not have been at equilibrium. Meanwhile, the model likely underestimated dissolved lead in the presence of SR NOM, as the model did not take into account the interactions between NOM and oxidized lead. NOM can increase the release of dissolved lead by altering the structure of lead corrosion scales, complexing with lead, or by stabilizing colloidal particles (Dryer & Korshin, 2007; Korshin et al., 1999; Korshin et al., 2000; Korshin et al., 2005; Korshin & Liu, 2019; Lin & Valentine, 2008a; Lin & Valentine, 2009; Trueman & Gagnon, 2016a; Trueman et al., 2017; Trueman et al., 2018; Trueman et al., 2019a; Valentine & Lin, 2009). This outcome clearly highlights the negative impact that NOM can have on the release of dissolved lead and its ability to increase the concentration of dissolved lead above the theoretical solubility based on a model that does not incorporate NOM.

3.3.4 Changes to NOM Characteristics Following Stagnation

3.3.4.1 FEEM Results

The intensity of the fulvic and humic acid FEEM fractions in the synthetic waters with SR NOM before and after a 48-hour stagnation period in the test pieces are shown in Figures 3.5a and 3.5b, while the protein-like materials fraction is shown in Figure B.6a. The intensity of the humic acids ranged from 268 au (TP10) to 475 au (TP2) prior to stagnation and from 244 au (TP10) to 444 au (TP8) after stagnation. The intensity of the humic acids decreased significantly ($p < 0.05$) in all of the synthetic waters with SR NOM following stagnation (Table B.8). The largest decrease in humic acid intensity was in TP3 (107 au) while the smallest decrease was in TP10 (24 au). The intensity of the fulvic acids ranged from 192 au (TP10) to 373 au (TP2) prior to stagnation and from 179 au (TP10) to 347 au (TP2) after stagnation. The intensity of the fulvic acids decreased upon stagnation and the decrease was significant ($p < 0.05$) in all of the test pieces with SR NOM except TP10 (Table B.8). The largest decrease in fulvic acid intensity was in TP3 (74 au) while the smallest decrease was in TP9 (12 au).

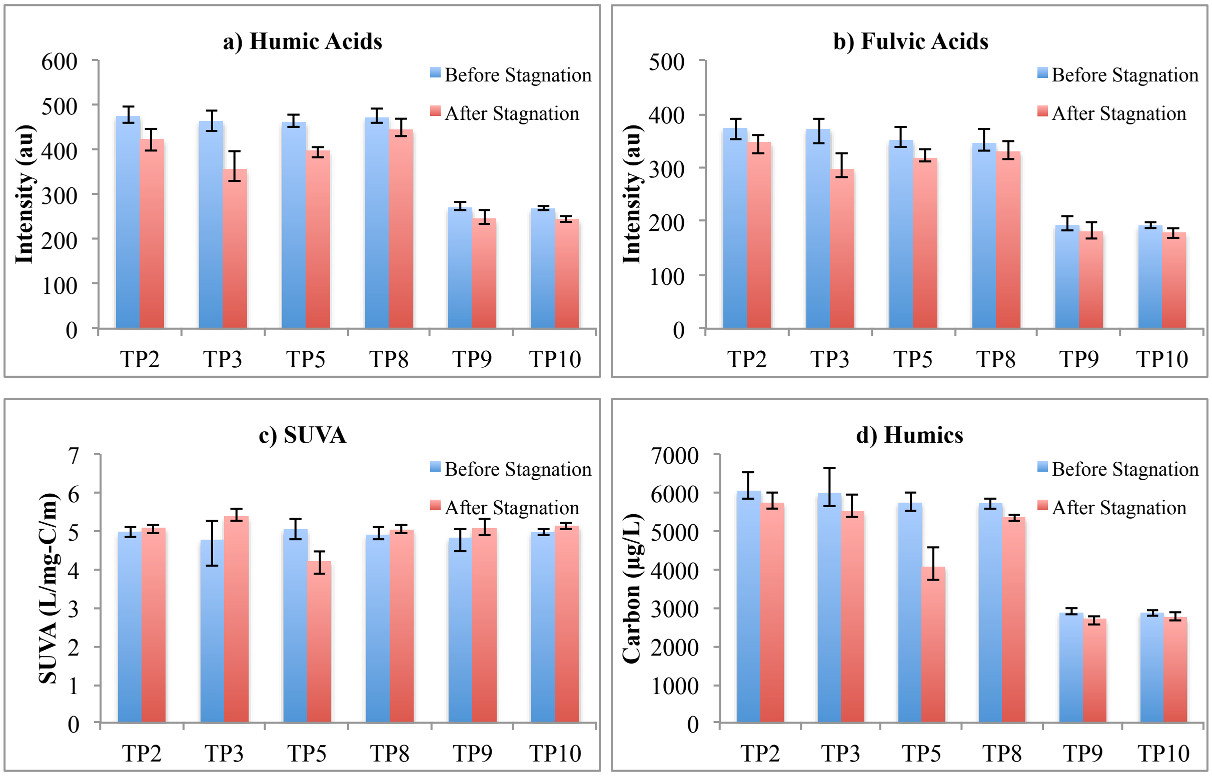


Figure 3.5 Average values for FEEM NOM fractions in weeks 12, 16, and 20 for a) humic acids and b) fulvic acids. Average values for LC-OCD NOM fractions in weeks 3, 7, 12, 16 and 20 for c) SUVA and d) humics. Error bars represent minimum and maximum values. TP2, TP3, TP5, and TP8 were dosed with 7 mg DOC/L of SR NOM, while TP9 and TP10 were dosed with 3.5 mg DOC/L of SR NOM.

A strong correlation between the decrease in humic acid intensity and dissolved lead release ($R^2 = 0.88$; $p < 0.001$), and the decrease in fulvic acid intensity and dissolved lead release ($R^2 = 0.78$; $p < 0.001$) were observed in the synthetic waters with SR NOM, as shown in Figures B.7a and B.7b. To the author's knowledge, this is the first study to identify a correlation between dissolved lead release and a decrease in humic and fulvic acid intensities using FEEM. This relationship suggests that interactions between SR NOM and oxidized lead increased the release of dissolved lead. Indeed, both humic and fulvic acids have been found to increase the release of dissolved and colloidal lead in previous research (Arnold, 2011; Korshin et al., 1999; Korshin & Liu, 2019; Trueman et al., 2017). This result indicates that the molecules that make up the humic and fulvic acids were altered in a manner that was proportional to the amount of dissolved lead that was released. Similar changes in the FEEM intensity of NOM have been documented during the water treatment process (Croft, 2012). It is possible that certain aromatic groups in the humic and fulvic acids were altered or destroyed after interacting with lead and may have adsorbed to corrosion scales leading to colloidal dispersion or complexation (Korshin et al., 1999; Korshin et al., 2000; Korshin et al., 2005; Korshin & Liu, 2019; Trueman & Gagnon, 2016a; Trueman et al., 2017; Trueman et al., 2018; Trueman et al., 2019a). Using a novel technique with SEC coupled with ICP-MS and UV_{254} detection, Trueman et al. (2017) found a strong relationship between the ^{208}Pb and UV_{254} chromatograms when sodium humate (Aldrich) was added to the water, and suggested that this was due to the formation of lead-humate complexes. The findings of the current study are in agreement with the formation of such a complex, as a drop in the humic acid intensity would be expected upon the formation of lead-humate complexes. Further research investigating the impact of different types of NOM on dissolved lead release with a variety of humic and fulvic acid intensities prior to stagnation would be useful, in order to determine if FEEM could be used as a tool for assessing the aggressiveness of the NOM towards lead prior to stagnation.

3.3.4.2 LC-OCD Results

The SUVA (by-pass peak) and humics concentration for the synthetic waters with SR NOM determined by LC-OCD analysis before and after a 48-hour stagnation period in the test pieces are shown in Figures 3.5c and 3.5d respectively. The DOC, biopolymers, building blocks, low molecular weight (LMW) neutrals, and LMW acids/humics concentrations determined by LC-OCD are shown in Figures B.6b-f. The DOC concentration ranged from 3,660 µg/L (TP10) to 8,090 µg/L (TP3) prior to stagnation and from 3,560 µg/L (TP9) to 7,360 µg/L (TP2) following stagnation. The DOC concentration decreased in all of the synthetic waters with SR NOM following stagnation in the test pieces and the decrease was significant in TP3, TP5, and TP8 ($p < 0.05$). The SUVA ranged from 4.76 L/mg-C/m (TP3) to 5.04 L/mg-C/m (TP5) prior to stagnation and from 4.20 L/mg-C/m (TP5) to 5.37 L/mg-C/m (TP3) following stagnation. The SUVA increased in all of the synthetic waters with SR NOM except for TP5, which decreased. The increase in SUVA was significant in TP3 and TP10 ($p < 0.05$) and the decrease in SUVA in TP5 was also significant ($p = 0.009$). The change in SUVA is complex and is dependent on how the humics concentration changes relative to the DOC concentration. Some perspective on this is described in the next paragraph based on the FEEM results. The humics concentration ranged from 2,860 µg C/L (TP9) to 6,040 µg C/L (TP2) prior to stagnation and from 2,700 µg C/L (TP9) to 5,720 µg C/L (TP2) following stagnation. The humics concentration decreased significantly ($p < 0.05$) following stagnation in all of the test pieces. This finding is consistent with the decrease in humic and fulvic acid intensities following stagnation that were identified using FEEM. Other than a significant decrease in the concentration of LMW neutrals ($p = 0.013$) in TP8, none of the other NOM fractions measured by LC-OCD changed significantly following stagnation in the test pieces.

No correlation was observed between the decrease in the SUVA and dissolved lead release ($R^2 = 0.02$; $p = 0.626$; Figure B.7c). As the results were mixed with regards to the change in SUVA during stagnation, it does not appear that the aromaticity of the NOM was substantially altered. However, it has been suggested that waters with a higher UV_{254} and SUVA are more reductive to lead (IV) (Dryer & Korshin, 2007; Lin & Valentine, 2008a; Lin & Valentine, 2009). A weak correlation was observed between a decrease in the humics concentration and dissolved lead release ($R^2 = 0.15$; $p = 0.098$; Figure B.7d). This is in contrast to the FEEM results, where a strong correlation was observed between the decrease in humic and fulvic acid intensities and dissolved lead release. This result made sense, as FEEM is more sensitive to changes in structural and functional groups within the NOM, which would result from complexation with lead. Interestingly, the NOM fractions in TP5 decreased more substantially than in the other test pieces. This test piece also had the highest average turbidity following stagnation (8.17 NTU), and perhaps these two observations were linked (Table B.10). It is possible that other mechanisms in addition to complexation, such as adsorption to corrosion scales and microbial corrosion, may have decreased the humics and DOC concentrations in this test piece (Gao et al., 2018; Korshin et al., 1999; Korshin et al., 2000; Korshin et al., 2005; Trueman et al., 2017). It would be useful to repeat the experiments with different types of NOM to see if the composition as analyzed using LC-OCD plays a role with regards to dissolved and colloidal lead release.

3.3.5 Scale Analysis

XRD results for the lead pipes of the test pieces are shown in Figure 3.6 and Table 3.4 and the XRD results for the copper pipes are shown in Figure B.8 and Table B.4. The ICP-MS results for the scales are summarized in Tables B.5 and B.6, and the SEM-EDS results are displayed in Figures B.9-B.18. The XRD results indicated that cerussite was present on all of the lead pipes. Several other lead solids were also detected including plattnerite (TP1, TP2, TP5, TP7, TP8, TP10), hydrocerussite (TP2, TP3, TP5, TP8-10), litharge (TP1, TP3, TP5, TP7-10), and elemental lead (TP1-3, TP5-7, TP9, TP10). The SEM-EDS analysis indicated that the scales that formed were thin and less than 10 μm in thickness. The scales that formed were more complex than either cerussite or hydrocerussite, which were predicted by the tidyphreeqc modelling software. This finding is in accordance with several studies that have found that corrosion scales on lead pipes are more complex than predicted by solubility models (Cantor, 2017; Schock et al., 2014; Tully et al., 2019). It is interesting that a complex mixture of lead corrosion scales were observed on the lead pipes following only 20 weeks of “dump and fill” experiments that used synthetic waters of consistent chemistry. The complexity of the scales may partially explain why the dissolved lead concentrations were lower in the synthetic waters without NOM than predicted by tidyphreeqc.

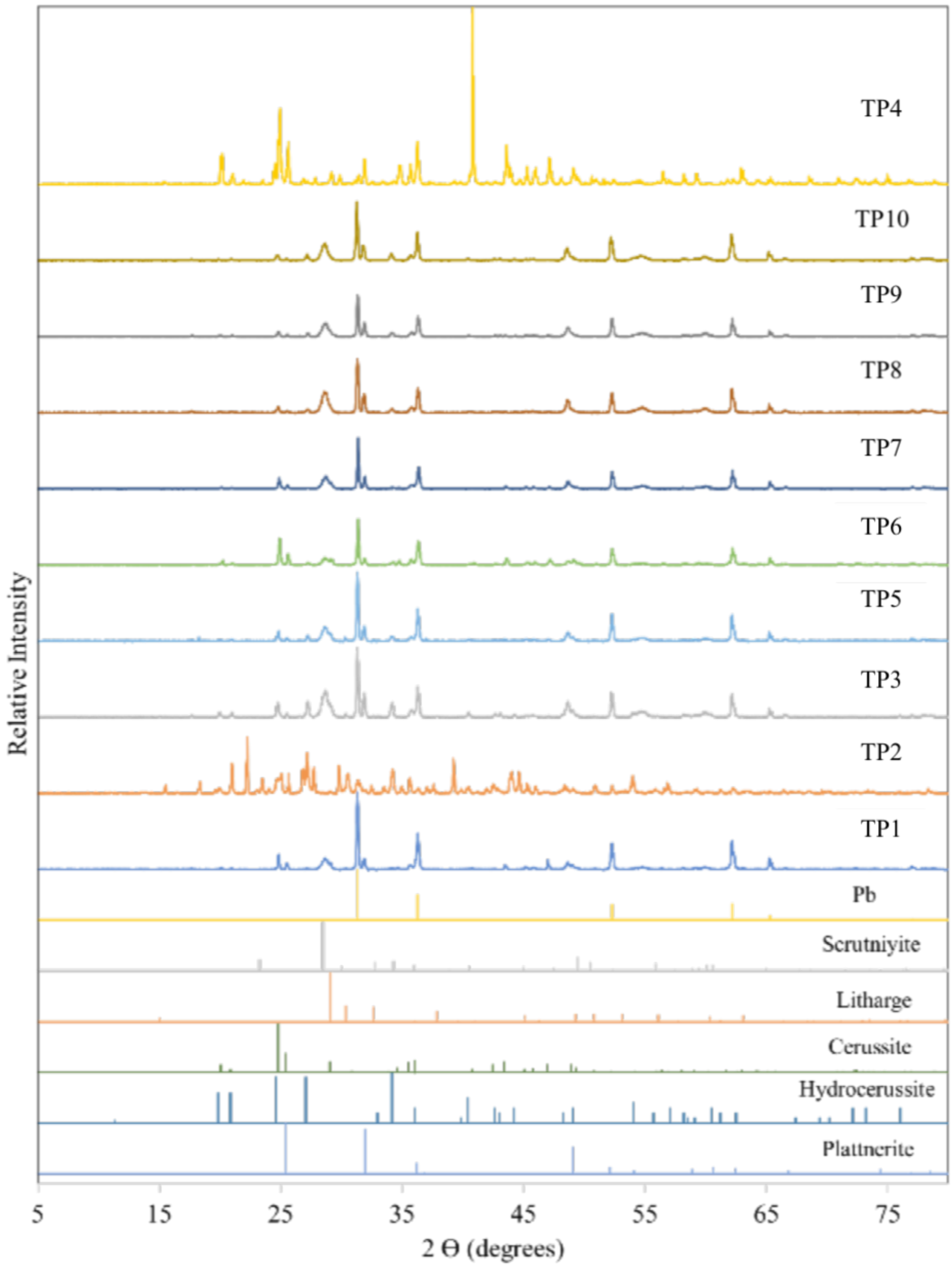


Figure 3.6 XRD patterns obtained from the surface of the lead pipes for a range of 5° to 80° 2θ. The patterns at the bottom are the reference patterns of the solids that had peaks identified in the samples.

Table 3.4 Summary of Results from XRD Conducted on the Powdered Samples from the Lead Pipe Surface

	Cerussite ($PbCO_3$)	Hydrocerussite ($Pb_3(CO_3)_2(OH)_2$)	Litharge (PbO)	Plattnerite (PbO_2)	Lead (Pb)
TP1	+		+	+	+
TP2	+	+		+	+
TP3	+	+	+		+
TP4	+				
TP5	+	+	+	+	+
TP6	+				+
TP7	+		+	+	+
TP8	+	+	+	+	
TP9	+	+	+		+
TP10	+	+	+	+	+

*‘+’ indicates the presence of certain mineral (greater than approximately 1%).

The discovery that plattnerite formed on some of the pipes was unexpected, as no disinfectant was added to the synthetic waters and free chlorine is normally required to maintain a redox potential high enough to oxidize lead (0) to lead (IV) (Brown et al., 2013; Edwards & Dudi, 2004; Rajasekharan et al., 2007; Switzer et al., 2006). However, free chlorine was added to the NSF extraction water during pretesting and it is possible that the plattnerite had already formed in some of the test pieces prior to the regular “dump and fill” experiments. The scale analysis did not indicate that protective calcium carbonate films formed on the lead pipes, however calcite magnesian and calcium carbonate were detected on some of the copper pipes.

SR NOM promoted the formation of hydrocerussite, as it was detected on all of the lead pipes that were exposed to NOM but on none of the lead pipes that were not exposed to NOM. The SR NOM also changed the colour of the lead corrosion scales, as the lead pipes not in contact with NOM formed white corrosion scales while the lead pipes in contact with SR NOM formed corrosion scales that were white, green, greenish-yellow, yellow, yellowish-white, yellowish-brown, brownish-white, or brown. This coloration is likely due to humic substances being incorporated into the lead corrosion scales (Korshin et al., 1999; Korshin et al., 2000; Korshin et al., 2005; Trueman et al., 2017). In the current study, the structure of the corrosion scales appeared to be similar in the test pieces exposed to water with and without SR NOM. This is in contrast to previous research, which found that in the presence of untreated NOM (from a concentrated natural source), cerussite and hydrocerussite were less crystalline and contained an amorphous layer at the surface (Korshin et al., 1999; Korshin et al., 2000; Korshin et al., 2005). This may be due to the high DIC concentration and hardness in the waters in the current study and the short duration (20 weeks) of the "dump and fill" experiments. As well, Korshin et al. (2005) found that NOM prevented the formation of cerussite and hindered the growth of hydrocerussite crystals. This is also in contrast to the current study, where cerussite was found on all of the lead pipes and SR NOM appeared to promote the formation of hydrocerussite. This may be because the lead coupons in Korshin et al. (2005) were exposed to the water with a lower DIC concentration of approximately 4.3 mg/L (alkalinity = 15 mg $CaCO_3$/L) compared to between 10 mg/L and 80 mg/L in the current work. It is also possible that the galvanic connection between lead and copper may have increased the generation of cerussite and hydrocerussite corrosion scales in the current work.

NOM can act as a reductant and reduce lead (IV) to lead (II), hence it was expected that the lead (IV) solid plattnerite would be more abundant on the lead pipes exposed to water without SR NOM (Dryer & Korshin, 2007; Korshin & Liu, 2019; Lin & Valentine, 2008a; Lin & Valentine, 2009; Valentine & Lin, 2009; Winning et al., 2017). However, no relationship was identified between the absence of NOM and the presence of plattnerite. This may be because there was no disinfectant added to the synthetic waters, which would have limited the production of lead (IV). In all, the scale analysis suggested that SR NOM was incorporated into the lead corrosion scales and may have increased the release of dissolved lead through colloidal dispersion and complexation.

3.3.6 Relevance of Results for Drinking Water with Free Chlorine or Chloramine

In the present study, no disinfectant was added to the synthetic waters as it would have complicated the preparation of the waters, made the water quality less stable, and added another factor to be considered in the results. Therefore, the redox potential in the synthetic waters was probably lower than in drinking water with either free chlorine or chloramine added as a disinfectant. According to Figure 2.2 in Chapter 2, it is presumed that the waters in the present study had a redox potential that would have promoted the oxidation of lead (0) to lead (II) and not lead (0) to lead (IV), and therefore the results are more applicable for drinking water with chloramine than drinking water with free chlorine. However, lead (II) scales can still form in water with free chlorine, so the results are still relevant in many distribution systems using chlorinated water (Tully et al., 2019). Besides the redox potential, a disinfectant may have altered the results by reacting with the SR NOM. This likely would have reduced the increase in dissolved lead in the presence of NOM by altering the aromatic groups of the NOM, with the impacts being more notable if free chlorine was added as a disinfectant than chloramine (Lin & Valentine, 2009; Valentine & Lin, 2009). Regardless, an increase in dissolved lead release due to the addition of SR NOM would be anticipated even if a disinfectant had been added.

3.3.7 Implications for the Water Treatment Industry

The fact that SR NOM increased dissolved lead concentrations by approximately an order of magnitude in this study should be of interest to utilities that have not optimized NOM removal. Furthermore, the results of this study suggest that even in hard waters, NOM can greatly increase the concentration of dissolved lead. For instance TP8, which had a pH of 8.5, DIC concentration of 80 mg/L, a hardness of 450 mg $CaCO_3$/L, and a DOC concentration of 7 mg/L, released an average of 578 µg/L of dissolved lead following a 48-hour stagnation period. This was much greater than the solubility of 264 µg/L that was predicted by tidyphreeqc. As evidenced through the FEEM and LC-OCD analyses, the characteristics of the NOM were altered during stagnation in the test pieces. It is believed that SR NOM increased the concentration of dissolved lead by modifying the structure of corrosion scales, promoting colloidal dispersion, and forming lead-NOM complexes, as has been suggested in previous research (Korshin et al., 1999; Korshin et al., 2000; Korshin et al., 2005, Korshin & Liu, 2019; Trueman & Gagnon, 2016a; Trueman et al., 2017; Trueman et al., 2018; Trueman et al., 2019a; Willison & Boyer, 2012). Improvements in the removal or treatment of NOM in the water treatment process are expected to remove the strongest complexing fractions and will likely decrease lead concentrations in consumer’s taps. This is in line with multi-barrier treatment decision-making.

As well, the results of this study suggested that an increase in the DIC concentration did not reduce the release of lead resulting from galvanic corrosion. In this study, the pH buffering capacity that resulted from an increase in the alkalinity was not sufficient to overcome an increase in the galvanic current due to an increase in the conductivity, and this finding is in accordance with previous research (Nguyen et al., 2011a; Zhou et al., 2015). This implies that in the case of galvanic corrosion, increasing the DIC concentration over 10 mg/L is not an effective means of reducing the release of lead. This finding is consistent with several studies that have suggested that an optimal alkalinity is around 30-75 mg $CaCO_3$/L (Giammar et al., 2010; Kim et al., 2011; Noel et al., 2014; Schock & Gardels, 1983, Wilzcak et al., 2010). Therefore, pH adjustment is recommended over alkalinity adjustment as a means of reducing lead release (Wilczak et al., 2010). As many of the synthetic waters in this study were oversaturated with calcium carbonate, attempting to form calcium carbonate scales on lead pipes did not appear to be an effective corrosion control strategy. However, it is possible that several years may be required to form protective calcium carbonate films on lead pipes and that the current study was too short to observe this. Nonetheless, these results are in accordance with previous literature that has suggested that corrosion has little to do with calcium carbonate precipitation (AwwaRF, 1990; Richards et al., 2018; Schock, 1989; Wilczak et al., 2010). Additionally, hardness was not found to have a significant impact on lead release. These results suggests that having hard water does not necessarily guarantee that lead concentrations in consumer's taps will be below regulated values

3.4 Conclusions

The following conclusions were made based on the results of a 20-week "dump and fill" experiment that utilized a 2^{4-1} fractional factorial design to examine the impact of pH, DIC, hardness, and NOM on the galvanic corrosion of lead.

- pH was found to potentially have a significant effect on the release of total lead, with an increase in pH from 7 to 8.5 decreasing total lead release by an average of 4,390 µg/L. DIC was found to potentially significantly increase the galvanic current, with an increase in the DIC from 10 mg/L to 80 mg/L increasing galvanic current by an average of 28.4 µA. Hardness did not have a significant impact on the galvanic current or lead release. SR NOM had a potentially significant impact on the release of dissolved lead, with the addition of SR NOM at a concentration of 7 mg DOC/L increasing the release of dissolved lead by an average of 2,320 µg/L.
- Solubility modelling using tidyphreeqc software did not accurately predict the release of dissolved lead. Potential reasons for this discrepancy include more complex lead

corrosion scales forming than either cerussite or hydrocerussite, and interactions between NOM and oxidized lead causing complexation and colloidal dispersion.

- Strong correlations were identified between the release of dissolved lead and a decrease in the humic ($R^2 = 0.88$; $p < 0.001$) and fulvic ($R^2 = 0.78$; $p < 0.001$) acid intensities measured by FEEM. This result provides indirect evidence of complexation between lead and SR NOM.
- The synthetic waters with SR NOM formed yellowish-brown corrosion scales on the lead pipes, while the synthetic waters without NOM formed white corrosion scales on the lead pipes. This suggested that SR NOM was incorporated into the lead corrosion scales, although the scales were too thin to identify any differences in structure. SR NOM also appeared to promote the formation of hydrocerussite, as this solid was only detected on the lead pipes exposed to SR NOM.
- The scale analysis did not suggest that hardness films such as calcium carbonate formed on the lead pipes, suggesting that the precipitation of calcium carbonate did not offer protection against corrosion in this study. The results of this study indicate that hard water could still be aggressive to lead, at least in some scenarios.

Chapter 4

Role of NOM on the Galvanic Corrosion of Lead in Real and Synthetic Drinking Water

This chapter is based on an article that at the time of writing was being prepared for submission to Water Research tentatively titled “Role of NOM on the Galvanic Corrosion of Lead in Real and Synthetic Drinking Water”. The cited references in this chapter are included in the list of references at the end of the thesis.

This article focuses on the results of a bench scale “dump and fill” experiment to assess the role of different types and concentrations of NOM on galvanic corrosion and lead release (Phase II). As identified in Chapters 2 and 3, NOM is a water quality factor that is known to increase the release of lead, in particular dissolved and colloidal lead, but has not been studied as thoroughly as many other water quality factors such as pH and DIC. Appendix D contains supplemental information referenced in this chapter, while Appendix E contains the raw data that was collected. The scale analysis section (section 4.3.8) in this chapter only includes results for XRD and ICP-MS. Scales were to be analyzed using SEM and EDS as well, but this was unable to be completed in time for the thesis submission due to the COVID-19 pandemic.

The author would like to acknowledge the contributions of the individuals who will be the coauthors of the manuscript that will be submitted for this chapter: Dr. Benjamin Trueman, Dr. Sigrid Peldszus, Anushka Mishrra, Kimia Aghasadeghi, Dr. Graham Gagnon, Dr. Daniel Giammar, and Dr. Peter M. Huck. Please refer to the Statement of Contributions in the front matter of the thesis for a detailed description of the work that was completed by the coauthors and lab assistants.

Summary

Galvanic current, lead release, and copper release from test pieces consisting of new lead and copper pipes exposed to a variety of real and synthetic waters were monitored throughout a 21-week “dump and fill” experiment. The two real waters consisted of unchlorinated, but otherwise treated river water, and raw water from a municipal well in Southern Ontario**.** Each of the real

waters was modelled using two synthetic waters, one with SR NOM and another without NOM, for a total of four synthetic waters**.** The galvanic current between the lead and copper pipes of the test pieces was the highest in the synthetic water modelling the well water with SR NOM, and this was likely due to a combination of SR NOM and a high concentration of DIC. No significant differences were identified among the different water types regarding the release of total and particulate lead due to high variability in the release of particulate lead. However, dissolved lead release did vary among the different water types. The synthetic waters with SR NOM released the most dissolved lead, followed by the real waters, and finally by the synthetic waters without SR NOM**.** FFF combined with ICP-MS and UV_{254} identified that complexation and colloidal dispersion were responsible for the increase in dissolved lead associated with the NOM**.** Furthermore, changes to the humics concentration measured by LC-OCD and the humic and fulvic acid intensities measured using FEEM suggested that humic substances may be the fraction of NOM that is most responsible for complexing with lead**.** Utilities that have yet to optimize NOM treatment or removal should do so, in order to minimize lead concentrations in consumers' taps.

4.1 Introduction

Major sources of lead in drinking water include lead service lines, lead solder, lead containing plumbing fixtures, and galvanized pipes (Clark et al., 2015; Giammar et al., 2010; Latham et al., 2015). The exposure to lead in drinking water is linked to elevated BLLs, which has been proven to cause neurological and neurodevelopmental disorders in children (Edwards et al., 2009; Evens et al., 2015; Hanna-Attisha et al., 2016; Shadbegian et al., 2019; Triantafyllidou & Edwards, 2012). Due to the health effects that are associated with lead in drinking water, it is a regulated contaminant in many jurisdictions. Health Canada has set a MAC guideline of 5 µg/L for lead in drinking water (Health Canada, 2019). In Ontario, the enforceable MAC for lead is 10 µg/L and is regulated by the MECP (Government of Ontario, 2020). However, as the Health Canada guideline was recently lowered from 10 µg/L to 5 µg/L, it is possible that the enforceable MAC in Ontario will be lowered to 5 µg/L in the near future, which may require several municipalities not currently implementing corrosion control programs to do so (Health Canada, 2019).

Corrosion and the release of lead are accelerated if lead is connected to another metal, such as copper or brass (Brown et al., 2013; Kogo et al. 2017; Triantafyllidou & Edwards, 2010; Triantafyllidou & Edwards, 2011). This can occur if there has been a PLSLR when part of a lead service line is replaced with copper (Triantafyllidou & Edwards, 2010). In this situation, near the galvanic connection lead acts as the anode and is preferentially sacrificed, while copper acts as the cathode and is protected against corrosion (Brown et al., 2013; Triantafyllidou & Edwards, 2010). Additionally, lead (II) is a Lewis acid, so a local drop in pH can occur near the surface of the lead at the lead-copper junction. Therefore, galvanic corrosion can increase the release of lead by increasing the corrosion rate and by lowering the pH of the water near the surface of the lead (Ma et al., 2016; Triantafyllidou & Edwards, 2010). Copper released upstream from the copper pipe can also deposit on the surface of the downstream lead pipe causing deposition corrosion, which can further increase the release of lead (Hu et al., 2012).

NOM is a common constituent in drinking water and it is comprised of a mixture of organic compounds with varying chemical properties and compositions. Several studies have identified that NOM can act as a reductant and accelerate the reduction of relatively insoluble lead (IV) into more soluble lead (II) (Dryer & Korshin, 2007; Korshin & Liu, 2019; Lin & Valentine, 2008a; Lin & Valentine, 2009; Valentine & Lin, 2009; Winning, et al., 2017). As well, NOM can adsorb to corrosion scales, which can hinder the formation of cerussite and hydrocerussite, and form a thin amorphous film on the surface of the metal (Korshin et al., 1999; Korshin et al., 2000; Korshin et al., 2005; Liu et al., 2010; Valentine & Lin, 2009). It is presumed that the amorphous film contains NOM that has adsorbed to the corrosion scales (Korshin et al., 1999; Trueman et al., 2017). Furthermore, the adsorption of NOM to corrosion scales can result in a negative shift in the zeta potential of nanoparticles, which increases their stability and results in colloidal dispersion (Korshin et al., 2005; Korshin & Liu, 2019; Liu et al., 2010). For instance, Korshin and Liu (2019) found that the addition of Suwannee River standard fulvic acid to water resulted in a negative shift in the zeta potential of Pb(IV) corrosion scales and greatly increased the concentration of colloidal lead, which they defined as particles between 0.1 μm and 0.45 μm in size. Finally, NOM can form dissolved and colloidal complexes with lead, which can also greatly increase the concentration of dissolved lead (Korshin et al., 1999; Korshin et al., 2000; Trueman & Gagnon, 2016a; Trueman et al., 2017; Trueman et al., 2018; Trueman et al., 2019a;

Willison & Boyer, 2012). Previous studies by Trueman and colleagues that have employed the novel techniques of SEC or FFF combined with ICP-MS and UV_{254} detection have found that both the formation of lead-NOM complexes and colloidal dispersion can greatly increase the release of dissolved and colloidal lead (Trueman & Gagnon, 2016a; Trueman et al., 2017; Trueman et al., 2018; Trueman et al., 2019a).

However, it is not well understood which components of NOM are responsible for adsorbing to lead corrosion scales, complexing with lead, and causing colloidal dispersion (Gao et al., 2018; Korshin et al., 2005; Korshin & Liu, 2019; Winning et al., 2017). Characterizing the NOM before and after stagnation would provide greater insight into the mechanisms of how NOM increases the release of dissolved lead and which fractions of NOM are the most important. Furthermore, as NOM is made up of a diverse collection of organic compounds, NOM from different sources may have different impacts on lead release. For instance, the impacts of NOM on lead release are less substantial if the water has been coagulated, chlorinated or ozonated (Korshin et al., 2005; Lin & Valentine, 2008a; Lin & Valentine, 2009; Trueman et al., 2018; Valentine & Lin, 2009). Hence, there is also a need to evaluate the impact of different types and concentrations of NOM on corrosion and lead release.

The main objective of this work was to investigate the impact of different types and concentrations of NOM on galvanic corrosion and lead release. In addition, the properties of the NOM and colloidal particles were investigated to provide insight into the mechanisms of how NOM increases the concentration of dissolved and colloidal lead**.** As well, the aggressiveness of real and synthetic waters to lead were compared, to determine if real NOM and SR NOM interact with lead in a similar manner. This study was conducted over a period of 21 weeks, utilized 12 lead and copper test pieces, and followed a “dump and fill” protocol similar to that used by Triantafyllidou and Edwards (2010). The test pieces consisted of lead and copper pipes with an external galvanic connection to simulate a PLSLR. A total of six different water types, two real and four synthetic, were included in this study. One of the real waters was collected prior to chlorination from a surface water treatment plant in Southern Ontario**.** The other real water was collected from a municipal well in Southern Ontario prior to treatment. Two synthetic waters modelled each of the real waters, one without any NOM and another with SR NOM, at a similar concentration as in the real water**.**

4.2 Methods and Materials

4.2.1 Preparation of Lead and Copper Test Pieces

The test pieces were constructed based on a design in a previous study by Parks et al. (2014) and consisted of lead and copper pipes with an external galvanic connection as illustrated in Figure 4.1. A total of 14 test pieces were built, and following assembly they were cleaned and pretested following methodology similar to that used by Parks et al. (2014). Of the 14 test pieces, the 12 test pieces with the most consistent total lead release during the pretesting were used for the experimental work to allow for six water types to be tested with duplication. A detailed description of the design of the test pieces and pretesting procedure can be found in section 3.2.1 of Chapter 3.

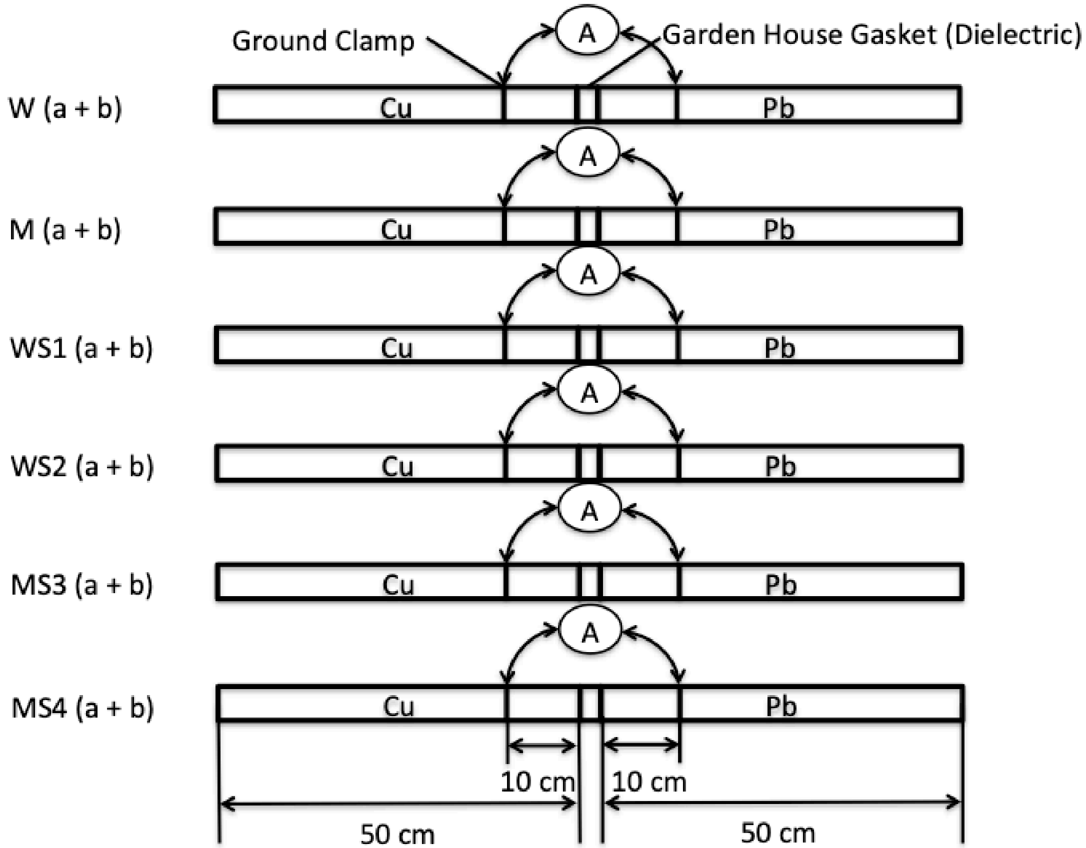


Figure 4.1 Experimental set-up. Each water type was tested in duplicate (a + b) for a total of 12 test pieces. WS1 and WS2 modelled the W water without and with SR NOM respectively. MS3 and MS4 modelled the M water without and with SR NOM respectively.

4.2.2 Source Waters and Synthetic Waters

A total of six different water types were compared in this study, two real waters and four synthetic waters modelling the real waters. The water quality of the different water types is summarized in Table 4.1 (for more information see Tables D.9, D.10, D.13). Some of the waters are missing measurements for DOC and SUVA because they were not measured on a weekly basis or could not be analyzed by the LC-OCD due to a low DOC concentration. However, the DOC was measured at least once for each water type over the 21-week experiment to ensure that there was minimal contamination. One of the real waters was collected from a municipal well (W) in Cambridge Ontario (Region of Waterloo) prior to treatment (raw water). This water was hard water with a near neutral pH, high DIC concentration, high hardness, and low DOC concentration. The other real water was collected from the Mannheim Water Treatment Plant (M) in the Region of Waterloo that draws water from the Grand River. The M water was also considered to be hard water, but compared to the W water had a slightly higher pH, lower DIC concentration and hardness, and higher DOC concentration. The treatment process at the facility consisted of coagulation, flocculation, sedimentation, oxidation, filtration, ultraviolet (UV) disinfection, and chloramination, and consisted of two parallel treatment trains. PACl was added as a coagulant at a concentration of approximately 36 mg/L and polymer (filter aid) was added at a concentration of approximately 0.25 mg/L. The aluminum concentration in the collected water was low and approximately 0.05 mg/L (Table D.13). Ozone was added as a primary oxidant in one of the trains, while free chlorine (weeks 1-15) or ozone (weeks 16-21) were added in the other train, with each train contributing about 50% of the treated water that was collected. The ozone was dosed between 2-3 mg/L in weeks 1-6 and between 1-2.25 mg/L in weeks 7-21 and did not provide any residual. The free chlorine was dosed between 1.05-1.7 mg/L and had a residual of 0.05-0.17 mg/L following primary oxidation. However, it is likely that the chlorine residual was negligible at the point of collection due to the subsequent filtration step. The M water was treated with UV light as the primary means for disinfection and the treated water was collected following the UV treatment and prior to chloramination. The W and M waters were collected on a weekly basis with the exception of a few weeks, when water that had been collected in the previous week was utilized due to operational issues.

Table 4.1 Measured Average Water Quality Parameters for Water Entering the Test Pieces

Parameter	Units	Weeks	W	M	WS1	WS2	MS3	MS4
pH	pH unit	1-4	7.30	7.56	7.12	7.16	7.51	7.51
		5-21	7.19	7.45	7.16	7.19	7.55	7.59
DIC	mg C/L	1-21	71.0	43.1	67.2	67.0	49.7	49.5
Hardness	mg $CaCO_3$/L	1-21	312	264	322	325	266	270
DOC	mg C/L	1-4	1.77	3.65	n.m.	n.m.	n.m.	n.m.
		5-19	1.35	3.40	0.07	1.76	n.m.	3.49
		20-21	1.08	3.93	n.m.	2.45	0.20	5.18
Alkalinity	mg $CaCO_3$/L	1-21	262	167	243	243	195	195
Specific Conductance	µS/cm	1-4	705	671	1,341	1,348	657	890
		5-21	744	645	1,689	1,682	1,159	1,168
Turbidity	NTU	1-21	0.16	0.13	0.48	0.61	0.20	0.66
Chloride	mg/L	1-4	66	81	265	250	217	216
		5-21	66	80	343	343	213	214
Sulfate	mg/L	1-4	21	29	111	112	85	85
		5-21	25	33	106	106	86	86
CSMR	-	1-4	3.15	2.82	2.38	2.24	2.54	2.54
		5-21	2.64	2.46	3.23	3.23	2.50	2.50
Nitrate	mg/L	1-21	1.9	11.3	n.d.	n.d.	n.d.	n.d.
SUVA	L/mg-C/m	1-21	2.86	2.19	4.83	n.m.	4.83	n.m.

*n.m. Not measured

**n.d. Not detected

***The water quality in the synthetic waters was adjusted in weeks 5 and 20, and therefore some parameters have different values provided for the three different time periods.

A total of four different synthetic waters were prepared on a weekly basis to model the real waters. Each of the real waters was modelled with two synthetic waters, one with NOM and one without NOM. WS1 (no NOM) and WS2 (SR NOM added) modelled the W water while MS3 (no NOM) and MS4 (SR NOM added) modelled the M water. The pH, concentration of DIC, DOC, calcium, magnesium, and the CSMR in the synthetic waters were controlled to match the real waters' chemistry as much as possible. After week 4, the pH, DOC concentration and CSMR were adjusted in some of the synthetic waters to better match the real waters' chemistry. However, the chemistry of the real waters did change somewhat during the duration of the experiment and thus it was impossible to match the chemistry exactly. In addition, the DOC concentration in WS2 and MS4 were increased by a factor of about 1.45 in weeks 20 and 21 due to an issue preparing the stock solution.

The synthetic waters were prepared by adding several different chemicals to ultrapure MilliQ water. The pH was adjusted in the synthetic waters by adding either sodium hydroxide (Sigma-Aldrich) from a 0.1 M stock solution or hydrochloric acid (BDH) from a 0.1 M stock solution. DIC was added from a 0.4 M stock solution of sodium bicarbonate (BDH), calcium was added from a 0.15 M stock solution of calcium chloride dihydrate (EMD Millipore), and magnesium was added from a 0.075 M stock solution of magnesium sulfate heptahydrate (EMD). The CSMR was adjusted by adding sodium chloride from a 0.25 M stock solution (Sigma-Aldrich). The NOM was added from a stock solution of reference SR NOM (IHSS; 2R101N) with a DOC concentration of approximately 165 mg/L (Zhou et al., 2015). The composition of the SR NOM according to the IHSS (n.d.a) is 50.70 wt% carbon, 3.97 wt% hydrogen, 41.48 wt% oxygen, 1.27 wt% nitrogen, 1.78 wt% sulfur, and an ash content of 4.01 wt%. The stock solution of SR NOM was prepared by dissolving 200 mg of SR NOM into a 500 mL solution with 20 mL of 0.1 M sodium hydroxide (Zhou et al., 2015). The sodium bicarbonate, calcium chloride dihydrate, magnesium sulfate heptahydrate, and sodium chloride were prepared on a weekly basis. The SR NOM was prepared biweekly while the sodium hydroxide and sulfuric acid were prepared on an as needed basis. 4 L of each water type were collected or prepared weekly in LDPE bottles and were transferred and stored headspace free in four 1 L glass bottles for testing or stagnation in the test pieces.

4.2.3 Dump and Fill Experiments

All of the experimental work was completed in a laboratory setting at room temperature (approximately 20^0C). This study followed a “dump and fill” protocol similar to the one employed by Triantafyllidou and Edwards (2010), as described in section 3.2.4 in Chapter 3. The real and synthetic waters were collected or prepared on Tuesdays for the subsequent week’s “dump and fill” events in order to decrease the age of the water prior to stagnation. Water quality parameters were measured on at least a monthly basis in the synthetic waters and almost weekly in the real waters prior to stagnation in the test pieces (Tables 4.2, D.9, D.10, D.13, Appendix E). At the end of the final 48-hour stagnation event of the week (Wednesdays), the galvanic current between the lead and copper pipes in the test pieces was measured.

Table 4.2 Schedule of Water Quality Analyses

Parameter	Unstagnated		Stagnated
	W, M	WS1, WS2, MS3, MS4	All Water Types
Alkalinity	1-21	4,8,12,15,18	4,8,12,15,18
FEEM*	1-21	3,7,11,16,21	3,7,11,16,21
FFF/ICP-MS (48 Hour Stagnation)	-	-	16,17,21
Galvanic Current	-	-	1-21**
IC (Chloride, Nitrate and Sulfate)	1-21	4,12,18	4,12,18
LC-OCD*	1,2,4,5,7-21	7,11,16,21	3,7,11,16,21
Lead and Copper - Total (Composite)	-	-	1-21
Lead and Copper - Total (48 Hour Stagnation)	-	-	1,3,5,7,9,11,13,16,17,20,21
Lead and Copper - Dissolved (48 Hour Stagnation)	-	-	1,3,5,7,9,11,13,16,17,20,21
Metals (Total)	18,21	18,21	-
pH	1-21	1-21	1-21
Specific Conductance	1-21	4,8,12,15,18	4,8,12,15,18
TOC*	21	21	21
DOC*	21	21	-
Turbidity	1-21	1,3,5,7,9,11,13,16,17,20,21	1,3,5,7,9,11,13,16,17,20,21

*Only one synthetic water without NOM (WS1 or MS3) was analyzed per week as a blank.
**On week 13 the galvanic current was only measured in Wa, Wb, Ma, Mb, WS1a, MS4a, and MS4b

Stagnated water from the test pieces was collected in accordance with the method outlined in section 3.2.4 of Chapter 3. Total lead and copper were measured from the weekly composite samples. Meanwhile, dissolved lead and copper were measured following the final 48-hour stagnation event on weeks 1, 3, 5, 7, 9, 11, 13, 16, 17, 20, and 21 (Table 4.2). Therefore, the total lead concentrations are not equal to the sum of the dissolved and particulate lead concentrations as they originate from different data sets. Filtered samples were also taken on weeks 16, 17, and 21 for FFF/ICP-MS and FFF/UV_{254} analyses. These samples were not acidified and instead were stored at 4^0C prior to analysis. Several other water quality analyses were also performed on the water collected after the final 48-hour stagnation event of the week, to investigate the changes in water quality during stagnation, as outlined in Table 4.2 (also see Tables D.9, D.11, D.12, Appendix E).

4.2.4 Analytical Methods

The analytical methods for pH, alkalinity, DIC, CRC ICP-MS, hardness, specific conductance, turbidity, IC, galvanic current, ICP-MS, LC-OCD, and FEEM are described in section 3.2.5 in Chapter 3. The FFF/ICP-MS and FFF/UV_{254} analyses were completed at Dalhousie University following the method outlined in Trueman et al. (2019a). FFF samples were separated into three primary fractions based on the retention volume: peak 1 (void volume; ~12 mL peak retention volume), peak 2 (NOM peak; ~14 mL peak retention volume), and peak 3 (larger colloidal peak; ~20.5 mL peak retention volume) that likely represented dispersed metal oxides. After the 21 week long "dump and fill" experiment was completed, the scales in the test pieces were analyzed using XRD and ICP-MS at Washington University in St. Louis. This procedure is outlined in section 3.2.5 in Chapter 3.

4.2.5 Data Analysis

As the water quality in the synthetic waters was altered in weeks 5 and 20, the statistical analysis for galvanic current, lead release, and copper release were performed on the data from weeks 5 to 19. It was determined that the galvanic current data did not require a transformation but the lead and copper data did. The Box Cox method was utilized to improve the normality of the data and it was deemed that a natural log transformation ($\lambda = 0$) of the lead and copper data was appropriate (Montgomery, 2013). ANOVA was completed for the galvanic current, lead, and copper data to determine if there were significant differences in the response variables among the different water types. If ANOVA suggested that there were significant differences among the water types, the Tukey-Kramer test (also referred to as Tukey's Honestly Significant Difference Procedure) was used to identify which water types were different than one another (Montgomery, 2013). The data transformations, ANOVA, and Tukey-Kramer tests were computed using MATLAB®. Due to a high amount of variability, the significance for galvanic current, lead release, and copper release were reported at 10% ($p = 0.1$). 10% significance was deemed to be appropriate as many differences were almost significant at the standard 5% and a few other corrosion studies have used significance at 10% (Dodrill & Edwards, 1995; Doré et al., 2019; Tam & Elefsiniotis, 2009). Differences that were significant at the 5% level or better ($p < 0.05$) were considered to be significant, while differences between 5% and 10% were considered to be potentially significant ($0.05 < p < 0.10$).

The galvanic current results were used to estimate the amount of lead that was oxidized throughout the 21-week experiment using Faraday's Law (Cartier et al., 2012; Dudi, 2004). According to Faraday's Law, one coulomb of charge is equal to one mole of electrons. It was assumed that two moles of electrons were required to oxidize one mole of lead (0) to lead (II). It was also assumed that the galvanic current was constant throughout the entire week and equal to the measurement made at the end of the final 48-hour stagnation event. The mass of lead (II) produced and the mass of total lead released from the weekly composite samples were then compared, to estimate the fraction of oxidized lead that was released and the fraction that was stored as a corrosion scale.

The solubility modelling for lead was completed by Dr. Benjamin Trueman at Dalhousie University using an R package for solubility modelling in PHREEQC called tidyphreeqc (Dunnington, 2019; Garnier, 2018; Parkhurst & Appelo, 2013; Wickham, 2017; Wickham & Bryan, 2019). The PHREEQC "minteq" database was modified to be in accordance with Table 4-14 in Schock et al. (1996). This model incorporated the pH, DIC, sulfate, chloride, sodium, calcium, and magnesium concentrations, but did not incorporate the DOC concentration.

Dr. Benjamin Trueman at Dalhousie University integrated the fractograms that were eluted using FFF/ICP-MS and FFF/UV_{254}, in order to determine the semi-quantitative lead and copper concentrations in each fraction. The concentrations of the three fractions were calculated as the sum of the instantaneous concentrations that were measured across the peaks multiplied by the retention volume and divided by the injection volume (Trueman et al., 2019a). The peaks were modelled as skewed Gaussian distributions described by

$$y = h \times e^{-\frac{(x-\mu)^2}{2\sigma}} \times (1 + \mathrm{erf}\left(\gamma \frac{(x-\mu)}{\sqrt{2\sigma}}\right)) \tag{7}$$

where y denotes the instantaneous concentration, x the retention volume, h the peak height, μ the mean, σ the standard deviation, γ the skewness parameter, and *erf* the error function. The lead fractograms for samples with SR NOM (WS2 and MS4) were modeled as three skewed Gaussian distributions (peaks) while the lead fractograms for the other samples (W, M, WS1, and MS3) were modeled as two skewed Gaussian distributions (peaks). Meanwhile, the copper fractograms for all of the samples were modeled as three skewed Gaussian distributions (peaks).

Two-tailed paired sample t-tests were completed to compare the NOM fractions from FEEM and LC-OCD before and after stagnation in the test pieces to determine if there were significant differences ($p < 0.05$). The statistical calculations for FEEM and LC-OCD were completed using Excel. Several correlations between the changes in NOM fractions and lead release were investigated to provide insight into how NOM can increase the release of dissolved lead.

4.3 Results and Discussion

4.3.1 Galvanic Current

A time series plot of the galvanic current that was measured between the lead and copper pipes of the test pieces is shown in Figure 4.2, while the average galvanic current in the test pieces during weeks 5 to 19 are listed in Table 4.3. WS2 had the highest average galvanic current (69.2 μA), and the difference was significant between WS2 and all of the water types ($p < 0.05$) except for W, which was just potentially significant ($p < 0.1$; Table D.1). MS3 had the lowest average galvanic current (35.4 μA), although it was only significantly lower than WS2 ($p = 0.003$) and potentially significantly lower than W ($p = 0.088$; Table D.1). There were no significant differences in the galvanic current among any of the other water types. The average galvanic current in the duplicate test pieces were fairly close to one other for all of the water types except for W. Test piece Wa had an average galvanic current of 59.3 μA which was much higher than Wb, with an average galvanic current of only 44.1 μA. Furthermore, the standard deviation for galvanic current in Wa was 15.3 μA compared to Wb which was only 5.2 μA (Table D.8). For this reason, it is suspected that there may have been an issue with the galvanic connection for the Wa test piece, but it was not clear what caused this to occur.

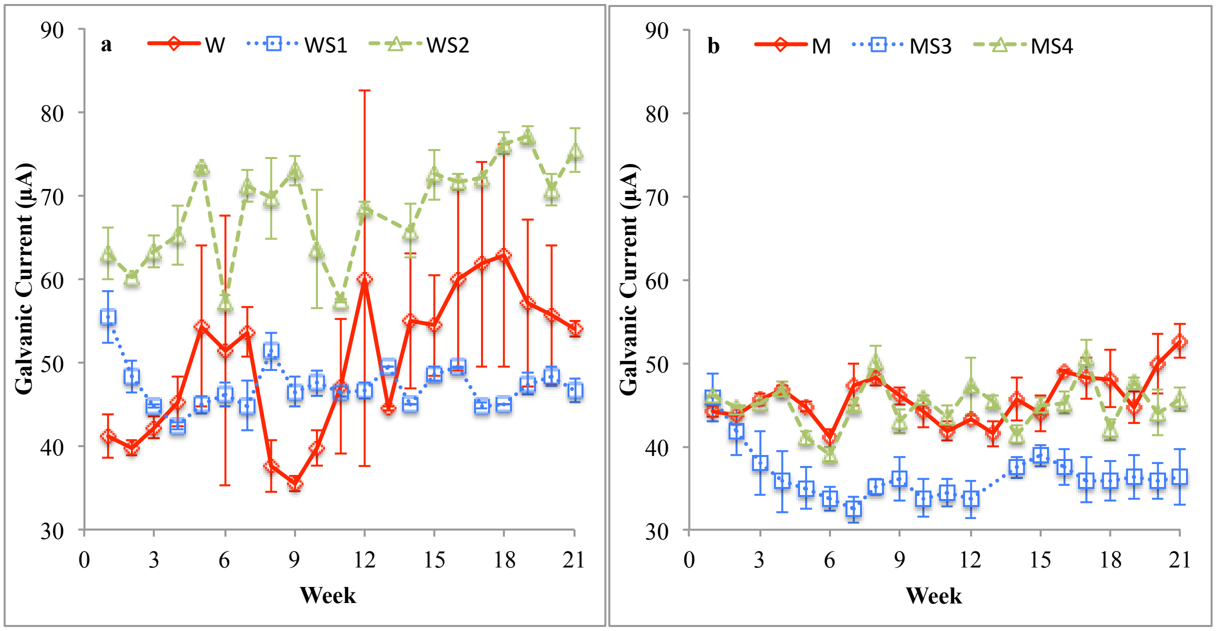


Figure 4.2 Time series plot of the galvanic current for a) W, WS1, and WS2, and b) M, MS3, and MS4. Markers represent the mean of the duplicate test pieces while the error bars represent the duplicate measurements. The galvanic current was measured at the end of the final 48-hour stagnation period of the week.

Table 4.3 Average Galvanic Current, Lead Release, and Copper Release from the Test Pieces

Parameter		W	M	WS1	WS2	MS3	MS4
Galvanic Current (µA)	*mean*	51.7	45.2	46.8	69.2	35.4	44.8
	a	59.3	43.7	47.7	68.5	34.4	42.9
	b	44.1	46.7	45.9	69.9	36.5	46.7
Total Lead (µg/L)	*mean*	1,890	1,260	1,090	7,320	1,830	2,690
	a	3,120	459	1,530	10,600	549	2,270
	b	674	2,060	650	4,010	3,120	3,100
Dissolved Lead (µg/L)	*mean*	441	887	144	1,980	79.0	1,780
	a	436	417	89.5	2,030	85.0	1,600
	b	446	1,360	117	1,920	73.0	1,950
Particulate Lead (µg/L)	*mean*	2,180	911	850	13,600	1,700	1,760
	a	3,730	103	1,110	23,200	657	1,530
	b	621	1,720	595	4,100	2,740	1,990
Total Copper (µg/L)	*mean*	845	397	33.8	149	18.5	111
	a	851	412	31.8	122	18.1	104
	b	839	382	35.7	176	19.0	118
Dissolved Copper (µg/L)	*mean*	861	380	16.7	74.6	6.90	71.2
	a	882	390	17.8	65.3	7.73	71.2
	b	841	370	15.7	83.9	6.08	71.3
Particulate Copper (µg/L)	*mean*	107	60.8	14.9	59.1	9.78	45.0
	a	91.2	68.0	16.0	58.3	8.40	42.6
	b	123	53.7	13.8	59.8	11.2	47.4

*Galvanic current was measured at the end of the final 48-hour stagnation period of the week (weeks 5-19)

**Total metals were measured from the weekly composite samples (weeks 5-19)

***Dissolved and particulate metals were measured from samples collected following select 48-hour stagnation events (weeks 5,7,9,11,13,16, and 17)

****a and b are duplicate test pieces filled with the same water type

It is believed that WS2 had the highest galvanic current due to a combination of having a higher concentration of DIC and SR NOM. Several studies, including Chapter 3 of this thesis, identified that increasing the concentration of DIC increases galvanic current when lead is connected to copper (Nguyen et al., 2011a; Triantafyllidou & Edwards, 2010; Triantafyllidou & Edwards, 2011; Zhou et al., 2015). The increase in galvanic current associated with galvanic corrosion is likely due to an increase in the conductivity of the water (Nguyen et al., 2011a; Triantafyllidou & Edwards, 2010; Triantafyllidou & Edwards, 2011; Zhou et al., 2015). Using similar test pieces and methodology that were utilized in the current study, Zhou et al. (2015) identified that the DIC concentration had a larger impact on galvanic current when SR NOM was added. The results of the current study are consistent with this finding, as WS2 had a significantly higher galvanic current than WS1, with the only difference in the chemistry of the waters being the presence of SR NOM in WS2. As well, the galvanic current in the W test pieces were on average lower than in the WS2 test pieces (p = 0.065), which were exposed to water with a similar DOC concentration but different sources of NOM (i.e. SR NOM in WS2 compared to groundwater NOM in W). This may have been due to different types of NOM or a difference in the conductivity, as the average specific conductance in the WS2 water was 1,350 µS/cm compared to only 705 µS/cm in the W water. It is not immediately clear how NOM can increase galvanic current, but research looking into this would be useful as it may be another mechanism that explains how NOM can increase lead release.

4.3.2 Lead Release

4.3.2.1 Total Lead

A time series plot of the total lead release from the test pieces over the 21-week experiment is included in Figure 4.3, the average total lead release from weeks 5 to 19 is listed in Table 4.3, and summary statistics are provided in Table D.8. WS2a on average had the highest concentration of total lead (10,600 µg/L), while Ma had the lowest concentration of total lead (459 µg/L). The release of total lead was highly variable in the test pieces, with coefficients of variation ranging from 15.6% (MS4b) to 92.3% (WS1a). Furthermore, there were very large differences in the lead release between the duplicate test pieces. For example, WS2a released an average of 10,600 µg/L of total lead compared to WS2b which released an average of only 4,010 µg/L. The large difference in the lead release between the duplicate test pieces resulted in ANOVA not finding any significant differences in total lead release among the different water types (p = 0.306). As discussed in section 4.3.2.2, the high variability in lead release can be mainly attributed to the large amounts of particulate lead.

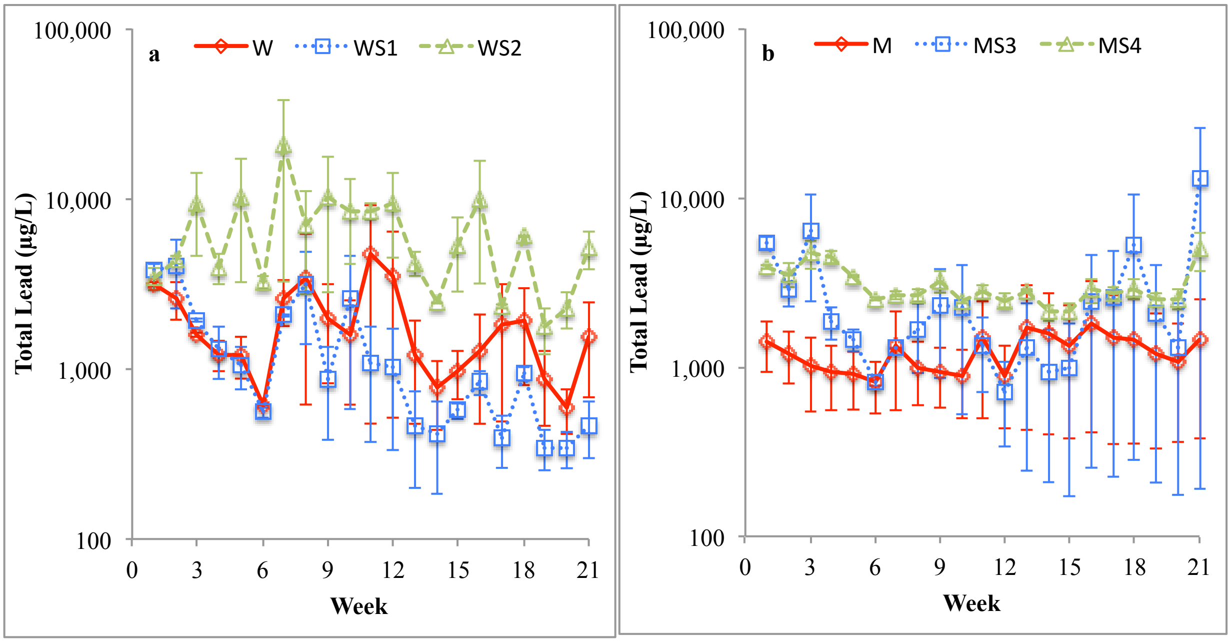


Figure 4.3 Time series plot of total lead release for a) W, WS1, WS2 and b) M, MS3, MS4. Markers represent the mean of the duplicate test pieces while the error bars represent the duplicate measurements. Total lead was measured in the weekly composite samples.

Although no significant differences were detected among the different water types, it does appear that SR NOM may have increased the release of total lead. Both of the synthetic waters with SR NOM (WS2 and MS4) released more total lead than their respective synthetic waters without SR NOM (WS1 and MS3). As well, the synthetic waters with SR NOM (WS2 and MS4) also released more total lead than the real waters (W and M), suggesting that the SR NOM may have interacted more with the oxidized lead than the NOM in the real waters. The impact of the NOM on lead release was more apparent when dissolved lead release was studied, as is discussed in the next section (4.3.2.2).

4.3.2.2 Dissolved and Particulate Lead

The average dissolved and particulate lead release following the select 48-hour stagnation events is displayed in Figure 4.4 and listed in Table 4.3, and summary statistics are provided in Table D.8. The dissolved lead concentrations were measured from filtered samples (0.45 µm), while the particulate lead concentrations were calculated as the difference between the total lead concentrations and the dissolved lead concentrations measured from the samples collected after the select 48-hour stagnation events. As a reminder, the total lead concentrations in section

4.3.2.1 were measured from the weekly composite samples and therefore the sum of the dissolved and particulate lead concentrations in this section are similar but not equal to the total lead concentrations in section 4.3.2.1. The average dissolved lead concentrations in weeks 5 to 19 varied from 73.0 µg/L in MS3b to 2,030 µg/L in WS2a. The dissolved lead release from the test pieces was less variable than total and particulate lead release, and had coefficients of variation ranging from 9.1% (Wa) to 73.5% (WS1b). The average particulate lead release in weeks 5 to 19 varied from 103 µg/L in Ma to 23,200 µg/L in WS2a. The particulate lead release from the test pieces was highly variable and had coefficients of variation ranging from 47.6% (MS3a) to 168% (Wb).

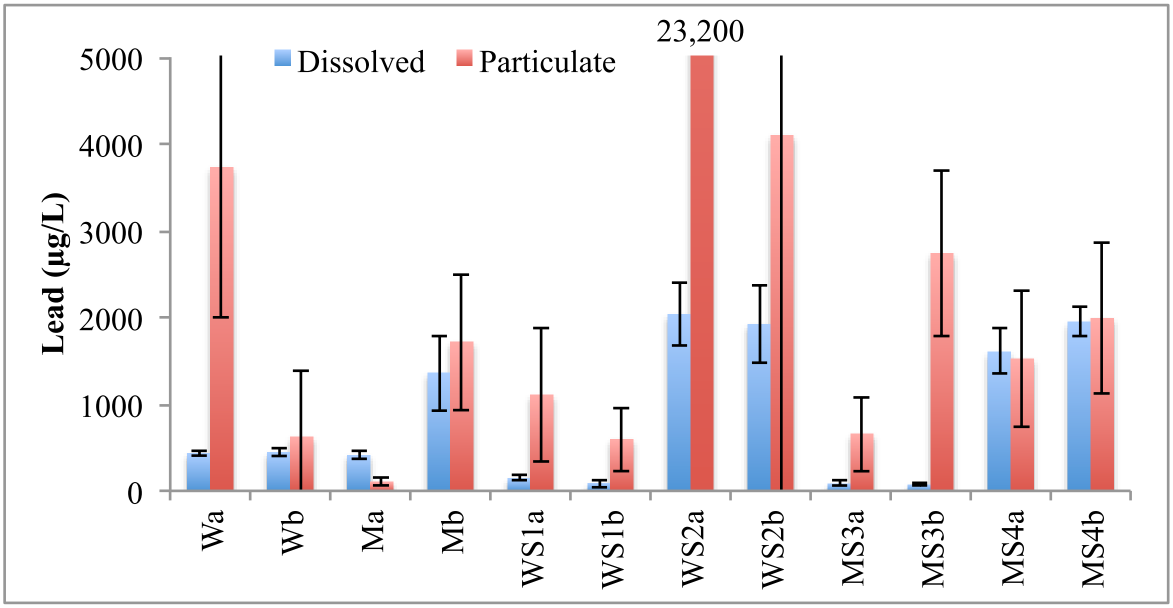


Figure 4.4 Dissolved and particulate lead release during 48-hour stagnation events on weeks 5, 7, 9, 11, 13, 16, and 17. The solid bars represent average values for the water type while the error bars represent the 90% confidence interval.

A time series plot of the dissolved lead release throughout the duration of the experiment is shown in Figure 4.5. Based on ANOVA, significant differences among the different water types and the release of dissolved lead were detected. The Tukey-Kramer test identified that WS2 (SR NOM) had significantly higher dissolved lead release than WS1 (no NOM; p = 0.002) and potentially had a significantly higher dissolved lead release than W (groundwater NOM; p = 0.054). Meanwhile, MS4 (SR NOM) released more dissolved lead than both M (river NOM) and MS3 (no NOM), but it was only significantly higher than MS3 (p = 0.001; Table D.1). As well, W (groundwater NOM) was found to potentially have a significantly higher dissolved lead release than WS1 (no NOM; p = 0.054), while M (river NOM) was found to have significantly higher dissolved lead release than MS3 (no NOM; p = 0.007; Table D.1). To summarize, dissolved lead release was the highest in the synthetic waters with SR NOM (WS2 and MS4), followed by the real waters (W and M), while the synthetic waters without NOM released the least dissolved lead (WS1 and MS3). Thus, these results indicate that NOM, especially SR NOM, increased the release of dissolved lead. The increase in dissolved lead was likely due to complexation between lead and NOM or colloidal dispersion of lead with NOM (Korshin et al., 1999; Korshin et al., 2000; Korshin et al., 2005, Korshin & Liu, 2019; Trueman & Gagnon, 2016a; Trueman et al., 2017; Trueman et al., 2018; Trueman et al., 2019a; Willison & Boyer, 2012) and the contribution of these mechanisms is explored in more detail in section 4.3.6. The order of magnitude increase in dissolved lead release associated with the SR NOM is consistent with Chapter 3. Interestingly, in this experiment the SR NOM was dosed at much lower DOC concentrations (WS2 = 1.76 mg/L, MS4 = 3.49 mg/L) than in Chapter 3 (3.5 mg/L and 7 mg/L). Therefore, even at relatively low concentrations, SR NOM is able to greatly increase the release of dissolved lead. The order of magnitude increase associated with the addition of SR NOM is also consistent with the literature (Willison & Boyer, 2012; Zhou et al., 2015).

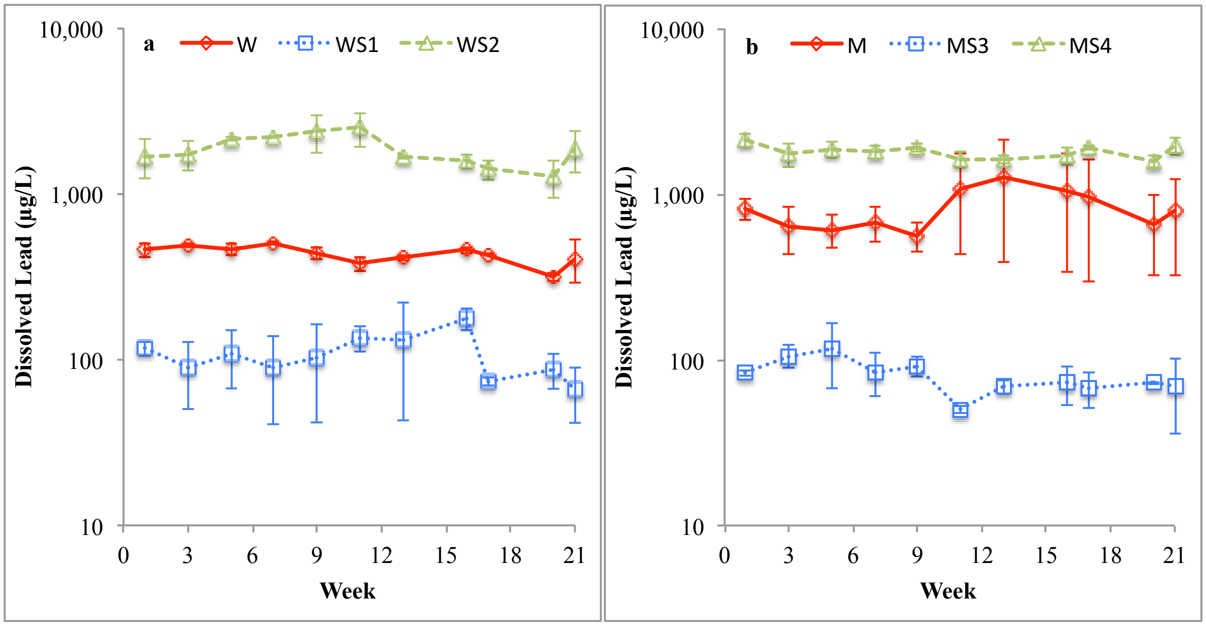


Figure 4.5 Time series plot of dissolved lead release for a) W, WS1, WS2 and b) M, MS3, MS4. Markers represent the mean of the two duplicate test pieces while the error bars represent the duplicate measurements. Dissolved lead was measured from samples collected after select 48-hour stagnation events.

The results of this study show that excluding NOM from synthetic water resulted in substantially lower dissolved lead release compared to the real water it was simulating. In contrast, adding NOM from a concentrated source with different characteristics, such as SR NOM, resulted in substantially higher dissolved lead release than in the real water with a similar DOC concentration. This finding highlights the difficulty of accurately simulating real waters with synthetic waters in corrosion work, and how NOM is one of the parameters responsible for this complexity. The treatment of the M water prior to collection may have contributed to its lower aggressiveness towards lead than the MS4 water with SR NOM, as the characteristics of the NOM would have been altered during treatment as discussed in section 4.3.7. In particular, the humic and fulvic acid intensities measured by FEEM were much lower in the M water than in the MS4 water, despite having a similar DOC concentration. This highlights that the characteristics of the NOM influences the release of dissolved lead. Several studies have shown that treatment such as coagulation, chlorination, and ozonation, can mitigate the negative impacts associated with NOM on the release of dissolved lead, by altering the characteristics of the NOM and by reducing the DOC concentration (Korshin et al., 2005; Lin & Valentine, 2008a; Lin & Valentine, 2009; Trueman et al., 2018; Valentine & Lin, 2009). Although not treated, the NOM in the W water may not have been as aggressive towards lead as the SR NOM due to the reduction in the concentration of humic substances as the water travelled through the aquifer (Juhna et al., 2003; Kaiser et al., 1996), which would have had a similar effect as treating the NOM. Indeed, the NOM characteristics of the W water were more similar to the M water than the synthetic waters with SR NOM (WS2 and MS4), as discussed in section 4.3.7.

Interestingly, similar dissolved lead release was observed in the two synthetic waters with SR NOM, WS2 (1,980 μg/L) and MS4 (1,780 μg/L), despite MS4 having an average DOC concentration of 3.49 mg/L compared to only 1.76 mg/L in WS2 from weeks 5 to 19. This may be due to the higher galvanic current in the test pieces exposed to WS2 (69.2 μA) than MS4 (44.8 μA), which would have resulted in the increased production of oxidized lead. As well, the average pH of WS2 was 7.19 compared to 7.59 in MS4 and previous research has found that NOM has a larger impact in waters with a lower pH (Korshin et al., 1999; Lin & Valentine, 2008a; Chapter 3). In addition, the marginal increase in dissolved lead due to increasing the DOC concentration has been found to decrease once the DOC is higher than about 1-3.5 mg/L

(Korshin et al., 1999; Korshin et al., 2000; Korshin et al., 2005; Korshin and Liu, 2019). Thus, it seems that in this study the higher galvanic current in the WS2 test pieces and lower pH in the WS2 water, was enough to offset the higher DOC concentration in the MS4 water.

As the particulate lead release in most of the water types was substantially higher than dissolved lead release, the trends for particulate lead were expected to follow similar trends as total lead. ANOVA did not detect any significant differences in the release of particulate lead among the different water types. This was not surprising as the release of particulate lead was sporadic and highly variable. Interestingly, some test pieces seemed to be more susceptible to the release of very high amounts of particulate lead than others and this was not necessarily related to the water quality. For instance, WS2a released an average of 23,200 µg/L of particulate lead compared to only 4,100 µg/L in WS2b. Furthermore, the higher particulate lead release in WS2a than WS2b was consistent and occurred in six out of seven of the 48-hour stagnation events from weeks 5 to 19. It is likely that slight changes in the connection between the lead and copper pipes were responsible, and resulted in more corrosion scales being dislodged in WS2a than WS2b. This outcome highlights the difficulties of using a static "dump and fill" method, which allows for large amounts of particulate lead to build up due to long stagnation periods and low non-uniform flow velocities when the pipes were being emptied.

4.3.3 Copper Release

A time series plot of the total copper release from the test pieces over the 21-week experiment is included in Figure D.1, the average total, dissolved, and particulate copper release from weeks 5 to 19 are listed in Table 4.3, and summary statistics are provided in Table D.8. As was expected based on the galvanic series, the release of total copper was much lower than total lead and ranged from 18.1 µg/L (MS3a) to 851 µg/L (Wa). Furthermore, the total copper release was not as variable as the release of total lead, with the coefficients of variation ranging from 14.5% (WS1a) to 56.2% (MS4a). Using ANOVA and the Tukey-Kramer test, it was identified that all of the differences in total copper release among the different water types were significant ($p < 0.05$) except the difference between WS2 and MS4 ($p = 0.313$; Table D.1).

The copper results suggested that the real waters (W and M) released the most copper, followed by the synthetic waters with SR NOM (WS2 and MS4), and the synthetic waters without NOM (WS1 and MS3). This is in contrast to the lead results, as the synthetic waters with NOM (WS2 and MS4) released more lead than the real waters (W and M). The high copper release in the real waters is investigated in section 4.3.6, and appears to be due to the formation of dispersed copper oxides or copper-rich colloids. Looking strictly at the synthetic waters, it does appear that NOM increased the release of copper and this has been documented in previous research (Arnold et al., 2012b; Boulay & Edwards, 2001; Edwards & Sprague, 2001b; Korshin et al., 1996). NOM can form complexes with copper and cause colloidal dispersion in a similar fashion as for lead, thus increasing the concentration of dissolved copper (Edwards & Sprague, 2001b). In addition, NOM can impact the aging process of copper materials and the formation of corrosion scales (Arnold et al., 2012b; Korshin et al., 1996). Both the pH and DIC concentration also had an impact on the release of copper in this study, as W (845 µg/L) released significantly more copper than M (397 µg/L; $p = 0.006$), and WS1 (33.8 µg/L) released significantly more copper than MS3 (18.5 µg/L; $p = 0.022$). WS2 (149 µg/L) also released more copper than MS4 (111 µg/L), but the difference was not significant ($p = 0.313$). This is consistent with previous research including Chapter 3, that have identified that waters with a low pH and high DIC concentration are the most aggressive to copper (Dodrill & Edwards, 1995; Edwards et al., 1996; Xiao et al., 2007).

4.3.4 Lead Release Predicted by Faraday's Law

The amount of lead that was oxidized in the test pieces due to galvanic corrosion was predicted using Faraday's Law (Cartier et al., 2012; Dudi, 2004). Figure D.2 shows a comparison between the amount of oxidized lead that was predicted to have been produced and the total lead release that was measured in the weekly composite samples. As summarized in Table D.2, a relatively small portion of the oxidized lead was actually released into the water as either dissolved or particulate lead, ranging from 1.7% (Ma) to 23.6% (WS2a). Meanwhile, it was assumed that the remainder of the oxidized lead was stored as a corrosion scale and was not released into the water (76.4% to 98.3%). Previous research, including Chapter 3, that have used Faraday's Law to predict the release of lead resulting from galvanic corrosion also found that the majority of oxidized lead was stored as a corrosion scale and not released into the water (Cartier et al., 2012;

Zhou et al., 2015; Chapter 3). The large quantities of corrosion scales that were produced in this study explain why the particulate lead concentrations were very high and susceptible to large spikes.

4.3.5 Solubility Modelling with Tidyphreeqc

The theoretical solubility of lead for the different waters was estimated using tidyphreeqc. This model assumed that the lead solids that could form were either cerussite or hydrocerussite and therefore lead solubility was largely controlled by the pH and DIC concentration. The model also incorporated complexes that could form between lead and other dissolved species as mentioned in section 4.2.5. However, this model did not incorporate lead-NOM complexes that could form. This model also did not consider colloidal lead that can be incorporated into the dissolved lead fraction (< 0.45 μm). According to the tidyphreeqc modelling software, cerussite corrosion scales were expected to form on all of the lead pipes. The lead solubility predicted by the model was very consistent in all of the different water types, ranging from 229 μg/L (MS4) to 238 μg/L (WS1). A comparison between the dissolved lead concentrations and the solubility predicted by the tidyphreeqc software is displayed in Figure D.3. The model did not accurately predict the dissolved lead that was released from the lead pipes, overestimating lead release in the test pieces without NOM (WS1 and MS3) and underestimating lead release in the test pieces with NOM (W, M, WS2, and MS4). This finding is consistent with the solubility modelling that was completed in Chapter 3. It is possible that the model overestimated the dissolved lead concentrations in the synthetic waters without NOM (WS1 and MS3), as the corrosion scales that formed were more complex than predicted (section 4.3.8) and the system may not have reached equilibrium after a 48-hour stagnation period. It is likely that the model greatly underestimated the concentration of dissolved lead in the presence of SR NOM (WS2 and MS4) due to the alteration of the structure of the corrosion scales, colloidal dispersion, or complexation (Dryer & Korshin, 2007; Korshin et al., 1999; Korshin et al., 2000; Korshin et al., 2005; Korshin & Liu, 2019; Lin & Valentine, 2008a; Lin & Valentine, 2009; Trueman & Gagnon, 2016a; Trueman et al., 2017; Trueman et al., 2018; Trueman et al., 2019a; Valentine & Lin, 2009). To a lesser extent, NOM may also have increased dissolved lead concentrations in the real waters (W and M), but other water quality parameters such as trace metals or nitrate also could have played a role (Knowles et al., 2015; Schock et al., 2014; Trueman & Gagnon, 2016b; Trueman et al., 2019b).

4.3.6 Field Flow Fractionation Paired with Inductively Coupled Plasma Mass Spectrometry

FFF/ICP-MS and FFF/UV_{254} fractograms for the sampling events on weeks 16, 17, and 21 are displayed in Figure D.4 and semi-quantitative lead and copper concentrations are tabulated in Table D.3. Average fractograms across the three sampling events are displayed in Figure 4.6. Either two- or three-peak models were used to describe the fractograms as shown in Figure D.5. Two-peak models were used to describe the fractograms for lead for the real waters (W and M) and synthetic waters without NOM (WS1 and MS3). Three-peak models were used to describe the fractograms for lead for the synthetic waters with SR NOM (WS2 and MS4) and for all of the waters for copper. Peaks 1, 2, and 3 occurred at retention volumes of approximately 12 mL, 14 mL, and 20.5 mL respectively, but varied among the water types. The variations in retention volumes can be explained by differences in the size distributions and secondary interactions. The two- and three-peak models described their respective fractograms well, with root mean square errors ranging from 0.11 µg/L to 0.69 µg/L for lead and 0.02 µg/L to 0.07 µg/L for copper. Several of the peaks exhibited tailing (positive skewness) that is characteristic of heavy metals in chromatographic separations (Brown & Grushka, 2000).

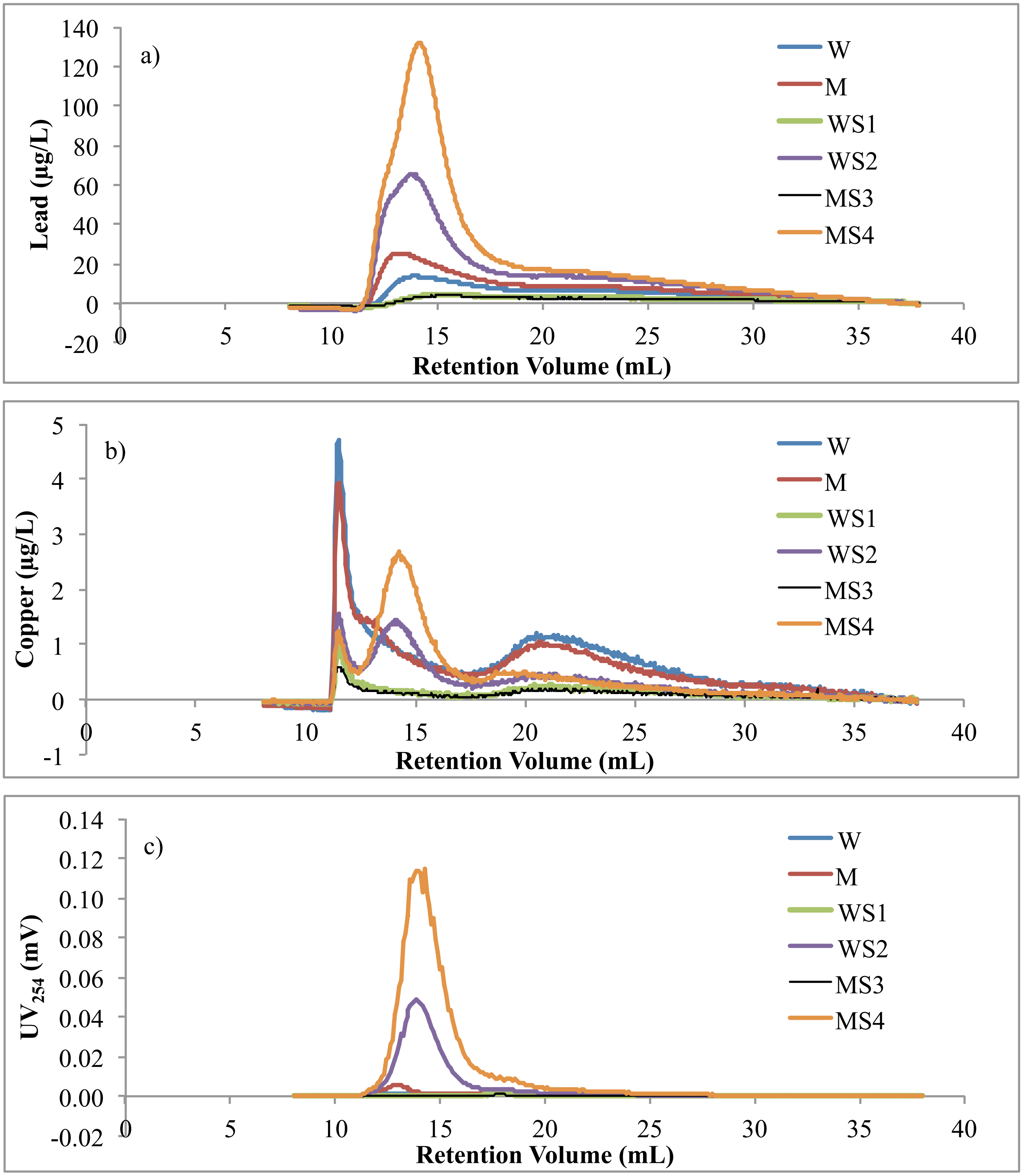


Figure 4.6 Averaged field flow fractograms representing all six samples for a) lead, b) copper, and c) UV_{254} absorbance. UV_{254} is shown as the raw detector output expressed in mV. The filtered samples (< 0.45 µm) were separated into three primary fractions: (1) the void volume (~12 mL peak retention volume), representing soluble and unfocused species, (2) the NOM peak (~14 mL peak retention volume), and (3) a larger colloidal peak (~20.5 mL peak retention volume) that probably represents dispersed metal oxides.

For lead, peak 1 is the void volume fraction and represents soluble and unfocused species (Figure 4.6a). The retention volume for peak 1 varied widely for lead, which may be explained by variations in the composition/size distributions. Since it is much larger in the samples with the SR NOM, it may include lead-NOM complexes that were too small to be effectively separated by the cross-flow. Secondary interactions with the membrane may also explain the variance in the peak retention volume. In the lead fractograms for WS2 and MS4, peak 2 is the NOM fraction and represents high molecular weight (~1 kDa) SR NOM and the lead that was bound to it. This corresponds to the peak in the UV_{254} signal at a retention volume of approximately 14 mL (Figure 4.6c). This is consistent with the expected binding of lead to NOM. This peak was unable to be separated from the void volume peak in the waters without SR NOM (W, M, WS1, and MS3). Previous work by Trueman and colleagues that employed either SEC/ICP-MS or FFF/ICP-MS found that complexation between lead and colloidal NOM is a dominant mechanism for mobilizing oxidized lead (Trueman & Gagnon, 2016a; Trueman et al., 2017; Trueman et al., 2018; Trueman et al., 2019a). There was some evidence of lead-NOM complexation in samples W and M as well (peak 1), although the UV_{254} signals were substantially weaker. The signals were likely lower in these waters than in the synthetic waters with SR NOM (WS2 and MS4) due to less complexation and reduced NOM recovery in these waters (Trueman et al., 2019a).

Peak 3, the larger colloidal peak, represents larger colloids (> 1000 kDa) and possibly lead species that desorbed as the cross-flow was decreased. Peak 3 was lower and more elongated than peak 1 or peak 2 and was the highest in the synthetic waters with NOM. These findings stress the importance of proper NOM removal and treatment in order to mitigate its impact on the release of lead. As is discussed in section 4.3.7, the differences in the NOM characteristics between the real waters and the SR NOM can be attributed to this difference in behavior. In particular, differences in the properties of the humic substances may have played an important role. Consistent with previous findings, the treatment of the NOM in the M water likely decreased complexation and colloidal dispersion in comparison to waters with untreated NOM (Korshin et al., 2005; Lin & Valentine, 2008a; Lin & Valentine, 2009; Trueman et al., 2018; Valentine & Lin, 2009). As well, the NOM in W appeared to complex less with lead compared to the untreated SR NOM. This was likely due to the removal of the strongest complexing fractions in the NOM when the water passed through the aquifer (Juhna et al., 2003; Kaiser et al., 1996).

The recovery for copper was relatively low, as evidenced by the low copper concentrations measured using FFF/ICP-MS for copper (Table D.3) (Trueman et al., 2019a). Nonetheless, useful inferences into the composition of colloidal copper could still be made. As with lead, peak 1 for copper represented soluble and unfocused species, and some NOM that had complexed with copper (Figure 4.6b). Peak 2 represented the NOM fraction for the synthetic waters with SR NOM (WS2 and MS4) and this corresponded to the peak in the UV_{254} signal (Figure 4.6c). Therefore, it was evident that complexation between copper and NOM occurred in these samples. It has been shown that complexation between copper and NOM can greatly increase the solubility of copper in the presence of NOM (Edwards & Sprague, 2001b). Peak 2 was also identified at a slightly lower retention volume in the other waters (W, M, WS1, and MS3), but it was unclear what the composition of this fraction was. It did appear that for M at least some of the copper in peak 2 was complexed with NOM, as there was a peak in the UV_{254} signal around that retention volume. However, the NOM in the W water did not appear to complex with copper, as peak 2 did not correspond to the small peak in the UV_{254} signal for that water. Copper was also present in peak 3, which may represent dispersed copper oxides or other copper-rich colloids. Peak 1 and peak 3 were noticeably higher in the real waters (W and M) than in the synthetic waters with SR NOM (WS2 and MS4), suggesting that these fractions may be responsible for the higher dissolved copper concentrations in the real waters. The real waters may have had more copper in peak 1 and peak 3 due to the presence of trace metals (Table D.13).

4.3.7 Changes to NOM Characteristics Following Stagnation

4.3.7.1 FEEM

NOM fractions measured by FEEM for weeks 5-19 for the real waters (W and M) and weeks 7, 11, and 16 for the synthetic waters with SR NOM (WS2 and MS4) are displayed in Figure 4.7. Only measurements made from weeks 5-19 were included due to changes in the water chemistry in weeks 5 and 20. It is clear that the humic and fulvic acid intensities measured by FEEM were quite different in the real waters (W and M) and the synthetic waters modelling them with SR

NOM (WS2 and MS4), despite having similar DOC concentrations. WS2 had higher average humic (133 au vs 101 au) and fulvic (95 au vs 92 au) acid intensities than W, while MS4 had higher average humic (255 au vs 133 au) and fulvic (180 au vs 116 au) acid intensities than M. Fluorophores are responsible for generating the signal that is measured by FEEM, which are aromatic groups that are able to complex with compounds such as lead. Therefore, it is plausible that the differences in the humic and fulvic acid intensities are indicative of the propensity of the NOM to interact with lead. The lower humic and fulvic acid intensities in the real waters compared to the synthetic waters was likely due to the removal or alteration of the fractions of NOM most likely to complex with lead. In the M water, coagulation and oxidation using ozone or free chlorine would have measurably decreased the humic and fulvic acid intensities. Although the W water was not treated prior to collection, humics would have been removed as the water travelled through the aquifer. This has been noted in previous studies that have determined that humic acids are preferentially removed as water passes through an aquifer (Juhna et al., 2003; Kaiser et al., 1996).

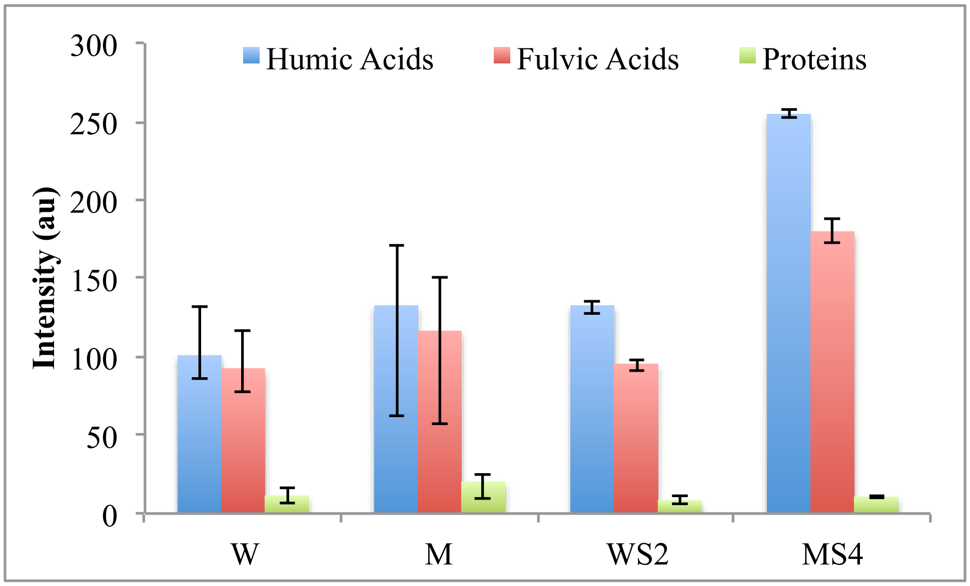


Figure 4.7 FEEM NOM fractions for real and synthetic waters with SR NOM prior to stagnation for humic acids, fulvic acids, and protein like materials. Bars represent average intensities while the error bars represent minimum and maximum intensities. Measurements were made on weeks 5-19 for W and M, and weeks 7, 11, and 16 for WS2 and MS4.

The percent decrease in the humic and fulvic acid intensities measured using FEEM in the real and synthetic waters with NOM following a 48-hour stagnation period in the test pieces are displayed in Figures 4.8a and b respectively, while the percent change in the protein-like materials fraction is shown in Figure D.6a. The values reported are averages of the percent decreases that were calculated from the individual events. The intensity of the humic acids ranged from 103 au (W) to 274 au (MS4) prior to stagnation and from 71 au (Wa) to 248 au (MS4a) following stagnation. The intensity of the humic acids decreased significantly ($p < 0.05$) in all of the waters with NOM following stagnation (Table D.9). The largest percent decrease in the humic acid intensity was in Wa (28.8%) and the smallest percent decrease was in MS4a (9.6%). The intensity of the fulvic acids ranged from 95 au (W) to 194 au (MS4) prior to stagnation and from 67 au (Wa) to 178 au (MS4) following stagnation. The intensity of the fulvic acids decreased significantly ($p < 0.05$) in all of the waters with NOM following stagnation (Table D.9). The largest percent decrease in the fulvic acid intensity was in Wa (25.9%) and the smallest percent decrease was in MS4a (8.1%).

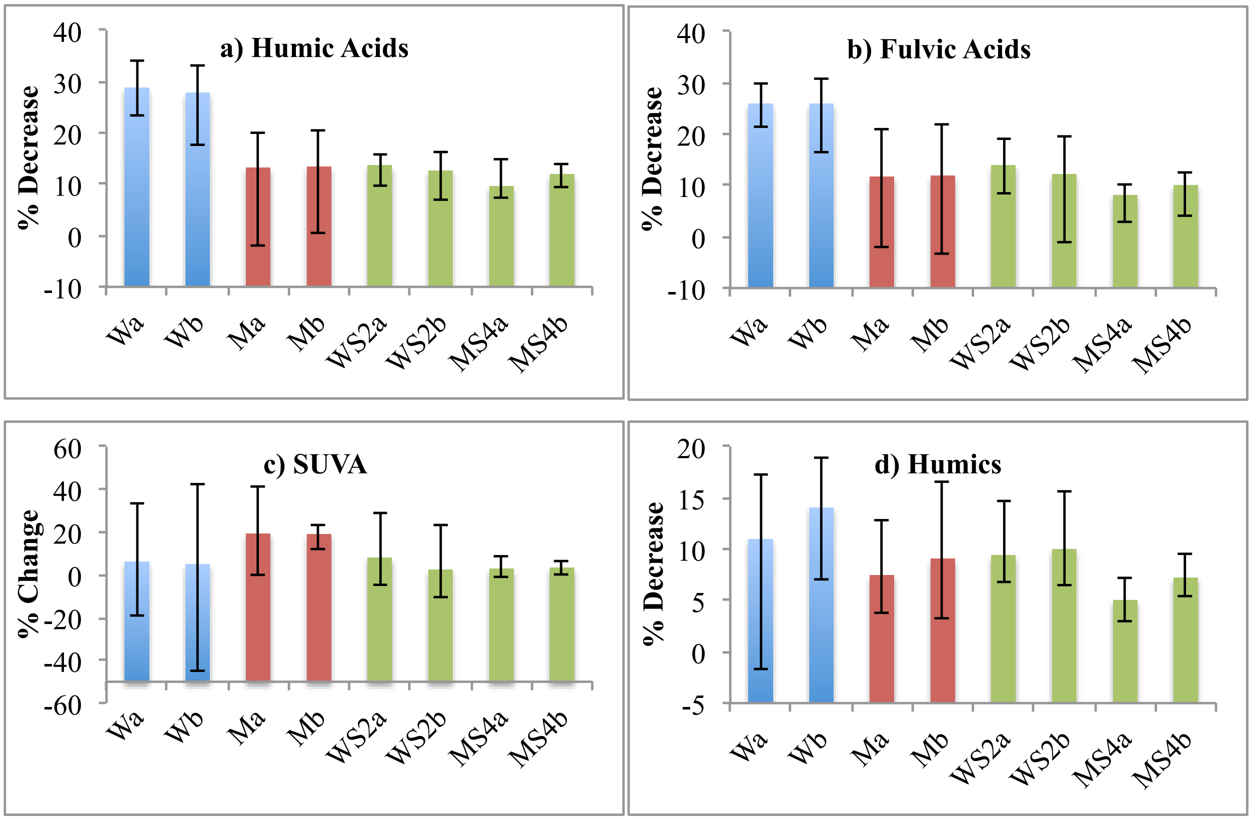


Figure 4.8 Average percent decrease in FEEM NOM fractions for a) humic acids and b) fulvic acids. Average percent change or decrease in LC-OCD NOM fractions for c) SUVA and d) humics. Error bars represent the minimum and maximum percent decrease or change. The percent decrease in FEEM fractions were measured on weeks 3, 7, 11, 16, and 21. The percent decrease or change in the LC-OCD fractions were measured on weeks 7, 11, 16 and 21. The values were determined by calculating the percent decrease or change per event and then averaging them.

Very weak correlations were identified between the initial humic ($R^2 = 0.28$; $p = 0.016$) and fulvic acid ($R^2 = 0.15$; $p = 0.091$) intensities measured using FEEM and the release of dissolved lead (Figure D.7a and b). This suggests that humic acids, and to a lesser extent fulvic acids, may have played a role with regards to dissolved lead release. In section 3.3.4.1 in Chapter 3, a strong correlation was identified between the decrease in humic and fulvic acid intensities during stagnation and dissolved lead release when SR NOM was added to the synthetic waters. Interestingly, the present study did not find a correlation between the decrease in the humic and fulvic acid intensities and dissolved lead release, even when the synthetic waters with SR NOM were looked at exclusively. It is noted that the DOC concentrations were higher in Chapter 3 at 3.5 mg/L and 7 mg/L compared to less than 3.5 mg/L in the present study. This suggests that a change in these parameters measured by FEEM was only indicative of dissolved lead release when SR NOM was added at a higher concentration of DOC (> 3.5 mg/L).

Relatively strong correlations were identified between the initial humic ($R^2 = 0.76$; $p = 0.005$) and fulvic acid ($R^2 = 0.71$; $p = 0.008$) intensities and the concentration of lead in peak 1 (void volume) measured using FFF/ICP-MS (Figures D.9a and b). The initial humic ($R^2 = 0.64$; $p = 0.202$) and fulvic ($R^2 = 0.54$; $p = 0.262$) acid intensities measured using FEEM and the concentration of lead in peak 2 (NOM fraction) measured using FFF/ICP-MS were also moderately correlated to one another (Figures D.11a and b). As well, correlations between the decrease in humic ($R^2 = 0.98$; $p = 0.010$) and fulvic ($R^2 = 0.59$; $p = 0.230$) acid intensities upon stagnation and the concentration of lead in peak 2 (NOM fraction) were identified (Figures D.12a and b). These findings provide further evidence that humic acids, and to a lesser extent fulvic acids, increased the concentration of colloidal lead by forming lead-NOM complexes. It is possible that if the NOM concentrations were higher, a correlation between the decrease in the humic and fulvic acid intensities and the release of dissolved lead would have been identified, as the NOM fraction measured by FFF/ICP-MS would have become a more dominant component of the dissolved lead.

4.3.7.2 LC-OCD

The composition of the NOM in the real waters (W and M) and synthetic waters with SR NOM (WS2 and MS4) was determined by LC-OCD. The percentage breakdown of the operationally defined hydrophilic DOC (CDOC) is shown in Figure 4.9 and the breakdown of the total DOC, including the operationally defined hydrophobic DOC (HOC), is tabulated in Table D.4. The NOM in the real waters (W and M) were similar in composition to one another with the exception of the substantially larger percentage of biopolymers in the M water (6.4% vs 0.2%). The biopolymer fraction consists mainly of polysaccharides, proteins, and aminosugars (Huber et al., 2011), and it is expected that river water would contain more of these organic compounds than groundwater. The composition of the NOM in the WS2 and MS4 waters were very similar as was anticipated, because SR NOM was added in both of these waters. However, there were considerable differences in the composition of the NOM in the real waters (W and M) and in the synthetic waters with SR NOM (WS2 and MS4). The humics comprised a much larger portion of the NOM in the waters with SR NOM (WS2 and MS4) than in the real waters (W and M). Conversely, the building blocks, LMW neutrals, and LMW Acids/Humics fractions composed a larger portion of the NOM in the real waters (W and M). As the SR NOM was sourced from the Suwannee River in Georgia, while the real waters were sourced in Southern Ontario, substantial differences in the characteristics of the NOM were expected. In addition, the humics concentration in the SR NOM may be relatively higher than in the real waters, due to the alteration of the composition of the SR NOM when it was prepared using reverse osmosis followed by freeze-drying (lyophilisation) by the IHSS (International Humic Substances Society, n.d.b). It is also possible that humics were preferentially removed in M during the water treatment process and humics in W were preferentially removed as the groundwater travelled through the aquifer.

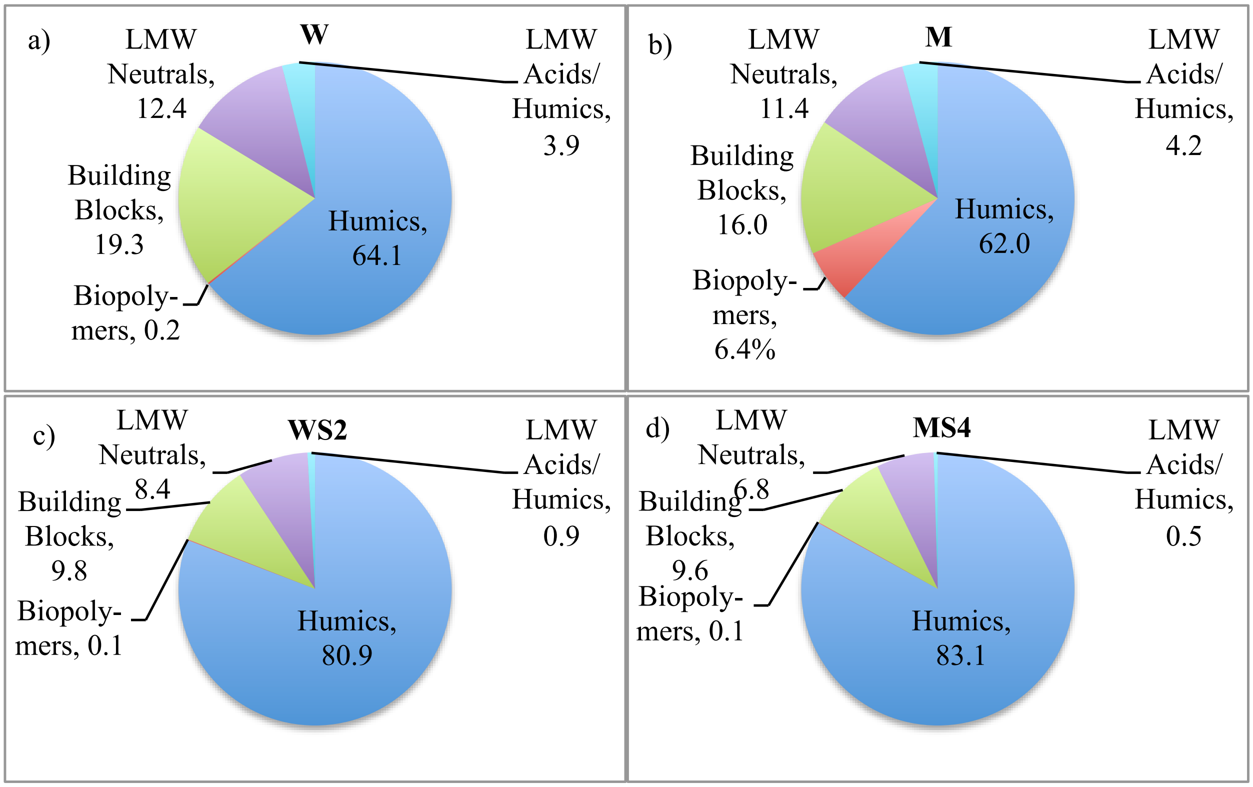


Figure 4.9 Average percentage composition of CDOC in a) W, b) M, c) WS2, and d) MS4 using LC-OCD. The measurements were completed on weeks 1, 2, 4, 5, 7-21 for W and M, and in weeks 7, 11, 16, and 21 for WS2 and MS4.

The percent change in the SUVA measured in the LC-OCD bypass peak and percent decrease in the humics concentration for the real and synthetic waters with NOM determined by LC-OCD analysis during a 48-hour stagnation period in the test pieces, are shown in Figures 4.8c and d respectively. Meanwhile, the percent change or decrease in the DOC, biopolymers (Ma and Mb only), building blocks, LMW neutrals, and LMW acids/humics concentrations determined by LC-OCD are shown in Figures D.6b-f. The DOC concentration ranged from 1,390 µg/L (W) to 3,920 µg/L (MS4) prior to stagnation and from 1,300 µg/L (Wb) to 3,550 µg/L (MS4a) following stagnation. The DOC concentration decreased in all of the waters with NOM, but the decrease was only significant ($p < 0.05$) in four out of eight of the waters (Mb, WS2a, WS2b, MS4b; Table D.9). The SUVA ranged from 2.19 L/mg-C/m (M) to 4.83 L/mg-C/m (MS4) prior to stagnation and from 2.44 L/mg-C/m (Ma) to 5.13 L/mg-C/m (WS2a) following stagnation. The SUVA increased in all of the waters with NOM, but the increase was only significant in Mb ($p = 0.003$; Table D.9). The humics concentration ranged from 791 µg/L (W) to 3,020 µg/L (MS4) prior to stagnation and from 675 µg/L (Wb) to 2,780 µg/L (MS4a) following stagnation.

The humics concentration decreased in all of the waters with NOM and the decrease was significant ($p < 0.05$) in all of the waters except for Wa (Table D.9). This is in accordance with the decrease in the humic and fulvic acid intensities that were identified using FEEM. In most of the waters, the other NOM fractions measured by LC-OCD decreased during stagnation, but only a few of the changes were found to be significant (Table D.9).

A moderate correlation was identified between the initial SUVA and the release of dissolved lead ($R^2 = 0.50$; $p = 0.002$), as well as a very weak correlation between the initial humics concentration ($R^2 = 0.25$; $p = 0.048$) and the release of dissolved lead (Figures D.7c and d). However, the correlation between SUVA and dissolved lead was mainly due to differences in the real and synthetic waters with SR NOM, so more data would be required before a strong relationship between SUVA and dissolved lead could be identified. Such a relationship would not be surprising though, as it has been suggested that aromatic components of NOM can interact more with lead than non-aromatic components (Dryer & Korshin, 2007; Lin & Valentine, 2009; Valentine & Lin, 2009). A very weak correlation was identified between the decrease in the humics concentration and dissolved lead release ($R^2 = 0.25$; $p = 0.004$; Figure D.8d), which is consistent with the results in Chapter 3. This may indicate that some of the humics were lost by adsorbing to corrosion scales or by complexing with lead, and to the author's knowledge this is the second study (after Chapter 3) to show a link between a decrease in humics and dissolved lead release.

Relatively strong correlations between the initial humics concentration and the lead in peak 1 (void volume; $R^2 = 0.70$; $p = 0.010$) and peak 2 (NOM fraction; $R^2 = 0.76$; $p = 0.131$) measured using FFF/ICP-MS were found (Figures D.9d and D.11d). In addition, a strong correlation between the decrease in humics concentration and the lead in peak 2 (NOM fraction; $R^2 = 0.94$; $p = 0.030$) were also identified (Figure D.12d). This is consistent with the correlations between the humic and fulvic acid intensities and the concentration of NOM in these lead fractions that were identified using FEEM. It would be useful to repeat these experiments with a more diverse set of waters to evaluate if FEEM and LC-OCD could be useful tools for evaluating the potential of lead-NOM complexes to form in certain water types.

4.3.8 Scale Analysis

XRD results for the lead pipes of the test pieces are shown in Figure 4.10 and Table 4.4, while the XRD results for the copper pipes are shown in Figure D.13 and Table D.5. The ICP-MS results for the scales are summarized in Tables D.6 (lead) and D.7 (copper). The XRD results suggested that the corrosion scales that formed on all of the lead pipes were similar and contained elemental lead, litharge, hydrocerussite, and cerussite. Furthermore, the ICP-MS results identified that lead, calcium, iron, magnesium, potassium, copper, and sodium were present in the corrosion scales on most of the lead pipes. Trace amounts of aluminum were also identified in the corrosion scales of Mb and WS2b, and manganese in MS4b. The lead corrosion scales on the lead pipes were white in colour except for Wa and Wb, which were red or purple and only on one half of the pipe. This may have been due to iron that precipitated out of the water during stagnation in the test pieces. The presence of iron was apparent in the XRD patterns, with small humps being identified between 10 to 15 degrees that resulted from the normalization of the background intensity of an otherwise elevated XRD pattern.

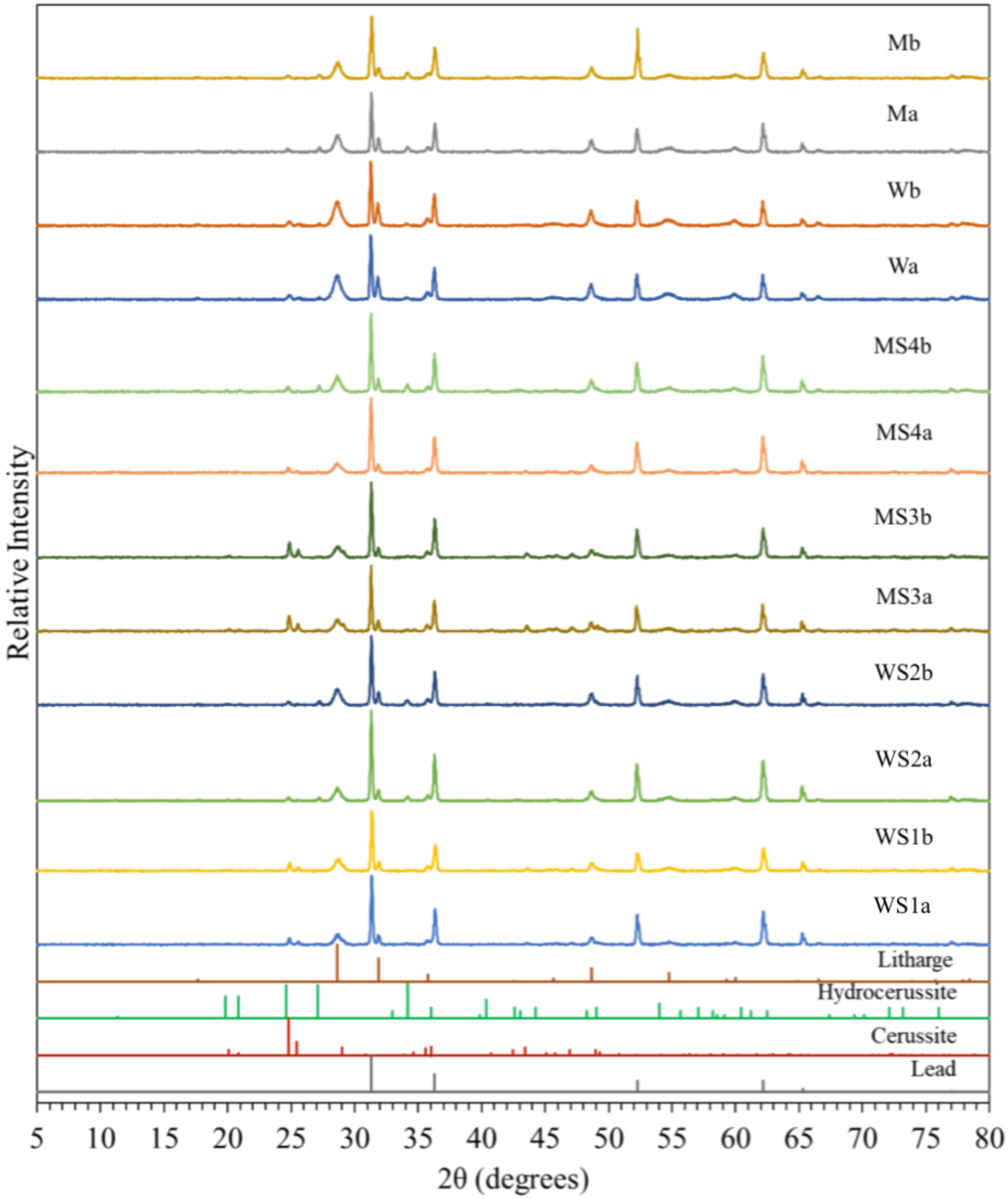


Figure 4.10 XRD patterns obtained from the surface of the lead pipes for a range of 5° to 80° 2θ. The patterns at the bottom are the reference patterns of the solids that had peaks identified in the samples.

Table 4.4 Summary of Results from XRD Conducted on the Powdered Samples from the Lead Pipe Surface

	Lead	Litharge	Hydrocerussite	Cerussite
Wa	+++	++	+	+
Wb	+++	++	+	+
Ma	+++	++	+	+
Mb	+++	++	+	+
WS1a	+++	++	+	+
WS1b	+++	++	+	+
WS2a	+++	++	+	+
WS2b	+++	++	+	+
MS3a	+++	++	+	+
MS3b	+++	++	+	+
MS4a	+++	++	+	+
MS4b	+++	++	+	+

*'+' indicates the abundance of a certain mineral (greater than approximately 1%)
**'+++' indicates the most abundant mineral, followed by the '++' mineral and then the '+' minerals

Clearly, the corrosion scales that formed on the lead pipes were more complex than predicted by the tidyphreeqc modelling software. This is consistent with several other studies that have determined that corrosion scales that form are more complex than predicted by solubility theory (Cantor, 2017; Schock et al., 2014; Tully et al., 2019; Chapter 3). This may also explain why the measured dissolved lead release was lower than predicted by tidyphreeqc in the absence of NOM. The scale analysis results are somewhat different than the Chapter 3 results in that the SR NOM was not found to alter the structure of the corrosion scales on the lead pipes. In Chapter 3, SR NOM gave the lead corrosion scales a yellowish brown colour while in the current study the lead corrosion scales in the test pieces with SR NOM were white in colour. This may be due to the waters with SR NOM in this study having lower DOC concentrations than in Chapter 3.

In contrast to the lead pipes, the copper pipes had varying scale compositions depending on the water type. The corrosion scales on the copper pipes of Wa and Wb were patchy and green in colour, and consisted of cuprite, calcite magnesian, and malachite. The corrosion scales on the copper pipes of Ma, Mb, and MS4b were patchy and black, while MS4a had minimal scaling. The corrosion scales on these pipes consisted mainly of elemental copper, elemental lead, and litharge. The corrosion scales on the copper pipes of WS1a, MS3a and MS3b were patchy and black, while WS1b was patchy and greenish white. The corrosion scales on these pipes were mostly a mixture of elemental copper, cuprite, and calcite magnesian. The corrosion scales on the copper pipes of WS2a and WS2b were patchy and black with tiny white dots and contained a mixture of elemental copper, cuprite, calcite, and elemental lead.

NOM at a higher concentration in the M and MS4 waters did appear to inhibit the formation of the copper corrosion scales, as the most abundant species identified using XRD were elemental copper, elemental lead, and litharge, and not copper carbonates or oxides. This finding is consistent with previous research that has suggested that NOM slows the natural aging process of copper and inhibits the formation of low solubility malachite corrosion scales (Arnold et al., 2012b; Edwards et al., 1994; Edwards & Sprague, 2001b; Korshin et al., 1996). Another interesting finding was that malachite only formed on the copper pipes exposed to the W water, and this was likely why the corrosion scales on these pipes were green. However, malachite does not appear to have been the solubility-controlling solid on these pipes, as the solubility of malachite is generally less than 200 µg/L (Edwards & Sprague, 2001b) and the average dissolved copper concentrations in Wa and Wb were 882 µg/L and 841 µg/L respectively. In fact, the W water released more dissolved copper than any of the other water types despite forming low solubility malachite corrosion scales.

4.3.9 Relevance of Results for Drinking Water with Free Chlorine or Chloramine

As discussed in section 3.3.6 in Chapter 3, as no disinfectant was added to the waters in the present study, the results are more similar to chloraminated drinking water than chlorinated drinking water. However, in many cases lead (II) scales can form even in drinking water with free chlorine, and therefore the results are still relevant for utilities that use chlorinated drinking water (Tully et al., 2019). As well, if a disinfectant would have been added to the synthetic waters with SR NOM, it is likely that the dissolved lead release would have been lower as the disinfectant would have reacted with the SR NOM and decreased its ability to complex with lead (Lin & Valentine, 2009; Valentine & Lin, 2009). Dissolved lead may also have been lower in the real waters if a disinfectant had been added. However, it is likely that this reduction would be less noticeable in the real waters than in the synthetic waters with SR NOM, as the humic substances in the real NOM was less able to complex with lead. This may have been due to the removal of the strongest complexing fractions in the W water as it passed through the aquifer (Juhna et al., 2003; Kaiser et al., 1996) and by the oxidation of the M water with ozone or free chlorine at the treatment plant.

4.4 Conclusions

Several conclusions were made from the results of a 21-week "dump and fill" experiment examining the impact of NOM in real and synthetic drinking waters on the galvanic corrosion of lead.

- Dissolved lead release was the highest in the synthetic waters with SR NOM, followed by the real drinking waters and then the synthetic waters without NOM. This confirmed that the addition of SR NOM greatly increased the release of dissolved lead and this effect is evident even at a DOC concentration of only 1.76 mg/L in WS2 compared to 3.5 mg/L in Chapter 3. These results suggest that synthetic drinking waters with NOM added from a concentrated source are likely to overestimate the release of lead, while synthetic waters without NOM will likely underestimate the release of lead, when compared to real waters. This can be attributed to the different characteristics of the NOM in the real waters and in the synthetic waters with SR NOM.
- FFF/ICP-MS analysis showed that both complexation between lead and NOM and colloidal dispersion caused by NOM increased the release of dissolved lead, although complexation was likely a more important mechanism for the synthetic waters with SR NOM. Therefore, improvements in the treatment of NOM will likely lower lead concentrations in consumers' taps for utilities that currently have suboptimal treatment.
- FEEM and LC-OCD analyses indicated respectively that there were decreases in humic and fulvic acid concentrations and decreases in humic substances concentrations after stagnation in the test pieces. In particular, strong correlations between a decrease in these parameters and peak 2 (NOM fraction) measured using FFF/ICP-MS were identified. This suggests that the characteristics of the NOM were altered upon interacting with the oxidized lead and it appears that at least part of this decrease can be attributed to complexation.
- The galvanic current between the lead and copper pipes of WS2 was significantly higher than in any of the other water types except W, which it was potentially significantly

higher than, indicating that the combination of a high DIC concentration and SR NOM increased the galvanic current and the subsequent oxidation of lead. This result suggests that in some cases NOM could be more detrimental in hard waters than in soft waters, in particular if a galvanic connection is present.

- The dissolved lead release was similar in the synthetic waters with 3.5 mg DOC/L (MS4) and 1.8 mg DOC/L (WS2) of SR NOM, suggesting that even for NOM with the same characteristics, the DOC concentration cannot directly be used to predict the release of dissolved lead. Other water quality factors, such as pH and DIC, need to be considered as well.
- Solubility modelling using tidyphreeqc grossly underestimated the release of dissolved lead in the synthetic waters with SR NOM (WS2 and MS4) and in the real waters (W and M). This result stresses the need to develop solubility models for lead that can incorporate the impacts of NOM on lead solubility.
- Copper release was the highest in the real waters (W and M), followed be the synthetic waters with SR NOM (WS2 and MS4), and lastly by the synthetic waters without NOM (WS1 and MS3). Furthermore, FFF/ICP-MS results suggested that the real waters (W and M) had substantially more copper in peak 1 (void volume) and peak 3 (larger colloidal fraction) than the synthetic waters (WS1, WS2, MS3, and MS4). This result suggested that the synthetic waters did not accurately model the real waters with regards to copper release, however NOM did not appear to be a major reason for this discrepancy.
- The corrosion scales on all of the lead pipes consisted of a mixture of elemental lead, litharge, hydrocerussite, and cerussite. This indicates that NOM did not significantly alter the composition of the lead corrosion scales in this study. However, NOM in M and SR NOM in WS2 and MS4 did appear to inhibit the formation of corrosion scales on the copper pipes.

Chapter 5

Summary, Conclusions, and Recommendations

5.1 Project Approach and Challenges

The main goals of this project were to assess the aggressiveness of hard waters towards lead and to determine if NOM is a water quality factor in real Southern Ontario drinking water that can influence the release of lead. The specific case of galvanic corrosion was studied as it was anticipated to provide a worst-case scenario and to accelerate the corrosion process. The majority of previous lead corrosion research has focused on soft waters with a low concentration of DIC and hardness, as they are thought to be the most aggressive towards lead. However, a few research studies have proven that lead release can still be an issue in hard waters, depending on water quality (Colling et al., 1987; Colling et al., 1992). In particular, a pilot study by Colling et al. (1992) suggested that NOM could greatly increase the aggressiveness of groundwaters towards lead. The outcomes of that study required further consideration, as the water quality was not well controlled making it difficult to definitively prove the role of NOM on corrosion in hard water. The current study was conducted in two phases and provided an investigation into the impact of water quality on galvanic corrosion and lead release with a focus on hard water and NOM.

Phase I involved an investigation into the impact of pH, DIC, hardness, and NOM on galvanic corrosion and lead release, as described in Chapter 3. This study employed test pieces consisting of new lead and copper pipes with an external galvanic connection and followed a “dump and fill” protocol for a total duration of 20 weeks. In order to control the different water quality factors of interest, synthetic waters were utilized with NOM added as SR NOM. The galvanic current, and the total, dissolved, and particulate lead and copper concentrations were routinely measured, in order to determine the effect of the water quality factors on those parameters. In addition, the waters were analyzed before and after stagnation using FEEM and LC-OCD, to identify if certain NOM fractions were correlated with the release of dissolved lead. Scale analysis was also conducted to see if water quality had an impact on the composition and structure of the lead corrosion scales that formed. The findings of Phase I suggested that certain hard waters could be aggressive to lead and that SR NOM can increase the release of dissolved lead in a variety of water types.

Based on the findings in Phase I (Chapter 3), Phase II examined the impact of different types of NOM in real and synthetic drinking waters on galvanic corrosion and lead release, and is discussed in detail in Chapter 4. The real waters included raw water from a municipal well in Southern Ontario (W), and unchlorinated but otherwise treated water from the Grand River in Southern Ontario (M). A total of four synthetic waters were also included in this study, with each of the two real waters being modeled by two synthetic waters, one with SR NOM (WS2 and MS4) and one without NOM (WS1 and MS3). Phase II utilized test pieces of the same design as in Phase I and followed the same "dump and fill" protocol for a period of 21 weeks. Each condition was tested in duplicate, for a total of 12 test pieces. The same parameters that were measured in Phase I were also measured in Phase II. In addition, in Phase II samples were sent to Dalhousie University to be analyzed using FFF/ICP-MS and FFF/UV_{254} to provide further insight into the size distribution and properties of lead, copper and NOM containing colloidal particles.

In order to reduce the number of water quality factors to be considered and to simplify the preparation of the synthetic waters, no disinfectant was added to any of the waters in Chapters 3 or 4. Thus, the redox potential in the waters were likely lower than the redox potential in chloraminated or chlorinated drinking water. As lead (II) was expected to form in all of the waters in Chapters 3 and 4, it is likely that the results are more applicable to drinking water with chloramine than free chlorine. However, lead (II) corrosion scales can form even in drinking water with free chlorine, and hence the results in the present study are still relevant for chlorinated drinking water. As well, adding a disinfectant to the waters in Chapters 3 and 4 would have likely decreased the ability of the SR NOM, and to a lesser extent the NOM in the real waters, to complex with lead. Therefore, it is likely that NOM will not have as substantial of an effect on lead release in chlorinated or chloraminated drinking water as reported in this thesis, but nonetheless could be of concern for utilities.

Some notable challenges that arose in the current study are listed below:

1. During Phase I it was identified that several test pieces were susceptible to releasing extremely high amounts of particulate lead on a sporadic basis, and that the handling and emptying of the water from the test pieces had an influence on this. Starting in week 13 of Phase I and continuing throughout Phase II, the same individual completed all of the "dump and fill" events (with the exception of a couple weeks due to vacation and a conference) to ensure more consistent methodology.
2. In Phase II, some of the synthetic waters were found to have a high initial turbidity due to an interaction between the calcium chloride and the sodium bicarbonate. The problem was addressed by altering the mixing procedure to lower the concentrations during preparation. Initially, the stock solutions were added to 1 L of MilliQ water, which was further diluted to make 4 L of synthetic water. This procedure was adjusted by adding the stock solutions to 2 L of MilliQ water instead of 1 L, and then further diluting the solution to make 4 L of synthetic water. In addition, the mixing time prior to the turbidity measurements was increased to get more accurate measurements. However, water quality testing indicated the water chemistry was not impacted by the high initial turbidity and it is not believed that this had an impact on lead release.
3. Operational issues at the municipal well and water treatment facility prevented the collection of the real waters in Phase II on a couple instances. On the first occurrence, assistance from operators was required to collect the water sample at the municipal well and this resulted in long work hours in the laboratory to remain on schedule. Afterwards, a two-week supply of the real waters was collected during every sampling event to prevent this situation from occurring again.
4. The Natural Sciences and Engineering Research Council of Canada (NSERC) Chair's TOC analyzer was not operational in both Phase I and II due to a variety of mechanical issues. To overcome this difficulty, the DOC concentration was measured using LC-OCD routinely in the synthetic waters (about once a month) and weekly in the real waters. All of the DOC concentrations included in the main body of the thesis (Chapters 3 and 4) were measured using LC-OCD. Since the LC-OCD uses a vastly different method for measuring DOC than a TOC analyzer, one set of samples in each Phase were analyzed using a TOC analyzer as a control measurement for both DOC and TOC. Another research group in the Civil and Environmental Engineering Department at the University

of Waterloo measured DOC and TOC on a TOC analyzer in Phase I. ALS Environmental measured DOC and TOC on a TOC analyzer in Phase II.

5. It was initially proposed that the IC in the UW Civil and Environmental Engineering laboratory could be used to measure the calcium, magnesium, and sodium concentrations in the waters. However, this machine was found to be incapable of accurately measuring these concentrations, even after several attempts. Thus, samples were sent out for CRC ICP-MS analysis once in Phase I and twice in Phase II to ALS Environmental. This provided the additional benefit of measuring a wide variety of metals in the waters. In addition, hardness titrations (HACH® 5B Hardness Test Kit) were performed weekly in the real waters and monthly in the synthetic waters in Phase II, in order to verify that the hardness was consistent.

5.2 Summary of Findings and Conclusions

The results of Phase I (Chapter 3) indicated that hard waters could potentially be aggressive to lead and that SR NOM can greatly increase the release of dissolved lead. Specific conclusions relating to Phase I are as follows;

- Increasing the pH had a potentially significant effect ($p = 0.089$) on the release of total lead, with an increase in pH from 7 to 8.5 decreasing total lead concentrations by an average of 4,390 µg/L. Increasing the DIC concentration from 10 mg/L to 80 mg/L did not impact lead release, but it did potentially significantly ($p = 0.051$) increase the galvanic current between the lead and copper pipes by an average of 28.4 µA. The hardness did not significantly affect the galvanic current or lead release. NOM had a profound impact on the release of dissolved lead ($p = 0.060$); with the addition of 7 mg DOC/L of SR NOM increasing dissolved lead release by an average of 2,320 µg/L.
- Analyzing the waters before and after stagnation using FEEM identified correlations between a decrease in the humic acid intensity ($R^2 = 0.88$; $p < 0.001$) and fulvic acid intensity ($R^2 = 0.78$; $p < 0.001$) and dissolved lead release, providing indirect evidence of complexation between SR NOM and lead.
- SR NOM appeared to alter the structure of the corrosion scales that formed, for example scale analysis using XRD identified that SR NOM promoted the formation of hydrocerussite. Furthermore, visual observations suggested that SR NOM was

incorporated into the corrosion scales and imparted a yellowish-brown colour in contrast to the white corrosion scales that formed in the test pieces not exposed to NOM.

- The interaction between hardness and DIC did not have a significant effect on lead release in this experiment. In addition, the XRD and ICP-MS results from the scale analysis did not indicate that protective calcium carbonate films formed on the lead pipes. Therefore, it does not appear that the precipitation of lead carbonate decreased the release of lead.

The results of Phase II (Chapter 4) suggested that SR NOM was more aggressive towards lead than real NOM in the river water (M) and groundwater (W), and that the synthetic waters did not accurately model the real waters. Specific conclusions for Phase II are listed below;

- The synthetic waters did not accurately model the real waters and at least some of the differences can be attributed to the presence and characteristics of the NOM. The synthetic waters with SR NOM (WS2 and MS4) released more dissolved lead than the real waters (W and M). Meanwhile, the synthetic waters without SR NOM (WS1 and MS3) released significantly less dissolved lead than the real waters (W and M). The differences in the behaviour of the real NOM and the SR NOM can be attributed to differences in the composition of the NOM, in particular humic acids.
- Even at the relatively low to moderate concentrations of DOC in the real waters (W = 1.35 mg/L and M = 3.40 mg/L), NOM was capable of increasing the release of dissolved lead. This suggests that NOM can be a water quality factor that influences the release of lead in real Southern Ontario drinking water.
- Using FFF/ICP-MS and FFF/UV_{254}, it was apparent that SR NOM formed dissolved complexes with lead. Complexation between lead and NOM was also identified in the real waters, but the signals were substantially weaker. Colloidal dispersion was another mechanism that increased the concentration of dissolved lead in the synthetic waters with SR NOM and the real waters.
- Correlations were identified between a decrease in the humic ($R^2 = 0.98$; $p = 0.010$) and fulvic ($R^2 = 0.59$; $p = 0.230$) acid intensities measured using FEEM and the concentration of lead in peak 2 (NOM fraction) measured using FFF/ICP-MS after stagnation. There was also a correlation between the decrease in the humics concentration measured using

LC-OCD and the concentration of lead in peak 2 ($R^2 = 0.94$; $p = 0.030$). This indicates that the characteristics of the NOM may have been altered due to complexation with lead.

Significant conclusions from Phase I and II of this study are listed below:

- Several real and synthetic hard waters were included in Phases I and II, and lead release was relatively high in all of these waters with an average total lead concentration greater than 450 µg/L. Furthermore, in Phase I it was determined that the hardness did not have a significant effect on lead release or galvanic current and scale analysis did not indicate that there was any significant formation of protective hardness films. Therefore, it appears that at least in certain situations hard waters can be aggressive to lead.
- NOM, in particular SR NOM, substantially increased the release of dissolved lead. Important mechanisms included complexation between dissolved lead and NOM, and colloidal dispersion from NOM interacting with lead. However, the DOC concentration was not a good indicator of the release of dissolved lead. In some cases, synthetic waters with SR NOM released more dissolved lead than other synthetic waters with higher concentrations of DOC. This was likely due to an interaction between NOM and other water quality factors, such as pH and DIC. Therefore, the NOM characteristics and the background water quality need to be considered when anticipating the impacts of NOM on lead release.
- Upon stagnation in the test pieces, the humic and fulvic acid intensities measured by FEEM decreased consistently. The humics concentration measured by LC-OCD also decreased following stagnation. This suggested that the characteristics and concentration of the NOM was altered during stagnation. There was some evidence that this may have been related to complexation with lead, but it is also possible that some of the NOM was incorporated into the corrosion scales and was lost from the system.
- SR NOM at high concentrations in Phase I (3.5-7 mg DOC/L) appeared to promote the formation of hydrocerussite and gave the corrosion scales a yellowish-brown colour instead of a white colour that is more typical for lead carbonates. However, SR NOM and real NOM at lower concentrations (1.35-3.49 mg DOC/L) in Phase II did not appear to alter the composition of the lead corrosion scales. This suggests that under the

experimental conditions that were studied, NOM at low concentrations may not noticeably alter the structure of lead corrosion scales.

- Tidyphreeqc modelling software did not accurately predict the release of dissolved lead from the test pieces due to limitations in the model. For instance, the model assumed the only lead corrosion scales that could form were either cerussite or hydrocerussite, while scale analysis proved that the lead corrosion scales were far more complex. Another major reason for the discrepancy was that the model did not incorporate interactions between lead and NOM, which included the formation of lead-NOM complexes and colloidal dispersion.

5.3 Implications for the Water Treatment Industry

Based on the findings from this study, several implications for the water treatment industry were identified as listed below:

1. In at least some scenarios hard water can be aggressive to lead and having hard water does not necessarily mean that lead in drinking water will not be an issue for a utility. Therefore, it is possible that some utilities with hard water will need to implement corrosion control programs in the future in order to meet increasingly stringent regulations.
2. Calcium carbonate did not offer protection against galvanic corrosion and lead release in this study. Although it is plausible that a longer-term study could find some evidence of calcium carbonate precipitation, at the current time oversaturating drinking water with calcium carbonate cannot be recommended as a corrosion control strategy. Instead, it is advised that the pH and DIC concentration be adjusted to minimize the solubility of lead (II) carbonates (cerussite and hydrocerussite).
3. The synthetic waters used in Phase II of this study did not accurately model the real waters. Therefore, before implementing a corrosion control program it is recommended that a utility perform pilot studies with actual treated water used in the distribution system, to assess the impact of changes to water quality on lead release.
4. NOM in raw water from a well and treated but unchlorinated water from the Grand River in Southern Ontario was able to complex with lead and cause colloidal dispersion. Although chlorination would likely mitigate the negative impacts to an extent, NOM in

real waters do appear to increase the release of dissolved lead. It is recommended that utilities optimize NOM removal and treatment in order to minimize lead in consumers' taps. Improvements to the removal of NOM will also provide benefits with other aspects of treatment, such as minimizing the formation of disinfection by-products.

5. The DOC concentration alone cannot be used to predict the propensity of NOM to complex with lead. Instead, the humic and fulvic acid intensities measured by FEEM appear to be better predictors of this propensity. Therefore, it is recommended that utilities characterize waters with FEEM following changes to treatment to predict if the NOM will be more or less likely to complex with lead.
6. Analyzing samples using FFF/ICP-MS and FFF/UV_{254} can provide insight into the characteristics of dissolved and colloidal lead and NOM containing particles that are less than 0.45 μm in size. For instance, in this study FFF/ICP-MS and FFF/UV_{254} analysis indicated that much of the dissolved lead in the synthetic waters with SR NOM could be attributed to complexation between lead and the SR NOM. Understanding the drivers for elevated lead concentrations in consumers' taps may help to develop a more effective corrosion control program.

5.4 Future Research

1. Investigate if calcium carbonate films can form and mitigate lead release in a longer-term (> 2 years) pilot scale study.
2. Compare the aggressiveness of a wider variety of hard waters towards lead, in particular evaluate the effect of the hardness to alkalinity ratio and trace metals such as iron and manganese.
3. Investigate the impact of changing water quality on the release of lead to simulate conditions in distribution systems where multiple source waters are utilized.
4. Conduct a field study measuring lead in consumers' taps in a utility with hard drinking water, to verify that lead release can be an issue in hard water as was observed in this study.
5. Evaluate the impact of NOM on lead corrosion in a wider range of real waters and look into whether or not FEEM and LC-OCD can be used to predict the propensity of the NOM for complexing with lead or causing colloidal dispersion.

6. Evaluate if intermittent spikes in the DOC concentration can cause notable increases in the release of lead.
7. Determine the effectiveness of corrosion inhibitors in hard water, in particular orthophosphate.
8. Develop a solubility model for lead that can incorporate NOM with a variety of input parameters measured by FEEM and LC-OCD.
9. Develop a software program that can predict lead “hotspots” in a large municipality based on the water quality and age of the homes.

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Appendix A

Supplemental Information for Chapter 2

Table A.1 Summary of Select Studies That Have Investigated the Impact of DIC or Alkalinity on Lead Release

Reference	Type	Material	Stagnation Period	Results
Arnold, 2011	Dump and fill	Lead pipe connected to PVC Lead pipe connected to copper Lead solder connected to copper Brass connected to copper	2 and 3 days	A high alkalinity of 250 mg $CaCO_3$/L increased lead release from lead tin solder and decreased lead release from lead pipe connected to copper compared to a low alkalinity of 12 mg $CaCO_3$/L. The alkalinity had no impact on lead release from brass connected to copper but a higher alkalinity increased the variability of lead release from lead connected to PVC.
Boyd et al., 2012	Recirculating pipe loop	Lead pipe Lead pipe connected to copper Lead pipe connected to brass	Constant flow rate of 0.5 gpm	Increasing alkalinity reduced the release of lead.
Churchill et al., 2000	Flow through pipe loop	50/50 lead tin solder Cast brass mixing faucet	8 and 16 hours	Increasing the alkalinity from 2.5-3.7 to 20-30 mg $CaCO_3$/L did not affect lead release from the 50/50 lead tin solder but reduced lead release from the cast brass mixing faucets.
Dodrill & Edwards, 1995	Survey of 365 utilities	Various	Various	90th percentile lead concentrations were much higher in utilities using water with an alkalinity under 30 mg $CaCO_3$/L than over 30 mg $CaCO_3$/L. Low alkalinity waters were more corrosive to lead at a low pH (<8.4) than high alkalinity waters. The corrosiveness of low and high alkalinity waters at a pH higher than 8.4 were similar.
Edwards et al., 2001a	Dump and fill	Lead pipe	2 and 3 days	Increasing the alkalinity from 15 to 40 mg $CaCO_3$/L reduced lead release. Lead release did not change significantly when the alkalinity increased from 40 to 300 mg $CaCO_3$/L.
Edwards & McNeill, 2002	Dump and fill	Lead pipe	2 and 3 days	Increasing the alkalinity from 15 to 45 mg $CaCO_3$/L substantially reduced lead release. Increasing the alkalinity from 45 to 300 mg $CaCO_3$/L only slightly decreased lead release.

Table A.1 Summary of Select Studies That Have Investigated the Impact of DIC or Alkalinity on Lead Release

Reference	Type	Material	Stagnation Period	Results
Giammar et al., 2010	Continuous flow stirred tank reactor	Hydrocerussite and plattnerite solids	Hydraulic residence time of 60 min for hydrocerussite and 30 min for plattnerite	Increasing the DIC concentration from 0 to 50 mg C/L decreased the dissolution rate of hydrocerussite and increased the dissolution rate of plattnerite.
Liu et al., 2010	Dump and fill	50/50 lead tin solder in copper coupons	7 days	Increasing the alkalinity of desalinated water from 30 to 120 mg $CaCO_3$/L slightly increased lead release.
Nguyen et al., 2010	Dump and fill	50/50 lead tin solder	2 and 3 days	Test pieces that had the alkalinity increased from 25 mg $CaCO_3$/L to 100 mg $CaCO_3$/L had a larger reduction in lead release over time than test pieces that remained at an alkalinity of 25 mg $CaCO_3$/L.
Nguyen et al., 2011a	Dump and fill	50/50 lead tin solder	3 and 4 days	Increasing the alkalinity up to 25 mg $CaCO_3$/L decreased lead release in lab prepared and utility "A" water. Increasing the alkalinity from 8 to 20 mg $CaCO_3$/L increased lead release in utility "B" water. Increasing the alkalinity from 80 to 110 mg $CaCO_3$/L increased lead release in utility "C" water.
Noel et al., 2014	Continuous flow stirred tank reactor	Hydrocerussite solid	Hydraulic residence time of 30 and 60 min	Increasing the DIC concentration from 0 to 10 mg C/L decreased the dissolution rate. Increasing the DIC concentration from 10 to 50 mg C/L had no impact on the dissolution rate.
Schock, 1980	Flow through pipe loop	Lead pipe	15-30 min	Water with an alkalinity of 30-200 mg $CaCO_3$/L released less lead than water with little or no alkalinity.
Tam & Elefsiniotis, 2009	Dump and fill	Brass fittings	3 days	At a pH of 7, water with high alkalinity (100-150 mg $CaCO_3$/L) increased lead release compared to water with an alkalinity of 20 mg $CaCO_3$/L. At a pH > 8, alkalinity did not impact the release of lead.

Table A.1 Summary of Select Studies That Have Investigated the Impact of DIC or Alkalinity on Lead Release

Reference	Type	Material	Stagnation Period	Results
Tang et al., 2006	Pilot distribution system and flow through lead corrosion loop	Lead coupon	6 hours	No relationship was found between the alkalinity and lead release in an uncontrolled experiment. In a controlled experiment, lead release decreased as alkalinity increased from 80 to 240 mg $CaCO_3$/L.
Triantafyllidou & Edwards, 2010	Dump and fill	Lead pipe connected to copper	2 and 3 days	Increasing the alkalinity from 15 to 100 mg $CaCO_3$/L did not impact lead release.
Valentine & Lin, 2009	Bench scale dissolution	Plattnerite solid	1 to 7 days	Rate of Pb(II) formation and monochloramine decay increased with increasing TIC concentration.
Xie et al., 2010	Continuous flow stirred tank reactor	Plattnerite solid	Hydraulic residence time of 30 min	At pH values of 7.5 to 10, the dissolution of plattnerite increased with increasing DIC concentration.
Xie & Giammar, 2011	Dump and fill	Lead pipes	0-24 hours	Water with a DIC concentration of 10 mg C/L and a pH of 10 had a lower scale dissolution rate than water with a DIC concentration of 50 mg C/L and a pH of 8.5.
Zhou et al., 2015	Dump and fill	Lead pipe connected to copper	2 and 3 days	Increasing the alkalinity from 15 to 250 mg $CaCO_3$/L inreased the galvanic current but did not increase lead release.

Table A.2 Summary of Select Studies That Have Investigated the Impact of NOM on Lead Release

Reference	Type	Material	Stagnation Period	Results
Arnold, 2011	Dump and fill	Lead pipe connected to PVC Lead pipe connected to copper Lead solder connected to copper Brass connected to copper	2 and 3 days	NOM was added from a stock solution consisting mainly of fulvic acids. NOM tended to increase the release of lead and was more pronounced when the TOC concentration was 4 mg/L compared to 1 mg/L. In some cases, 1 mg/L of TOC decreased lead release. Waters with a high concentration of NOM required more orthophosphate for effective corrosion control.
Colling et al., 1992	Flow through	Lead pipe	Constant flow rate of 30 mL/h	Increasing the TOC concentration in the less aggressive hard water from 0.5 mg/L to 1.6 mg/L by adding a peat slurry significantly increased lead release. Meanwhile, decreasing the TOC concentration from 1.2 to 0.2 mg/L by passing more aggressive hard water through a GAC column significantly decreased lead release.
Dryer & Korshin, 2007	Bench scale dissolution	Lead dioxide solid	1 to 53 days	NOM isolated from the Potomac River increased lead release, and most of the increase was when the DOC concentration was increased from 1 to 5 mg/L. The lead released in the presence of NOM was mainly dissolved. The UV_{254} absorbance decreased over the duration of the experiment, suggesting that there was a destruction in the aromatic groups of the NOM.
Gao et al., 2018	Bench scale	Lead coupon connected to iron (III) oxide disk	8 hours	Cytochrome c was added to represent electrochemically active small sized proteins. Cytochrome c interacted with DO and cells on the cathode side, suggesting it can be oxidized by DO and facilitate oxidation by DO. Cytochrome c also altered the molecular weight size distribution of lead. Biofilms could potentially trap and accumulate trace amounts of redox-active functional groups in NOM.

Table A.2 Summary of Select Studies That Have Investigated the Impact of NOM on Lead Release

Reference	Type	Material	Stagnation Period	Results
Korshin et al., 1999	Dump and fill Recirculating loop	Leaded brass coupon Lead tin solder coupon Lead coupon	Dump and fill: 7 days Recirculating loop: 8 hours and 1.5 hours, water was replaced every 7 days	Both Aldrich humic acid and NOM isolated from the Judy Reservoir in Mt. Vernon Washington were found to increase lead release from all three sources of lead in preliminary dump and fill and long term recirculating loop experiments. During the first eight weeks, there was a near linear relationship between NOM and lead release from the brass. In all the materials, there was a large increase in lead release when the DOC concentration was increased from 0 to 2 or 3 mg/L, but minimal additional lead release was observed if the DOC concentration was raised higher than this. NOM completely blocked the formation of cerussite and hydrocerussite crystals and formed an amorphous coating on the surface.
Korshin et al., 2000	Dump and fill Recirculating loop	C36000 brass rod C36000 brass tube	Dump and fill: 7 days Recirculating loop:1 week	NOM was isolated from the Judy Reservoir in Mt. Vernon Washington. Lead release increased greatly as the DOC concentration was increased from 0 to 2 mg/L, but not as substantially when the DOC concentration was increased above 2 mg/L. Organic free water formed hydrocerussite crystals while water with NOM formed an amorphous layer.
Korshin et al., 2005	Bench scale	Lead coupon Lead tin solder coupon	6 to 19 months	NOM was isolated from the Judy Reservoir in Mt. Vernon Washington. Corrosion scales that formed in organic free water were a mixture of cerussite and hydrocerussite, prismatic and platy in structure, and white in colour. Meanwhile, the scales that formed in water with NOM were hydrocerussite, smooth in structure and dull grey in colour. An increase in NOM altered the zeta potential up to a DOC concentration of about 3.5 mg/L. NOM increased the number of particles that were less than 5 μm in size, but decreased the number of particles that were greater than 5 μm in size. Unaltered NOM had more of an impact on the corrosion scales than NOM treated with chlorine or ozone.

Table A.2 Summary of Select Studies That Have Investigated the Impact of NOM on Lead Release

Reference	Type	Material	Stagnation Period	Results
Korshin & Liu, 2019	Bench scale dissolution	Lead dioxide solid	1 to 15 days	NOM was added as Suwannee River standard fulvic acid. The addition of NOM resulted in a 20 mV negative shift in the zeta potential. There was a large increase in lead release when the DOC concentration was increased from 0 to 1 mg/L, and a proportionately smaller increase in lead release when the DOC concentration was increased from 1 to 5 mg/L. Less than 10% of lead release was from particles less than 0.1 µm in size, so most of the lead release was from colloidal particles between 0.1 and 0.45 µm in size. Chloramine did not have a large impact on lead release when NOM was present. The NOM made the surface of the PbO_2 less crystalline. Phosphate was found to mitigate the impacts of the NOM on colloidal
Lin & Valentine, 2008a	Bench scale dissolution	Lead dioxide solid	1 to 28 days	Iowa River hydrophobic acid was used as a source of NOM. The reduction of lead (II) was enhanced by a higher concentration of NOM and a lower pH. After 15 days, in water without NOM the dissolution rates decreased but in water with NOM they did not decrease even after 28 days. The effect of pH was more pronounced in the presence of NOM, perhaps due to the involvement of protons in the reduction process. Pre-chlorination of NOM lowered the rate of lead (II) release and decreased the SUVA.
Lin & Valentine, 2009	Bench scale dissolution	Lead dioxide solid	1 to 21 days	NOM was isolated from the Iowa River. The highest lead (II) concentrations were in the presence of NOM without a disinfectant. Chlorine and chloramine can oxidize NOM to supress the remaining reductive capacity of the NOM. Higher lead (II) concentrations were associated with a higher UV_{254} residual and a lower disinfectant residual.
Liu et al., 2010	Dump and fill	50/50 lead tin solder in copper coupons	7 days	NOM caused a negative shift in the zeta potential and caused dissolved lead concentrations to be higher than predicted thermodynamically.
Triantafyllidou & Edwards, 2007	Dump and fill	C36000 brass rod soldered to copper tube	16 hours	NOM was added as SR NOM. Adding 0.5 mg/L of SR NOM did not have a significant impact on lead release.
Trueman, & Gagnon, 2016a	Household sampling	Various	6 hours	NOM was present in the source water at a DOC concentration of 1.5 mg/L. NOM was present in colloidal species along with iron and lead.

Table A.2 Summary of Select Studies That Have Investigated the Impact of NOM on Lead Release

Reference	Type	Material	Stagnation Period	Results
Trueman et al., 2017	Dump and fill	Lead coupons connected to iron coupons	2 days	NOM was added as Aldrich sodium humate at a DOC concentration of 1.8 mg/L. The addition of NOM increased lead release. SEC-ICP/MS results suggested that this was due to the formation of lead humate colloidal particles.
Trueman et al., 2018	Household sampling	Various	Random daytime	NOM was present in the source water at a DOC concentration of 1.6-1.9 mg/L. NOM was not found to complex with lead, but may have induced colloidal dispersion in one system.
Trueman et al., 2019a	Household sampling	Various	Random daytime	NOM was present in the drinking water at a DOC concentration of 2.8-3.2 mg/L. Lead was present as an organic complex at approximately 0.9 kDa.
Willison & Boyer, 2012	Dump and fill	Lead tin solder connected to copper tubing	3 and 4 days	NOM was added as SR NOM, salicylic acid, and tryptophan. At a DOC concentration of 1.5 mg/L, the water with SR NOM released far more lead than the waters with salicylic acid and tryptophan. There were no significant differences in lead release for low and high concentrations of salicylic acid and tryptophan.
Winning et al., 2017	Batch scale dissolution	Lead dioxide solid	12 hours to 21 days	The removal of AHS decreased the TOC concentration from 7.1 to 4.9 mg/L and decreased lead release by 6%. The reduction of TOC by 50% decreased lead release by 75%.
Zhou et al., 2015	Dump and fill	Lead pipe connected to copper pipe	2 and 3 days	NOM was added as SR NOM. A DOC concentration of 7 mg/L increased galvanic current, total lead release, and dissolved lead release compared to a DOC concentration of 1 mg/L.

Appendix B

Supplemental Information for Chapter 3

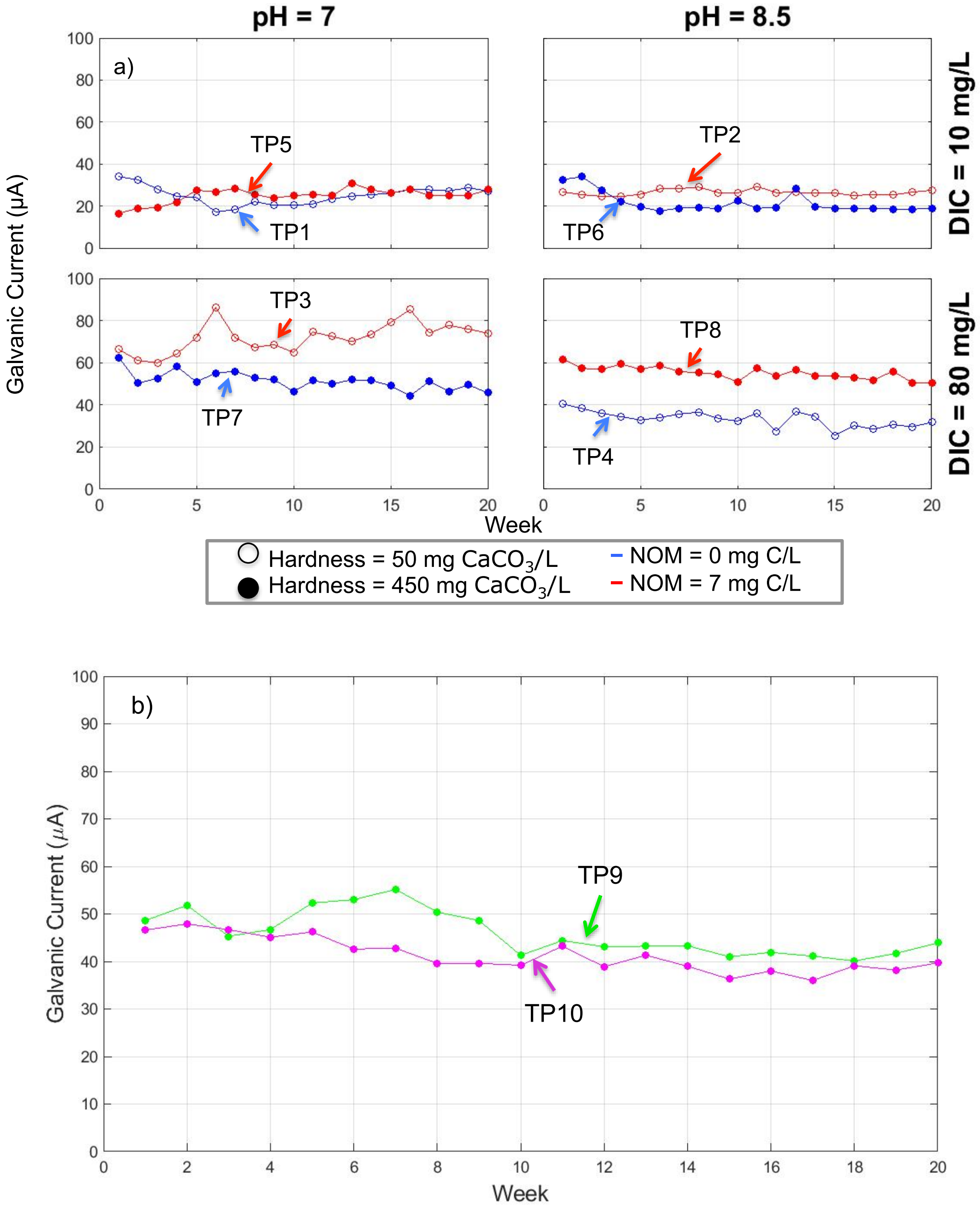


Figure B.1 Panel plot of the galvanic current between the lead and copper pipes of the test pieces during the 20-week study for a) TP1-8 and b) TP9-10. The galvanic current was measured following a 48-hour stagnation period.

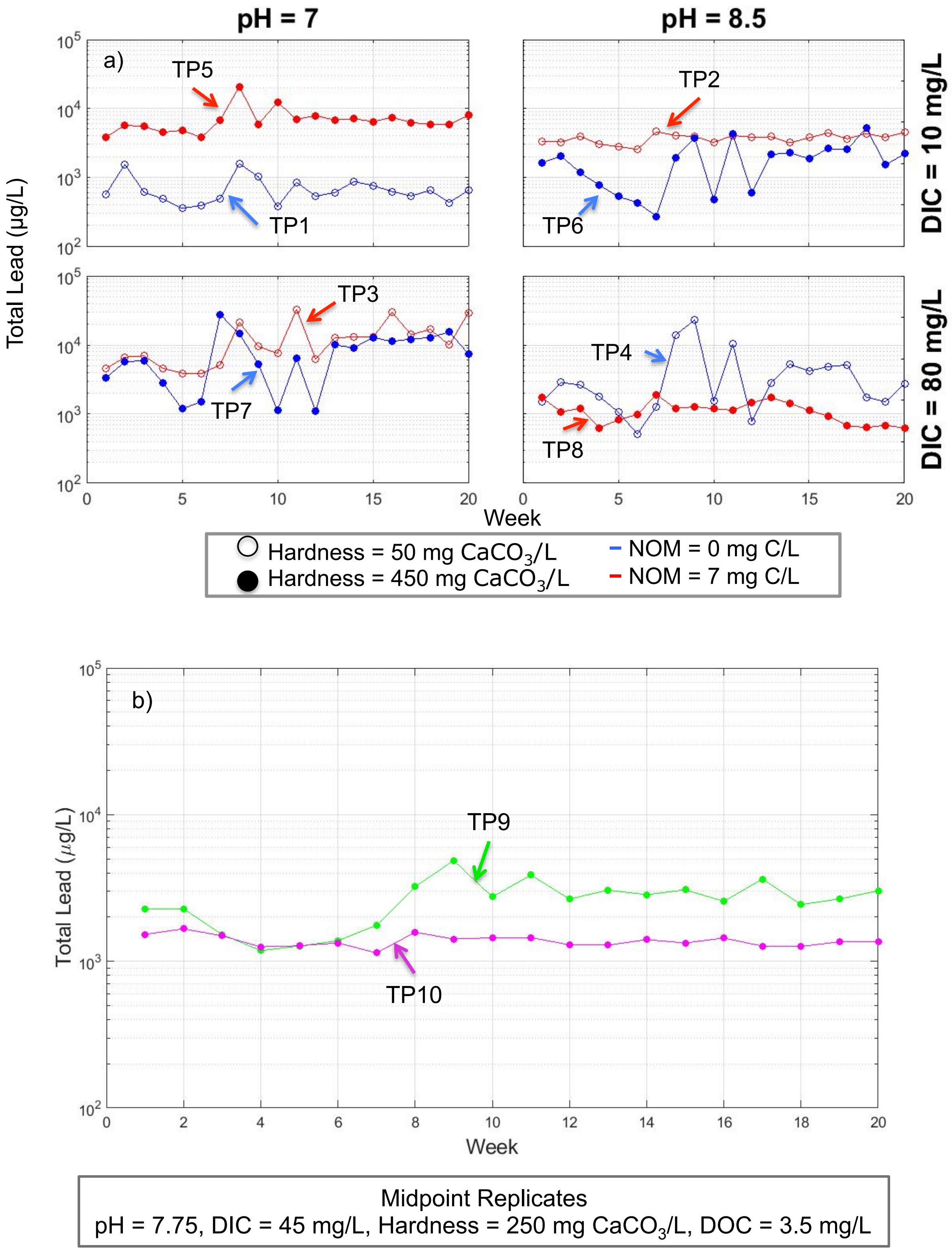


Figure B.2 Panel plot of total lead concentrations in the stagnated water from a) TP1-8 and b) TP9-10. Total lead was measured from composite samples combining stagnated water from the week's three dump and fill events.

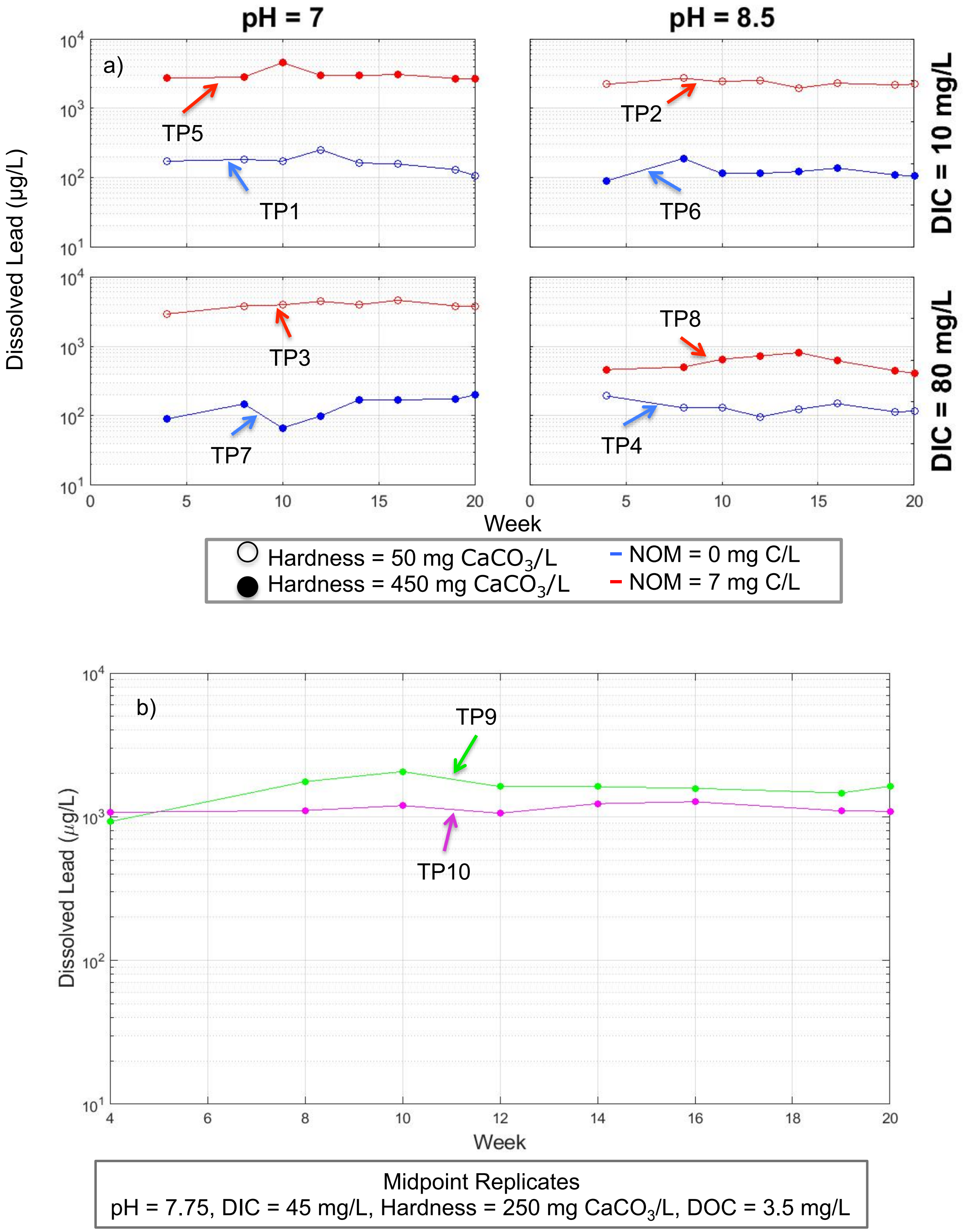


Figure B.3 Panel plot of dissolved lead concentrations in the stagnated water from a) TP1-8 and b) TP9-10. Dissolved lead was measured from water samples collected following a 48-hour stagnation period on select weeks.

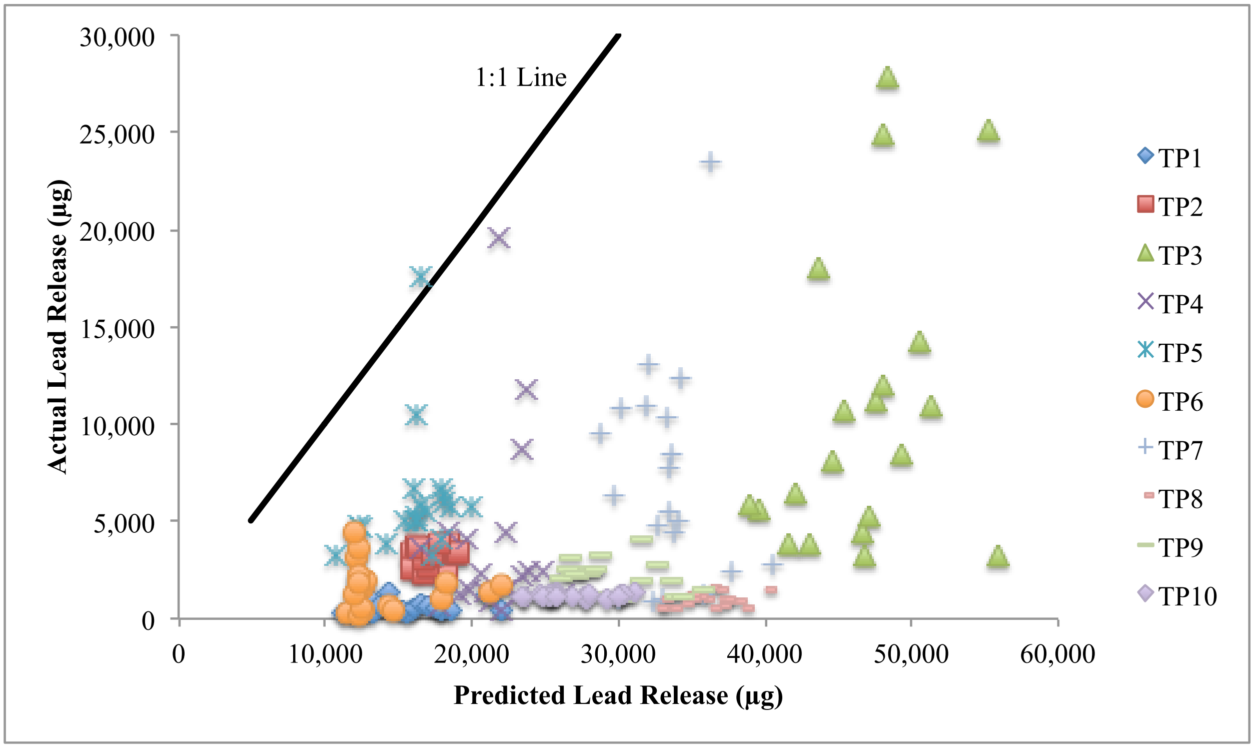


Figure B.4 Predicted weekly lead release calculated based on galvanic current and Faraday's Law versus actual weekly lead release from the weekly composite samples.

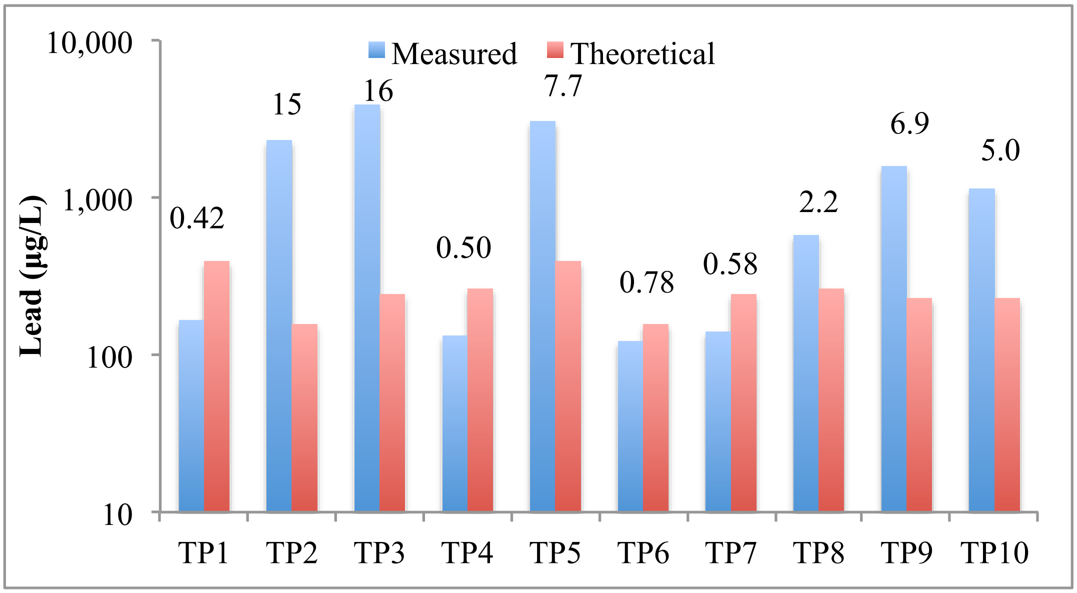


Figure B.5 Comparison of average measured dissolved lead concentrations to theoretical lead solubility predicted by tidyphreeqc. Numbers on top of the bars represent the ratio of measured dissolved lead concentrations to theoretical solubility.

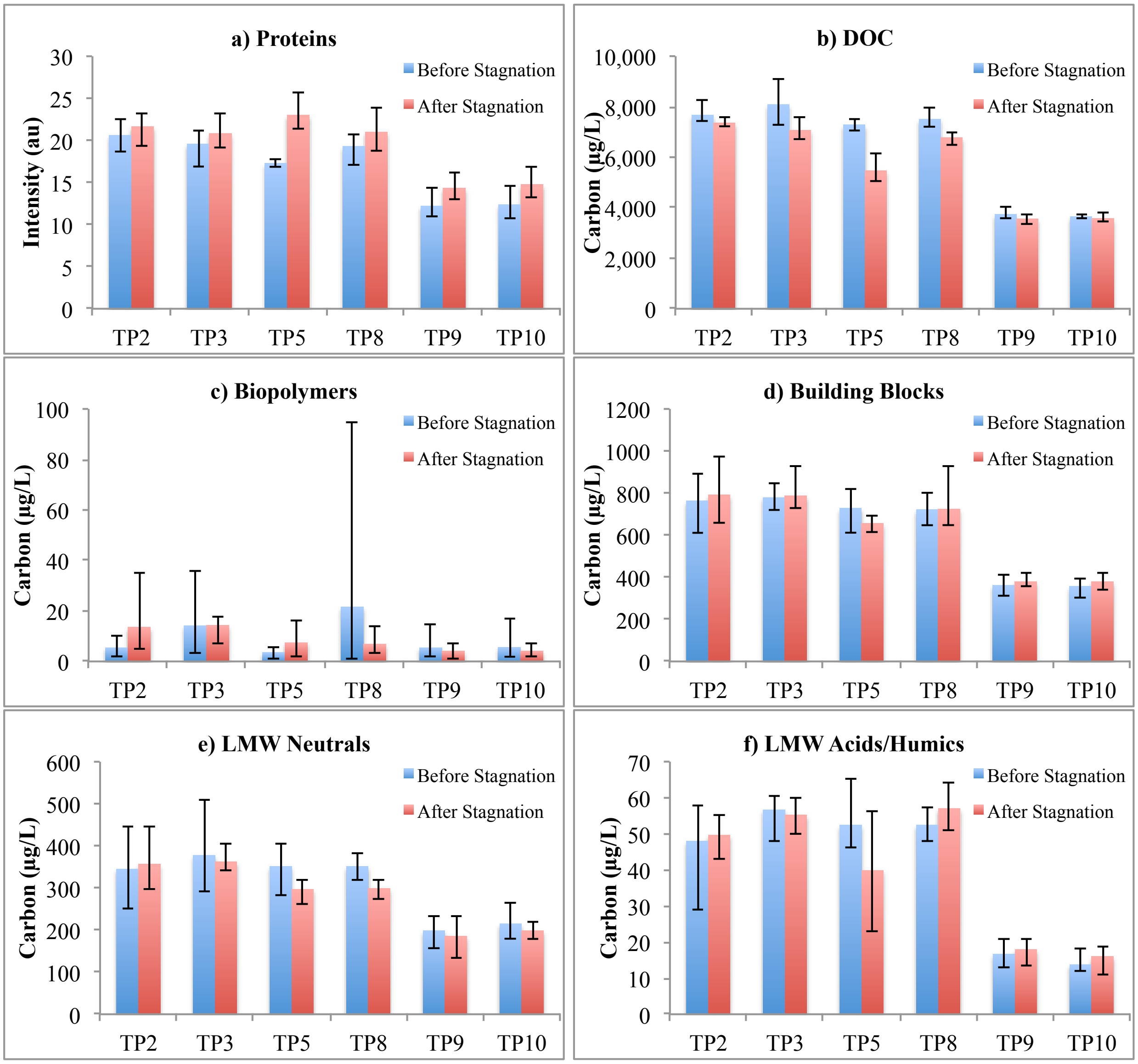
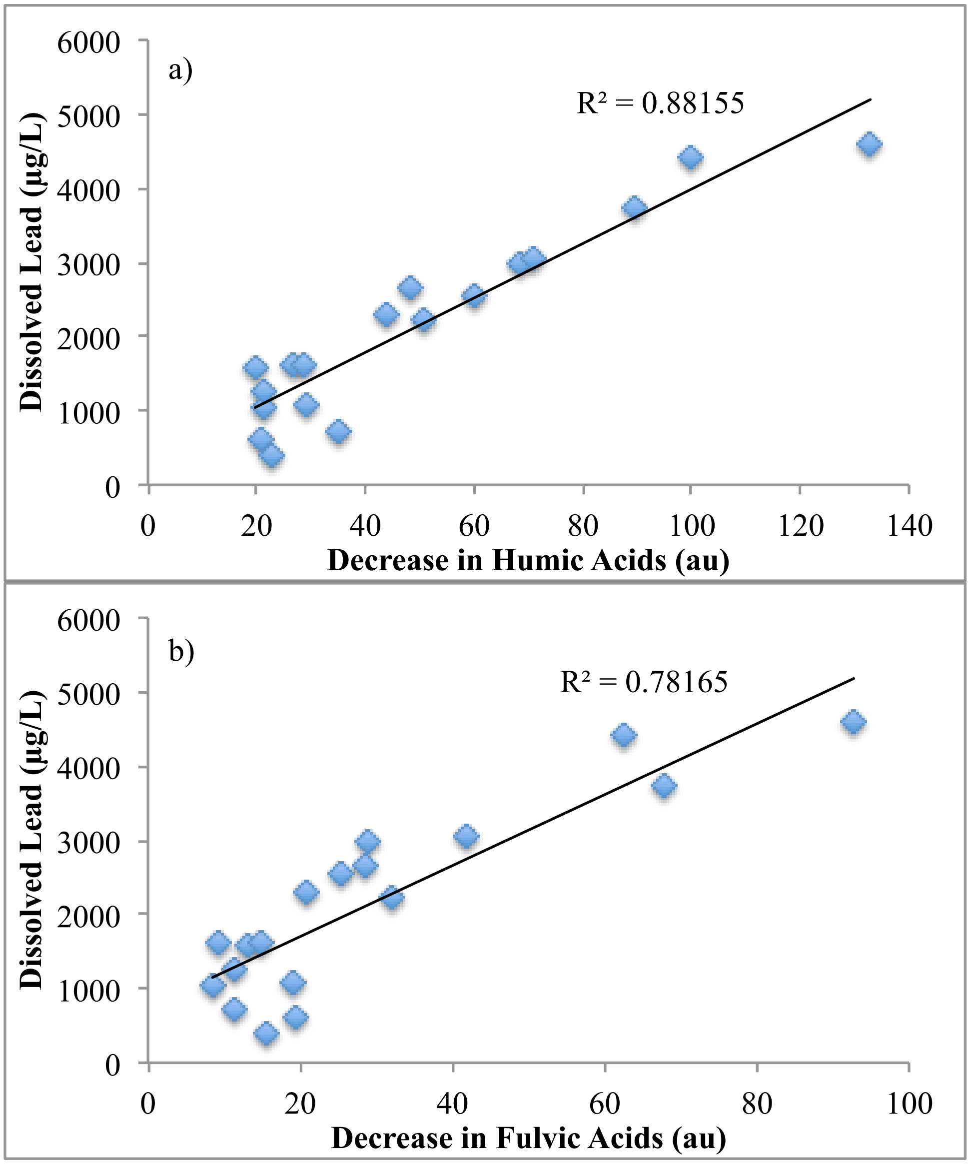


Figure B.6 Average values for FEEM NOM fractions in weeks 12, 16, and 20 for a) Proteins. Average values for LC-OCD NOM fractions in weeks 3, 7, 12, 16 and 20 for b) DOC, c) Biopolymers, d) Building Blocks, e) LMW Neutrals, f) LMW Acids/Humics. Error bars represent minimum and maximum values. TP2, TP3, TP5, and TP8 were dosed with 7 mg DOC/L of SR NOM while TP9 and TP10 were dosed with 3.5 mg DOC/L of SR NOM.


a)
R² = 0.88155
Dissolved Lead (µg/L)
6000
5000
4000
3000
2000
1000
0
0
20
40
60
80
100
120
140
Decrease in Humic Acids (au)
b)
R² = 0.78165
Dissolved Lead (µg/L)
6000
5000
4000
3000
2000
1000
0
0
20
40
60
80
100
Decrease in Fulvic Acids (au)

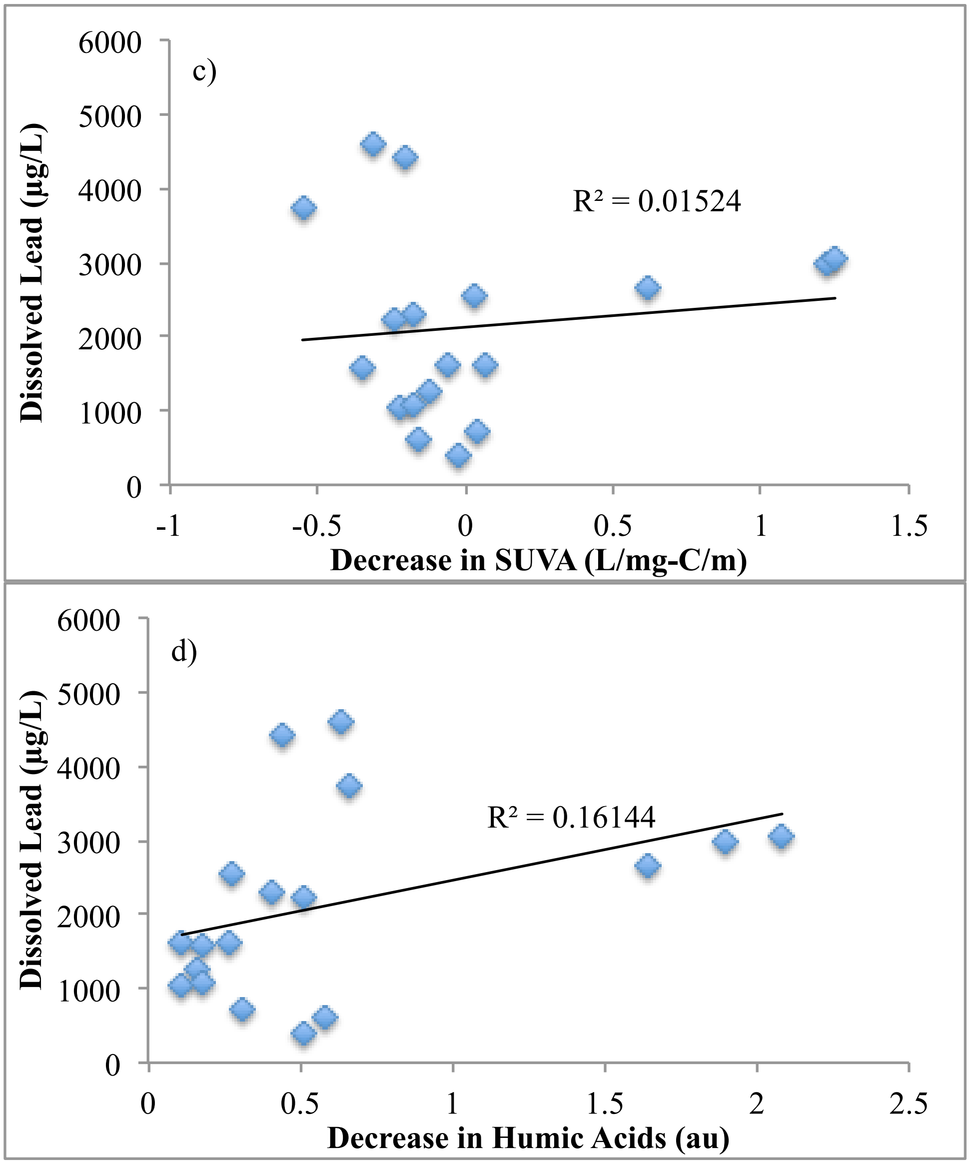


Figure B.7 a) Correlation between dissolved lead and decrease in humic acid intensity upon stagnation in the test pieces measured using FEEM. b) Correlation between dissolved lead and decrease in fulvic acid intensity upon stagnation in the test pieces measured using FEEM. c) Correlation between dissolved lead and decrease in SUVA upon stagnation in the test pieces measured using LC-OCD. d) Correlation between dissolved lead and decrease in humics concentration upon stagnation in the test pieces measured using LC-OCD. The data plotted is from TP2, TP3, TP5, TP8, TP9 and TP10 on weeks 12, 16 and 20.

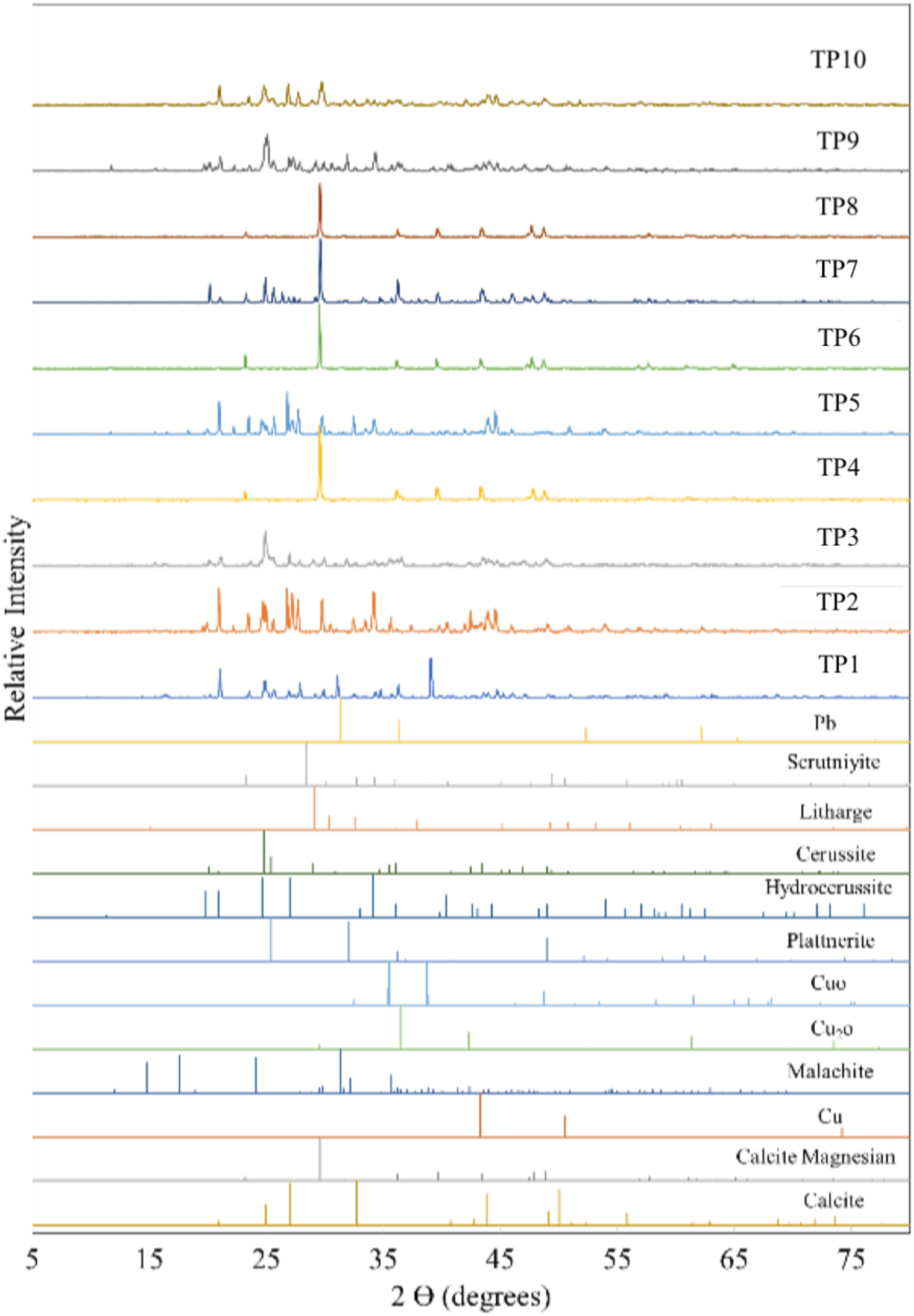


Figure B.8 XRD patterns obtained from the surface of the copper pipes for a range of 5° to 80° 2θ. The patterns at the bottom are the reference patterns of the solids that had peaks identified in the samples.

Table B.1 Chemical Doses for Synthetic Waters

Test Piece	$NaHCO_3$ (mg/L)	$CaCl_2$ (mg/L)	$MgSO_4$ (mg/L)	NaCl (mg/L)	Na_2SO_4 (mg/L)	NOM* (mg/L)	H_2SO_4** (mg/L)	NaOH** (mg/L)
TP1	70	39	18	327	199	0	6.8	0
TP2	70	39	18	327	199	7.0	0	0.44
TP3	560	39	18	327	199	7.0	54	0
TP4	560	39	18	327	199	0	0	2.6
TP5	70	349	162	0	28	7.0	6.8	0
TP6	70	349	162	0	28	0	0	0.44
TP7	560	349	162	0	28	0	54.2	0
TP8	560	349	162	0	28	7.0	0	2.6
TP9	315	194	90	164	114	3.5	5.8	0
TP10	315	194	90	164	114	3.5	5.8	0

*SR NOM concentration required to achieve the DOC target

**Concentrations of H_2SO_4 and NaOH varied in order to achieve the pH target

Table B.2 Schedule of Water Quality Analyses

Parameter	Weeks Measured
Alkalinity	1,5,9,13,17
FEEM*	12,16,20
Galvanic Current	1-20
IC (Chloride and Sulfate)	2,6,11,19
LC-OCD*	3,7,12,16,20
Lead and Copper - Total (Composite)	1-20
Lead and Copper - Total (48 Hour Stagnation)	4,8,10,12,14,16,19,20
Lead and Copper - Dissolved (48 Hour Stagnation)	4,8,10,12,14,16,19,20
Metals (Total)	11
pH	1-20
Specific Conductance	1,5,9,13,17
TOC and DOC*	20
Turbidity	1,5,9,10,12,14,16,18-20

*For synthetic waters with NOM, only one synthetic water without NOM analyzed these weeks as a blank

Table B.3 Percent of Oxidized Lead in the Test Pieces Released into the Water and Stored as Corrosion Scale Based on Faraday's Law

Test Piece	% of Oxidized Lead Released	% of Oxidized Lead Stored as a Corrosion Scale
TP1	3.6	96.4
TP2	18.3	81.7
TP3	22.9	77.1
TP4	17.6	82.4
TP5	37.3	62.7
TP6	11.5	88.5
TP7	21.4	78.6
TP8	2.7	97.3
TP9	7.5	92.5
TP10	4.4	95.6

Table B.4 Summary of Results from XRD Conducted on the Powdered Samples from the Copper Pipe Surface

	Cerussite ($PbCO_3$)	Cuprite (Cu_2O)	Calcite Magnesian ($CaO.MgO$)/ Calcium Carbonate ($CaCO_3$)	Tenorite (CuO)	Plattnerite (PbO_2)	Copper (Cu)	Malachite ($Cu_2(CO_3)(OH)_2$)
TP1	+			+			
TP2	HC		+		+	+	
TP3	+	+	CC				
TP4			+			+	
TP5	+ HC		+	+			+
TP6	+	+	+				
TP7	+	+	CC				
TP8	+	+	+				
TP9	+ HC	+	CC				
TP10	+		+	+			

*'+' indicates the presence of certain mineral (greater than approximately 1%).
**HC stands for hydrocerussite. It is present in minor quantities.
***CC stands for calcium carbonate.

Table B.5 Mass Percentage of Elements in the Lead Pipe Pit and Pit-Containing Scales Determined by Acid Digestion of Solids Followed by Analysis with ICP-MS

	Cu	Ca	Mg	Na	Zn	Pb
TP1	T	T	-	1.2	T	58.4
TP2	T	-	-	-	-	86.9
TP3	T	-	-	-	T	72.4
TP4	T	-	T	-	T	55.8
TP5	T	T	-	1.4	T	57.9
TP5	T	-	-	T	-	64.7
TP7	T	T	T	-	T	58.0
TP9	T	-	-	T	T	57.4
TP10	T	T	-	1.7	T	57.2
Scales on the side of connection						
TP1	T	T	-	1.3	T	48.1
TP3	T	T	-	-	-	76.5
TP5	T	T	-	1.8	T	59.5
TP6	T	-	-	-	-	78.8
TP7	T	-	-	T	-	65.6
TP8	T	T	-	1.3	T	35.5
TP9	0.1	1.9	T	T	-	29.3
TP10	T	T	-	2.0	T	49.5

*‘T’ is trace quantity (< 0.1%) and ‘-’ is not detected.

Table B.6 Mass Percentage of Elements in the Copper Pipe Pit and Pit-Containing Scales Determined by Acid Digestion of Solids Followed by Analysis with ICP-MS

	Cu	Ca	Mg	Na	Zn	Pb
TP1	14.3	-	T	0.1	T	6.2
TP2	4.2	T	T	0.1	T	0.5
TP3	27.8	T	T	0.1	T	5.7
TP4	29.8	7.4	0.1	T	0.1	0.3
TP5	25.2	37.5	0.3	4.8	T	0.2
TP6	51.0	8.3	0.1	T	T	5.6
TP7	50.0	18.5	0.1	0.1	T	0.4
TP8	29.5	0.6	0.1	-	T	6.4
TP9	8.1	0.8	T	0.4	T	6.4
TP10	T	T	-	-	-	7.0

*‘T’ is trace quantity (< 0.01%) and ‘-’ is not detected

Table B.7 Summary of Galvanic Current, Lead Release, and Copper Release

		TP1	TP2	TP3	TP4	TP5	TP6	TP7	TP8	TP9	TP10
Galvanic Current (µA)	Average	25.0	26.5	71.9	33.2	25.0	21.6	51.4	55.2	45.8	41.3
	Standard Deviation	4.4	1.4	7.0	3.8	3.5	4.9	4.3	3.1	4.7	3.6
	Coefficient of Variation (%)	17.5	5.2	9.8	11.4	14.2	22.7	8.4	5.5	10.1	8.8
	95% C.I. Lower Bound	23.0	25.8	68.6	31.5	23.3	19.3	49.4	53.7	43.7	39.6
	95% C.I. Upper Bound	27.1	27.1	75.2	35.0	26.6	23.9	53.4	56.6	48.0	43.0
	Median	25.1	26.3	72.3	33.8	25.3	19.2	51.4	55.5	44.2	39.7
	25th Percentile	21.3	25.5	66.5	30.3	24.0	18.9	49.2	53.1	41.8	38.9
	75th Percentile	27.7	27.3	75.6	36.1	27.7	22.4	52.7	57.2	50.0	44.6
	Minimum	17.2	24.5	60.0	25.5	16.5	17.7	44.3	50.3	40.1	36.0
	Maximum	34.0	29.3	86.1	40.4	30.9	33.9	62.5	61.7	55.2	47.9
	Number of Measurements	20	20	20	20	20	20	20	20	20	20
Total Lead (µg/L)	Average	693	3695	12580	4483	7110	1903	8388	1125	2619	1380
	Standard Deviation	343	569	9055	5496	3690	1328	6533	386	925	126
	Coefficient of Variation (%)	49.4	15.4	72.0	122.6	51.9	69.8	77.9	34.3	35.3	9.1
	95% C.I. Lower Bound	533	3429	8342	1912	5383	1282	5330	944	2185	1321
	95% C.I. Upper Bound	854	3961	16817	7055	8837	2524	11445	1306	3052	1439
	Median	602	3813	9752	2683	6332	1886	6958	1133	2660	1360
	25th Percentile	484	3219	5450	1498	5522	636	2953	722	1892	1279
	75th Percentile	823	4043	16125	5094	7325	2466	12663	1392	3068	1451
	Minimum	353	2534	3830	516	3788	272	1090	630	1184	1141
	Maximum	1587	4584	32760	23070	20720	5215	27620	1907	4866	1665
	Number of Measurements	20	20	20	20	20	20	20	20	20	20
Dissolved Lead (µg/L)	Average	166	2310	3893	132	3046	122	140	578	1581	1141
	Standard Deviation	42	230	503	29	620	30	48	145	319	81
	Coefficient of Variation (%)	25.3	10.0	12.9	21.9	20.4	24.6	34.4	25.2	20.2	7.1
	95% C.I. Lower Bound	131	2117	3472	108	2527	97	100	456	1314	1073
	95% C.I. Upper Bound	201	2502	4314	156	3564	147	180	699	1848	1208
	Median	166	2256	3867	127	2882	114	159	561	1620	1102
	25th Percentile	136	2175	3746	115	2686	105	93	449	1493	1078
	75th Percentile	179	2505	4308	145	3039	133	172	708	1723	1224
	Minimum	106	1955	2913	97	2658	89	67	407	924	1058
	Maximum	250	2691	4587	193	4535	188	201	809	2063	1271
	Number of Measurements	8	8	8	8	8	8	8	8	8	8

Table B.7 Summary of Galvanic Current, Lead Release, and Copper Release

		TP1	TP2	TP3	TP4	TP5	TP6	TP7	TP8	TP9	TP10
Particulate Lead (µg/L)	Average	399	1801	18082	3842	4595	1402	9486	250	1319	260
	Standard Deviation	244	1286	22191	4678	2473	1280	9941	171	718	100
	Coefficient of Variation (%)	61.3	71.4	122.7	121.8	53.8	91.3	104.8	68.5	54.4	38.6
	95% C.I. Lower Bound	194	726	-473	-70	2527	332	1174	107	719	176
	95% C.I. Upper Bound	603	2876	36637	7754	6662	2472	17798	393	1919	344
	Median	283	1483	10330	1357	4291	876	5830	179	1251	264
	25th Percentile	208	671	4081	606	2826	551	2253	125	778	167
	75th Percentile	581	3089	25626	8151	5532	2544	17264	334	1975	322
	Minimum	190	472	1808	377	1664	194	1814	96	271	130
	Maximum	868	3928	68391	12620	9772	3791	29028	612	2442	431
	Number of Measurements	8	8	8	8	8	8	8	8	8	8
Total Copper (µg/L)	Average	10.9	91.4	437.5	25.8	80.7	7.5	55.1	98.4	84.5	69.7
	Standard Deviation	5.5	75.9	151.9	8.4	24.1	5.5	32.4	23.0	26.6	16.7
	Coefficient of Variation (%)	50.1	83.0	34.7	32.7	29.9	72.7	58.8	23.3	31.5	24.0
	95% C.I. Lower Bound	8.3	55.9	366.4	21.9	69.5	5.0	39.9	87.7	72.1	61.9
	95% C.I. Upper Bound	13.4	126.9	508.6	29.8	92.0	10.1	70.3	109.2	96.9	77.6
	Median	8.8	69.1	388.3	23.5	71.9	6.2	46.5	96.8	75.8	62.1
	25th Percentile	6.3	54.6	345.5	21.0	60.7	4.2	42.5	77.8	65.9	58.7
	75th Percentile	15.0	89.2	465.3	29.0	101.2	7.6	60.3	117.3	95.0	82.5
	Minimum	4.9	46.7	270.8	16.9	55.8	3.1	27.9	66.1	59.0	51.4
	Maximum	21.4	353.3	799.3	53.0	132.0	26.1	184.3	141.6	162.5	112.4
	Number of Measurements	20	20	20	20	20	20	20	20	20	20
Dissolved Copper (µg/L)	Average	2.9	47.2	326.0	12.1	29.5	1.4	39.8	71.8	55.4	44.9
	Standard Deviation	2.6	9.1	89.3	3.4	6.0	1.2	16.4	16.2	7.8	5.3
	Coefficient of Variation (%)	88.5	19.2	27.4	27.9	20.4	84.9	41.3	22.6	14.1	11.8
	95% C.I. Lower Bound	0.8	39.6	251.3	9.3	24.5	0.4	26.1	58.3	48.8	40.4
	95% C.I. Upper Bound	5.1	54.7	400.6	14.9	34.6	2.4	53.5	85.4	61.9	49.3
	Median	2.4	43.4	324.7	11.5	29.3	1.0	36.6	66.8	55.5	44.8
	25th Percentile	1.3	39.7	249.2	9.5	24.5	n.d.	26.0	60.7	47.9	40.3
	75th Percentile	3.0	56.6	358.7	15.2	31.3	1.5	51.9	85.3	59.0	46.3
	Minimum	1.1	38.2	217.9	8.1	23.0	n.d.	19.8	53.0	45.3	38.7
	Maximum	9.0	61.9	507.0	17.8	42.3	4.1	69.0	101.8	69.9	55.9
	Number of Measurements	8	8	8	8	8	8	8	8	8	8

Table B.7 Summary of Galvanic Current, Lead Release, and Copper Release

		TP1	TP2	TP3	TP4	TP5	TP6	TP7	TP8	TP9	TP10
Particulate Copper (µg/L)	Average	6.9	29.9	66.7	9.5	46.0	9.0	31.7	21.2	20.9	17.4
	Standard Deviation	6.6	53.4	25.8	5.1	20.3	9.1	34.3	8.9	10.1	4.0
	Coefficient of Variation (%)	95.5	178.4	38.7	53.6	44.2	101.2	108.3	42.1	48.3	22.9
	95% C.I. Lower Bound	1.4	-14.7	45.1	5.2	29.0	1.4	3.0	13.7	12.5	14.0
	95% C.I. Upper Bound	12.3	74.5	88.3	13.7	63.0	16.6	60.3	28.6	29.3	20.7
	Median	7.2	12.2	63.1	8.4	38.7	4.0	13.9	20.0	18.6	16.8
	25th Percentile	3.3	8.2	45.1	5.1	31.4	2.8	11.0	17.2	14.9	13.8
	75th Percentile	8.8	20.4	84.8	11.9	60.6	17.3	59.5	28.9	20.3	19.6
	Minimum	n.d.	n.d.	40.1	4.0	29.5	2.6	9.8	6.7	13.7	12.9
	Maximum	19.7	161.0	116.8	19.7	87.0	26.2	99.2	35.6	45.1	25.2
	Number of Measurements	8	8	8	8	8	8	8	8	8	8

*Detection limit of 0.4 µg/L for lead and 0.7 µg/L for copper

** n.d. below detection limit

Table B.8 Summary of FEEM, LC-OCD, and TOC Analyzer Results

			Average Before	Average After	Change	p-Value
FEEM	Humic Acids (au)	TP2	474.91	423.29	-51.62	**0.008**
		TP3	463.19	355.75	-107.43	**0.015**
		TP5	460.52	397.95	-62.57	**0.013**
		TP8	470.95	444.71	-26.24	**0.028**
		TP9	270.48	245.38	-25.09	**0.012**
		TP10	268.24	244.23	-24.00	**0.012**
	Fulvic Acids (au)	TP2	373.07	346.99	-26.08	**0.015**
		TP3	371.44	297.05	-74.38	**0.015**
		TP5	350.87	317.86	-33.01	**0.017**
		TP8	345.46	329.91	-15.55	**0.022**
		TP9	193.06	180.58	-12.48	**0.017**
		TP10	191.59	178.62	-12.98	0.056
	Proteins (au)	TP2	20.63	21.64	1.01	0.122
		TP3	19.58	20.81	1.24	0.304
		TP5	17.29	23.00	5.72	0.076
		TP8	19.32	21.02	1.69	0.181
		TP9	12.20	14.36	2.17	**0.043**
		TP10	12.39	14.77	2.38	0.065
LC-OCD	DOC (mg/L)	TP2	7.677	7.361	-0.316	0.058
		TP3	8.090	7.072	-1.019	**0.043**
		TP5	7.279	5.465	-1.815	**0.000**
		TP8	7.502	6.787	-0.715	**0.005**
		TP9	3.738	3.560	-0.178	0.154
		TP10	3.656	3.576	-0.080	0.223
	SUVA (L-mg/C-m)	TP2	4.97	5.07	0.10	0.101
		TP3	4.76	5.37	0.61	**0.026**
		TP5	5.04	4.20	-0.84	**0.009**
		TP8	4.90	5.02	0.13	0.112
		TP9	4.81	5.06	0.25	0.203
		TP10	4.96	5.13	0.17	**0.005**
	Hydrophobic (µg C/L)	TP2	475	427	-48	0.704
		TP3	889	345	-544	0.187
		TP5	412	396	-16	0.641
		TP8	626	356	-270	0.112
		TP9	292	266	-26	0.739
		TP10	202	234	33	0.277

Table B.8 Summary of FEEM, LC-OCD, and TOC Analyzer Results

			Average Before	Average After	Change	p-Value
LC-OCD	Biopolymers (µg C/L)	TP2	6	14	8	0.247
		TP3	14	14	0	0.979
		TP5	4	8	4	0.285
		TP8	22	7	-15	0.422
		TP9	6	4	-1	0.634
		TP10	6	4	-2	0.706
	Humics (µg C/L)	TP2	6040	5722	-318	**0.007**
		TP3	5976	5508	-468	**0.005**
		TP5	5732	4067	-1665	**0.001**
		TP8	5719	5344	-375	**0.008**
		TP9	2859	2706	-153	**0.010**
		TP10	2863	2743	-120	**0.005**
	Building Blocks (µg C/L)	TP2	764	793	29	0.598
		TP3	780	787	7	0.885
		TP5	728	657	-71	0.215
		TP8	722	724	2	0.965
		TP9	362	380	17	0.595
		TP10	357	380	23	0.442
	LMW Neutrals (µg C/L)	TP2	345	357	11	0.680
		TP3	378	363	-15	0.696
		TP5	352	297	-54	0.143
		TP8	351	299	-52	**0.013**
		TP9	199	186	-13	0.500
		TP10	216	198	-17	0.354
	LMW Acids/Humics (µg C/L)	TP2	48	50	2	0.777
		TP3	57	55	-2	0.500
		TP5	52	40	-13	0.229
		TP8	53	57	4	0.163
		TP9	17	18	1	0.605
		TP10	14	16	2	0.232
TOC Analyzer	TOC (mg/L)	TP2	8.0	7.8	-0.2	-
		TP3	7.8	8.7	0.8	-
		TP5	7.2	6.4	-0.8	-
		TP8	7.1	6.9	-0.2	-
		TP9	3.6	3.5	-0.1	-
		TP10	3.5	3.5	0.0	-

Table B.8 Summary of FEEM, LC-OCD, and TOC Analyzer Results

			Average Before	Average After	Change	p-Value
TOC Analyzer	DOC (mg/L)	TP2	7.8	7.4	-0.4	-
		TP3	8.1	7.4	-0.7	-
		TP5	7.7	5.7	-2.1	-
		TP8	7.0	6.5	-0.5	-
		TP9	3.7	3.4	-0.3	-
		TP10	3.6	3.4	-0.2	-
	POC (mg/L)	TP2	0.2	0.4	0.2	-
		TP3	-0.3	1.3	1.6	-
		TP5	-0.5	0.8	1.3	-
		TP8	0.1	0.4	0.3	-
		TP9	-0.1	0.1	0.2	-
		TP10	-0.1	0.1	0.2	-

*FEEM measured weeks 12, 16, and 20

**LC-OCD measured weeks 3, 7, 12, 16 and 20

***TOC analyzer measurements on week 20

**** POC calculated as the difference between TOC and DOC

Table B.9 Chemistry of Synthetic Waters Prior to Stagnation in the Test Pieces

	pH				DIC (mg/L)			
	target	average	min	max	target	average	min	max
TP1	7	7.08	6.91	7.20	10	9.70	7.37	10.81
TP2	8.5	8.49	8.30	8.69	10	11.30	10.93	11.90
TP3	7	7.08	6.87	7.19	80	77.52	74.79	78.86
TP4	8.5	8.44	8.33	8.59	80	77.03	75.67	79.32
TP5	7	7.07	6.83	7.20	10	11.11	10.28	11.74
TP6	8.5	8.44	8.30	8.64	10	10.96	10.47	11.88
TP7	7	7.08	6.95	7.20	80	75.33	74.07	77.21
TP8	8.5	8.40	8.30	8.57	80	78.85	78.07	79.20
TP9	7.75	7.81	7.56	7.95	45	42.89	42.13	43.35
TP10	7.75	7.84	7.64	7.95	45	43.12	42.13	43.90

*n.m. not measured

Table B.9 Chemistry of Synthetic Waters Prior to Stagnation in the Test Pieces

	Hardness (mg $CaCO_3$/L)		DOC (mg/L)				Alkalinity (mg $CaCO_3$/L)		
	target	measured	target	average	min	max	average	min	max
TP1	50	48.07	0	0.033	n.m.	n.m.	34	26	38
TP2	50	47.37	7	7.677	7.400	8.284	48	46	50
TP3	50	45.25	7	8.090	7.255	9.063	276	270	282
TP4	50	47.90	0	0.063	n.m.	n.m.	322	316	332
TP5	450	403.6	7	7.279	7.034	7.489	38	36	40
TP6	450	403.2	0	n.m.	n.m.	n.m.	46	44	50
TP7	450	415.2	0	n.m.	n.m.	n.m.	264	262	266
TP8	450	409.4	7.0	7.502	7.182	7.932	329	326	330
TP9	250	199.2	3.5	3.738	3.567	4.003	173	170	176
TP10	250	232.5	3.5	3.656	3.553	3.729	174	170	178

*n.m. not measured

Table B.9 Chemistry of Synthetic Waters Prior to Stagnation in the Test Pieces

	SPC (µS/cm)			Turbidity (NTU)			Chloride (mg/L)		
	average	min	max	average	min	max	average	min	max
TP1	1221	1187	1299	0.08	0.06	0.13	234	229	239
TP2	1230	1181	1280	0.15	0.12	0.22	235	228	245
TP3	1608	1566	1634	0.15	0.12	0.18	233	224	240
TP4	1669	1611	1675	0.09	0.07	0.12	233	225	241
TP5	1071	787	1169	0.16	0.14	0.22	233	223	241
TP6	1260	1122	1655	0.07	0.06	0.08	234	225	243
TP7	1515	1486	1593	0.08	0.07	0.10	235	225	244
TP8	1483	1046	1640	0.16	0.13	0.17	235	224	242
TP9	1377	1297	1471	0.12	0.10	0.15	237	230	245
TP10	1323	1004	1418	0.11	0.10	0.13	239	231	248

*n.m. not measured

Table B.9 Chemistry of Synthetic Waters Prior to Stagnation in the Test Pieces

	Sulfate (mg/L)			CSMR			SUVA		
	average	min	max	average	min	max	average	min	max
TP1	182	161	192	1.29	1.24	1.43	6.12	n.m.	n.m.
TP2	188	180	193	1.25	1.23	1.27	4.97	4.84	5.11
TP3	185	178	191	1.26	1.25	1.26	4.76	4.08	5.25
TP4	187	179	193	1.25	1.24	1.26	3.27	n.m.	n.m.
TP5	199	195	204	1.17	1.14	1.18	5.04	4.76	5.30
TP6	196	191	202	1.19	1.17	1.21	n.m.	n.m.	n.m.
TP7	199	195	204	1.18	1.15	1.20	n.m.	n.m.	n.m.
TP8	188	160	202	1.25	1.19	1.40	4.90	4.76	5.10
TP9	188	152	204	1.27	1.18	1.51	4.81	4.47	5.04
TP10	200	194	207	1.19	1.19	1.20	4.96	4.89	5.03

*n.m. not measured

Table B.10 Chemistry of Synthetic Waters Following Stagnation in the Test Pieces

	pH			DIC (mg/L)			Hardness (mg $CaCO_3$/L)
	average	min	max	average	min	max	measured
TP1	8.75	8.22	9.18	7.99	6.26	9.26	50.53
TP2	8.91	8.75	9.11	12.31	11.60	13.03	49.98
TP3	7.71	7.52	7.87	65.88	64.89	67.84	47.95
TP4	8.55	8.42	8.77	75.11	73.04	76.75	42.91
TP5	8.01	7.77	8.31	10.40	9.74	11.19	426.4
TP6	8.22	7.98	9.10	10.49	8.24	13.50	419.3
TP7	7.61	7.34	7.80	62.01	60.34	63.74	439.7
TP8	8.27	8.13	8.37	74.13	72.10	77.14	415.5
TP9	8.26	8.10	8.42	41.87	41.24	42.76	206.8
TP10	8.25	8.10	8.40	42.06	41.41	43.36	242.3

*n.m. not measured

Table B.10 Chemistry of Synthetic Waters Following Stagnation in the Test Pieces

	DOC (mg/L)			Turbidity (NTU)			SUVA		
	average	min	max	average	min	max	average	min	max
TP1	n.m.	n.m.	n.m.	0.56	0.20	1.09	n.m.	n.m.	n.m.
TP2	7.361	7.224	7.608	1.14	0.67	2.05	5.07	4.94	5.14
TP3	7.072	6.716	7.592	5.36	0.84	21.40	5.37	5.26	5.57
TP4	0.127	0.119	0.135	0.38	0.17	0.81	3.13	2.53	3.72
TP5	5.465	5.055	6.182	8.17	3.62	19.10	4.20	3.87	4.45
TP6	n.m.	n.m.	n.m.	0.29	0.12	1.10	n.m.	n.m.	n.m.
TP7	n.m.	n.m.	n.m.	1.16	0.60	2.54	n.m.	n.m.	n.m.
TP8	6.787	6.489	7.000	0.52	0.35	0.89	5.02	4.94	5.14
TP9	3.560	3.333	3.772	0.53	0.29	0.88	5.06	4.88	5.31
TP10	3.576	3.457	3.782	0.33	0.25	0.56	5.13	5.02	5.21

*n.m. not measured

Table B.11 Changes to the Chemistry of the Synthetic Waters During Stagnation

	pH			DIC (mg/L)			Hardness (mg $CaCO_3$/L)		
	initial	final	change	initial	final	change	initial	final	change
TP1	7.08	8.75	1.67	9.70	7.99	-1.72	48.07	50.53	2.46
TP2	8.49	8.91	0.42	11.30	12.31	1.02	47.37	49.98	2.61
TP3	7.08	7.71	0.63	77.52	65.88	-11.65	45.25	47.95	2.70
TP4	8.44	8.55	0.12	77.03	75.11	-1.92	47.90	42.91	-4.99
TP5	7.07	8.01	0.94	11.11	10.40	-0.71	403.6	426.4	22.8
TP6	8.44	8.22	-0.22	10.96	10.49	-0.47	403.2	419.3	16.1
TP7	7.08	7.61	0.54	75.33	62.01	-13.33	415.2	439.7	24.5
TP8	8.40	8.27	-0.13	78.85	74.13	-4.71	409.4	415.5	6.1
TP9	7.81	8.26	0.45	42.89	41.87	-1.02	199.2	206.8	7.6
TP10	7.84	8.25	0.41	43.12	42.06	-1.07	232.5	242.3	9.8

*n.m. not measured

Table B.11 Changes to the Chemistry of the Synthetic Waters During Stagnation

	DOC (mg/L)			Turbidity (NTU)			SUVA		
	initial	final	change	initial	final	change	initial	final	change
TP1	0.033	n.m.	n.m.	0.08	0.56	0.48	6.12	n.m.	n.m.
TP2	7.677	7.361	-0.316	0.15	1.14	0.99	4.97	5.07	0.10
TP3	8.090	7.072	-1.019	0.15	5.36	5.21	4.76	5.37	0.61
TP4	0.063	0.127	0.064	0.09	0.38	0.30	3.27	3.13	-0.15
TP5	7.279	5.465	-1.815	0.16	8.17	8.02	5.04	4.20	-0.84
TP6	n.m.	n.m.	n.m.	0.07	0.29	0.22	n.m.	n.m.	n.m.
TP7	n.m.	n.m.	n.m.	0.08	1.16	1.07	n.m.	n.m.	n.m.
TP8	7.502	6.787	-0.715	0.16	0.52	0.36	4.90	5.02	0.13
TP9	3.738	3.560	-0.178	0.12	0.53	0.41	4.81	5.06	0.25
TP10	3.656	3.576	-0.080	0.11	0.33	0.22	4.96	5.13	0.17

*n.m. not measured

Table B.12 Metals Concentrations Before and After Stagnation Measured Using CRC ICP-MS

		Hardness (mg $CaCO_3$/L)	Aluminum	Antimony	Arsenic	Barium	Bismuth	Cadmium
TP1	Before	48	<0.0050	<0.00010	<0.00010	0.00033	<0.000050	<0.0000050
	After	50	<0.0050	0.00011	<0.00010	0.00049	<0.000050	0.0000177
TP2	Before	47	0.0117	<0.00010	<0.00010	0.00044	<0.000050	<0.0000050
	After	50	<0.050	<0.0010	<0.0010	<0.0010	<0.00050	0.00012
TP3	Before	45	<0.050	<0.0010	<0.0010	<0.0010	<0.00050	<0.000050
	After	48	<0.050	<0.0010	<0.0010	<0.0010	0.00052	<0.000050
TP4	Before	48	<0.050	<0.0010	<0.0010	<0.0010	<0.00050	<0.000050
	After	43	<0.050	<0.0010	<0.0010	<0.0010	<0.00050	0.000053
TP5	Before	404	0.0129	<0.00010	<0.00010	0.0016	<0.000050	<0.0000050
	After	426	<0.050	<0.0010	<0.0010	0.0018	<0.00050	<0.000050
TP6	Before	404	<0.0050	<0.00010	<0.00010	0.0016	<0.000050	<0.0000050
	After	418	<0.0050	0.00031	<0.00010	0.00155	<0.000050	0.0000108
TP7	Before	414	<0.0050	<0.00010	<0.00010	0.00193	<0.000050	<0.0000050
	After	440	<0.050	<0.0010	<0.0010	0.002	<0.00050	0.000041
TP8	Before	417	0.01265	<0.00010	0.00012	0.001945	<0.000050	<0.0000050
	After	416	<0.050	<0.0010	<0.0010	0.0021	<0.00050	<0.000050
TP9	Before	199	0.0076	<0.00010	<0.00010	0.00114	<0.000050	<0.0000050
	After	207	<0.050	<0.0010	<0.0010	0.0014	<0.00050	<0.000050
TP10	Before	233	0.0075	<0.00010	<0.00010	0.00112	<0.000050	<0.0000050
	After	242	<0.050	<0.0010	<0.0010	0.0012	<0.00050	0.000119

* Concentrations in mg/L

** Measured before and after 48-hour stagnation during week 11

Table B.12 Metals Concentrations Before and After Stagnation Measured Using CRC ICP-MS

		Calcium	Chromium	Copper	Iron	Lead	Magnesium	Molybdenum	Phosphorus
TP1	Before	13	<0.00050	<0.0010	<0.010	0.00008	3.79	<0.000050	<0.050
	After	13.9	<0.00050	0.0042	<0.010	0.355	3.84	<0.000050	0.07
TP2	Before	12.9	0.00056	<0.0010	0.02	0.000199	3.68	<0.000050	<0.050
	After	13.7	<0.0050	0.073	<0.10	3.45	3.83	<0.00050	<0.50
TP3	Before	12.1	<0.0050	<0.010	<0.10	<0.00050	3.65	<0.00050	<0.50
	After	12.9	<0.0050	0.382	<0.10	6.09	3.82	<0.00050	<0.50
TP4	Before	12.9	<0.0050	<0.010	<0.10	<0.00050	3.81	<0.00050	<0.50
	After	11	<0.0050	0.022	<0.10	0.516	3.75	<0.00050	<0.50
TP5	Before	109	<0.00050	<0.0010	0.017	0.000195	31.9	0.000059	<0.050
	After	117	<0.0050	0.072	<0.10	6.09	32.6	<0.00050	<0.50
TP6	Before	110	<0.00050	<0.0010	<0.010	<0.000050	31.2	<0.000050	<0.050
	After	114	<0.00050	0.0034	<0.010	0.27	32.7	<0.000050	<0.050
TP7	Before	113	<0.00050	<0.0010	<0.010	0.000051	32.3	<0.000050	<0.050
	After	119	<0.0050	0.0845	<0.10	0.755	34.6	<0.00050	<0.50
TP8	Before	111.5	0.00063	<0.0010	0.017	0.0001715	31.8	0.000078	<0.050
	After	109	<0.0050	0.103	<0.10	0.808	34.8	<0.00050	<0.50
TP9	Before	64.5	<0.00050	<0.0010	<0.010	0.000128	9.27	0.000052	<0.050
	After	66.9	<0.0050	0.069	<0.10	2.3	9.66	<0.00050	<0.50
TP10	Before	63.9	<0.00050	<0.0010	<0.010	0.000135	17.7	<0.000050	<0.050
	After	66.2	<0.0050	0.06	<0.10	1.32	18.7	<0.00050	<0.50

* Concentrations in mg/L

** Measured before and after 48-hour stagnation during week 11

Table B.12 Metals Concentrations Before and After Stagnation Measured Using CRC ICP-MS

		Potassium	Silicon	Sodium	Strontium	Sulfur	Thallium	Tin	Titanium
TP1	Before	<0.050	<0.10	205	0.0063	55	<0.000010	<0.00010	<0.00030
	After	0.073	<0.10	205	0.0066	55.6	0.000069	<0.00010	<0.00030
TP2	Before	<0.050	0.12	212	0.0062	61.5	<0.000010	0.00018	<0.00030
	After	<0.50	<1.0	225	<0.010	57.7	<0.00010	<0.0010	<0.0030
TP3	Before	<0.50	<1.0	315	<0.010	58.3	<0.00010	<0.0010	<0.0030
	After	<0.50	<1.0	329	<0.010	64.5	0.00021	<0.0010	<0.0030
TP4	Before	<0.50	<1.0	340	<0.010	60.9	<0.00010	<0.0010	<0.0030
	After	<0.50	<1.0	348	<0.010	59.9	<0.00010	<0.0010	<0.0030
TP5	Before	<0.050	0.12	43	0.0525	64.5	<0.000010	0.00019	<0.00030
	After	<0.50	<1.0	45.8	0.055	60.7	<0.00010	<0.0010	<0.0030
TP6	Before	<0.050	<0.10	41.9	0.0526	63.1	<0.000010	<0.00010	<0.00030
	After	<0.050	<0.10	45.6	0.0538	64.7	0.000068	<0.00010	<0.00030
TP7	Before	<0.050	<0.10	148	0.0535	68.2	<0.000010	<0.00010	<0.00030
	After	<0.50	<1.0	151.5	0.0545	68.75	0.00014	<0.0010	<0.0030
TP8	Before	<0.050	0.13	166.5	0.05435	56.7	<0.000010	0.00018	0.00024
	After	<0.50	<1.0	172	0.053	50.9	0.0001	<0.0010	<0.0030
TP9	Before	<0.050	<0.10	195	0.0296	54.2	<0.000010	0.0001	<0.00030
	After	<0.50	<1.0	203	0.031	50.9	<0.00010	<0.0010	<0.0030
TP10	Before	<0.050	<0.10	193	0.0297	68.5	<0.000010	0.00011	<0.00030
	After	<0.50	<1.0	197	0.031	61.5	<0.00010	<0.0010	<0.0030

* Concentrations in mg/L

** Measured before and after 48-hour stagnation during week 11

Table B.12 Metals Concentrations Before and After Stagnation Measured Using CRC ICP-MS

		Zinc
TP1	Before	<0.0030
	After	0.0139
TP2	Before	<0.0030
	After	<0.030
TP3	Before	<0.030
	After	<0.030
TP4	Before	<0.030
	After	<0.030
TP5	Before	<0.0030
	After	<0.030
TP6	Before	<0.0030
	After	0.0125
TP7	Before	<0.0030
	After	<0.030
TP8	Before	<0.0030
	After	<0.030
TP9	Before	<0.0030
	After	<0.030
TP10	Before	<0.0030
	After	<0.030

* Concentrations in mg/L

** Measured before and after 48-hour stagnation during week 11

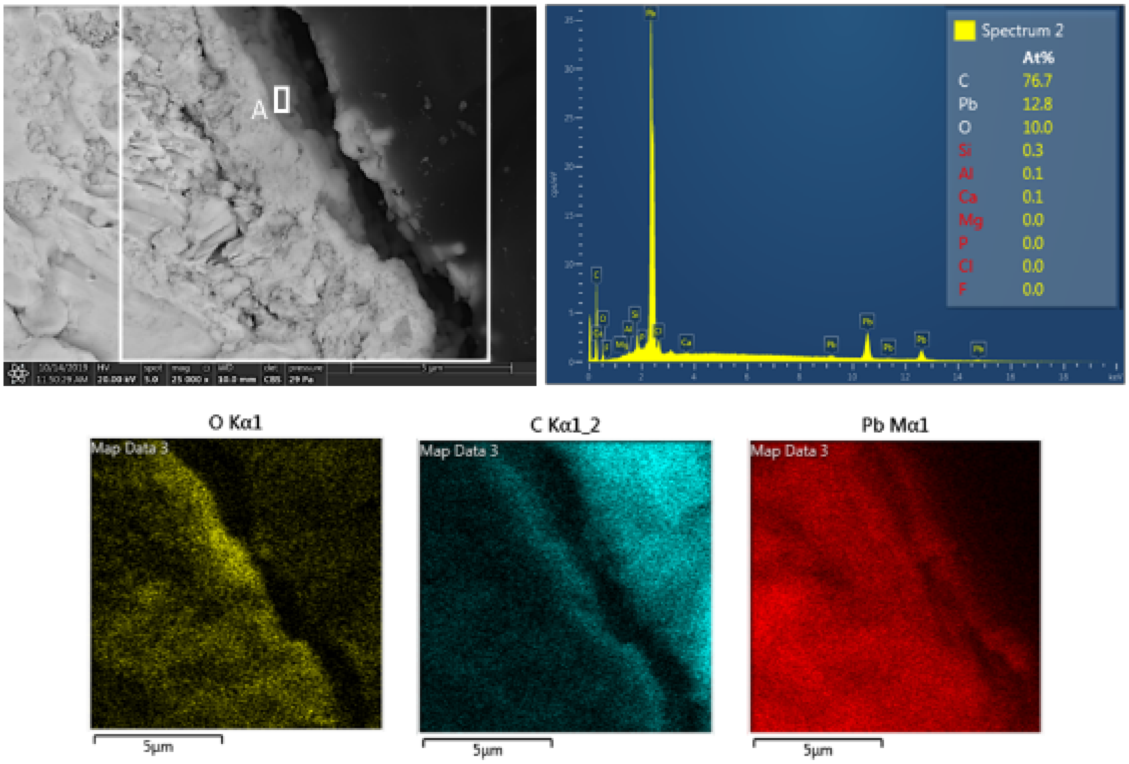


Figure B.9 (Top left) The SEM image of the lead pipe cross-section from TP1 with the highlighted region on which EDS was conducted; (top right) Semi-quantitative analysis of elements present on the scale surface at A; (bottom) mapping of the most abundant elements indicated by EDS i.e C, O, Pb on the highlighted region on the SEM Image.

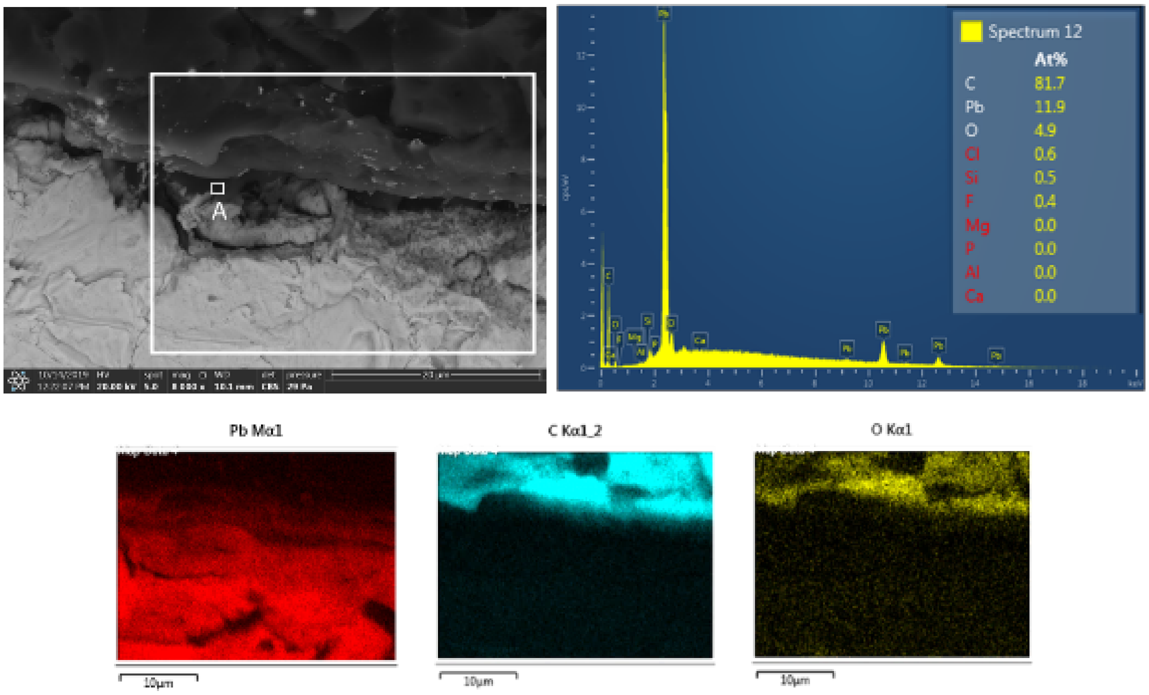


Figure B.10 (Top left) The SEM image of the lead pipe cross-section from TP2 with the highlighted region on which EDS was conducted; (top right) Semi-quantitative analysis of elements present on the scale surface at A; (bottom) mapping of the most abundant elements indicated by EDS (i.e. Pb, Ca, C, O) on the highlighted region of the SEM Image.

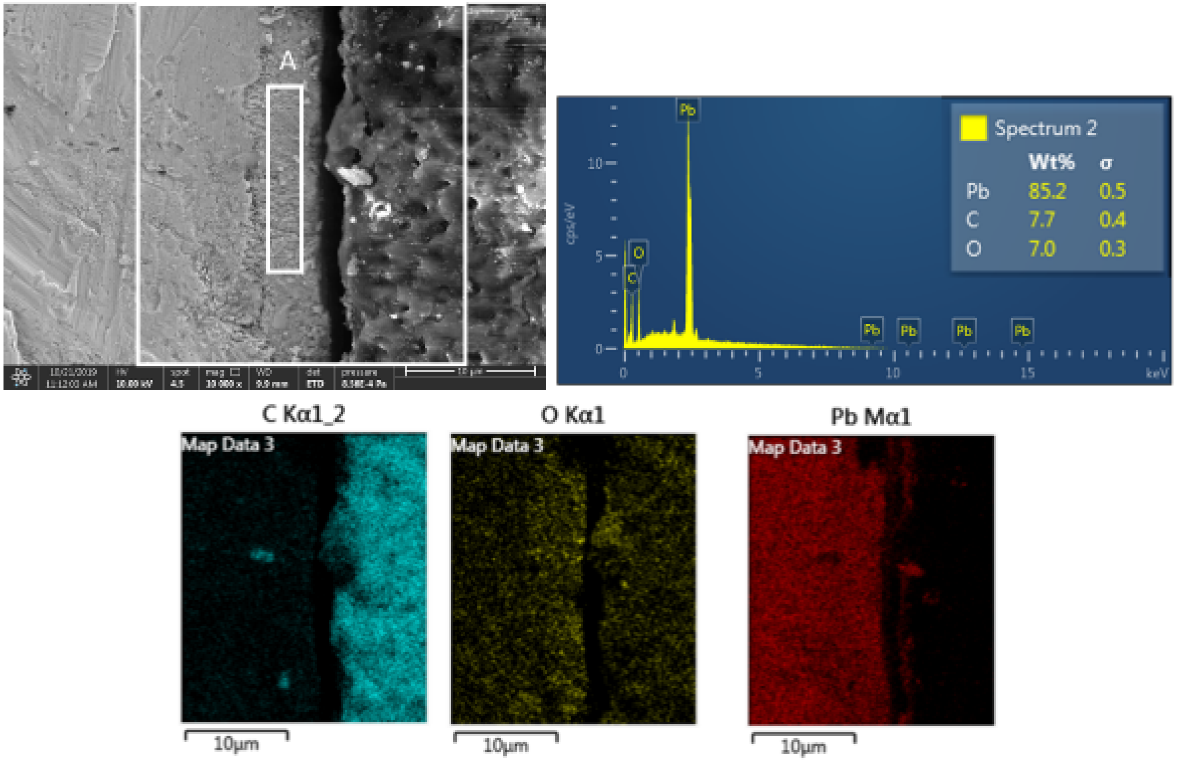
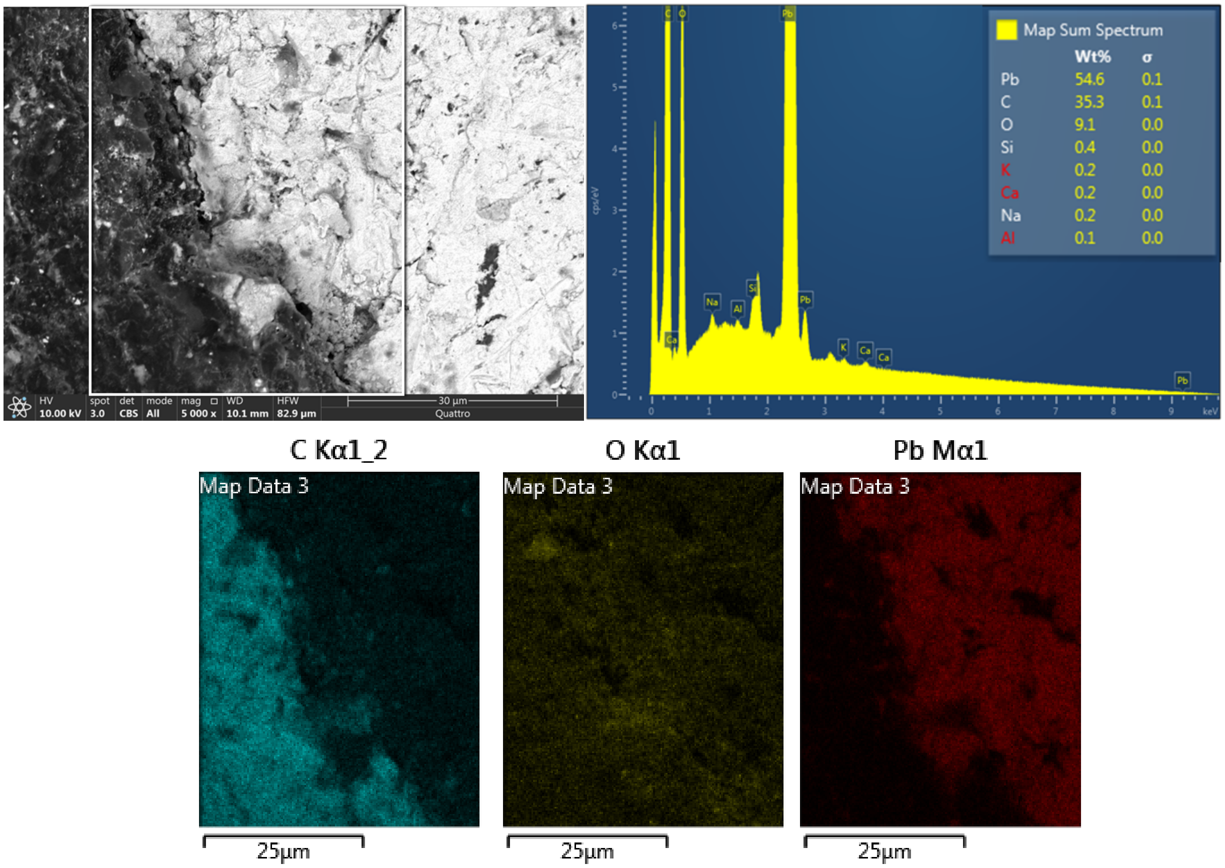


Figure B.11 (Top left) The SEM image of the lead pipe cross-section from TP3 with the highlighted region on which EDS was conducted; (top right) Semi-quantitative analysis of elements present on the scale surface at A; (bottom) mapping of the most abundant elements indicated by EDS (i.e. Pb, C, O) on the highlighted region on the SEM Image.



Map Sum Spectrum

	Wt%	σ
Pb	54.6	0.1
C	35.3	0.1
O	9.1	0.0
Si	0.4	0.0
K	0.2	0.0
Ca	0.2	0.0
Na	0.2	0.0
Al	0.1	0.0

Figure B.12 (Top left) The SEM image of the lead pipe cross-section from TP4 with the highlighted region on which EDS was conducted; (top right) Semi-quantitative analysis of elements present on the scale surface; (bottom) mapping of the most abundant elements indicated by EDS (i.e Pb, C, O) in the highlighted region of the SEM Image.

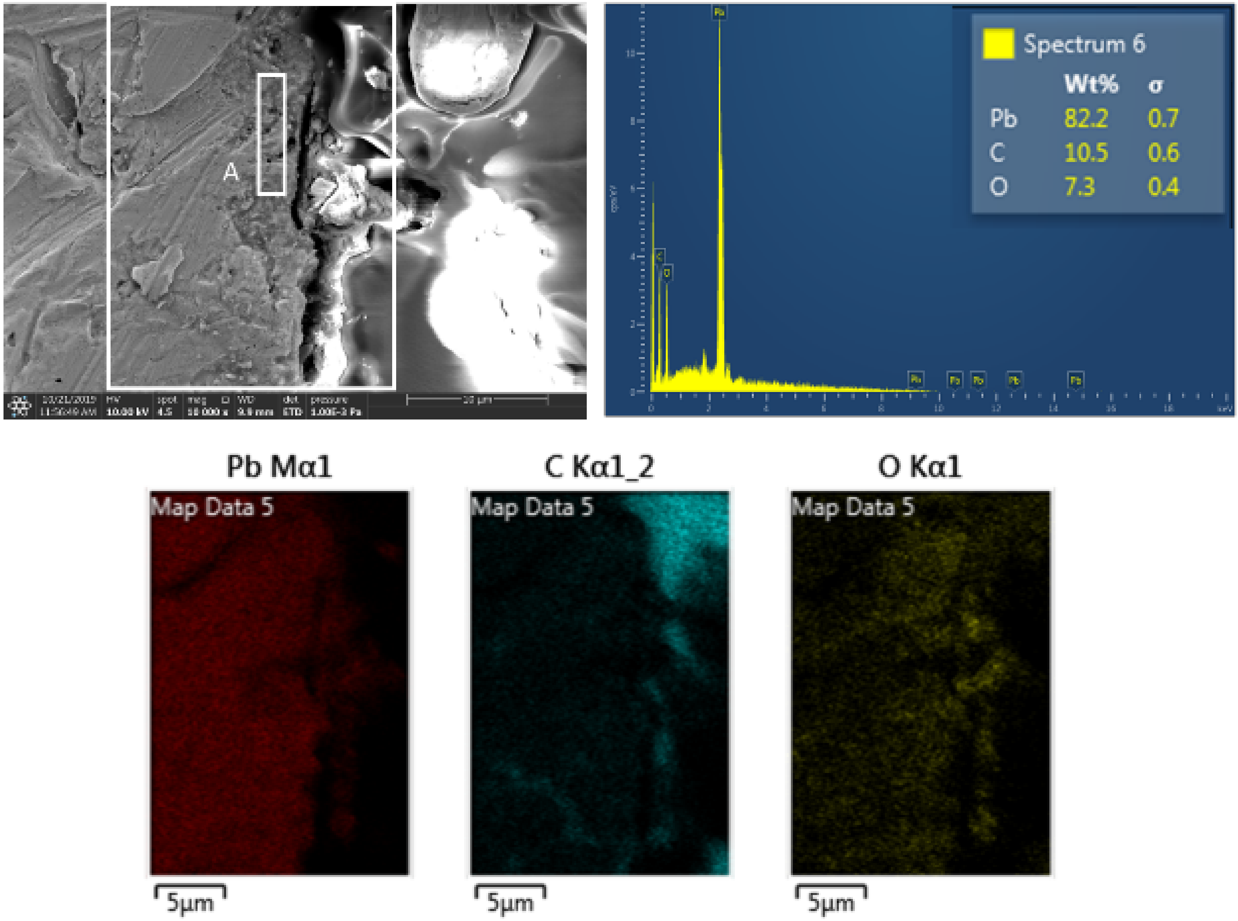


Figure B.13 (Top left) The SEM image of the lead pipe cross-section from TP5 with the highlighted region on which EDS was conducted; (top right) Semi-quantitative analysis of elements present on the scale surface at A; (bottom) mapping of the most abundant elements indicated by EDS (i.e. Pb, C, O) on the highlighted region on the SEM Image.

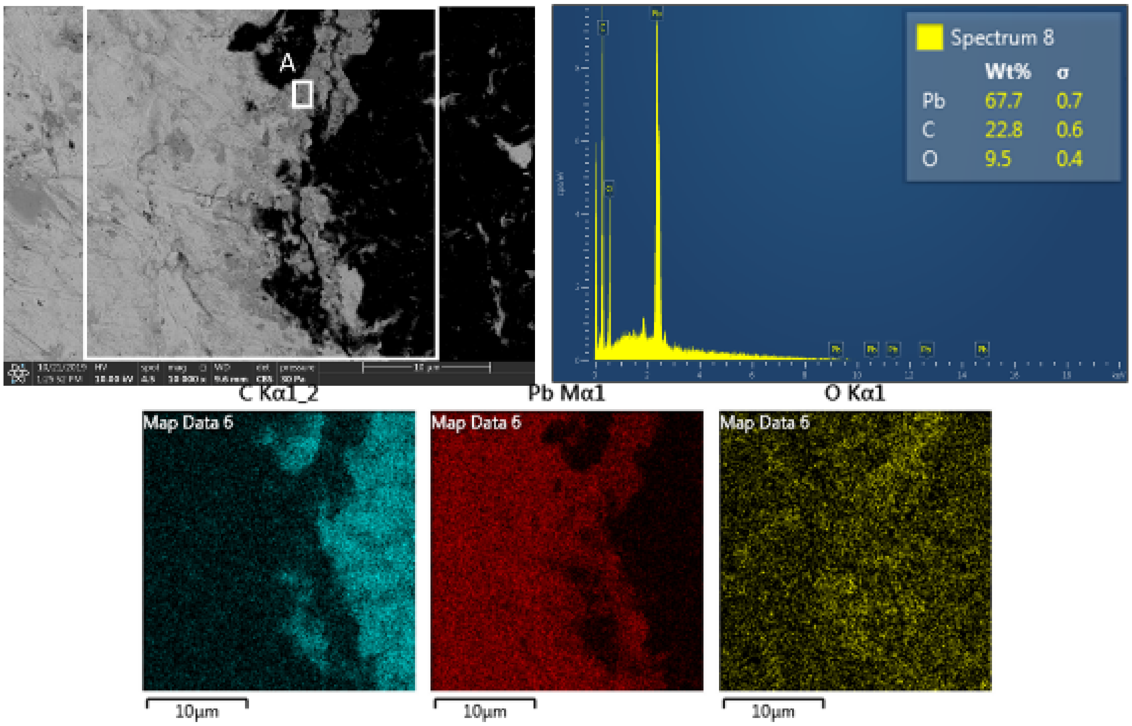
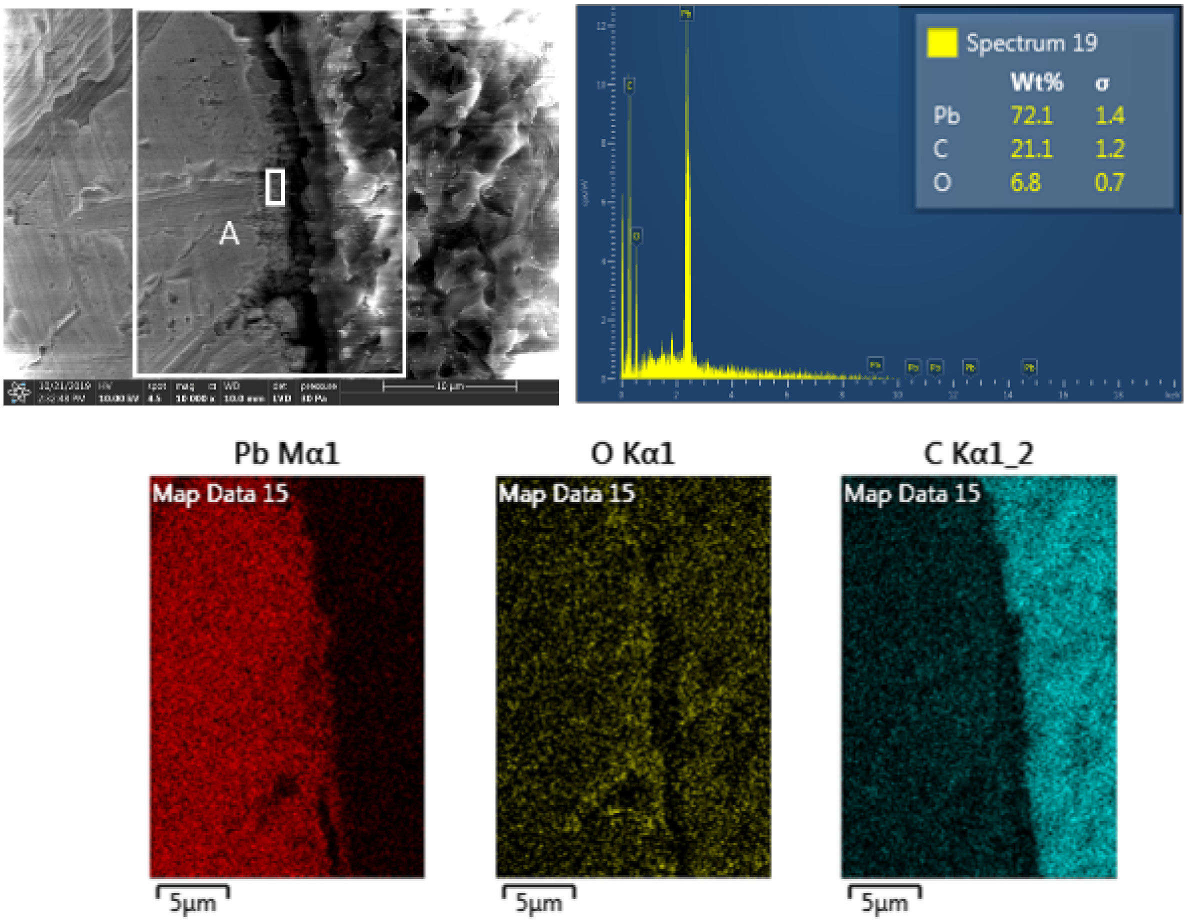


Figure B.14 (Top left) The SEM image of the lead pipe cross-section from TP6 with the highlighted region on which EDS was conducted; (top right) Semi-quantitative analysis of elements present on the scale surface at A; (bottom) mapping of the most abundant elements indicated by EDS (i.e. Pb, C, O) on the highlighted region on the SEM Image.



Spectrum 19

	Wt%	σ
Pb	72.1	1.4
C	21.1	1.2
O	6.8	0.7

Figure B.15 (Top left) The SEM image of the lead pipe cross-section from TP7 with the highlighted region on which EDS was conducted; (top right) Semi-quantitative analysis of elements present on the scale surface at A; (bottom) mapping of the most abundant elements indicated by EDS (i.e. Pb, C, O) on the highlighted region on the SEM Image.

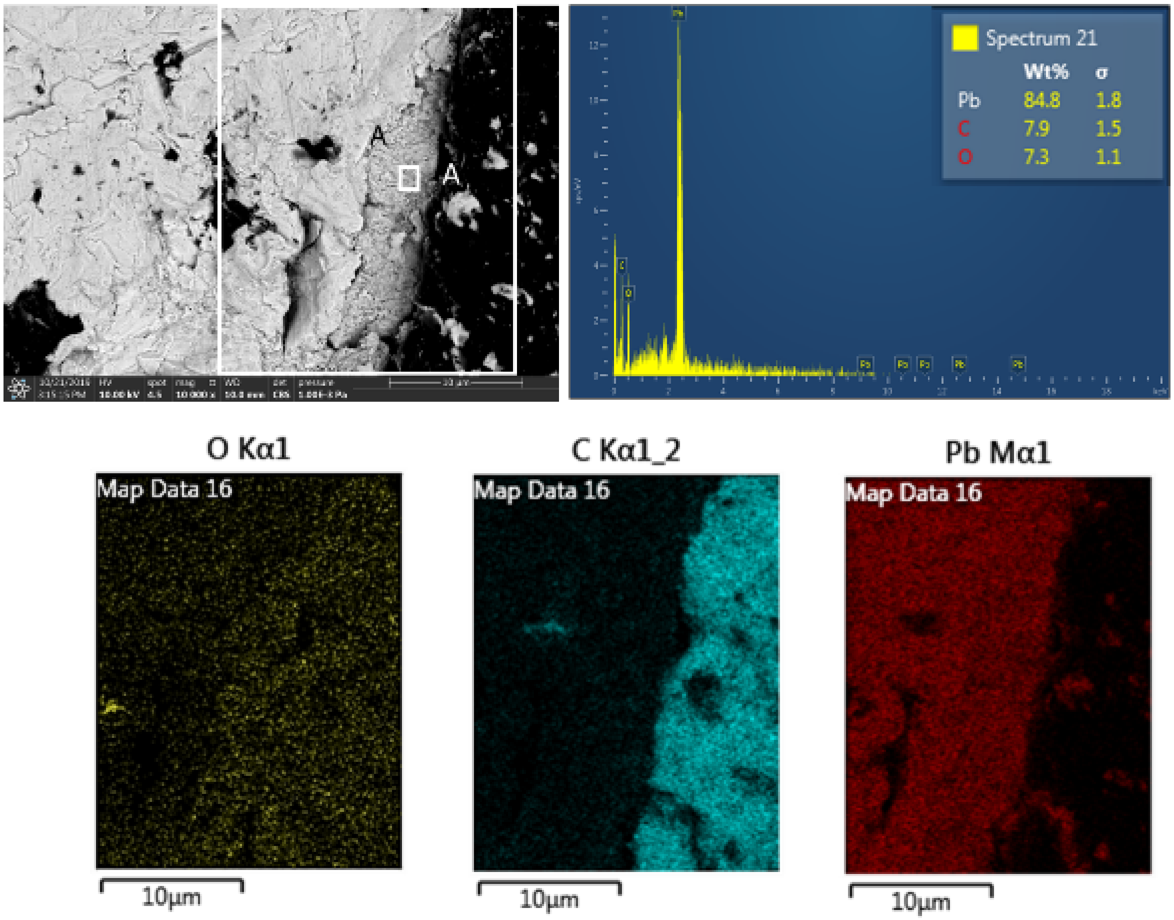


Figure B.16 (Top left) The SEM image of the lead pipe cross-section from TP8 with the highlighted region on which EDS was conducted; (top right) Semi-quantitative analysis of elements present on the scale surface at A; (bottom) mapping of the most abundant elements indicated by EDS (i.e. Pb, C, O) on the highlighted region on the SEM Image.

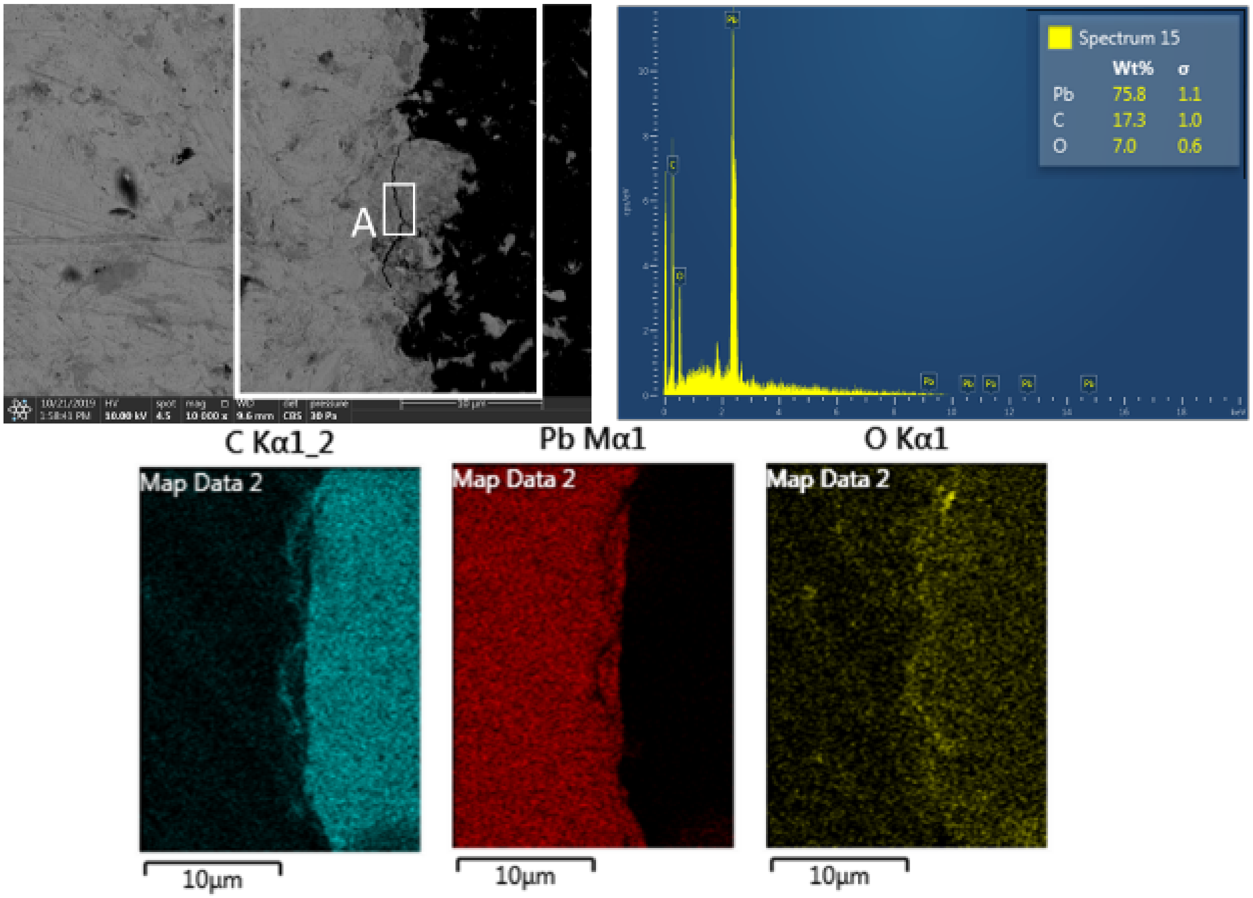
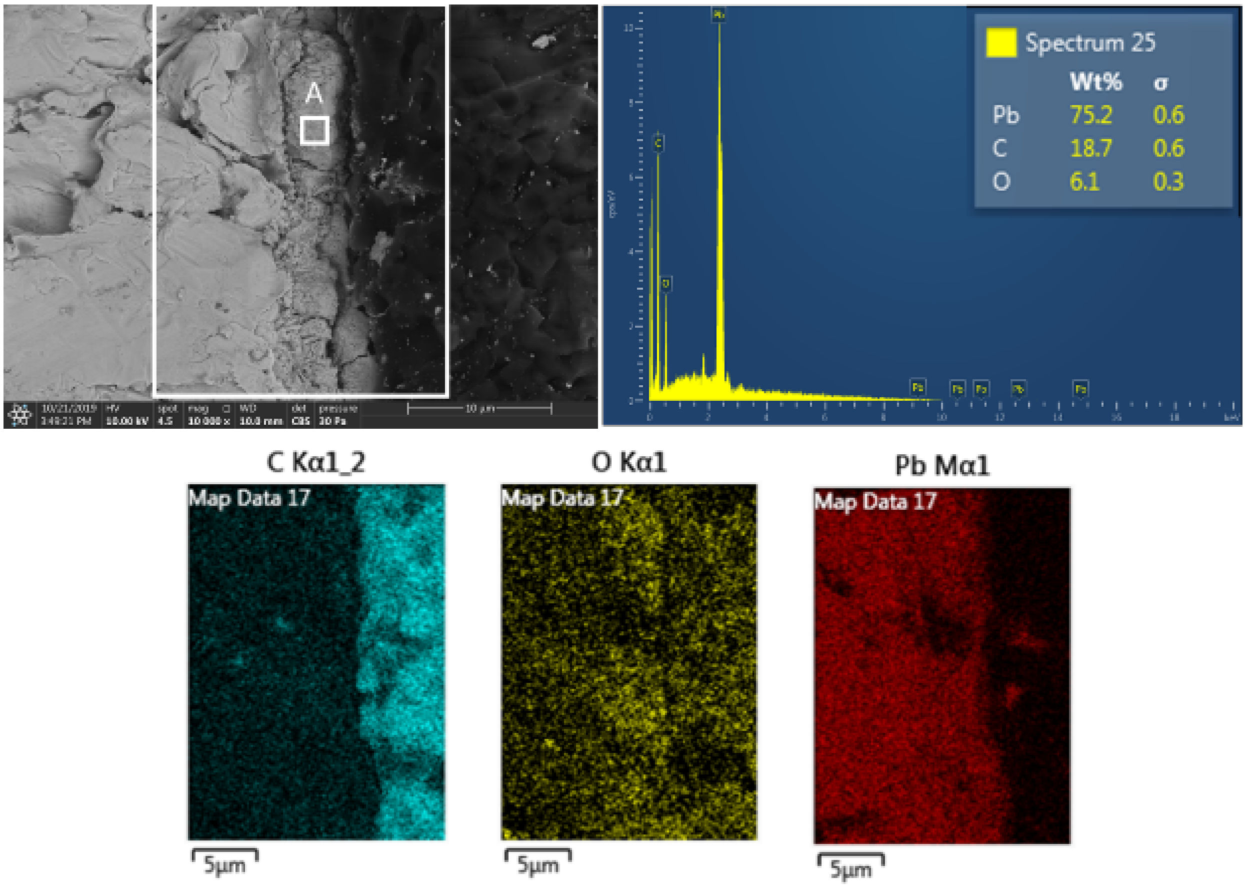


Figure B.17 (Top left) The SEM image of the lead pipe cross-section from TP9 with the highlighted region on which EDS was conducted; (top right) Semi-quantitative analysis of elements present on the scale surface at A; (bottom) mapping of the most abundant elements indicated by EDS (i.e. Pb, C, O) on the highlighted region on the SEM Image.



	Wt%	σ
Pb	75.2	0.6
C	18.7	0.6
O	6.1	0.3

Figure B.18 (Top left) The SEM image of the lead pipe cross-section from TP10 with the highlighted region on which EDS was conducted; (top right) Semi-quantitative analysis of elements present on the scale surface at A; (bottom) mapping of the most abundant elements indicated by EDS (i.e. Pb, C, O) on the highlighted region on the SEM Image.

Appendix C

Raw Data for Chapter 3

Galvanic Current (μA)

Test Piece	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12	Week 13
1	34.0	32.5	28.0	24.6	24.1	17.2	18.3	22.1	20.4	20.3	21.0	23.5	24.7
2	26.7	25.4	24.6	24.5	25.6	28.1	28.3	29.0	26.4	26.2	29.3	26.4	26.6
3	66.3	61	60.0	64.2	72.0	86.1	71.8	67.2	68.6	64.9	74.5	72.5	70.0
4	40.4	38.3	36.0	34.4	32.8	34.0	35.6	36.6	33.6	32.3	36.1	27.5	36.8
5	16.5	18.9	19.1	21.9	27.6	26.7	28.5	25.5	23.7	25.0	25.5	24.8	30.9
6	32.6	33.9	27.6	22.1	19.5	17.7	19.0	19.4	18.7	22.5	18.9	19.3	28.1
7	62.5	50.4	52.5	58.1	50.9	55.1	55.9	52.7	52.0	46.3	51.5	49.9	51.9
8	61.7	57.3	56.9	59.3	56.9	58.6	55.8	55.2	54.5	50.9	57.3	53.5	56.6
9	48.6	51.8	45.3	46.7	52.3	53.0	55.2	50.4	48.6	41.3	44.4	43.1	43.2
10	46.6	47.9	46.7	45.1	46.2	42.6	42.8	39.6	39.6	39.2	43.2	38.9	41.3

🟦 Duplicated measurement

Galvanic Current (µA)

Test Piece	Week 14	Week 15	Week 16	Week 17	Week 18	Week 19	Week 20
1	25.4	26.1	27.7	27.7	27.2	28.7	27.1
2	26.1	26.2	24.9	25.6	25.3	26.6	27.5
3	73.4	79.1	85.2	74.1	77.8	76.0	74.0
4	34.5	25.5	30.2	28.4	30.6	29.6	31.8
5	27.8	26.1	28.0	25.1	24.9	25.0	27.7
6	19.7	18.9	18.9	19.0	18.5	18.5	18.9
7	51.6	49.1	44.3	51.2	46.4	49.5	45.7
8	53.7	53.7	53.0	51.8	56.0	50.5	50.3
9	43.3	41.0	41.9	41.1	40.1	41.7	43.9
10	39.0	36.3	38.0	36.0	39.1	38.2	39.7

🟦 Duplicated measurement

Total Lead (μg/L) - Weekly Composite Samples

Test Piece	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12	Week 13
1	565.1	1537	605.9	482.1	353.4	388.0	488.3	1587	1010	374.3	844.4	531.1	598.1
2	3347	3251	3929	3023	2787	2534	4584	4036	3916	3209	4045	3808	3872
3	4530	6684	6959	4576	3905	3830	5188	21255	9503	7578	32760	6234	12630
4	1497	2876	2634	1805	1070	515.6	1290	13920	23070	1547	10315	784.0	2849
5	3810	5700	5462	4488	4806	3788	6799	20720	5910	12340	6920	7876	6781
6	1619	2032	1168	766.7	525.7	425.8	271.5	1920	3751	472.9	4216	592.1	2135
7	3340	5705	5963	2824	1187	1516	27620	14540	5303	1126	6452	1090	10000
8	1725	1085	1200	634.1	821.7	988.5	1907	1206	1278	1196	1137	1463	1724
9	2287	2283	1522	1184	1270	1382	1761	3228	4866	2748	3874	2660	3057
10	1526	1665	1491	1254	1276	1335	1141	1579	1419	1446	1452	1296	1288
FB	0.268	2.835	0.352	0.281	0.035	0.061	-0.03	-0.028	0.121	10.07	-0.018	0.029	-0.115

🟦	Duplicated measurement
FB	Field blank

Total Lead (µg/L) - Weekly Composite Samples

Test Piece	Week 14	Week 15	Week 16	Week 17	Week 18	Week 19	Week 20
1	865.8	758.4	620.4	534.5	645.7	428.2	646.2
2	3164	3764	4409	3622	4307	3818	4476
3	13150	12940	29660	14100	16800	10000	29310
4	5251	4213	4865	5170	1765	1502	2731
5	7098	6425	7401	6238	5869	5863	7901
6	2270	1852	2606	2531	5215	1507	2184
7	9115	12850	11240	12190	12820	15410	7464
8	1430	1129	937.1	680.7	638.0	689.4	629.6
9	2846	3071	2565	3637	2441	2660	3029
10	1405	1334	1441	1270	1264	1357	1363
FB	0.897	-0.052	0.001	0.063	-0.052	0.009	0.080

🟦 Duplicated measurement
FB Field blank

Lead (µg/L) - Samples from Individual 48-Hour Stagnation Events

	Week 4			Week 8			Week 10			Week 12		
Test Piece	Dissolved	Total	Particulate	Dissolved	Total	Particulate	Dissolved	Total	Particulate	Dissolved	Total	Particulate
1	172	456	285	181.4	462.5	281.1	172.5	362.9	190.4	249.9	451.4	201.6
2	2217	3177	960	2691	3265	574	2405	2877	472	2538	4620	2082
3	2913	4721	1808	3795	18310	14515	3932	8461	4529	4422	8354	3932
4	193	1286	1093	130.1	12750	12619.9	131.5	575.1	443.6	96.77	1364	1267
5	2697	4360	1664	2813	5461	2648	4535	10230	5695	2967	7750	4783
6	89	630	541	188.1	1633	1444.9	113.3	307.1	193.8	114.2	694.7	580.5
7	90	3397	3307	148.2	7648	7499.8	66.76	1881	1814.24	99.82	2001	1901
8	461	577	116	503.4	676.1	172.7	649.1	834.9	185.8	727.5	1339	611.5
9	924	1195	271	1754	2475	721	2063	3011	948	1620	3735	2115
10	1073	1203	130	1105	1428	323	1196	1354	158	1058	1287	229.0
FB	0.028	0.096	0.068	0.049	-0.028	-0.077	0.020	0.021	0.001	0.005	-0.100	-0.105
FIL	3.785	-	-	-0.017	-	-	0.041	-	-	0.011	-	-

🟦	Duplicated measurement
FB	Field blank
FIL	Filter blank

Lead (µg/L) - Samples from Individual 48-Hour Stagnation Events

	Week 14			Week 16			Week 19			Week 20		
Test Piece	Dissolved	Total	Particulate	Dissolved	Total	Particulate	Dissolved	Total	Particulate	Dissolved	Total	Particulate
1	161.2	704.1	542.9	156.0	750.1	594.1	129.6	356.1	226.5	106.2	974.5	868.3
2	1955	3159	1204	2291	6219	3928	2161	3923	1762	2220	5644	3424
3	3966	20720	16754	4587	33170	28583	3802	9946	6144	3729	72120	68391
4	124.4	4054	3930	149.3	9708	9559	113.9	491.3	377.4	116.3	1563	1446.7
5	2950	6748	3798	3063	8104	5041	2683	6041	3358	2658	12430	9772
6	121.3	1152	1031	136.3	3927	3791	108.5	3019	2910.5	104.1	824.6	720.5
7	170.1	7910	7740	171.4	20610	20439	171.9	29200	29028.1	201.1	4362	4160.9
8	808.5	1144	335.5	617.8	946.3	328.5	445.2	541.1	95.9	407.4	561.3	153.9
9	1619	2709	1090	1577	2989	1412	1465	3020	1555	1629	4071	2442
10	1233	1550	317	1271	1702	431.0	1098	1293	195	1092	1391	299
FB	-0.082	-0.107	-0.025	-0.083	-0.111	-0.028	-0.037	0.038	0.075	-0.009	-0.060	-0.051
FIL	-0.080	-	-	-0.100	-	-	-0.084	-	-	0.054	-	-

🟦	Duplicated measurement
FB	Field blank
FIL	Filter blank

Total Copper (µg/L) - Weekly Composite Samples

Test Piece	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12	Week 13
1	19.76	13.1	21.44	15.32	5.86	5.325	5.650	6.561	8.061	7.579	9.303	21.34	4.940
2	114	108.2	93.92	75.07	71.52	66.91	248.2	71.25	353.3	55.32	71.39	71.56	51.66
3	799.3	608	464.7	352.1	407.4	603.2	405.3	371.4	308.8	311.9	309.1	270.8	465.5
4	21.91	20.98	20.95	16.93	22.22	20.24	38.09	35.49	23.95	23.50	52.97	29.46	27.47
5	132	122.4	103.5	98.32	85.26	68.29	73.51	102.2	60.23	120.8	74.84	82.06	70.29
6	14.22	6.488	6.25	26.14	7.809	6.155	6.812	5.615	4.968	3.452	13.39	4.301	12.53
7	44.18	55.48	45.26	43.57	42.2	37.27	53.43	60.72	61.77	44.46	71.28	45.78	30.74
8	141.6	124.6	138.9	118.2	109.5	121.8	111.6	101	114.5	96.57	79.94	66.09	78.16
9	127.3	162.5	113.3	75.97	112.4	84.18	95.1	94.68	75.53	79.40	64.00	65.86	66.14
10	88.84	112.4	100.7	76.47	87.31	69.6	84.53	64.13	68.06	66.34	51.44	59.68	58.42
FB	0.189	2.568	0.401	0.458	0.527	0.294	0.003	0.046	-0.182	0.602	-0.467	-0.409	-0.116

🟦	Duplicate measurement
FB	Field blank

Total Copper (µg/L) - Weekly Composite Samples

Test Piece	Week 14	Week 15	Week 16	Week 17	Week 18	Week 19	Week 20
1	6.149	14.05	10.04	7.850	10.61	8.237	16.61
2	53.43	52.37	54.45	55.48	58.32	46.72	54.88
3	351.5	439.0	420.3	798.8	347.1	371.2	344.9
4	29.68	23.45	21.91	18.69	27.07	17.53	23.64
5	58.75	64.65	63.04	55.76	58.29	61.96	58.81
6	6.640	3.701	3.085	4.127	3.813	6.404	4.236
7	35.27	27.90	58.84	62.93	47.25	49.31	184.3
8	77.66	72.66	77.57	77.16	80.80	96.99	83.29
9	64.02	66.68	65.22	58.99	65.89	67.28	85.56
10	59.33	56.39	58.64	53.54	59.89	60.02	58.97
FB	0.607	0.068	0.119	0.523	0.091	0.761	0.084

🟦	Duplicate measurement
FB	Field blank

Copper (µg/L) - Samples from Individual Stagnation Events

	Week 4			Week 8			Week 10			Week 12		
Test Piece	Dissolved	Total	Particulate	Dissolved	Total	Particulate	Dissolved	Total	Particulate	Dissolved	Total	Particulate
1	2.202	11.06	8.858	9.036	5.755	-3.281	2.904	9.619	6.715	1.364	4.576	3.212
2	58	71.44	13.44	61.92	61.26	-0.66	39.48	51.99	12.51	52.38	75.15	22.77
3	364.9	416.4	51.5	294.2	337.2	43	340.0	404.7	64.70	217.9	281.6	63.7
4	11.97	16.45	4.48	17.81	24.86	7.05	12.18	16.15	3.970	10.93	30.60	19.67
5	42.33	84.95	42.63	30.76	60.21	29.45	23.02	110.00	86.98	31.45	97.67	66.22
6	1.515	5.061	3.546	4.124	13.78	9.656	0.729	3.602	2.873	0.479	3.250	2.771
7	30.29	41.38	11.09	40.96	140.2	99.24	24.52	35.44	10.92	48.32	63.78	15.46
8	101.8	121.9	20.1	76.19	107.7	31.51	68.82	89.84	21.02	52.99	70.72	17.73
9	55.78	70.12	14.34	59.78	80.2	20.42	45.32	65.22	19.90	45.63	63.10	17.47
10	55.88	73.89	18.01	39.25	52.36	13.11	44.23	61.52	17.29	38.66	58.76	20.1
FB	0.053	0.022	-0.031	-0.019	-0.06	-0.041	-0.294	4.082	4.376	-0.295	-3.979	-3.684
FIL	0.522	-	-	-0.041	-	-	-0.451	-	-	-0.436	-	-

🟦	Duplicate measurement
FB	Field blank
FIL	Filter blank

Copper (µg/L) - Samples from Individual Stagnation Events

	Week 14			Week 16			Week 19			Week 20		
Test Piece	Dissolved	Total	Particulate	Dissolved	Total	Particulate	Dissolved	Total	Particulate	Dissolved	Total	Particulate
1	1.220	4.746	3.526	2.547	10.22	7.673	1.061	9.512	8.452	3.058	22.8	19.74
2	40.54	201.5	161.0	44.36	56.17	11.81	38.15	45.22	7.070	42.42	53.83	11.41
3	314.5	354.6	40.10	507.0	598.5	91.5	334.9	397.3	62.4	234.2	351.0	116.8
4	16.23	25.05	8.820	8.114	19.96	11.846	9.303	21.25	11.947	9.981	17.87	7.88
5	26.04	56.84	30.8	29.48	73.16	43.68	23.99	57.32	33.33	29.10	63.94	34.84
6	1.392	5.891	4.499	0.867	3.493	2.626	0.678	20.59	19.91	1.225	27.42	26.20
7	32.30	42.05	9.755	53.03	124.8	71.77	19.75	32.05	12.300	69.03	91.72	22.69
8	64.79	84.63	19.84	60.52	77.52	17	88.30	95.02	6.720	61.30	96.92	35.62
9	54.82	71.37	16.55	56.71	76.39	19.68	55.18	68.91	13.730	69.93	115.0	45.07
10	45.59	61.52	15.93	45.42	61.81	16.385	46.50	59.41	12.91	43.33	68.55	25.22
FB	-0.116	-0.051	0.065	-0.117	-0.053	0.064	0.258	0.650	0.392	0.086	0.062	-0.02
FIL	-0.089	-	-	-0.308	-	-	-0.076	-	-	0.322	-	-

🟦	Duplicate measurement
FB	Field blank
FIL	Filter blank

pH

	Week 1					Week 2					Week 3				
Test Piece	U1	U2	U3	S3	Change	U1	U2	U3	S3	Change	U1	U2	U3	S3	Change
1	6.93	7.11	6.91	9.18	2.27	6.95	7.08	7.18	9.17	1.99	7.06	7.12	7.19	9.01	1.82
2	8.64	8.4	8.33	8.89	0.56	8.55	8.41	8.39	8.85	0.46	8.49	8.54	8.59	8.90	0.31
3	7.00	7.11	7.16	7.6	0.44	7.03	7.12	7.14	7.68	0.54	7.16	7.19	7.09	7.60	0.51
4	8.33	8.37	8.48	8.77	0.29	8.45	8.51	8.57	8.73	0.16	8.41	8.41	8.41	8.59	0.18
5	6.97	7.06	7.08	7.83	0.75	6.95	7.13	6.98	7.88	0.90	7.07	7.15	7.18	7.89	0.71
6	8.51	8.47	8.43	9.1	0.67	8.3	8.64	8.5	8.91	0.41	8.33	8.41	8.43	8.37	-0.06
7	6.95	7.05	7.03	7.62	0.59	6.99	7.19	7.15	7.62	0.47	7.04	7.18	7.05	7.57	0.52
8	8.3	8.32	8.41	8.34	-0.07	8.38	8.44	8.52	8.36	-0.16	8.43	8.42	8.39	8.37	-0.02
9	7.69	7.84	7.7	8.21	0.51	7.78	7.91	7.56	8.14	0.58	7.86	7.91	7.92	8.36	0.44
10	7.71	7.83	7.71	8.23	0.52	7.78	7.94	7.71	8.16	0.45	7.90	7.94	7.95	8.34	0.39
FB	6.03	-	-	-	-	-	-	-	6.11	-	-	-	5.83	5.82	-0.01

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
FB	Field blank

pH

	Week 4					Week 5					Week 6				
Test Piece	U1	U2	U3	S3	Change	U1	U2	U3	S3	Change	U1	U2	U3	S3	Change
1	6.95	7.06	7.10	8.86	1.76	6.99	7.13	7.18	8.78	1.60	6.98	7.09	7.20	8.43	1.23
2	8.54	8.42	8.36	8.96	0.60	8.48	8.33	8.64	8.98	0.33	8.63	8.54	8.42	8.99	0.57
3	7.01	7.17	7.15	7.77	0.62	7.08	7.10	7.10	7.68	0.58	7.07	7.11	6.87	7.63	0.76
4	8.42	8.43	8.52	8.58	0.06	8.40	8.45	8.48	8.55	0.07	8.41	8.41	8.44	8.56	0.12
5	6.96	7.02	7.18	7.89	0.71	6.97	7.12	6.98	8.01	1.03	6.97	7.09	7.15	8.02	0.87
6	8.36	8.45	8.47	8.28	-0.19	8.48	8.40	8.37	8.20	-0.17	8.50	8.39	8.41	8.19	-0.22
7	7.01	7.14	7.11	7.59	0.48	7.04	7.06	7.09	7.65	0.56	7.03	7.17	7.08	7.67	0.59
8	8.37	8.39	8.42	8.35	-0.06	8.38	8.40	8.40	8.28	-0.12	8.37	8.37	8.40	8.36	-0.04
9	7.81	7.86	7.93	8.37	0.44	7.81	7.95	7.58	8.25	0.67	7.81	7.88	7.80	8.35	0.55
10	7.81	7.90	7.92	8.33	0.41	7.83	7.94	7.67	8.18	0.51	7.83	7.92	7.94	8.33	0.38
FB	-	-	5.99	6.08	0.09	-	-	5.97	5.88	-0.09	-	-	6.09	6.11	0.02

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
FB	Field blank

pH

	Week 7					Week 8					Week 9				
Test Piece	U1	U2	U3	S3	Change	U1	U2	U3	S3	Change	U1	U2	U3	S3	Change
1	7.01	7.12	7.17	8.69	1.52	7.07	7.13	7.11	8.91	1.80	7.05	6.96	6.98	8.22	1.24
2	8.67	8.53	8.43	8.99	0.56	8.63	8.55	8.37	9.11	0.74	8.52	8.39	8.51	8.89	0.39
3	7.11	7.05	7.12	7.77	0.65	7.05	7.00	7.05	7.87	0.82	7.11	7.05	7.14	7.81	0.67
4	8.41	8.44	8.49	8.59	0.11	8.45	8.48	8.50	8.65	0.15	8.40	8.44	8.44	8.42	-0.02
5	6.99	7.15	7.15	8.31	1.16	6.96	7.09	7.05	8.26	1.21	7.03	7.19	7.20	8.17	0.97
6	8.50	8.43	8.42	8.21	-0.21	8.52	8.52	8.49	8.09	-0.40	8.48	8.43	8.42	8.16	-0.26
7	7.04	7.18	7.02	7.34	0.32	7.05	7.02	7.03	7.46	0.43	7.07	7.02	7.06	7.78	0.72
8	8.40	8.40	8.41	8.31	-0.10	8.47	8.51	8.43	8.23	-0.20	8.38	8.43	8.39	8.27	-0.12
9	7.82	7.91	7.67	8.27	0.60	7.89	7.70	7.70	8.31	0.61	7.83	7.91	7.77	8.32	0.55
10	7.82	7.94	7.90	8.17	0.27	7.90	7.69	7.94	8.38	0.44	7.81	7.93	7.92	8.33	0.41
FB	-	-	6.20	5.62	-0.58	-	-	6.49	5.86	-0.63	-	-	6.06	5.93	-0.13

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
FB	Field blank

pH

	Week 10					Week 11					Week 12				
Test Piece	U1	U2	U3	S3	Change	U1	U2	U3	S3	Change	U1	U2	U3	S3	Change
1	7.05	7.11	7.15	8.58	1.43	6.98	7.18	7.15	8.60	1.45	6.99	6.97	7.20	8.71	1.51
2	8.41	8.55	8.43	8.92	0.49	8.69	8.57	8.54	9.11	0.57	8.63	8.56	8.55	8.93	0.38
3	7.07	7.00	7.03	7.75	0.72	7.04	7.16	7.10	7.62	0.53	7.11	7.12	7.05	7.82	0.77
4	8.42	8.45	8.44	8.61	0.17	8.37	8.42	8.44	8.61	0.17	8.40	8.50	8.41	8.57	0.16
5	6.83	6.92	6.96	7.77	0.81	7.00	7.13	7.18	8.21	1.03	7.03	6.96	7.16	8.06	0.90
6	8.46	8.40	8.43	8.09	-0.34	8.47	8.42	8.37	8.23	-0.14	8.48	8.55	8.35	8.11	-0.24
7	7.06	7.19	7.03	7.62	0.59	7.01	7.19	7.06	7.52	0.46	7.04	7.10	7.01	7.66	0.65
8	8.38	8.37	8.38	8.26	-0.12	8.35	8.39	8.38	8.23	-0.15	8.36	8.49	8.34	8.25	-0.09
9	7.61	7.75	7.88	8.29	0.41	7.75	7.87	7.90	8.32	0.42	7.81	7.72	7.89	8.31	0.42
10	7.64	7.74	7.74	8.22	0.48	7.75	7.86	7.88	8.28	0.40	7.81	7.73	7.91	8.29	0.38
FB	-	-	5.85	5.82	-0.03	-	-	5.97	-	-	5.88	-	5.90	5.89	-0.01

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
FB	Field blank

pH

	Week 13					Week 14					Week 15				
Test Piece	U1	U2	U3	S3	Change	U1	U2	U3	S3	Change	U1	U2	U3	S3	Change
1	7.04	7.11	7.17	8.85	1.68	7.12	7.17	7.17	8.76	1.59	7.06	7.18	6.92	8.42	1.51
2	8.50	8.55	8.52	8.96	0.44	8.58	8.42	8.56	8.89	0.33	8.48	8.43	8.54	8.77	0.23
3	7.05	6.98	7.09	7.79	0.70	7.16	7.01	7.13	7.78	0.65	7.06	7.05	7.00	7.62	0.62
4	8.35	8.37	8.42	8.61	0.19	8.46	8.43	8.51	8.55	0.04	8.40	8.48	8.43	8.43	0.00
5	7.02	7.15	7.19	8.29	1.10	7.07	7.13	7.16	8.17	1.01	6.96	7.14	7.06	7.88	0.82
6	8.46	8.33	8.36	8.09	-0.27	8.56	8.48	8.50	8.19	-0.31	8.48	8.51	8.41	8.06	-0.35
7	7.04	7.20	7.07	7.80	0.73	7.14	7.12	7.07	7.79	0.72	7.18	7.16	7.18	7.63	0.45
8	8.35	8.36	8.41	8.37	-0.04	8.44	8.40	8.47	8.34	-0.13	8.37	8.43	8.40	8.19	-0.21
9	7.75	7.82	7.91	8.42	0.51	7.90	7.90	7.70	8.20	0.50	7.78	7.91	7.89	8.21	0.32
10	7.75	7.83	7.94	8.40	0.46	7.87	7.88	7.70	8.21	0.51	7.81	7.93	7.94	8.19	0.25
FB	-	-	6.02	6.07	0.05	-	-	5.95	5.95	0.00	-	-	5.82	5.74	-0.08

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
FB	Field blank

pH

	Week 16					Week 17					Week 18				
Test Piece	U1	U2	U3	S3	Change	U1	U2	U3	S3	Change	U1	U2	U3	S3	Change
1	6.98	7.20	7.03	8.55	1.52	7.03	6.94	7.20	8.91	1.71	6.95	7.11	7.09	8.73	1.64
2	8.48	8.43	8.37	8.75	0.38	8.55	8.50	8.55	8.85	0.30	8.41	8.30	8.44	8.77	0.33
3	7.10	7.04	7.09	7.52	0.44	7.08	7.10	7.10	7.76	0.66	7.01	7.18	7.06	7.63	0.57
4	8.38	8.48	8.59	8.48	-0.11	8.38	8.50	8.47	8.45	-0.02	8.34	8.47	8.43	8.43	0.00
5	6.99	7.15	7.00	7.81	0.81	6.95	7.19	7.18	8.02	0.84	6.96	7.13	7.08	7.85	0.77
6	8.43	8.47	8.52	7.98	-0.54	8.39	8.44	8.37	8.03	-0.34	8.41	8.43	8.37	8.02	-0.35
7	7.03	7.01	7.19	7.60	0.41	7.01	7.06	7.09	7.63	0.54	6.98	7.19	7.02	7.50	0.48
8	8.31	8.42	8.57	8.24	-0.33	8.32	8.42	8.40	8.21	-0.19	8.41	8.45	8.41	8.13	-0.28
9	7.71	7.92	7.78	8.10	0.32	7.73	7.94	7.94	8.28	0.34	7.70	7.84	7.83	8.17	0.34
10	7.76	7.68	7.82	8.10	0.28	7.73	7.94	7.91	8.22	0.31	7.70	7.83	7.88	8.18	0.30
FB	-	-	6.09	5.91	-0.18	-	-	5.93	5.88	-0.05	-	-	6.16	6.22	0.06

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
FB	Field blank

pH

	Week 19					Week 20				
Test Piece	U1	U2	U3	S3	Change	U1	U2	U3	S3	Change
1	7.01	7.18	7.18	8.80	1.62	7.06	7.20	7.19	8.81	1.62
2	8.43	8.39	8.54	8.86	0.32	8.30	8.53	8.51	8.91	0.40
3	7.04	7.02	7.07	7.65	0.58	7.13	7.06	7.12	7.77	0.65
4	8.35	8.45	8.50	8.50	0.00	8.33	8.43	8.44	8.42	-0.02
5	6.93	7.14	7.20	7.98	0.78	7.05	7.20	7.17	7.97	0.80
6	8.40	8.45	8.59	8.06	-0.53	8.43	8.47	8.38	8.07	-0.31
7	7.00	7.00	7.07	7.60	0.53	7.06	7.02	7.09	7.58	0.49
8	8.31	8.41	8.43	8.18	-0.25	8.34	8.41	8.36	8.15	-0.21
9	7.72	7.89	7.93	8.27	0.34	7.83	7.70	7.69	8.10	0.41
10	7.74	7.89	7.92	8.24	0.32	7.82	7.94	7.89	8.22	0.33
FB	-	-	5.92	5.95	0.03	-	-	6.09	5.91	-0.18

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
FB	Field blank

DIC (mg C/L) - Calculated Based on pH and Alkalinity

Test Piece	Week 1 - U	Week 1 - S	Week 1 Change	Week 5 - U	Week 5 - S	Week 5 Change	Week 9 - U
1	9.48	8.08	-1.39	10.69	8.42	-2.27	10.17
2	11.33	12.52	1.19	11.90	11.97	0.06	10.93
3	77.69	64.89	-12.80	78.86	65.84	-13.02	74.79
4	75.74	75.14	-0.60	79.32	75.43	-3.90	76.93
5	11.65	10.34	-1.30	11.06	9.74	-1.33	10.81
6	11.88	11.80	-0.08	10.47	13.50	3.03	10.95
7	77.21	63.74	-13.47	74.85	62.04	-12.81	74.07
8	79.20	77.14	-2.06	78.92	74.95	-3.97	78.92
9	43.35	42.42	-0.94	42.42	41.38	-1.04	43.34
10	43.79	41.41	-2.38	42.35	41.99	-0.36	43.90
FB	1.37	-	-	2	0.00	-	0

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
FB	Field blank

DIC (mg C/L) - Calculated Based on pH and Alkalinity

Test Piece	Week 9 - S	Week 9 Change	Week 13 - U	Week 13 - S	Week 13 Change	Week 17 - U	Week 17 - S
1	6.26	-3.91	7.37	7.91	0.54	10.81	9.26
2	11.60	0.67	10.94	12.44	1.51	11.39	13.03
3	65.10	-9.68	77.41	65.70	-11.71	78.86	67.84
4	73.04	-3.89	75.67	75.19	-0.49	77.48	76.75
5	10.14	-0.67	10.28	10.57	0.28	11.74	11.19
6	8.70	-2.25	10.48	8.24	-2.24	11.00	10.21
7	60.34	-13.73	74.28	60.74	-13.54	76.25	63.17
8	72.10	-6.82	78.07	73.21	-4.86	79.13	73.26
9	41.24	-2.09	42.13	41.53	-0.59	43.19	42.76
10	41.71	-2.19	42.13	41.81	-0.32	43.44	43.36
FB	-	-	-	1.30	-	-	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
FB	Field blank

DIC (mg C/L) - Calculated Based on pH and Alkalinity

Test Piece	Week 17 Change
1	-1.55
2	1.65
3	-11.02
4	-0.73
5	-0.55
6	-0.78
7	-13.07
8	-5.87
9	-0.43
10	-0.08
FB	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
FB	Field blank

DOC (mg C/L) - Measured using LC-OCD

	Week 3			Week 7			Week 12			Week 16		
Test Piece	U	S	Change	U	S	Change	U	S	Change	U	S	Change
1	-	-	-	-	-	-	-	-	-	-	-	-
2	7.424	7.418	-0.006	7.545	7.224	-0.321	7.400	7.288	-0.112	7.732	7.268	-0.464
3	8.276	7.184	-1.092	9.063	6.716	-2.347	7.255	6.800	-0.455	7.613	7.066	-0.547
4	-	-	-	-	0.135	-	0.063	-	-	-	0.119	-
5	7.482	6.182	-1.301	7.124	5.245	-1.879	7.034	5.055	-1.979	7.489	5.376	-2.113
6	-	-	-	-	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-	-	-	-	-
8	7.753	7.000	-0.753	7.932	6.786	-1.147	7.205	6.489	-0.716	7.437	6.821	-0.616
9	3.684	3.772	0.088	4.003	3.508	-0.495	3.567	3.553	-0.014	3.837	3.632	-0.206
10	3.651	3.782	0.131	3.701	3.586	-0.115	3.647	3.525	-0.122	3.729	3.530	-0.199
FIL	0.137	0.030	-0.107	0.025	0.038	0.013	0.044	0.111	0.067	0.024	0.037	0.013
FB	0.019	0.038	0.019	0.196	0.032	-0.164	0.043	0.043	0	0.028	0.025	-0.003

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
FIL	Filter blank
FB	Field blank

DOC (mg C/L) - Measured using LC-OCD

	Week 20		
Test Piece	U	S	Change
1	0.033	-	-
2	8.284	7.608	-0.676
3	8.245	7.592	-0.653
4	-	-	-
5	7.268	5.466	-1.802
6	-	-	-
7	-	-	-
8	7.182	6.839	-0.343
9	3.598	3.333	-0.265
10	3.553	3.457	-0.096
FIL	0.039	0.042	0.003
FB	0.019	0.035	0.016

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
FIL	Filter blank
FB	Field blank

DOC (mg C/L) - Measured using TOC Analyzer

		Week 20		
Test Piece	Target	U	S	Change
1	0	0.1	0.3	0.2
2	7	7.8	7.4	-0.4
3	7	8.1	7.4	-0.7
4	0	-	-	-
5	7	7.7	5.7	-2.05
6	0	-	-	-
7	0	-	-	-
8	7	7.0	6.5	-0.5
9	3.5	3.7	3.4	-0.25
10	3.5	3.6	3.4	-0.2
FIL	-	0.2	0.2	0
FB	-	0.2	0.2	0

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
FIL	Filter blank
FB	Field blank

TOC (mg C/L) - Measured using TOC Analyzer

	Week 20		
Test Piece	U	S	Change
1	0.2	0.3	0.1
2	8.0	7.8	-0.2
3	7.8	8.7	0.8
4	-	-	-
5	7.2	6.4	-0.8
6	-	-	-
7	-	-	-
8	7.1	6.9	-0.2
9	3.6	3.5	-0.1
10	3.5	3.5	0
FB	0.1	0.2	0.1

Alkalinity (mg $CaCO_3$/L)

	Week 1			Week 5			Week 9			Week 13			Week 17		
Test Piece	U	S	Change	U	S	Change	U	S	Change	U	S	Change	U	S	Change
1	32	36	4	37	36	-1	36	26	-10	26	34	8	38	40	2
2	48	54	6	50	52	2	46	50	4	46	54	8	48	56	8
3	270	258	-12	282	264	-18	270	264	-6	274	266	-8	282	274	-8
4	316	321	5	332	318	-14	322	306	-16	316	318	2	324	322	-2
5	40	42	2	38	40	2	38	42	4	36	44	8	40	46	6
6	50	52	2	44	56	12	46	36	-10	44	34	-10	46	42	-4
7	263	254	-9	264	248	-16	264	244	-20	262	246	-16	266	252	-14
8	330	322	-8	330	312	-18	330	300	-30	326	306	-20	330	304	-26
9	174	176	2	172	172	0	176	172	-4	170	174	4	174	178	4
10	176	172	-4	172	174	2	178	174	-4	170	175	5	175	180	5
FB	2	-	-	2	2	0	2	2	0	2	2	0	2	2	0

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
FB	Field blank

Specific Conductance (µS/cm)

	Week 1			Week 5			Week 9			Week 13			Week 17		
Test Piece	U	S	Change	U	S	Change	U	S	Change	U	S	Change	U	S	Change
1	1250	1230	-20	1239	1231	-8	1187	1192	5	1209	1176	-33	1221	1299	78
2	1229	1236	7	1255	1253	-2	1181	1170	-11	1230	1201	-29	1257	1280	23
3	1611	1604	-7	1621	1634	13	1566	1564	-2	1609	1590	-19	1633	1603	-30
4	1684	1663	-20.5	1710	1675	-35	1659	1641	-18	1680	1173	-507	1611	1447	-164
5	787	1149	362	1166	1164	-1.5	1123	1121	-2	1112	1101	-11	1169	1169	0
6	1200	1210	10	1163	1150	-13	1122	1112	-10	1653	1655	2.5	1163	1140	-23
7	1530	1518	-12	1547	1523	-24	1492	1468	-24	1486	1476	-10	1522	1593	71
8	1628	1613	-15	1624	1590	-34	1490	1474	-16	1046	1536	490	1625	1640	15
9	1415	1402	-13	1421	1419	-2	1362	1356	-6	1297	1273	-24	1388	1471	83
10	1415	1404	-11	1422	1418	-4	1360	1354	-6	1004	897	-107	1416	906	-510
FB	6.4	-	-	4.2	6.4	2.2	2.5	3.4	0.9	7.4	2.6	-4.8	5.5	4.7	-0.8

▨	Duplicated measurement
U	Unstagnated
S	Stagnated
FB	Field blank

Turbidity (NTU)

	Week 1			Week 5				Week 9				Week 10		Week 12			
Test Piece	U	S	Change	U	S	A	Change	U	S	A	Change	S	A	U	S	A	Change
1	0.06	0.66	0.60	0.08	0.57	0.17	0.49	0.08	0.21	0.17	0.13	0.40	0.20	0.13	0.23	0.24	0.10
2	0.16	2.05	1.89	0.14	1.39	0.69	1.25	0.13	0.84	0.93	0.71	1.11	0.53	0.22	0.86	0.70	0.64
3	0.15	3.13	2.98	0.14	0.84	0.77	0.7	0.13	3.80	0.90	3.67	5.57	0.91	0.18	5.35	0.80	5.17
4	0.10	0.37	0.27	0.12	0.67	0.39	0.55	0.09	0.81	0.20	0.72	0.20	0.14	0.08	0.41	0.25	0.33
5	0.15	3.62	3.47	0.17	5.85	0.58	5.68	0.14	5.76	0.97	5.62	19.1	0.67	0.22	13.1	0.80	12.88
6	0.07	1.10	1.03	0.08	0.36	0.15	0.28	0.07	0.21	0.14	0.14	0.12	0.11	0.07	0.15	0.12	0.08
7	0.07	1.53	1.47	0.08	0.60	0.13	0.52	0.07	0.74	0.29	0.67	0.81	0.14	0.10	0.64	0.18	0.54
8	0.17	0.45	0.28	0.16	0.60	0.77	0.44	0.13	0.40	0.86	0.27	0.60	0.82	0.17	0.52	0.69	0.35
9	0.1	0.88	0.78	0.11	0.29	0.47	0.18	0.15	0.57	0.75	0.42	0.57	0.38	0.13	0.43	0.46	0.30
10	0.12	0.56	0.44	0.11	0.45	0.52	0.34	0.10	0.36	0.6	0.26	0.30	0.39	0.13	0.25	0.51	0.12
FB	0.07	-	-	0.06	0.28	0.09	0.22	0.07	0.09	0.15	0.02	0.14	0.08	0.06	0.10	0.14	0.04

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
A	Acidified to pH < 2 with nitric acid
FB	Field blank
Change	S minus U

Turbidity (NTU)

	Week 14				Week 16				Week 18				Week 19	
Test Piece	U	S	A	Change	U	S	A	Change	U	S	A	Change	S	A
1	0.07	1.09	0.12	1.02	0.08	1.02	0.15	0.94	0.07	0.59	0.11	0.52	0.20	0.14
2	0.12	0.87	0.49	0.75	0.13	0.67	0.58	0.54	0.17	1.12	0.56	0.95	1.32	0.57
3	0.12	3.99	0.98	3.88	0.13	21.4	1.66	21.27	0.16	2.74	0.75	2.58	4.35	0.87
4	0.07	0.24	0.12	0.17	0.09	0.56	0.14	0.465	0.08	0.22	0.15	0.14	0.17	0.16
5	0.15	9.10	0.64	8.95	0.14	9.74	0.84	9.6	0.16	5.13	0.94	4.97	6.12	0.59
6	0.07	0.22	0.13	0.15	0.07	0.26	0.14	0.19	0.06	0.18	0.15	0.12	0.14	0.17
7	0.08	1.66	0.14	1.58	0.09	1.57	0.98	1.48	0.09	0.76	0.85	0.67	2.54	1.58
8	0.16	0.43	0.71	0.27	0.16	0.89	0.96	0.73	0.14	0.35	0.61	0.21	0.54	0.81
9	0.10	0.63	0.52	0.53	0.12	0.58	0.47	0.46	0.12	0.47	0.33	0.35	0.50	0.37
10	0.10	0.29	0.39	0.19	0.12	0.31	0.41	0.19	0.12	0.25	0.45	0.13	0.27	0.41
FB	0.06	0.08	0.08	0.02	0.08	0.08	0.08	0	0.06	0.10	0.07	0.04	0.08	0.10

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
A	Acidified to pH < 2 with nitric acid
FB	Field blank
Change	S minus U

Turbidity (NTU)

	Week 20			
Test Piece	U	S	A	Change
1	0.10	0.65	0.12	0.55
2	0.15	1.19	0.62	1.04
3	0.16	2.42	0.81	2.26
4	0.07	0.19	0.14	0.12
5	0.14	4.22	0.48	4.08
6	0.08	0.16	0.10	0.09
7	0.09	0.72	0.15	0.63
8	0.16	0.42	0.85	0.26
9	0.12	0.41	0.28	0.29
10	0.11	0.25	0.35	0.14
FB	0.07	0.06	0.07	-0.01

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
A	Acidified to pH < 2 with nitric acid
FB	Field blank
Change	S minus U

Anions (mg/L)

	Week 2 U			Week 2 S			Week 2 Change			Week 6 U		
Test Piece	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR
1	235	189	1.24	267	209	1.28	32	21	0.03	239	192	1.24
2	234	189	1.24	236	185	1.27	1	-4	0.03	245	193	1.27
3	231	185	1.25	227	197	1.15	-4	12	-0.09	240	191	1.26
4	230	185	1.24	216	174	1.24	-14	-12	0.00	241	193	1.25
5	233	197	1.18	210	180	1.17	-23	-17	-0.02	241	204	1.18
6	230	193	1.20	220	182	1.21	-11	-11	0.01	243	202	1.21
7	229	195	1.17	163	150	1.09	-66	-46	-0.08	244	204	1.20
8	233	191	1.22	232	189	1.22	-1	-2	0.00	242	202	1.19
9	231	195	1.18	214	188	1.14	-17	-7	-0.05	245	204	1.20
10	235	197	1.19	224	192	1.17	-11	-5	-0.03	248	207	1.20
FB	n.d.	n.d.	-	0.0893	n.d.	-	-	-	-	0.1106	n.d.	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
FB	Field blank
n.d.	Not detected

Anions (mg/L)

	Week 6 S			Week 6 Change			Week 11 U			Week 11 S		
Test Piece	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR
1	241	192	1.26	2	0	0.01	229	161	1.43	222	155	1.43
2	238	188	1.27	-7	-5	0.00	228	180	1.26	223	177	1.26
3	233	219	1.07	-7	28	-0.19	224	178	1.26	216	190	1.14
4	235	188	1.25	-6	-5	0.00	225	179	1.26	220	178	1.24
5	237	199	1.19	-3	-5	0.01	223	195	1.14	215	188	1.14
6	238	197	1.20	-5	-4	0.00	225	191	1.17	217	187	1.16
7	233	209	1.11	-11	6	-0.08	225	195	1.15	215	208	1.04
8	237	197	1.21	-4	-5	0.01	224	160	1.40	216	156	1.38
9	235	206	1.14	-9	1	-0.05	230	152	1.51	221	148	1.49
10	239	199	1.21	-9	-8	0.00	231	194	1.19	221	187	1.19
FB	0.0103	0.0198	0.52	-	-	-	n.d.	n.d.	-	0.0072	n.d.	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
FB	Field blank
n.d.	Not detected

Anions (mg/L)

	Week 11 Change			Week 19 U			Week 19 S			Week 19 Change		
Test Piece	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR
1	-8	-6	0.00	232	188	1.24	230	181	1.27	-3	-7	0.03
2	-5	-3	0.00	234	190	1.23	230	183	1.25	-4	-7	0.02
3	-8	12	-0.12	236	187	1.26	227	196	1.16	-9	9	-0.11
4	-5	-1	-0.02	235	189	1.24	226	183	1.24	-9	-7	0.00
5	-8	-7	0.00	236	201	1.18	227	193	1.18	-10	-8	0.00
6	-8	-5	-0.01	239	198	1.20	228	189	1.21	-10	-9	0.00
7	-9	12	-0.11	241	202	1.19	228	209	1.09	-13	7	-0.10
8	-8	-4	-0.01	240	199	1.21	229	191	1.20	-11	-9	0.00
9	-9	-4	-0.02	241	202	1.19	228	192	1.19	-13	-10	0.00
10	-9	-7	0.00	242	202	1.19	228	191	1.19	-14	-11	0.00
FB	-	-	-	0.0088	n.d.	-	0.0086	n.d.	-	-	-	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
FB	Field blank
n.d.	Not detected

SUVA (L/mg-C/m) - Measured on LC-OCD

	Week 3			Week 7			Week 12			Week 16			Week 20		
Test Piece	U	S	Change	U	S	Change	U	S	Change	U	S	Change	U	S	Change
1	-	-	-	-	-	-	-	-	-	-	-	-	6.12	-	-
2	5.06	5.11	0.05	4.87	4.94	0.07	5.11	5.08	-0.03	4.96	5.14	0.18	4.84	5.08	0.24
3	4.47	5.26	0.79	4.08	5.26	1.19	5.25	5.45	0.20	5.00	5.31	0.31	5.02	5.57	0.55
4	-	-	-	-	2.53	-	3.27	-	-	-	3.72	-	-	-	-
5	4.76	4.45	-0.31	5.08	4.27	-0.81	5.09	3.87	-1.22	5.30	4.05	-1.25	4.98	4.36	-0.62
6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
8	4.76	4.94	0.18	4.83	5.14	0.31	5.10	5.06	-0.04	4.83	4.99	0.16	4.97	4.99	0.02
9	4.82	4.88	0.06	4.47	5.31	0.84	5.00	5.06	0.06	4.73	5.08	0.35	5.04	4.97	-0.07
10	4.89	5.14	0.25	5.03	5.11	0.08	4.96	5.18	0.22	4.90	5.02	0.13	5.03	5.21	0.18
FIL	4.48	8.32	3.84	6.35	2.66	-3.69	8.02	2.82	-5.20	10.68	8.62	-2.06	3.07	7.16	4.09
FB	3.30	6.77	3.47	0.84	4.96	4.12	5.50	4.96	-0.54	9.93	12.99	3.06	11.37	7.83	-3.54

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
FIL	Filter blank
FB	Field blank

Hydrophobic (mg C/L) - LC-OCD

	Week 3			Week 7			Week 12			Week 16			Week 20		
Test Piece	U	S	Change	U	S	Change	U	S	Change	U	S	Change	U	S	Change
1	-	-	-	-	-	-	-	-	-	-	-	-	0.014	-	-
2	0.467	0.568	0.101	0.679	0.455	-0.224	0.294	0.585	0.291	0.456	0.425	-0.031	0.478	0.102	-0.376
3	1.470	0.514	-0.956	1.850	0.157	-1.693	0.270	0.293	0.023	0.415	0.489	0.074	0.440	0.272	-0.168
4	-	-	-	-	0.077	-	0.028	-	-	-	0.062	-	-	-	-
5	0.693	0.611	-0.082	0.236	0.148	-0.088	0.310	0.383	0.073	0.417	0.453	0.036	0.403	0.384	-0.019
6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
8	1.060	0.553	-0.507	0.947	0.332	-0.616	0.342	0.130	-0.212	0.402	0.259	-0.143	0.380	0.507	0.127
9	0.288	0.364	0.076	0.512	0.236	-0.276	0.138	0.284	0.146	0.287	0.297	0.010	0.237	0.151	-0.0865
10	0.280	0.405	0.125	0.091	0.134	0.043	0.233	0.222	-0.011	0.238	0.216	-0.022	0.167	0.194	0.027
FIL	0.076	0.011	-0.065	n.d.	0.023	-	0.027	0.037	0.010	0.008	0.012	0.004	0.017	0.021	0.004
FB	n.d.	0.020	-	0.144	0.012	-0.132	0.013	0.012	-0.001	0.014	0.003	-0.011	n.d.	0.011	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
FIL	Filter blank
FB	Field blank
n.d.	Not detected

Biopolymers (mg C/L) - LC-OCD

	Week 3			Week 7			Week 12			Week 16			Week 20		
Test Piece	U	S	Change	U	S	Change	U	S	Change	U	S	Change	U	S	Change
1	-	-	-	-	-	-	-	-	-	-	-	-	n.d.	n.d.	-
2	0.004	0.005	0.001	n.d.	0.008	-	0.010	0.013	0.003	0.006	0.007	0.001	0.002	0.035	0.033
3	n.d.	0.014	-	0.036	0.007	-0.029	0.013	0.018	0.005	0.003	0.015	0.012	0.005	0.018	0.013
4	-	-	-	-	0.002	-	n.d.	-	-	-	0.005	-	-	-	-
5	0.001	0.005	0.004	0.005	0.003	-0.002	0.002	0.012	0.010	0.004	0.016	0.012	0.006	0.002	-0.004
6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
8	0.001	0.003	0.002	0.095	0.014	-0.081	0.006	0.006	0.000	0.004	0.005	0.001	0.002	0.006	0.004
9	0.002	0.001	-0.001	0.015	0.003	-0.012	0.003	0.005	0.002	0.002	0.005	0.003	0.006	0.007	0.0015
10	0.004	0.002	-0.002	0.017	0.002	-0.015	0.002	0.007	0.006	0.002	0.007	0.005	0.004	0.003	-0.001
FIL	0.006	0.001	-0.005	0.002	0.002	0.000	0.001	n.d.	-	n.d.	0.003	-	0.002	0.003	0.001
FB	0.006	n.d.	-	n.d.	n.d.	-	0.002	n.d.	-	n.d.	0.008	-	0.002	0.003	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
FIL	Filter blank
FB	Field blank
n.d.	Not detected

Humic Substances (mg C/L) - LC-OCD

	Week 3			Week 7			Week 12			Week 16			Week 20		
Test Piece	U	S	Change	U	S	Change	U	S	Change	U	S	Change	U	S	Change
1	-	-	-	-	-	-	-	-	-	-	-	-	n.d.	-	-
2	5.940	5.784	-0.156	5.827	5.579	-0.248	5.890	5.619	-0.271	6.023	5.619	-0.404	6.520	6.009	-0.511
3	5.644	5.444	-0.200	5.803	5.410	-0.393	5.803	5.360	-0.443	6.012	5.374	-0.638	6.616	5.951	-0.665
4	-	-	-	-	n.d.	-	n.d.	-	-	-	n.d.	-	-	-	-
5	5.510	4.569	-0.941	5.820	4.052	-1.768	5.598	3.703	-1.895	5.995	3.912	-2.083	5.739	4.099	-1.64
6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
8	5.577	5.425	-0.152	5.761	5.440	-0.322	5.643	5.334	-0.309	5.852	5.271	-0.581	5.760	5.251	-0.509
9	2.817	2.737	-0.080	2.881	2.758	-0.123	2.813	2.701	-0.112	2.960	2.781	-0.180	2.822	2.554	-0.268
10	2.789	2.713	-0.076	2.932	2.860	-0.072	2.871	2.759	-0.112	2.900	2.737	-0.163	2.823	2.646	-0.177
FIL	n.d.	n.d.	-	n.d.	n.d.	-	n.d.	n.d.	-	n.d.	n.d.	-	n.d.	n.d.	-
FB	n.d.	n.d.	-	n.d.	n.d.	-	n.d.	n.d.	-	n.d.	n.d.	-	n.d.	n.d.	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
FIL	Filter blank
FB	Field blank
n.d.	Not detected

Building Blocks (mg C/L) - LC-OCD

	Week 3			Week 7			Week 12			Week 16			Week 20		
Test Piece	U	S	Change	U	S	Change	U	S	Change	U	S	Change	U	S	Change
1	-	-	-	-	-	-	-	-	-	-	-	-	0.006	-	-
2	0.611	0.659	0.048	0.736	0.785	0.049	0.803	0.720	-0.083	0.891	0.825	-0.066	0.779	0.974	0.195
3	0.719	0.748	0.029	0.805	0.735	-0.070	0.769	0.727	-0.042	0.844	0.792	-0.052	0.763	0.931	0.168
4	-	-	-	-	0.010	-	0.009	-	-	-	0.016	-	-	-	-
5	0.824	0.638	-0.187	0.612	0.693	0.081	0.775	0.615	-0.160	0.725	0.668	-0.057	0.704	0.673	-0.031
6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
8	0.675	0.681	0.006	0.707	0.653	-0.054	0.781	0.648	-0.133	0.802	0.924	0.122	0.645	0.715	0.07
9	0.311	0.417	0.106	0.359	0.359	0.000	0.398	0.355	-0.043	0.411	0.368	-0.044	0.332	0.399	0.067
10	0.300	0.422	0.122	0.390	0.382	-0.008	0.339	0.341	0.003	0.398	0.360	-0.038	0.357	0.395	0.038
FIL	0.013	0.006	-0.007	0.013	0.002	-0.011	0.004	0.007	0.003	0.004	0.008	0.004	0.007	0.004	-0.003
FB	0.002	0.002	0.000	0.004	0.006	0.002	0.008	0.012	0.004	0.004	n.d.	-	0.006	0.004	-0.002

▨	Duplicated measurement
U	Unstagnated
S	Stagnated
FIL	Filter blank
FB	Field blank
n.d.	Not detected

LMW Neutrals (mg C/L) - LC-OCD

	Week 3			Week 7			Week 12			Week 16			Week 20		
Test Piece	U	S	Change	U	S	Change	U	S	Change	U	S	Change	U	S	Change
1	-	-	-	-	-	-	-	-	-	-	-	-	0.009	-	-
2	0.372	0.353	-0.019	0.250	0.342	0.092	0.351	0.298	-0.054	0.307	0.345	0.038	0.447	0.445	-0.002
3	0.385	0.407	0.022	0.509	0.352	-0.157	0.344	0.342	-0.002	0.291	0.345	0.054	0.361	0.367	0.006
4	-	-	-	-	0.028	-	0.025	-	-	-	0.032	-	-	-	-
5	0.406	0.302	-0.104	0.395	0.300	-0.095	0.303	0.318	0.015	0.283	0.305	0.022	0.371	0.262	-0.109
6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
8	0.338	0.274	-0.064	0.371	0.289	-0.082	0.383	0.321	-0.062	0.319	0.309	-0.010	0.346	0.302	-0.044
9	0.231	0.232	0.001	0.215	0.134	-0.081	0.202	0.189	-0.013	0.157	0.170	0.013	0.189	0.204	0.015
10	0.266	0.221	-0.045	0.254	0.190	-0.064	0.191	0.179	-0.012	0.180	0.200	0.021	0.188	0.202	0.014
FIL	0.030	0.007	-0.023	0.023	0.008	-0.015	0.010	0.025	0.015	0.011	0.012	0.001	0.011	0.013	0.002
FB	0.016	0.009	-0.007	0.041	0.009	-0.032	0.016	0.019	0.003	0.007	0.008	0.001	0.009	0.015	0.006

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
FIL	Filter blank
FB	Field blank
n.d.	Not detected

LMW Acids (mg C/L) - LC-OCD

	Week 3			Week 7			Week 12			Week 16			Week 20		
Test Piece	U	S	Change	U	S	Change	U	S	Change	U	S	Change	U	S	Change
1	-	-	-	-	-	-	-	-	-	-	-	-	0.003	-	-
2	0.029	0.049	0.020	0.053	0.055	0.002	0.051	0.055	0.004	0.049	0.047	-0.002	0.058	0.043	-0.015
3	0.059	0.057	-0.002	0.061	0.056	-0.005	0.056	0.060	0.004	0.048	0.050	0.002	0.060	0.053	-0.007
4	-	-	-	-	0.019	-	0.001	-	-	-	0.004	-	-	-	-
5	0.047	0.057	0.010	0.057	0.048	-0.009	0.046	0.026	-0.020	0.065	0.023	-0.042	0.047	0.046	-0.001
6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
8	0.058	0.064	0.007	0.050	0.059	0.009	0.050	0.051	0.001	0.057	0.053	-0.004	0.048	0.058	0.01
9	0.017	0.021	0.004	0.021	0.018	-0.003	0.013	0.019	0.006	0.019	0.014	-0.006	0.014	0.019	0.005
10	0.012	0.019	0.007	0.018	0.018	0.000	0.012	0.016	0.004	0.013	0.011	-0.002	0.014	0.016	0.002
FIL	0.011	0.006	-0.005	0.008	0.004	-0.004	0.003	0.036	0.033	0.002	0.002	0.000	0.002	0.002	0.000
FB	0.002	0.006	0.004	0.007	0.003	-0.004	0.004	0.004	0.000	n.d.	0.006	-	0.003	0.002	-0.001

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
FIL	Filter blank
FB	Field blank
n.d.	Not detected

Humic Acids (au) - FEEM

	Week 12			Week 16			Week 20		
Test Piece	U	S	Change	U	S	Change	U	S	Change
1	-	-	-	-	-	-	1.6365	1.4588	-0.1777
2	457.9104	397.6946	-60.2158	471.3310	427.4046	-43.9265	495.4912	444.7739	-50.7173
3	440.7717	340.7553	-100.0164	462.8406	329.9652	-132.8754	485.9491	396.5426	-89.4065
4	0.1862	-	-	-	3.9391	-	-	-	-
5	450.0622	381.5418	-68.5204	476.6054	405.7763	-70.8291	454.8835	406.5317	-48.3518
6	-	2.4491	-	-	-	-	-	-	-
7	-	-	-	2.7443	-	-	-	-	-
8	465.1353	430.0114	-35.1239	489.9897	469.1409	-20.8488	457.7129	434.9704	-22.7425
9	266.0504	239.3272	-26.7232	282.5957	262.9004	-19.6953	262.7800	233.9263	-28.85365
10	263.1642	241.7531	-21.4110	273.8136	252.5035	-21.3101	267.7345	238.4474	-29.2871
FIL	0.2434	0.9024	0.6590	2.6193	2.9959	0.3766	0.5866	1.5373	0.9507
FB	0.5175	0.9323	0.4148	1.7621	2.8004	1.0383	0.0728	0.0272	-0.0456
MQ End	-0.3288	0.5487	0.8775	1.4495	3.2895	1.8400	-0.0738	0.1047	0.1785

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
FIL	Filter blank
FB	Field blank
MQ End	MQ blank

Fulvic Acids (au) - FEEM

	Week 12			Week 16			Week 20		
Test Piece	U	S	Change	U	S	Change	U	S	Change
1	-	-	-	-	-	-	2.0484	2.3068	0.2584
2	351.7381	326.5163	-25.2218	376.5315	355.5746	-20.9570	390.9277	358.8795	-32.0482
3	344.7008	282.1618	-62.5390	377.1588	284.4166	-92.7422	392.4542	324.5820	-67.8722
4	0.2430	-	-	-	4.4081	-	-	-	-
5	338.4169	309.7048	-28.7121	374.5761	332.7301	-41.8460	339.6119	311.1312	-28.4807
6	-	3.0727	-	-	-	-	-	-	-
7	-	-	-	2.7955	-	-	-	-	-
8	335.0573	323.6247	-11.4326	369.9652	350.3913	-19.5739	331.3720	315.7248	-15.6472
9	187.1410	177.7800	-9.3610	209.3929	196.2761	-13.1168	182.6374	167.6743	-14.96305
10	187.3732	178.9038	-8.4694	199.1026	187.8032	-11.2994	188.3068	169.1387	-19.1681
FIL	0.0769	0.8336	0.7567	2.5973	2.8163	0.2190	0.4721	1.6357	1.1636
FB	0.7057	0.7957	0.0900	1.8181	2.8948	1.0767	0.1299	0.1006	-0.0293
MQ End	-0.3413	0.5574	0.8987	1.5765	3.2942	1.7177	-0.0968	0.3055	0.4023

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
FIL	Filter blank
FB	Field blank
MQ End	MQ blank

Protein Like Materials (au) - FEEM

	Week 12			Week 16			Week 20		
Test Piece	U	S	Change	U	S	Change	U	S	Change
1	-	-	-	-	-	-	0.6238	4.5033	3.8795
2	18.6650	19.2844	0.6194	22.5426	23.1679	0.6253	20.6825	22.4806	1.7981
3	16.8999	19.1594	2.2595	21.1399	23.1602	2.0203	20.6860	20.1243	-0.5617
4	1.0411	-	-	-	7.1329	-	-	-	-
5	17.2010	21.8459	4.6449	16.8181	25.8078	8.9897	17.8448	21.3579	3.5131
6	-	4.9626	-	-	-	-	-	-	-
7	-	-	-	3.8330	-	-	-	-	-
8	17.1019	18.7764	1.6745	20.6507	23.8070	3.1563	20.2220	20.4709	0.2489
9	10.8921	13.9759	3.0838	14.4040	16.2025	1.7985	11.2929	12.9074	1.6145
10	10.7065	14.2513	3.5448	14.5836	16.8354	2.2519	11.8715	13.2137	1.3422
FIL	0.3809	2.8522	2.4713	3.2495	15.5146	12.2651	3.2750	1.3477	-1.9273
FB	0.9321	1.3794	0.4473	2.9775	8.0923	5.1148	0.3743	2.2813	1.9070
MQ End	-0.2819	0.1667	0.4486	1.3157	3.2480	1.9323	-0.1350	0.0389	0.1739

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
FIL	Filter blank
FB	Field blank
MQ End	MQ blank

Appendix D

Supplemental Information for Chapter 4

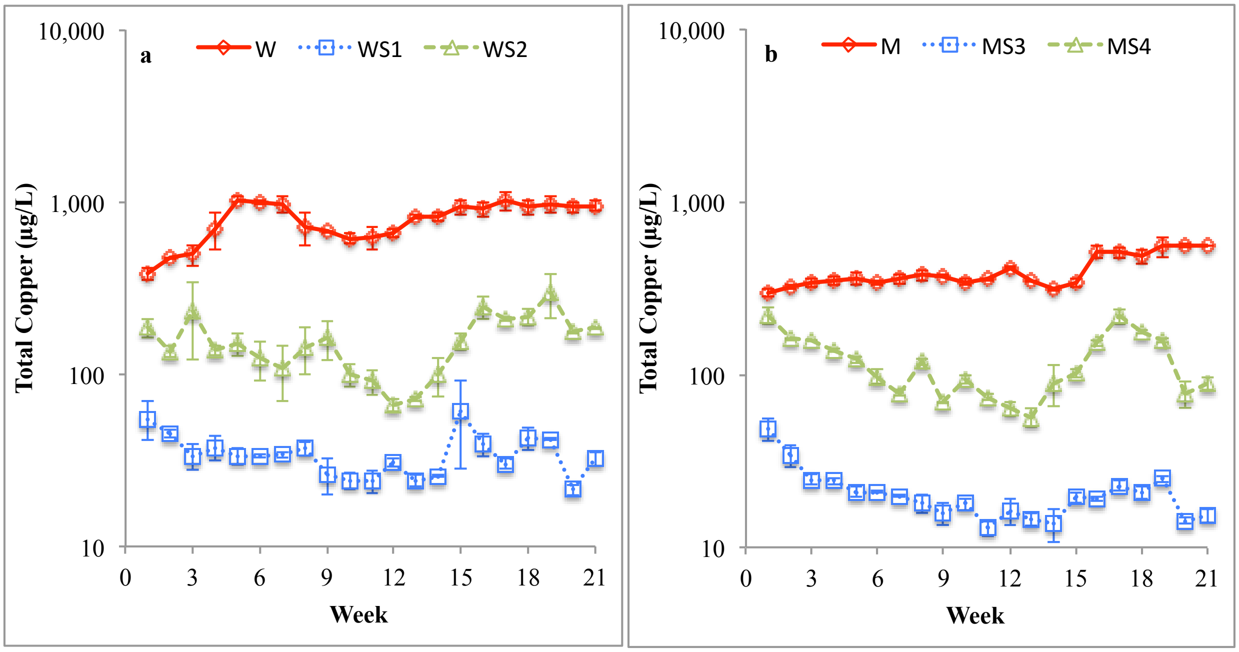


Figure D.1 Time series plot of total copper release for a) W, WS1, WS2 and b) M, MS3, MS4. Markers represent the mean of the two duplicate test pieces while the error bars represent the range of the duplicate measurements. Total copper was measured from the weekly composite samples.

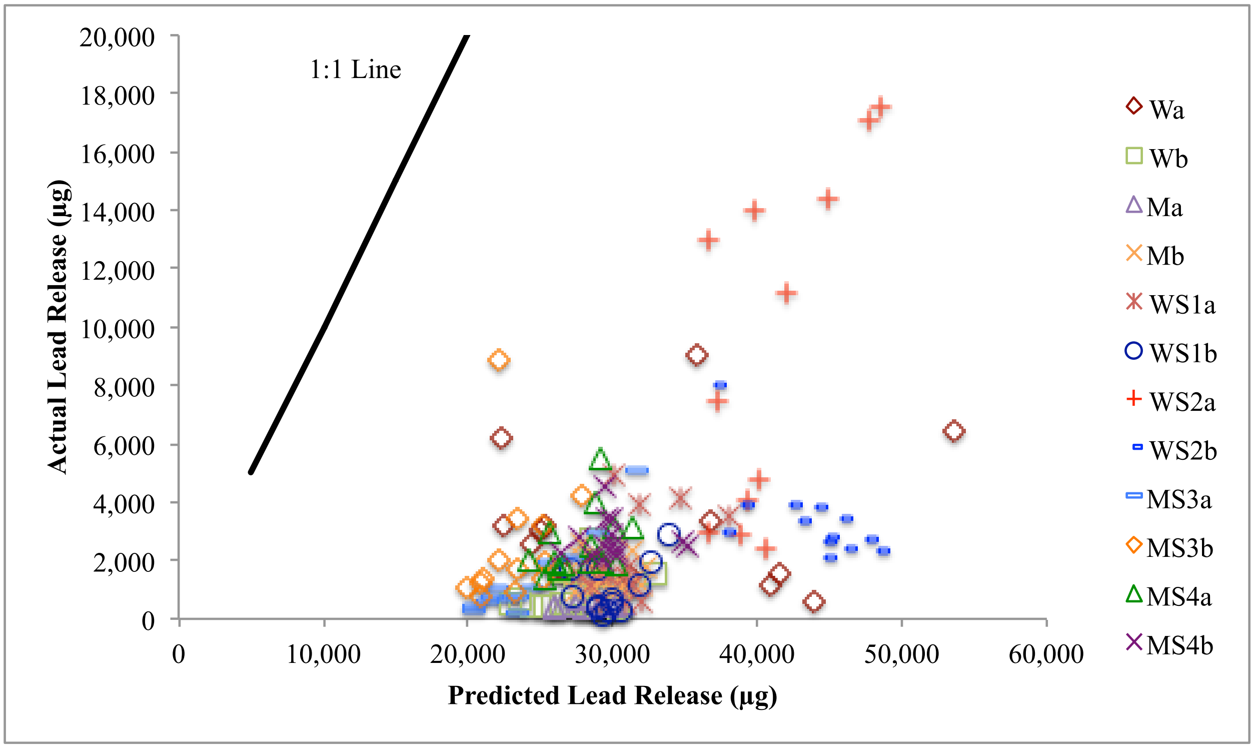


Figure D.2 Predicted weekly lead release calculated using galvanic current and Faraday's Law versus actual weekly lead release from the weekly composite samples.

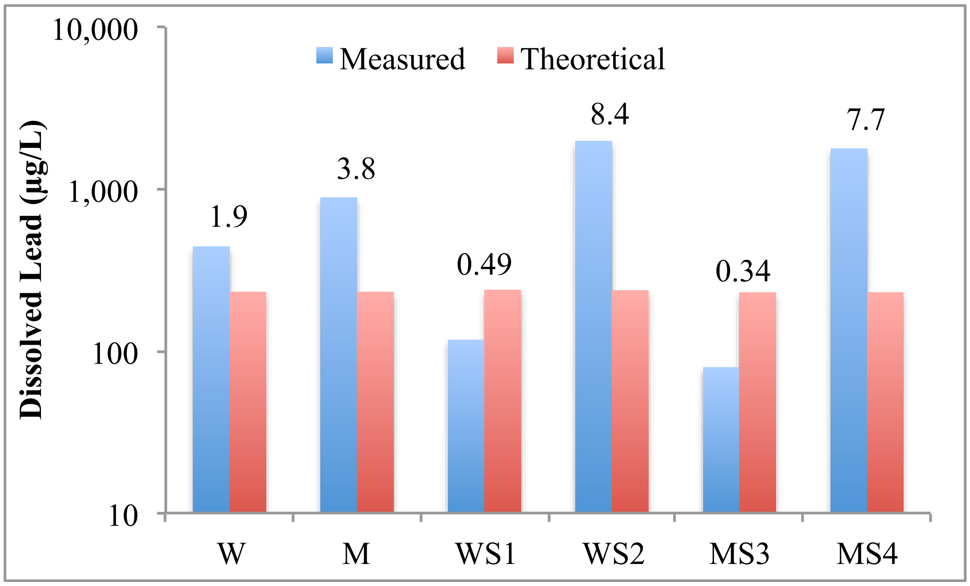


Figure D.3 Comparison of average measured dissolved lead concentrations (weeks 5-19) to theoretical lead solubility predicted by tidyphreeqc. Numbers on top of the bars represent the ratio of measured dissolved lead concentrations to the theoretical solubility.

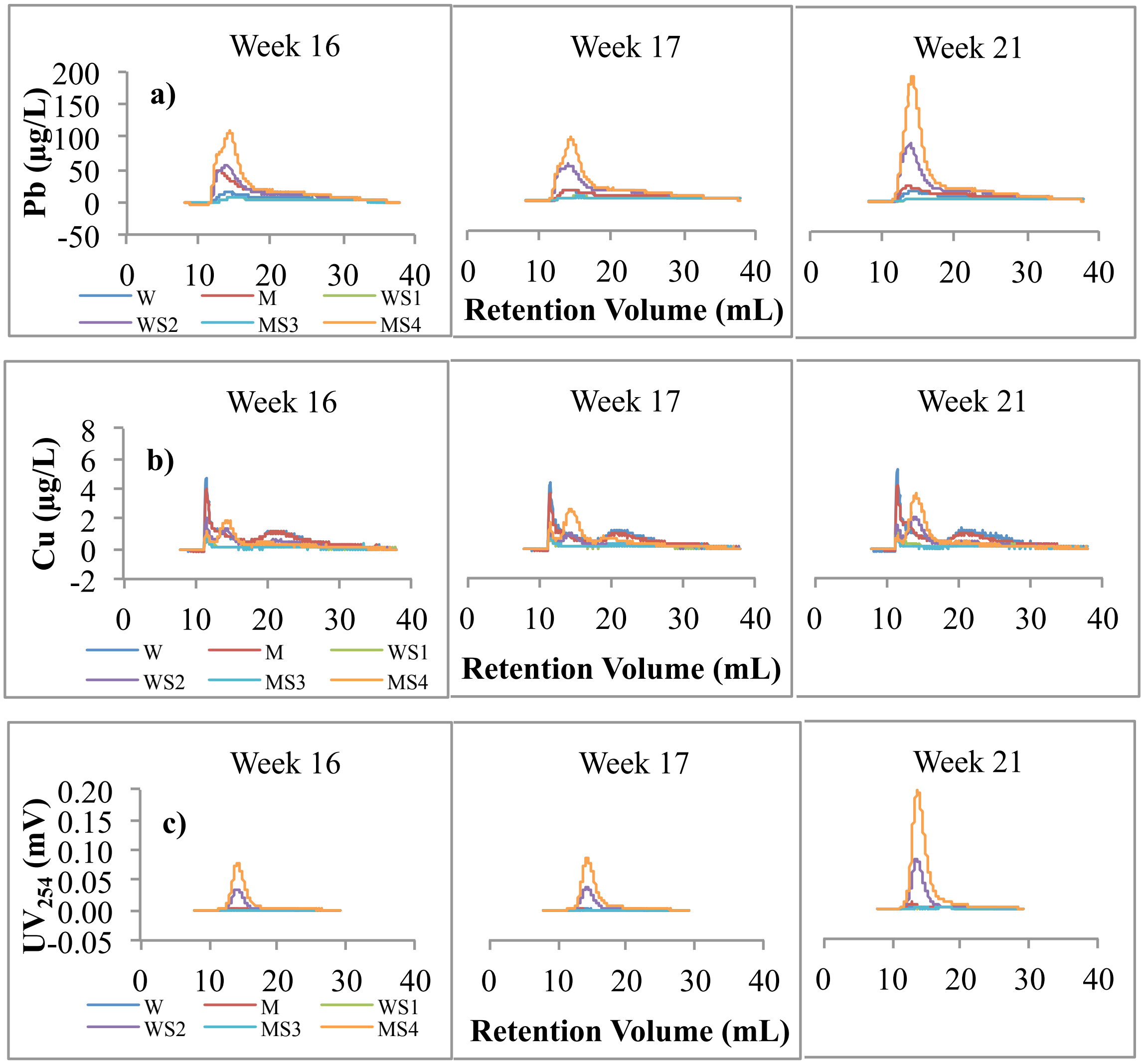


Figure D.4 Field flow fractograms by week representing all six samples for a) lead, b) copper, and c) UV_{254} absorbance. UV_{254} is shown as the raw detector output expressed in mV. The filtered samples (< 0.45 µm) were separated into three primary fractions: (1) the void volume (~12 mL peak retention volume), representing soluble and unfocused species, (2) the NOM peak (~14 mL peak retention volume), and (3) a larger colloidal peak (~20.5 mL peak retention volume) that probably represents dispersed metal oxides.

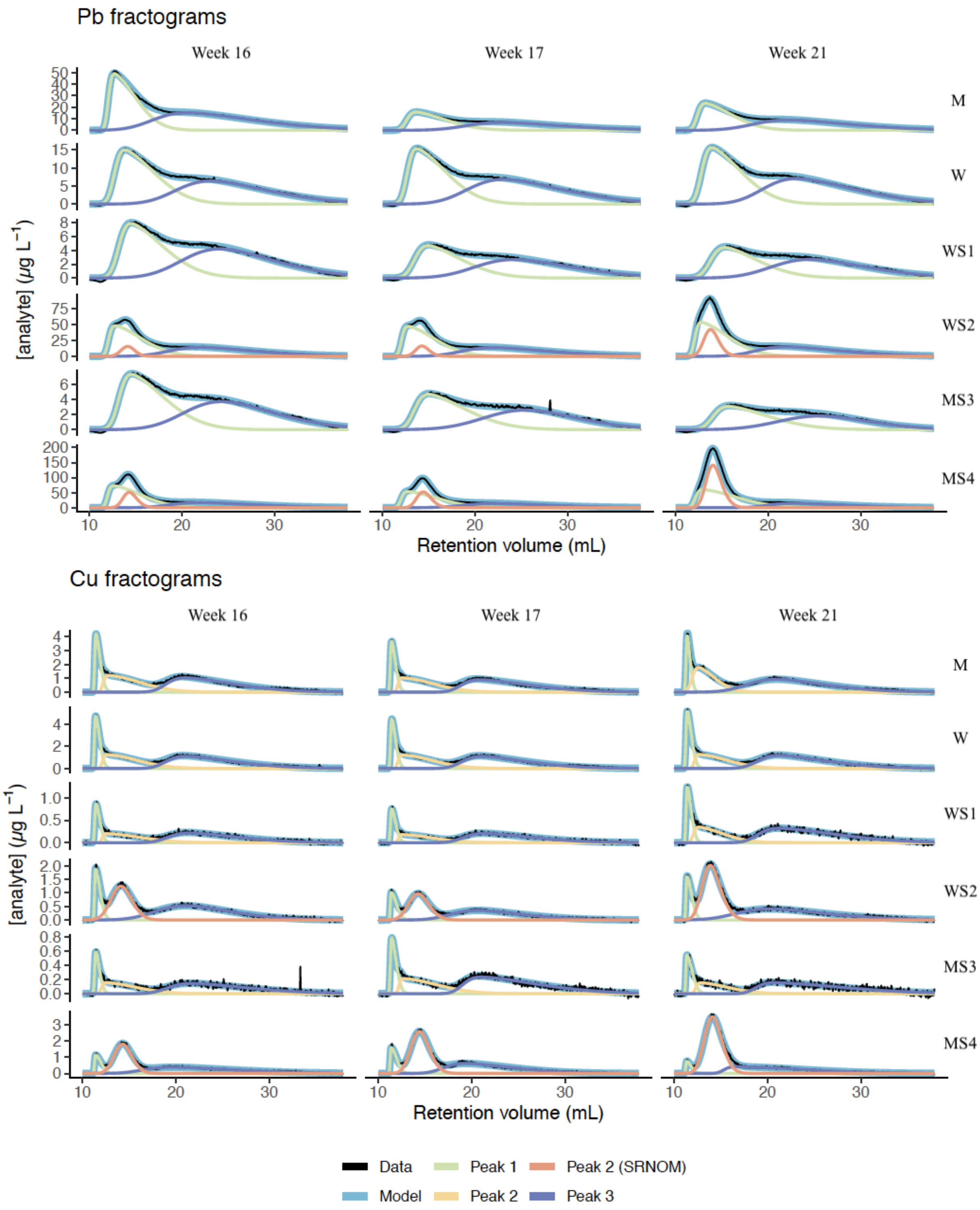


Figure D.5 Fractograms for lead and copper and their respective two- or three-peak models.

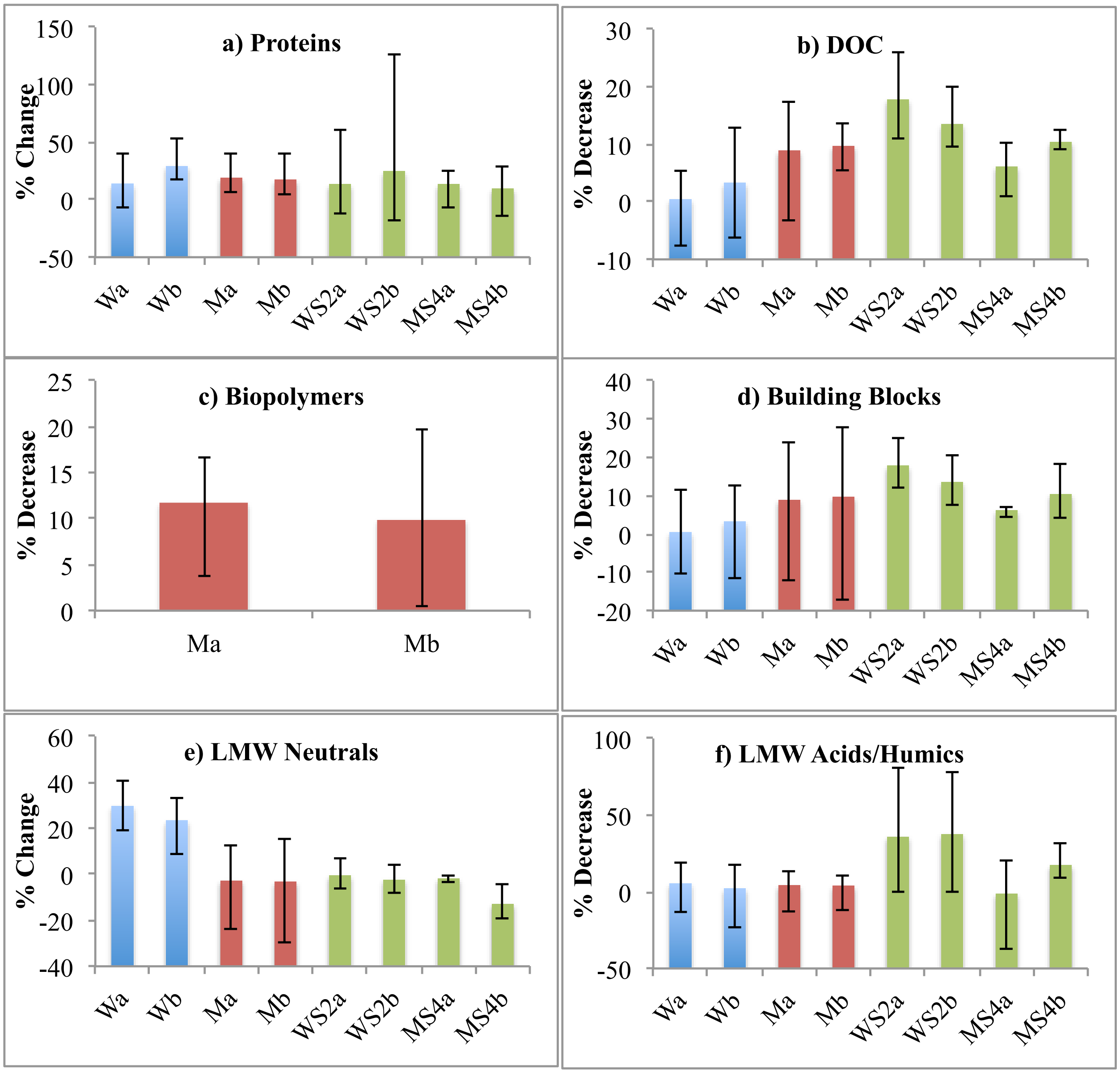
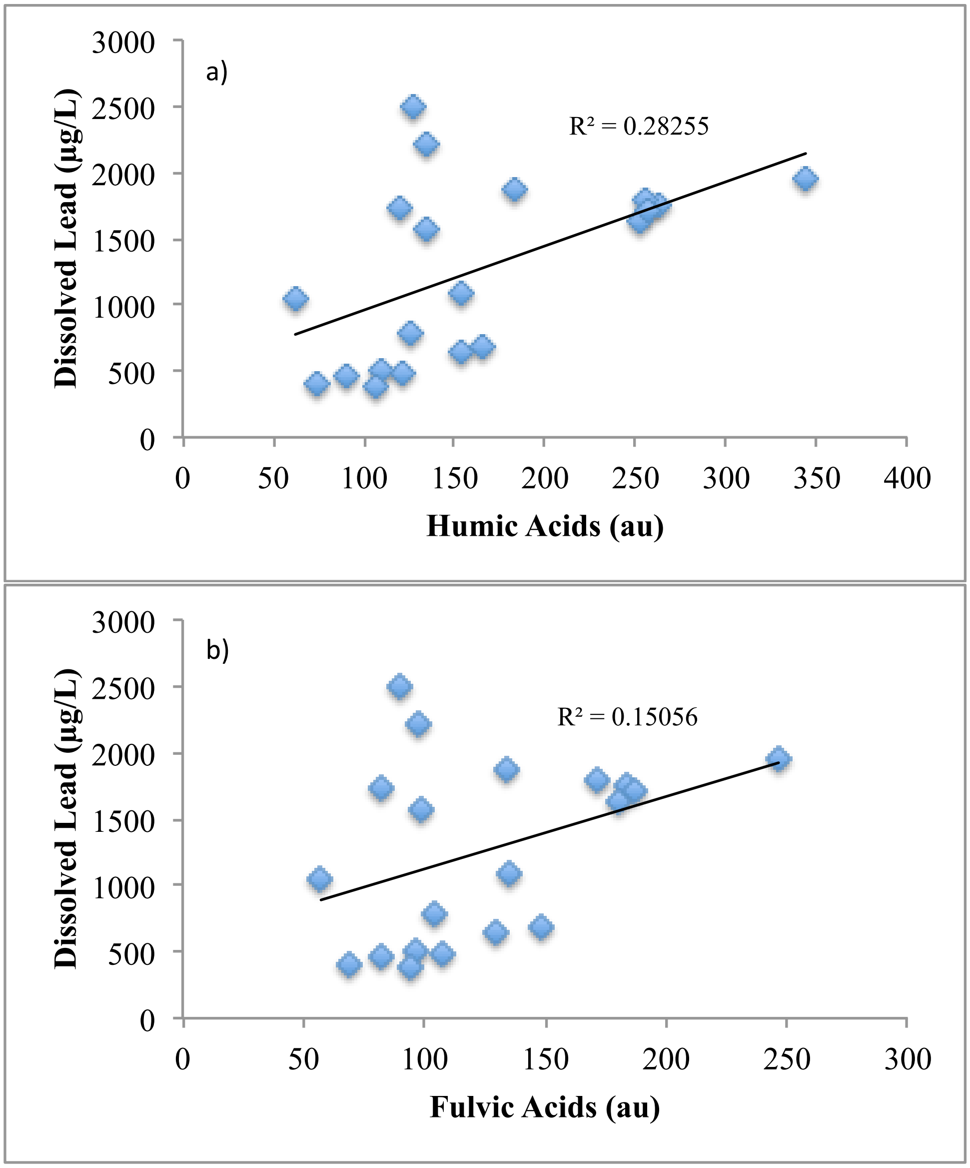


Figure D.6 Average percent change in FEEM NOM fraction for a) proteins. Average percent change or decrease in LC-OCD NOM fractions for b) DOC, c) biopolymers, d) building blocks, e) LMW neutrals, f) LMW acids/humics. Error bars represent the minimum and maximum values that were measured. The changes in FEEM fractions were measured on weeks 3, 7, 11, 16, and 21. The changes in the LC-OCD fractions were measured on weeks 7, 11, 16 and 21. Biopolymers were only included in Ma and Mb as they were below the detection limit for the other samples.


a)
R² = 0.28255
Dissolved Lead (µg/L)
3000
2500
2000
1500
1000
500
0
0
50
100
150
200
250
300
350
400
Humic Acids (au)
b)
R² = 0.15056
Dissolved Lead (µg/L)
3000
2500
2000
1500
1000
500
0
0
50
100
150
200
250
300
Fulvic Acids (au)

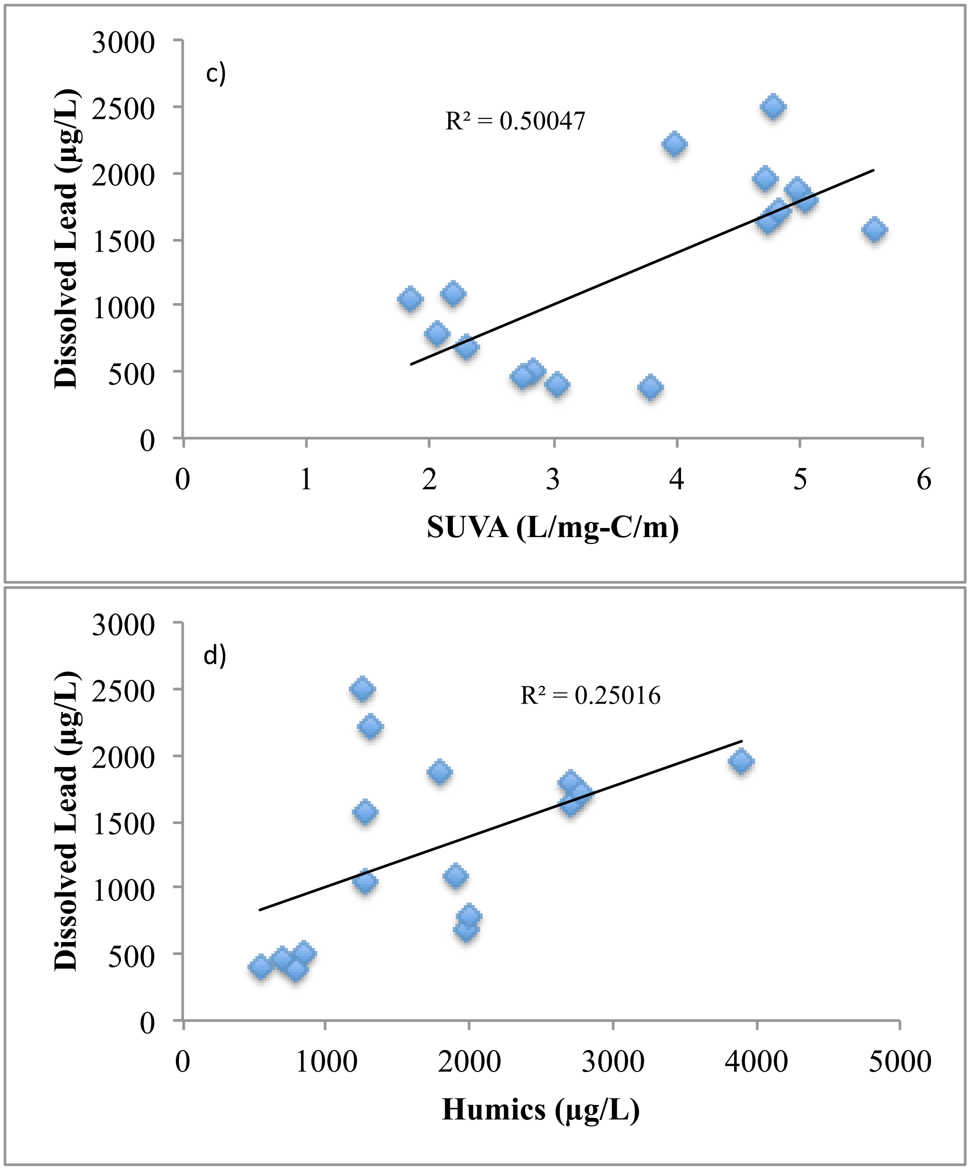
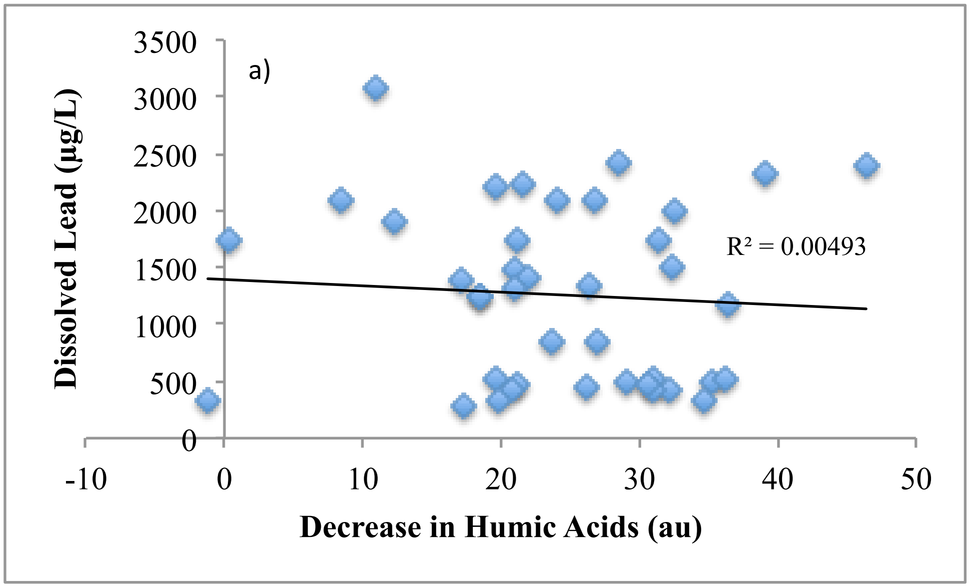
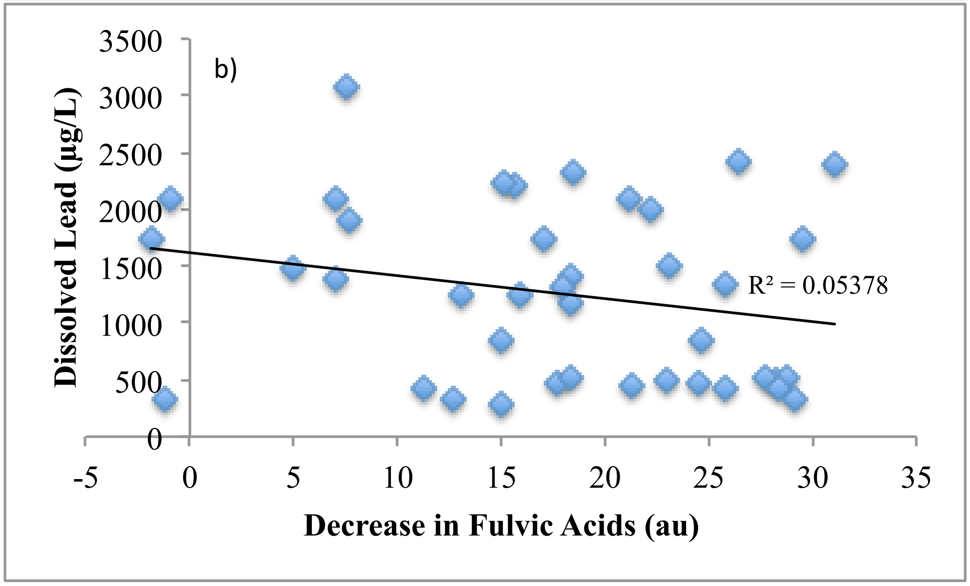


Figure D.7 Correlations between dissolved lead and a) initial humic acid intensity measured using FEEM, b) initial fulvic acid intensity measured using FEEM, c) initial SUVA measured using LC-OCD, and d) initial humics concentration measured using LC-OCD. The data plotted is for W, M, WS2, and MS4 measured on weeks 3, 7, 11, 16, and 21 for FEEM and weeks 7, 11, 16, and 21 for LC-OCD.


a)
Dissolved Lead (µg/L)
3500
3000
2500
2000
1500
1000
500
0
R² = 0.00493
-10
0
10
20
30
40
50
Decrease in Humic Acids (au)


b)
Dissolved Lead (µg/L)
3500
3000
2500
2000
1500
1000
500
0
R² = 0.05378
-5
0
5
10
15
20
25
30
35
Decrease in Fulvic Acids (au)

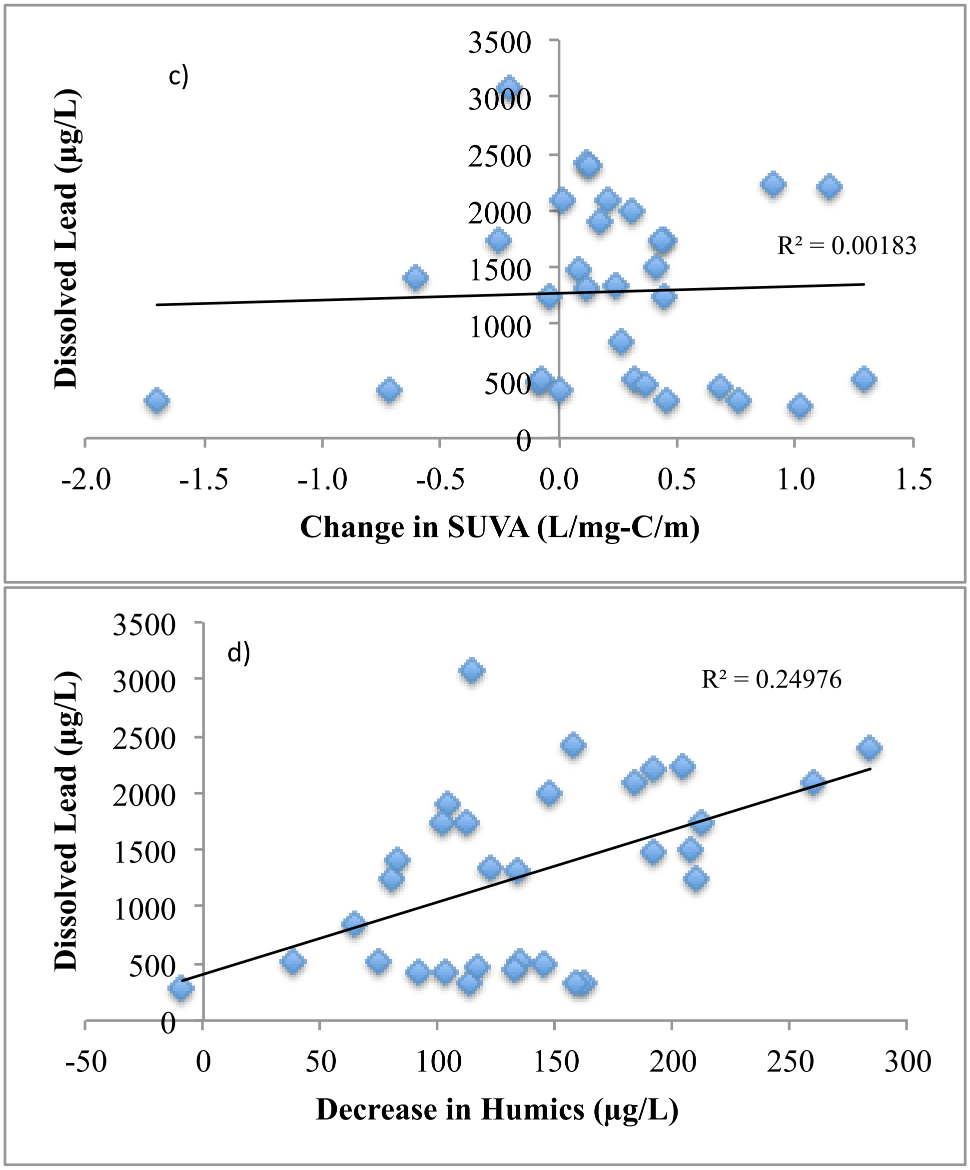
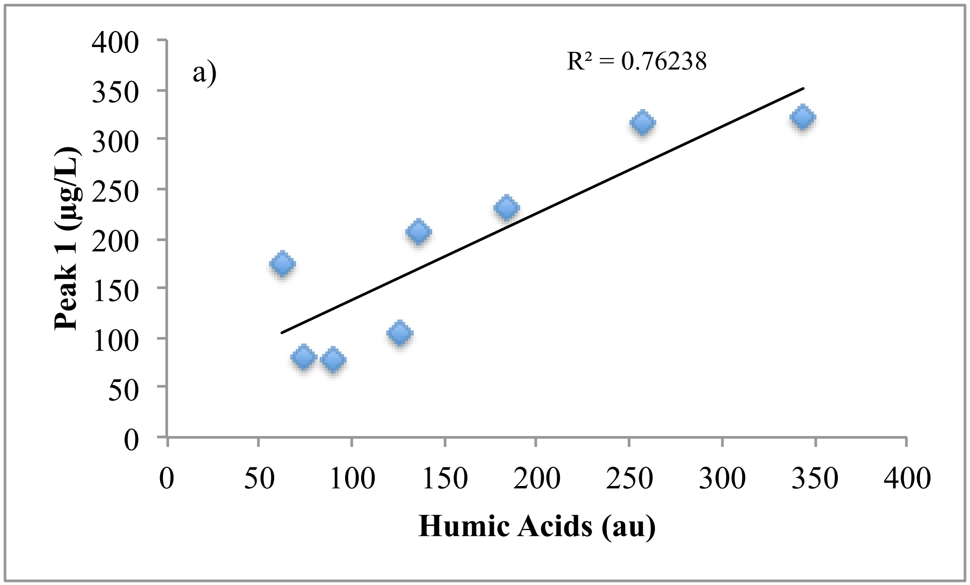
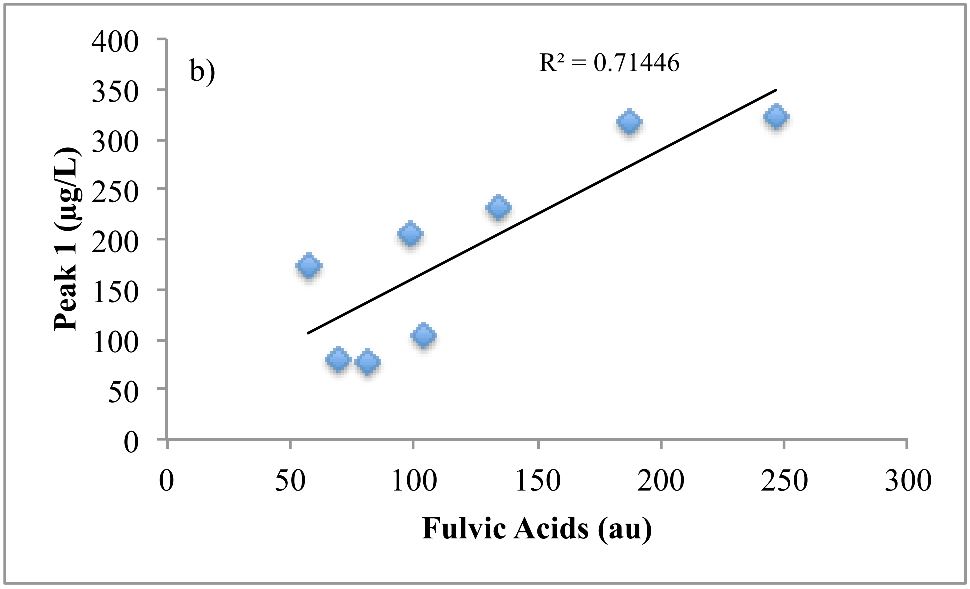


Figure D.8 Correlations between dissolved lead and a) decrease in humic acid intensity upon stagnation measured using FEEM, b) decrease in fulvic acid intensity upon stagnation measured using FEEM, c) change in SUVA upon stagnation measured using LC-OCD, and d) decrease in humics concentration upon stagnation measured using LC-OCD. The data plotted is for W, M, WS2, and MS4 measured on weeks 3, 7, 11, 16, and 21 for FEEM and weeks 7, 11, 16, and 21 for LC-OCD.


a)
R² = 0.76238
Peak 1 (µg/L)
400
350
300
250
200
150
100
50
0
0
50
100
150
200
250
300
350
400
Humic Acids (au)


b)
R² = 0.71446
Peak 1 (µg/L)
400
350
300
250
200
150
100
50
0
0
50
100
150
200
250
300
Fulvic Acids (au)

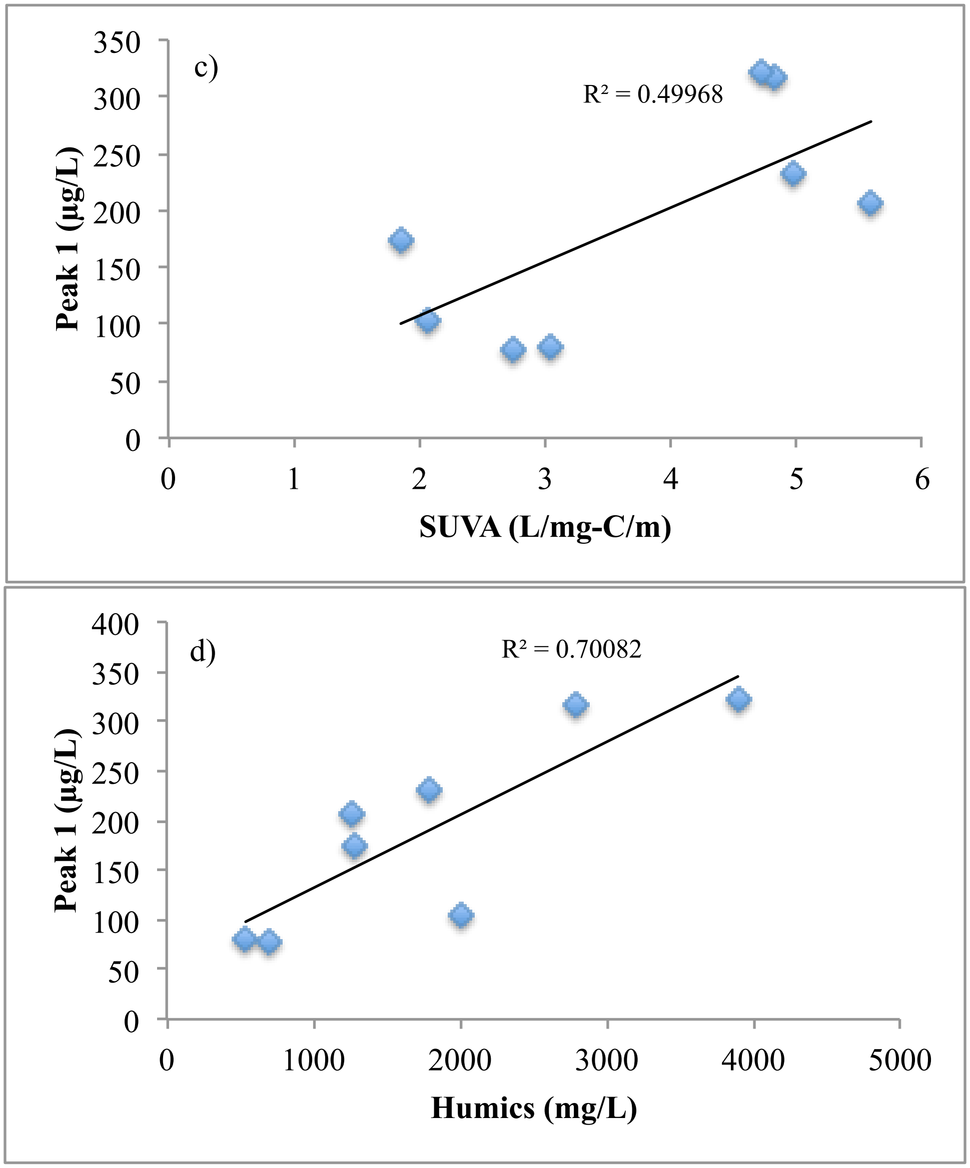
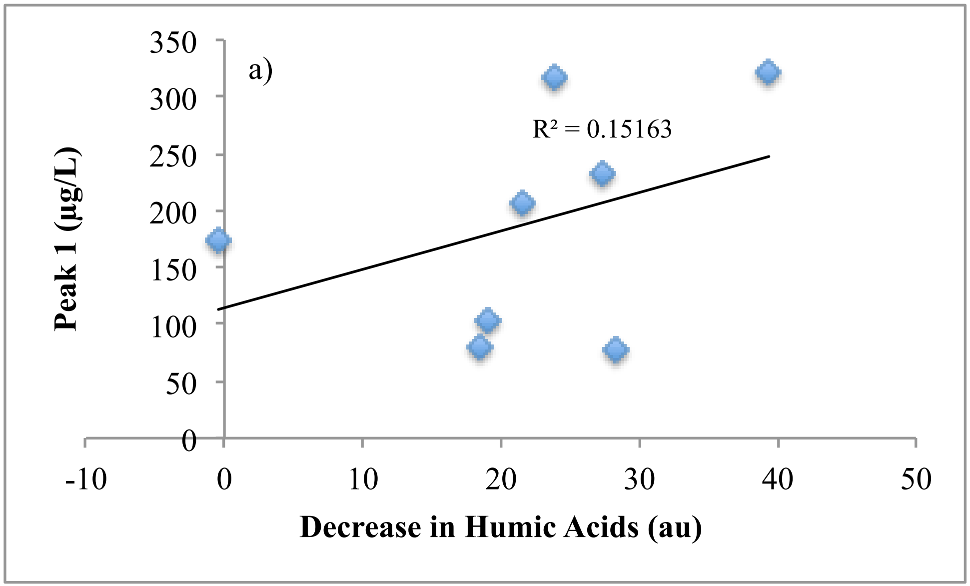
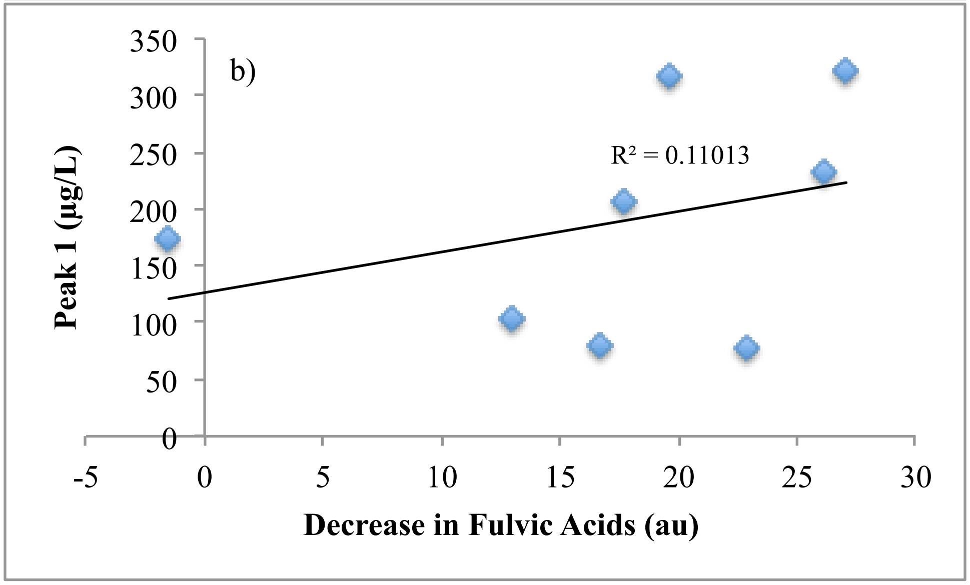


Figure D.9 Correlations between lead in peak 1 (void volume) measured with FFF/ICP-MS and a) initial humic acid intensity measured using FEEM, b) initial fulvic acid intensity measured using FEEM, c) initial SUVA measured using LC-OCD, and d) initial humics concentration measured using LC-OCD. The data plotted is for W, M, WS2, and MS4 measured on weeks 16 and 21.


a)
R² = 0.15163
Peak 1 (µg/L)
350
300
250
200
150
100
50
0
-10
0
10
20
30
40
50
Decrease in Humic Acids (au)


b)
R² = 0.11013
Peak 1 (µg/L)
350
300
250
200
150
100
50
0
-5
0
5
10
15
20
25
30
Decrease in Fulvic Acids (au)

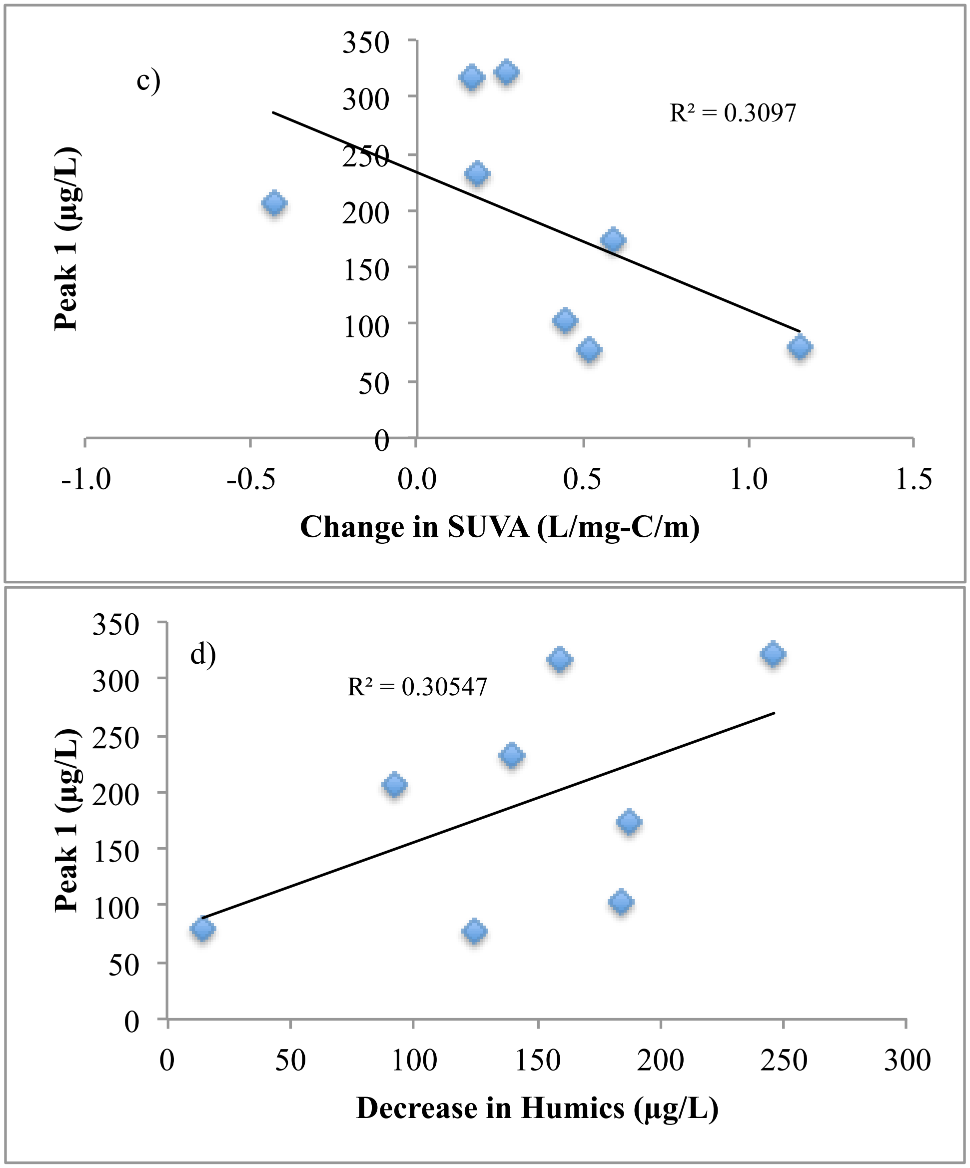
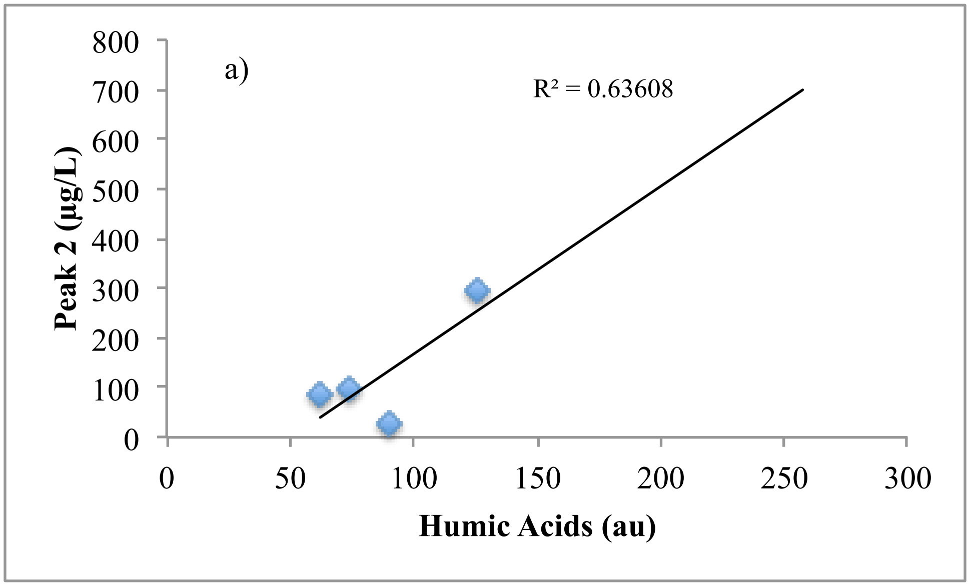
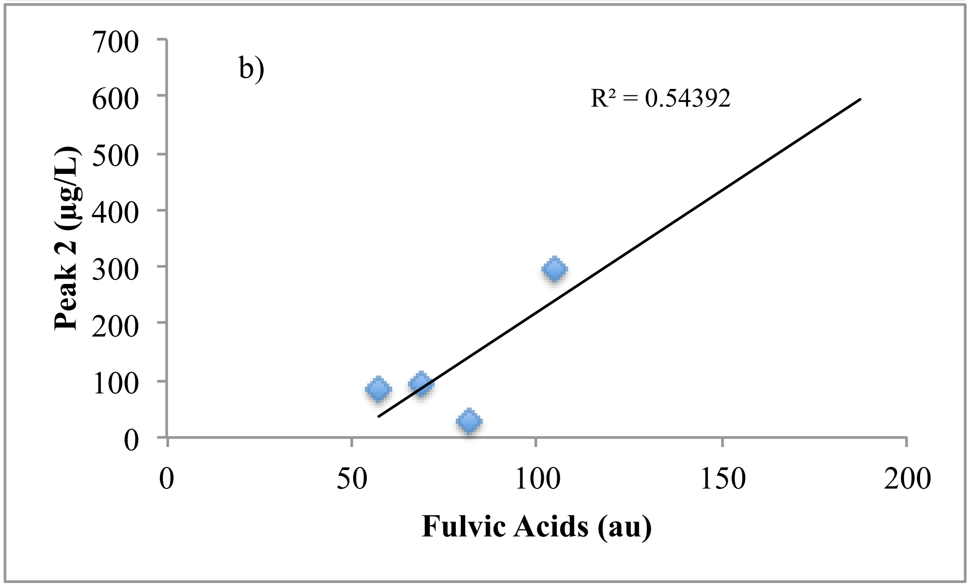


Figure D.10 Correlations between lead in peak 1 (void volume) measured with FFF/ICP-MS and a) decrease in humic acid intensity upon stagnation measured using FEEM, b) decrease in fulvic acid intensity upon stagnation measured using FEEM, c) change in SUVA upon stagnation measured using LC-OCD, and d) decrease in humics concentration upon stagnation measured using LC-OCD. The data plotted is for W, M, WS2, and MS4 measured on weeks 16 and 21.


a)
R² = 0.63608
Peak 2 (µg/L)
800
700
600
500
400
300
200
100
0
0
50
100
150
200
250
300
Humic Acids (au)


b)
R² = 0.54392
Peak 2 (µg/L)
700
600
500
400
300
200
100
0
0
50
100
150
200
Fulvic Acids (au)

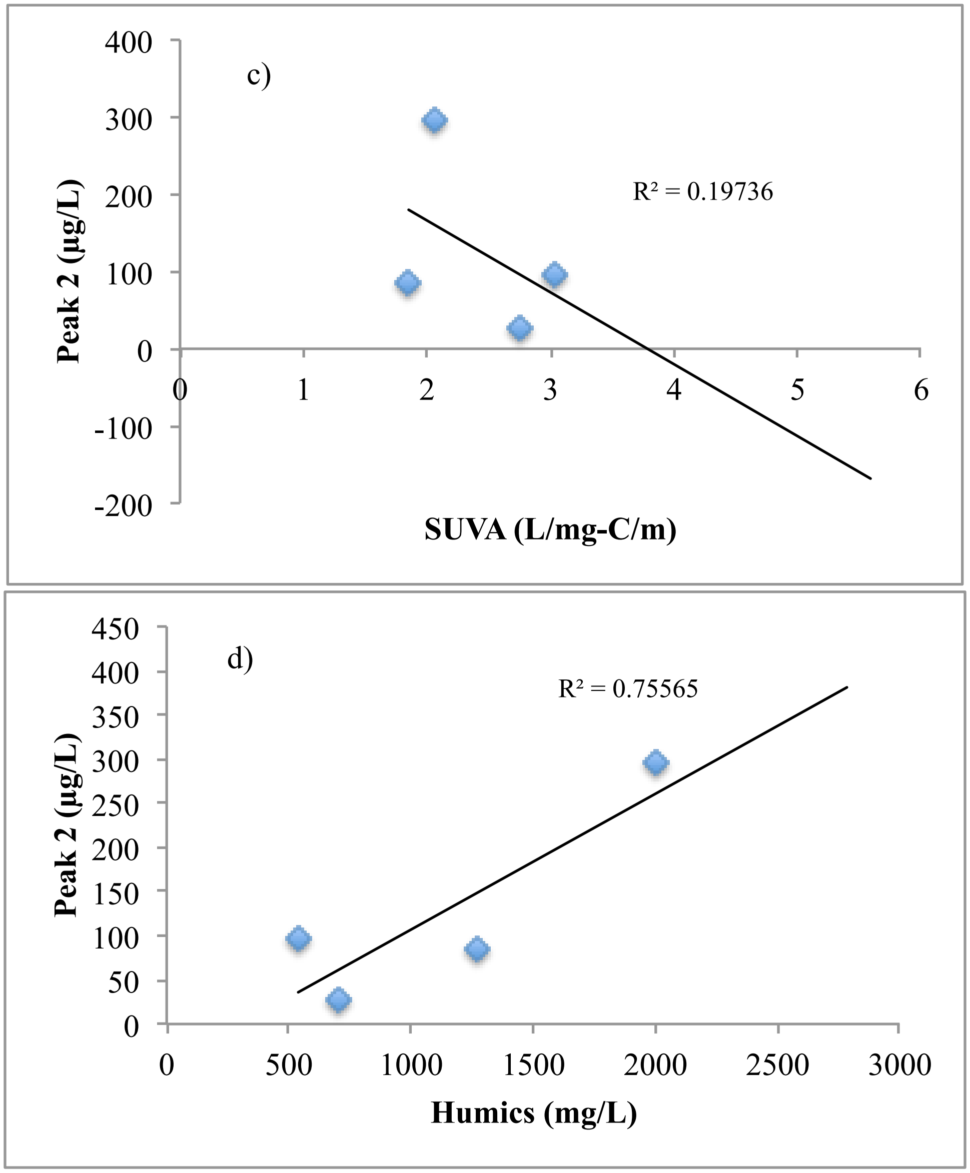
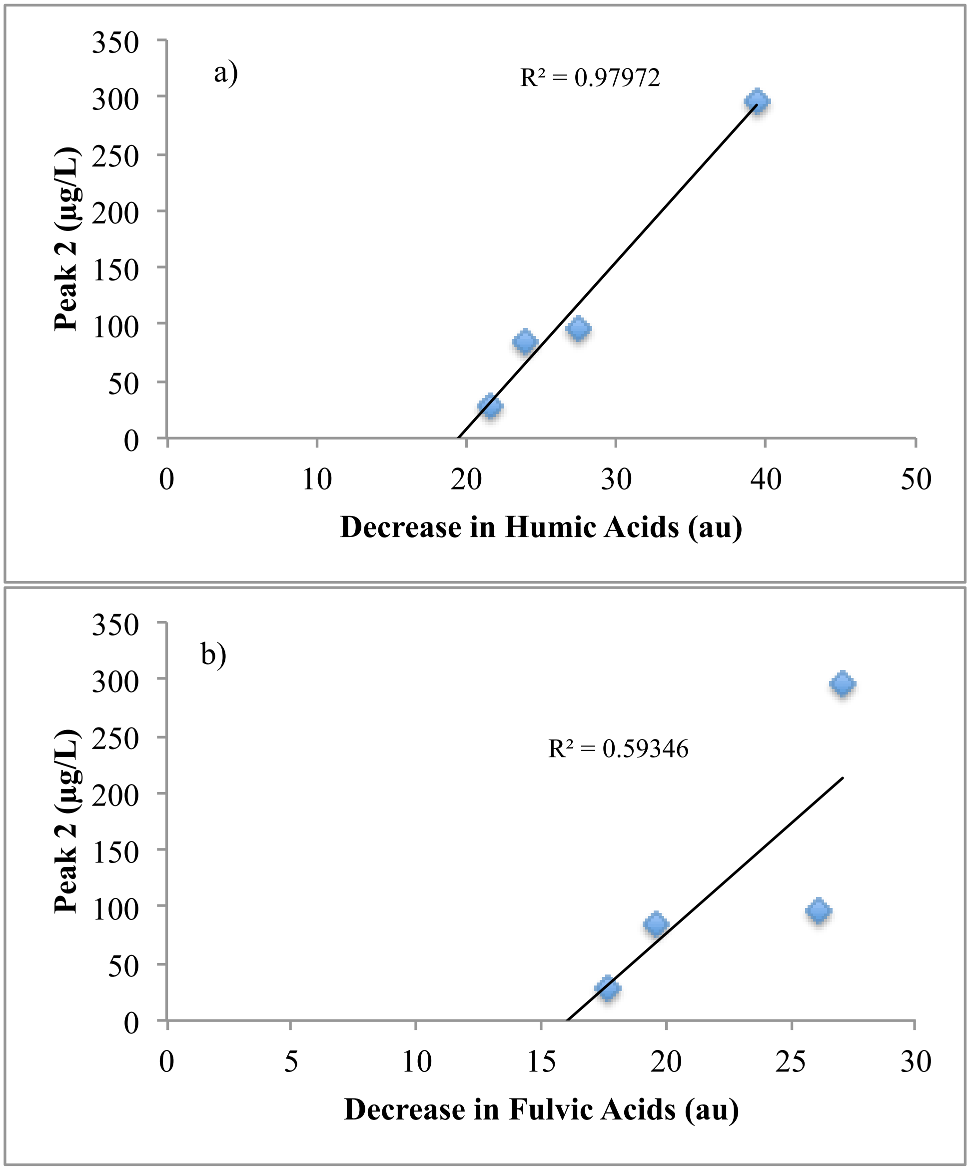


Figure D.11 Correlations between lead in peak 2 (NOM fraction) measured with FFF/ICP-MS and a) initial humic acid intensity measured using FEEM, b) initial fulvic acid intensity measured using FEEM, c) initial SUVA measured using LC-OCD, and d) initial humics concentration measured using LC-OCD. The data plotted is for WS2 and MS4 measured on weeks 16 and 21.


a)
R² = 0.97972
Peak 2 (µg/L)
350
300
250
200
150
100
50
0
0
10
20
30
40
50
Decrease in Humic Acids (au)
b)
R² = 0.59346
Peak 2 (µg/L)
350
300
250
200
150
100
50
0
0
5
10
15
20
25
30
Decrease in Fulvic Acids (au)

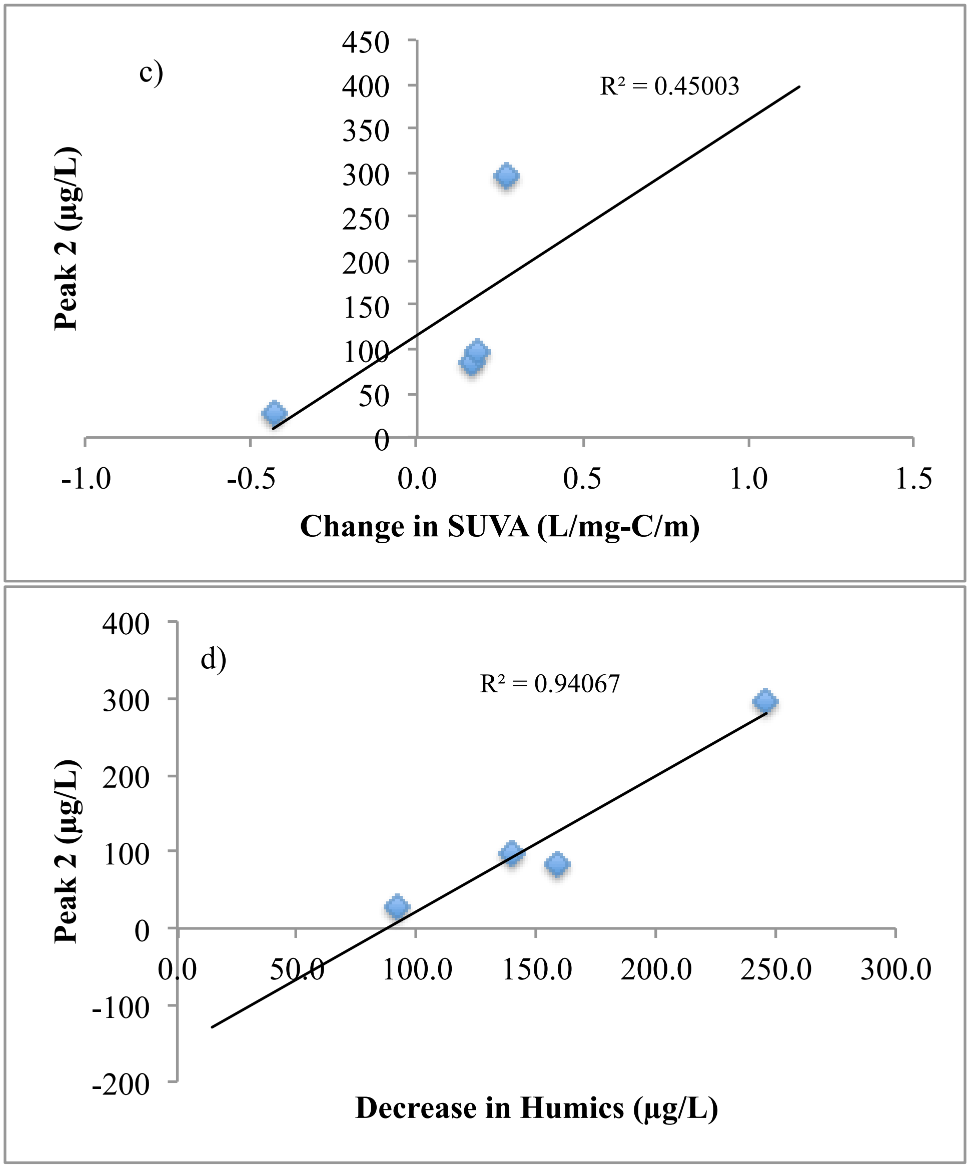


Figure D.12 Correlations between lead in peak 2 (primary NOM) fraction measured with FFF/ICP-MS and a) decrease in humic acid intensity upon stagnation measured using FEEM, b) decrease in fulvic acid intensity upon stagnation measured using FEEM, c) change in SUVA upon stagnation measured using LC-OCD, and d) decrease in humics concentration upon stagnation measured using LC-OCD. The data plotted is for WS2 and MS4 measured on weeks 16 and 21.

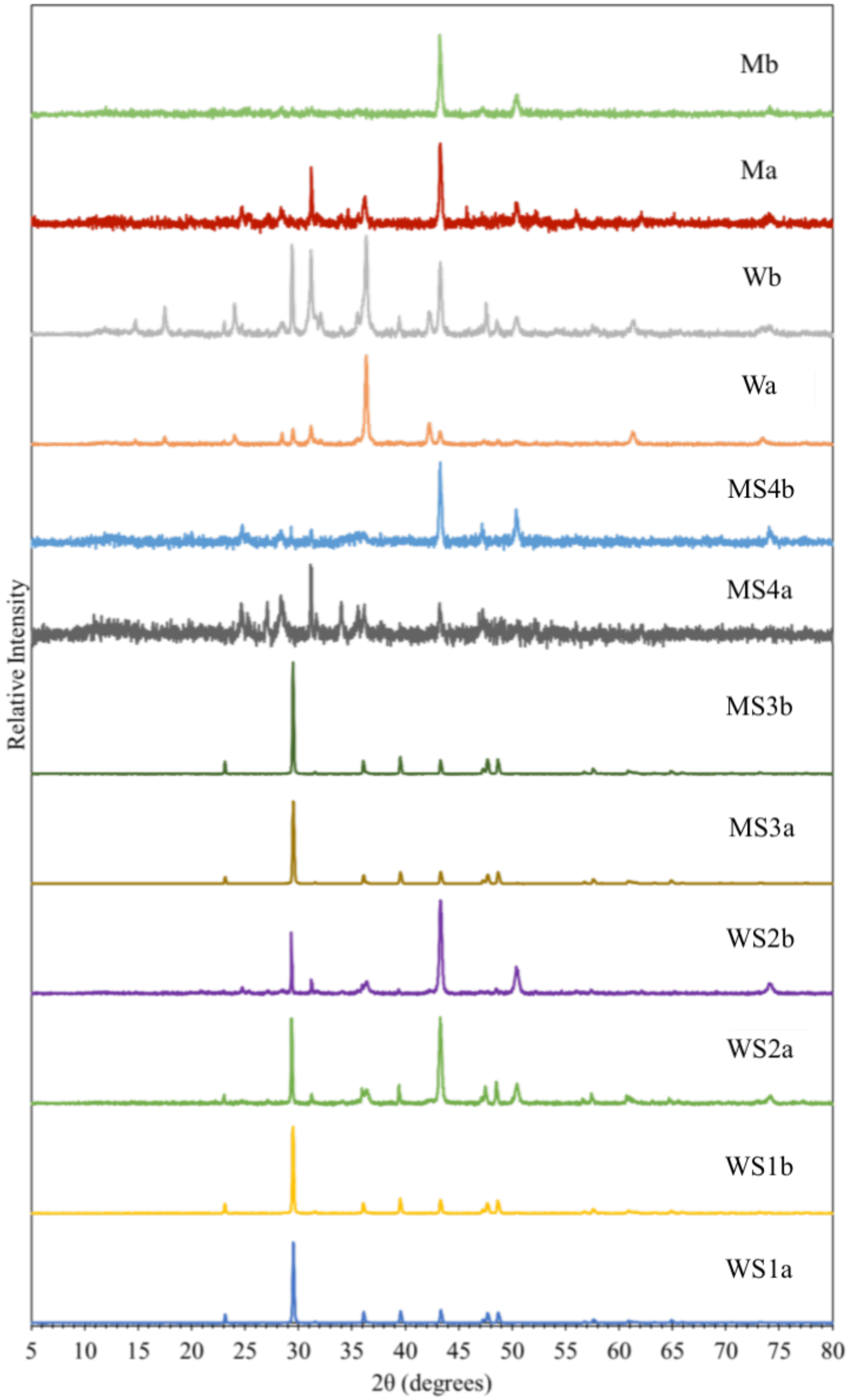


Figure D.13 XRD patterns obtained from the surface of the copper pipes for a range of 5° to 80° 2θ to represent their relative percentage. The XRD patterns have been rescaled due to the varying peak intensities arising from the varying abundance of minerals in the scale.

Table D.1 Significant Differences in Response Variables

Parameter	Higher	Lower	Difference	p-value
Galvanic Current (μA)	W (51.7)	MS3 (35.4)	16.2	0.065
	WS2 (69.2)	W (51.7)	17.6	0.088
		M (45.2)	24.0	0.016
		WS1 (46.8)	22.4	0.022
		MS3 (35.4)	33.8	0.003
		MS4 (44.8)	24.4	0.015
Dissolved Lead (μg/L)	W (441)	WS1 (117)	324	0.054
		MS3 (79.0)	362	0.024
	M (887)	WS1 (117)	770	0.015
		MS3 (79.0)	808	0.007
	WS2 (1,970)	W (441)	1,540	0.054
		WS1 (117)	1,860	0.002
		MS3 (79.0)	1,900	0.001
	MS4 (1,780)	W (441)	1,340	0.069
		WS1 (117)	1,660	0.002
		MS3 (79.0)	1,700	0.001
Total Copper (μg/L)	W (845)	M (397)	448	0.006
		WS1 (33.8)	811	<0.001
		WS2 (149)	696	<0.001
		MS3 (18.5)	826	<0.001
		MS4 (111)	734	<0.001
	M (397)	WS1 (33.8)	364	<0.001
		WS2 (149)	248	0.001
		MS3 (18.5)	379	<0.001
		MS4 (111)	286	<0.001
	WS1 (33.8)	MS3 (18.5)	15.2	0.022
	WS2 (149)	WS1 (33.8)	115	<0.001
		MS3 (18.5)	130	<0.001
	MS4 (111)	WS1 (33.8)	77.2	0.001
		MS3 (18.5)	92.5	<0.001

Table D.1 Significant Differences in Response Variables

Parameter	Higher	Lower	Difference	p-value
Dissolved Copper (μg/L)	W (861)	M (380)	482	0.005
		WS1 (16.7)	845	<0.001
		WS2 (74.6)	787	<0.001
		MS3 (6.90)	855	<0.001
		MS4 (71.2)	790	<0.001
	M (380)	WS1 (16.7)	362	<0.001
		WS2 (74.6)	305	<0.001
		MS3 (6.90)	373	<0.001
		MS4 (71.2)	308	<0.001
	WS1 (16.7)	MS3 (6.90)	9.84	0.003
	WS2 (74.6)	WS1 (16.7)	57.8	<0.001
		MS3 (6.90)	67.7	<0.001
	MS4 (71.2)	WS1 (16.7)	54.5	<0.001
		MS3 (6.90)	64.3	<0.001
Particulate Copper (μg/L)	W (107)	WS1 (14.9)	92.4	<0.001
		WS2 (59.1)	48.2	0.019
		MS3 (9.78)	97.6	<0.001
		MS4 (45.0)	62.3	0.002
	M (60.8)	WS1 (14.9)	45.9	0.001
		MS3 (9.78)	51.1	<0.001
		MS4 (45.0)	15.8	0.018
	WS2 (59.1)	WS1 (14.9)	44.2	0.003
		MS3 (9.78)	49.3	0.001
	MS4 (45.0)	WS1 (14.9)	30.1	0.034
		MS3 (9.78)	35.2	0.004

*ANOVA did not suggest there were significant differences between the water types for the release of total lead or particulate lead

** Significance was determined using the Tukey-Kramer test if ANOVA suggested that there were significant differences between the water types.

Table D.2 Percent of Oxidized Lead in the Test Pieces Released into the Water and Stored as a Corrosion Scale Based on Faraday's Law

Sample	% of Oxidized Lead Released	% of Oxidized Lead Stored as Corrosion Scale
Wa	8.4	91.6
Wb	3.3	96.7
Ma	1.7	98.3
Mb	5.0	95.0
WS1a	6.5	93.5
WS1b	3.3	96.7
WS2a	23.6	76.4
WS2b	7.8	92.2
MS3a	5.7	94.3
MS3b	10.7	89.3
MS4a	9.2	90.8
MS4b	9.1	90.9

Table D.3 Semi-Quantitative Concentrations Corresponding to the Integrated Peaks (1-3) by Element

Sample	Week	Lead (µg/L)			Copper (µg/L)		
		Peak 1	Peak 2	Peak 3	Peak 1	Peak 2	Peak 3
W	16	79	NA	77	3.2	5.6	9.6
	17	78	NA	85	3.0	5.5	9.2
	21	81	NA	84	3.7	5.3	10.5
	Average	79	NA	82	3.3	5.5	9.8
M	16	174	NA	199	3.0	5.7	9.0
	17	80	NA	83	2.5	4.7	7.9
	21	105	NA	111	2.3	5.2	9.5
	Average	120	NA	131	2.6	5.2	8.8
WS1	16	46	NA	52	0.6	1.0	1.9
	17	29	NA	34	0.5	0.8	1.8
	21	27	NA	33	0.8	1.3	3.2
	Average	34	NA	39	0.6	1.0	2.3
WS2	16	206	28	159	1.4	3.5	5.3
	17	204	29	154	0.8	2.6	3.4
	21	232	85	164	1.2	4.9	4.9
	Average	214	48	159	1.1	3.7	4.5
MS3	16	44	NA	45	0.4	0.7	1.5
	17	31	NA	32	0.6	1.1	2.2
	21	22	NA	22	0.5	0.6	1.7
	Average	32	NA	33	0.5	0.8	1.8
MS4	16	318	96	189	1.0	4.3	4.6
	17	255	104	158	1.3	6.3	5.6
	21	322	297	147	0.5	8.1	4.3
	Average	298	166	164	0.9	6.2	4.8

*Peak 1 = void volume, Peak 2 = NOM peak, Peak 3 = larger colloidal peak

Table D.4 Composition of Organic Matter Determined by LC-OCD

			W	M	WS2	MS4
HOC		% of DOC	11.2	11.7	10.3	7.1
CDOC		% of DOC	88.8	88.4	89.7	92.9
	Biopolymers	% of CDOC	0.2	6.4	0.1	0.1
	Humics	% of CDOC	64.1	62.0	80.9	83.1
	Building Blocks	% of CDOC	19.3	16.0	9.8	9.6
	LMW Neutrals	% of CDOC	12.4	11.4	8.4	6.8
	LMW Acids/Humics	% of CDOC	3.9	4.2	0.9	0.5

Table D.5 Summary of Results from XRD Conducted on the Powdered Samples from the Copper Pipe Surface

	Hydrocerussite	Cerussite	Litharge	Lead	Copper	Cuprite	Tenorite	Calcite Magnesian	Calcite	Malachite
Wa					++	+++		++		++
Wb	+	+	+		++	++		++		++
Ma	+	+	+	++	+++					
Mb			+	+	+++		+		+	
WS1a					+	+		+++		
WS1b					+	+		+++		
WS2a				++	+++	++			+++	
WS2b	+			++	+++	++			+++	
MS3a		+			+	+		+++		
MS3b					+	+		+++		
MS4a	+	+	+	+	++		+			
MS4b	+	+	++	+++			+		+	

*‘+’ indicates the abundance of a certain mineral (greater than approximately 1%)
**‘+++’ indicates the most abundant minerals, followed by the ‘++’ minerals and then the ‘+’ minerals

Table D.6 Mass Ratio (mg/g of Scale) of Elements in the Scales on the Lead Pipes Determined by Acid Digestion of Solids Followed by Analysis with ICP-MS

	Pb	Ca	Fe	Mg	K	Cu	Na	Al	Mn
Wa	473.3	n.d.	5.6	4.1	5.0	4.6	2.0	n.d.	n.d.
Wb	465.5	32.3	13.6	10.3	6.4	5.6	4.0	n.d.	n.d.
Ma	542.1	29.5	6.9	3.4	4.7	2.6	0.6	n.d.	n.d.
Mb	532.8	37.5	14.5	6.5	3.6	0.2	6.1	2.2	n.d.
WS1a	481.5	22.3	15.8	2.2	3.9	2.2	n.d.	n.d.	n.d.
WS1b	515.6	35.4	6.2	3.3	6.2	2.9	1.5	n.d.	n.d.
WS2a	342.7	22.9	4.3	3.5	3.4	2.5	1.2	n.d.	n.d.
WS2b	476.2	24.6	5.9	2.7	4.2	1.7	1.5	0.1	n.d.
MS3a	516.7	27.7	5.6	2.9	3.8	1.7	1.0	n.d.	n.d.
MS3b	446.8	20.4	4.2	1.9	2.7	1.0	0.9	n.d.	n.d.
MS4a	340.4	21.5	4.0	5.8	2.3	0.0	4.4	n.d.	n.d.
MS4b	428.8	29.3	6.6	6.8	4.3	3.3	2.1	n.d.	0.3

*n.d. not detected

Table D.7 Mass Ratio (mg/g of Scale) of Elements in the Scales on the Copper Pipes Determined by Acid Digestion of Solids Followed by Analysis with ICP-MS

	Ca	Cu	Fe	Mg	Pb	Al	Mn	Na
Wa	304.5	371.7	83.0	85.6	76.4	4.0	0.4	n.d.
Wb	320.6	222.5	87.1	42.2	58.2	n.d.	n.d.	1.7
Ma	329.6	86.6	74.4	47.6	23.3	n.d.	n.d.	n.d.
Mb	557.1	62.3	78.1	39.9	11.0	n.d.	1.9	n.d.
WS1a	67.8	51.2	11.5	7.3	4.5	0.6	n.d.	n.d.
WS1b	66.4	30.7	14.8	6.9	3.5	n.d.	n.d.	n.d.
WS2a	314.0	417.8	72.9	40.4	7.1	n.d.	n.d.	n.d.
WS2b	376.9	225.3	76.5	43.2	38.3	n.d.	n.d.	n.d.
MS3a	527.8	56.4	16.8	17.6	6.5	n.d.	n.d.	n.d.
MS3b	220.4	35.5	11.6	5.1	2.2	n.d.	n.d.	n.d.
MS4a	206.0	231.1	46.0	21.1	21.3	n.d.	n.d.	n.d.
MS4b	343.6	223.3	81.1	50.1	25.8	n.d.	n.d.	n.d.

*n.d. not detected

Table D.8 Summary of Galvanic Current, Lead Release, and Copper Release

		Wa	Wb	Ma	Mb	WS1a	WS1b	WS2a	WS2b	MS3a	MS3b	MS4a	MS4b
Galvanic Current (µA)	Average	59.3	44.1	43.7	46.7	47.7	45.9	68.5	69.9	34.4	36.5	42.9	46.7
	Standard Deviation	15.3	5.2	2.6	3.0	2.4	2.0	7.6	5.9	2.0	3.0	4.4	3.5
	Coefficient of Variation (%)	25.8	11.8	5.9	6.5	5.1	4.4	11.1	8.4	5.7	8.3	10.2	7.6
	90% C.I. Lower Bound	52.3	41.7	42.5	45.3	46.6	45.0	64.9	67.1	33.5	35.0	40.9	45.1
	90% C.I. Upper Bound	66.2	46.4	44.9	48.1	48.8	46.9	72.1	72.7	35.3	37.9	44.9	48.3
	95% C.I. Lower Bound	50.8	41.2	42.2	45.0	46.4	44.8	64.1	66.5	33.3	34.7	40.4	44.7
	95% C.I. Upper Bound	67.7	46.9	45.1	48.4	49.1	47.1	72.9	73.3	35.5	38.2	45.3	48.7
	Median	63.0	44.7	43.1	46.6	47.8	45.9	71.3	70.9	33.9	37.2	42.5	46.3
	25th Percentile	44.7	39.1	41.8	43.6	45.1	44.7	61.3	68.7	33.2	33.8	39.5	44.4
	75th Percentile	70.7	49.0	45.3	49.3	49.3	47.3	74.8	73.5	36.1	38.9	45.1	47.9
	Minimum	34.4	35.3	39.9	42.1	43.9	41.8	56.3	57.2	31.4	30.8	37.3	40.7
	Maximum	82.5	50.7	48.9	51.5	53.5	49.6	78.2	77.6	37.6	40.1	55.0	54.1
	Number of Measurements	15	15	15	15	15	14	14	14	14	14	15	15
Total Lead (µg/L)	Average	3122	674	459	2057	1532	650	10629	4007	549	3115	2268	3103
	Standard Deviation	2362	338	91	726	1414	514	9637	2177	387	2406	467	483
	Coefficient of Variation (%)	75.7	50.2	19.8	35.3	92.3	79.0	90.7	54.3	70.5	77.2	20.6	15.6
	90% C.I. Lower Bound	1868	506	407	1740	772	373	5390	3029	330	3325	2033	3151
	90% C.I. Upper Bound	4016	813	489	2400	2057	840	14154	5008	682	5513	2458	3590
	95% C.I. Lower Bound	1634	472	398	1668	632	322	4434	2813	292	3086	1987	3103
	95% C.I. Upper Bound	4251	847	498	2472	2197	891	15109	5224	721	5752	2505	3638
	Median	2552	610	434	2122	853	508	7463	3263	338	2358	2205	3018
	25th Percentile	1286	473	378	1304	633	262	2849	2739	225	1655	2003	2673
	75th Percentile	3352	803	554	2672	1766	968	16860	4511	861	4028	2337	3373
	Minimum	624	438	327	1082	434	185	2261	1219	173	869	1640	2542
	Maximum	9047	1785	595	3232	4921	2013	38220	9449	1282	10390	3528	4090
	Number of Measurements	15	15	15	15	15	15	15	15	15	15	15	15
Dissolved Lead (µg/L)	Average	436	446	414	1360	144	89	2034	1923	85	73	1604	1949
	Standard Deviation	40	59	77	593	44	66	487	623	44	14	357	236
	Coefficient of Variation (%)	9	13	19	44	30	73	24	32	52	19	22	12
	90% C.I. Lower Bound	407	402	357	925	112	41	1676	1465	53	63	1341	1776
	90% C.I. Upper Bound	465	489	470	1795	176	138	2391	2381	118	83	1866	2123
	95% C.I. Lower Bound	399	391	342	812	104	29	1583	1346	44	60	1273	1731
	95% C.I. Upper Bound	472	500	485	1908	185	150	2484	2500	126	86	1934	2168
	Median	428	437	431	1634	149	67	1911	1744	62	75	1492	2036
	25th Percentile	399	422	339	745	112	42	1622	1408	51	60	1305	1843
	75th Percentile	478	507	475	1748	162	159	2209	2225	110	85	1801	2103
	Minimum	397	341	298	667	78	41	1595	1214	48	53	1251	1457
	Maximum	501	512	517	2144	219	205	2983	3088	167	91	2277	2112
	Number of Measurements	7	7	7	7	7	7	7	7	7	7	7	7

Table D.8 Summary of Galvanic Current, Lead Release, and Copper Release

		Wa	Wb	Ma	Mb	WS1a	WS1b	WS2a	WS2b	MS3a	MS3b	MS4a	MS4b
Particulate Lead (µg/L)	Average	3729	621	103	1718	1106	595	23189	4099	657	2741	1525	1991
	Standard Deviation	2367	1044	54	1073	1045	500	19713	6696	586	1305	1075	1182
	Coefficient of Variation (%)	63.5	168.1	52.7	62.4	94.5	84.0	85.0	163.3	89.2	47.6	70.5	59.4
	90% C.I. Lower Bound	1991	-146	63	931	339	228	8713	-818	227	1782	735	1123
	90% C.I. Upper Bound	5467	1388	143	2506	1873	962	37666	9016	1087	3700	2315	2859
	95% C.I. Lower Bound	1540	-345	53	726	140	133	4957	-2094	115	1534	530	898
	95% C.I. Upper Bound	5918	1587	153	2710	2072	1057	41421	10292	1199	3948	2520	3085
	Median	2884	162	82	1724	643	301	22931	1620	274	2250	1062	1789
	25th Percentile	1832	118	70	751	603	173	4448	675	165	2016	878	1143
	75th Percentile	6728	717	156	2439	1099	1189	43168	3774	1226	4399	1916	2318
	Minimum	1420	110	26	335	292	160	948	397	133	873	608	903
	Maximum	7234	2938	182	3582	3385	1303	49131	19082	1453	4422	3764	4382
	Number of Measurements	7	7	7	7	7	7	7	7	7	7	7	7
Total Copper (µg/L)	Average	851	839	412	382	32	36	122	176	18	19	104	118
	Standard Deviation	209	133	99	57	5	18	55	83	4	3	58	40
	Coefficient of Variation (%)	24.6	15.8	24.0	15.0	14.5	51.1	45.2	47.4	24.5	16.3	56.2	33.6
	90% C.I. Lower Bound	711	751	346	344	29	24	86	120	15	17	65	92
	90% C.I. Upper Bound	990	928	478	420	35	48	159	231	21	21	143	144
	95% C.I. Lower Bound	681	732	332	336	28	21	78	108	14	16	57	86
	95% C.I. Upper Bound	1020	947	493	429	36	51	167	243	22	21	151	150
	Median	865	842	365	362	33	33	100	171	19	19	90	116
	25th Percentile	626	711	346	335	27	22	74	114	13	17	68	79
	75th Percentile	1016	891	529	438	34	41	191	215	21	21	140	165
	Minimum	524	656	306	314	26	20	69	61	11	13	41	68
	Maximum	1155	1077	623	477	42	93	211	381	26	24	257	176
	Number of Measurements	15	15	15	15	15	15	15	15	15	15	15	15
Dissolved Copper (µg/L)	Average	882	841	390	370	18	16	65	84	8	6	71	71
	Standard Deviation	259	201	82	56	4	5	21	27	2	2	53	17
	Coefficient of Variation (%)	29.3	23.9	20.9	15.1	20.9	33.4	32.6	31.6	25.3	36.6	74.2	23.5
	90% C.I. Lower Bound	692	693	330	329	15	12	50	64	6	4	32	59
	90% C.I. Upper Bound	1072	989	449	411	21	20	81	103	9	8	110	84
	95% C.I. Lower Bound	642	655	314	318	14	11	46	59	6	4	22	56
	95% C.I. Upper Bound	1121	1027	465	421	21	21	85	108	10	8	120	87
	Median	873	808	377	364	17	14	56	89	7	6	50	66
	25th Percentile	683	639	336	329	16	11	47	58	6	4	45	57
	75th Percentile	1189	1054	496	414	20	20	84	106	9	8	79	79
	Minimum	471	578	274	277	14	10	47	47	6	4	36	57
	Maximum	1194	1130	497	442	25	25	104	119	12	9	187	105
	Number of Measurements	7	7	7	7	7	7	7	7	7	7	7	7

Table D.8 Summary of Galvanic Current, Lead Release, and Copper Release

		Wa	Wb	Ma	Mb	WS1a	WS1b	WS2a	WS2b	MS3a	MS3b	MS4a	MS4b
Particulate Copper (µg/L)	Average	91	123	68	54	16	14	58	60	8	11	43	47
	Standard Deviation	25	46	30	45	2	6	45	41	3	2	42	38
	Coefficient of Variation (%)	27.7	37.0	44.0	83.0	14.5	46.1	77.2	69.1	37.8	21.3	99.7	81.1
	90% C.I. Lower Bound	73	90	46	21	14	9	25	29	6	9	11	19
	90% C.I. Upper Bound	110	157	90	86	18	18	91	90	11	13	74	76
	95% C.I. Lower Bound	68	81	40	12	14	8	17	22	5	9	3	12
	95% C.I. Upper Bound	115	166	96	95	18	20	100	98	11	13	82	83
	Median	101	126	65	64	17	12	29	41	7	12	26	41
	25th Percentile	60	88	51	53	14	8	21	36	6	10	10	10
	75th Percentile	112	131	74	74	18	20	102	108	12	13	95	100
	Minimum	59	72	35	-40	13	7	14	13	6	6	4	8
	Maximum	121	214	130	101	19	24	114	126	13	14	110	100
	Number of Measurements	7	7	7	7	7	7	7	7	7	7	7	7

*Detection limit of 0.4 µg/L for lead and 0.7 µg/L for copper

**Statistics are for the measurements during weeks 5-19

Table D.9 Summary of FEEM, LC-OCD, and TOC Analyzer Results

			Average Before	Average After	Average Change	p-Value
FEEM	Humic Acids (au)	Wa	103.18	71.06	-28.85	**0.001**
		Wb		72.34	-27.57	**0.001**
		Ma	139.18	111.71	-20.28	**0.026**
		Mb		111.85	-20.14	**0.020**
		WS2a	140.30	120.98	-19.32	**0.001**
		WS2b		122.02	-18.29	**0.008**
		MS4a	274.26	247.85	-26.40	**0.003**
		MS4b		241.01	-33.25	**0.001**
	Fulvic Acids (au)	Wa	94.93	66.60	-23.29	**0.000**
		Wb		66.86	-23.04	**0.001**
		Ma	121.56	99.10	-15.77	**0.047**
		Mb		98.79	-16.09	**0.041**
		WS2a	100.50	85.88	-14.62	**0.013**
		WS2b		87.22	-13.28	**0.047**
		MS4a	193.97	177.90	-16.07	**0.006**
		MS4b		174.00	-19.96	**0.007**
	Proteins (au)	Wa	11.63	11.56	1.13	0.182
		Wb		13.31	2.88	**0.003**
		Ma	20.42	21.80	3.13	**0.015**
		Mb		21.36	2.69	**0.014**
		WS2a	8.49	9.10	0.62	0.588
		WS2b		9.72	1.24	0.546
		MS4a	11.88	13.27	1.39	0.098
		MS4b		12.80	0.92	0.366
LC-OCD	DOC (mg/L)	Wa	1.39	1.33	-0.01	0.884
		Wb		1.30	-0.04	0.528
		Ma	3.49	3.18	-0.29	0.178
		Mb		3.14	-0.33	**0.022**
		WS2a	1.93	1.55	-0.34	**0.010**
		WS2b		1.61	-0.26	**0.011**
		MS4a	3.92	3.55	-0.26	0.091
		MS4b		3.48	-0.42	**0.012**

Table D.9 Summary of FEEM, LC-OCD, and TOC Analyzer Results

			Average Before	Average After	Average Change	p-Value
LC-OCD	SUVA (L-mg/C-m)	Wa	2.86	3.31	0.14	0.724
		Wb		3.12	0.05	0.946
		Ma	2.19	2.44	0.39	0.092
		Mb		2.48	0.39	**0.003**
		WS2a	4.83	5.13	0.32	0.353
		WS2b		4.81	0.05	0.881
		MS4a	4.83	4.94	0.14	0.240
		MS4b		4.97	0.16	0.082
	Hydrophobic (µg C/L)	Wa	156	195	50	0.127
		Wb		170	30	0.609
		Ma	410	366	-108	0.537
		Mb		335	-143	0.121
		WS2a	199	74	-127	0.256
		WS2b		156	-81	**0.042**
		MS4a	280	212	-75	0.290
		MS4b		178	-147	0.069
	Biopolymers (µg C/L)	Wa	3	14	11	-
		Wb		15	22	0.247
		Ma	198	159	-22	0.078
		Mb		161	-18	0.066
		WS2a	2	5	4	0.258
		WS2b		6	11	0.395
		MS4a	3	6	5	0.304
		MS4b		9	6	0.225
	Humics (µg C/L)	Wa	791	689	-86	0.082
		Wb		675	-105	**0.019**
		Ma	1914	1738	-125	**0.010**
		Mb		1718	-150	**0.027**
		WS2a	1404	1221	-130	**0.009**
		WS2b		1197	-139	**0.013**
		MS4a	3022	2784	-154	**0.013**
		MS4b		2759	-219	**0.006**

Table D.9 Summary of FEEM, LC-OCD, and TOC Analyzer Results

			Average Before	Average After	Average Change	p-Value
LC-OCD	Building Blocks (µg C/L)	Wa	239	229	-17	0.227
		Wb		237	-9	0.536
		Ma	493	473	-27	0.457
		Mb		488	-7	0.867
		WS2a	170	152	-14	**0.043**
		WS2b		142	-24	**0.013**
		MS4a	348	327	-15	**0.008**
		MS4b		322	-20	0.139
	LMW Neutrals (µg C/L)	Wa	153	167	37	0.058
		Wb		161	30	**0.037**
		Ma	352	328	-6	0.519
		Mb		319	-7	0.683
		WS2a	145	131	-4	0.879
		WS2b		134	-10	0.772
		MS4a	247	213	-13	0.599
		MS4b		206	-33	**0.040**
	LMW Acids/Humics (µg C/L)	Wa	48	38	-3	0.482
		Wb		39	-1	0.765
		Ma	129	114	-5	0.537
		Mb		114	-4	0.555
		WS2a	15	7	-8	0.257
		WS2b		7	-8	0.236
		MS4a	18	18	0	0.955
		MS4b		16	-3	**0.038**
TOC Analyzer	TOC (mg/L)	Wa	1.83	3.43	3.43	-
		Wb		3.44	3.44	-
		Ma	4.46	4.77	4.77	-
		Mb		4.68	4.68	-
		WS2a	3.20	3.30	3.30	-
		WS2b		3.14	3.14	-
		MS4a	6.15	6.14	6.14	-
		MS4b		6.11	6.11	-

Table D.9 Summary of FEEM, LC-OCD, and TOC Analyzer Results

			Average Before	Average After	Average Change	p-Value
TOC Analyzer	DOC (mg/L)	Wa		-	-	-
		Wb	1.36	-	-	-
		Ma		-	-	-
		Mb	4.20	-	-	-
		WS2a		-	-	-
		WS2b	3.01	-	-	-
		MS4a		-	-	-
		MS4b	5.59	-	-	-
	POC (mg/L)	Wa		-	-	-
		Wb	-1.36	-	-	-
		Ma		-	-	-
		Mb	-4.20	-	-	-
		WS2a		-	-	-
		WS2b	-3.01	-	-	-
		MS4a		-	-	-
		MS4b	-5.59	-	-	-

1. FEEM was measured on weeks 1-21 for W, M before stagnation, weeks 3,7,11,16, 21 for WS2, MS4 before stagnation, and weeks 3,7,11,16,21 for all samples after stagnation
2. Change in FEEM fractions were calculated for weeks 3,7,11,16,21
3. LC-OCD was measured on weeks 1,2,4,5,7-21 for W, M before stagnation, weeks 7,11,16,21 for WS2, MS4 before stagnation, and weeks 3,7,11,16,21 after stagnation
4. Change in LC-OCD fractions were calculated for weeks 7,11,16,21
5. TOC was measured on week 21 before and after stagnation and DOC was measured on week 21 before stagnation
6. Change in hydrophobic and biopolymer fraction data were omitted if data before or after stagnation was below the detection limit

Table D.10 Chemistry of Synthetic Waters Prior to Stagnation in the Test Pieces

	pH (Weeks 1-4)			pH (Weeks 5-21)			DIC (mg/L)		
Sample	Average	Min	Max	Average	Min	Max	Average	Min	Max
W	7.30	7.05	7.49	7.19	7.13	7.37	71.0	63.1	76.1
M	7.56	7.31	7.77	7.45	7.30	7.66	43.1	38.1	52.7
WS1	7.12	6.90	7.23	7.16	7.04	7.36	67.2	65.5	70.0
WS2	7.16	6.92	7.27	7.19	7.05	7.43	67.0	64.6	70.1
MS3	7.51	7.26	7.63	7.55	7.39	7.83	49.7	48.8	51.2
MS4	7.51	7.30	7.62	7.59	7.45	7.84	49.5	48.4	50.4

*n.m. not measured

**The pH, DOC, and CSMR in the synthetic waters were adjusted after week 4 to better simulate the real waters

***The DOC was increased by about 1.45x in the synthetic waters during weeks 20 and 21

****n.d Not detected

Table D.10 Chemistry of Synthetic Waters Prior to Stagnation in the Test Pieces

Sample	Hardness (mg $CaCO_3$/L)			DOC (mg/L) (Weeks 1-4)			DOC (mg/L) (Weeks 5-19)		
	Average	Min	Max	Average	Min	Max	Average	Min	Max
W	312	302	322	1.77	1.50	2.03	1.35	1.10	1.71
M	264	249	278	3.65	3.61	3.71	3.40	2.37	3.92
WS1	322	312	331	n.m.	n.m.	n.m.	0.07	-	-
WS2	325	315	335	n.m.	n.m.	n.m.	1.76	1.67	1.88
MS3	266	254	277	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
MS4	270	266	274	n.m.	n.m.	n.m.	3.49	3.35	3.57

*n.m. not measured

**The pH, DOC, and CSMR in the synthetic waters were adjusted after week 4 to better simulate the real waters

***The DOC was increased by about 1.45x in the synthetic waters during weeks 20 and 21

****n.d Not detected

Table D.10 Chemistry of Synthetic Waters Prior to Stagnation in the Test Pieces

	DOC (mg/L) (Weeks 20-21)			Alkalinity (mg $CaCO_3$/L)			SPC (µS/cm) (Weeks 1-4)		
Sample	Average	Min	Max	Average	Min	Max	Average	Min	Max
W	1.08	1.08	1.08	262	246	278	705	736	653
M	3.93	3.87	3.98	167	148	204	671	693	650
WS1	n.m.	n.m.	n.m.	243	238	246	1341	1341	1341
WS2	2.45	-	-	243	236	248	1348	1348	1348
MS3	0.20	-	-	195	190	202	657	657	657
MS4	5.18	-	-	195	188	200	890	890	890

*n.m. not measured

**The pH, DOC, and CSMR in the synthetic waters were adjusted after week 4 to better simulate the real waters

***The DOC was increased by about 1.45x in the synthetic waters during weeks 20 and 21

****n.d Not detected

Table D.10 Chemistry of Synthetic Waters Prior to Stagnation in the Test Pieces

Sample	SPC (µS/cm) (Weeks 5-21) Average	Min	Max	Turbidity (NTU) Average	Min	Max	Chloride (mg/L) (Weeks 1-4) Average	Min	Max
W	744	776	653	0.16	0.09	0.43	66	63	69
M	645	767	599	0.13	0.08	0.23	81	76	85
WS1	1689	1732	1664	0.48	0.09	2.42	265	-	-
WS2	1682	1729	1659	0.61	0.13	2.55	250	-	-
MS3	1159	1195	1135	0.20	0.10	0.33	217	-	-
MS4	1168	1189	1150	0.66	0.15	1.94	216	-	-

*n.m. not measured

**The pH, DOC, and CSMR in the synthetic waters were adjusted after week 4 to better simulate the real waters

***The DOC was increased by about 1.45x in the synthetic waters during weeks 20 and 21

****n.d Not detected

Table D.10 Chemistry of Synthetic Waters Prior to Stagnation in the Test Pieces

Sample	Chloride (mg/L) (Weeks 5-21)			Sulfate (mg/L) (Weeks 1-4)			Sulfate (mg/L) (Weeks 5-21)		
	Average	Min	Max	Average	Min	Max	Average	Min	Max
W	66	62	69	21	20	22	25	18	30
M	80	75	88	29	28	30	33	29	45
WS1	343	340	346	111	-	-	106	105	107
WS2	343	341	346	112	-	-	106	105	107
MS3	213	211	216	85	-	-	86	85	86
MS4	214	213	215	85	-	-	86	85	86

*n.m. not measured

**The pH, DOC, and CSMR in the synthetic waters were adjusted after week 4 to better simulate the real waters

***The DOC was increased by about 1.45x in the synthetic waters during weeks 20 and 21

****n.d Not detected

Table D.10 Chemistry of Synthetic Waters Prior to Stagnation in the Test Pieces

	CSMR (Weeks 1-4)			CSMR (Weeks 5-21)			Nitrate (mg/L)		
Sample	Average	Min	Max	Average	Min	Max	Average	Min	Max
W	3.15	3.07	3.22	2.64	2.12	3.43	1.9	1.4	2.5
M	2.82	2.73	3.04	2.46	1.99	2.64	11.3	7.7	21.6
WS1	2.38	-	-	3.23	3.23	3.23	n.d.	n.d.	n.d.
WS2	2.24	-	-	3.23	3.22	3.24	n.d.	n.d.	n.d.
MS3	2.54	-	-	2.50	2.48	2.51	n.d.	n.d.	n.d.
MS4	2.54	-	-	2.50	2.50	2.50	n.d.	n.d.	n.d.

*n.m. not measured

**The pH, DOC, and CSMR in the synthetic waters were adjusted after week 4 to better simulate the real waters

***The DOC was increased by about 1.45x in the synthetic waters during weeks 20 and 21

****n.d Not detected

Table D.10 Chemistry of Synthetic Waters Prior to Stagnation in the Test Pieces

Sample	SUVA (L/mg-C/m)		
	Average	Min	Max
W	2.86	2.09	3.79
M	2.19	1.70	2.73
WS1	10.23	-	-
WS2	4.83	3.98	5.59
MS3	3.48	3.48	3.48
MS4	4.83	4.73	5.04

*n.m. not measured

**The pH, DOC, and CSMR in the synthetic waters were adjusted after week 4 to better simulate the real waters

***The DOC was increased by about 1.45x in the synthetic waters during weeks 20 and 21

****n.d Not detected

Table D.11 Chemistry of Synthetic Waters Following Stagnation in the Test Pieces

	pH (weeks 1-4)			pH (weeks 5-21)			DIC (mg/L)		
Sample	average	min	max	average	min	max	average	min	max
Wa	7.59	7.43	7.75	7.76	7.65	7.90	66.1	63.7	68.0
Wb	7.66	7.53	7.92	7.74	7.59	7.85	67.0	64.7	68.5
Ma	7.76	7.66	7.94	7.77	7.61	7.90	40.9	36.3	44.2
Mb	7.84	7.75	7.93	7.87	7.67	8.01	40.5	36.1	44.7
WS1a	7.65	7.58	7.71	7.67	7.55	7.84	59.7	57.9	61.7
WS1b	7.64	7.61	7.68	7.65	7.55	7.76	60.5	58.6	62.2
WS2a	7.81	7.75	7.87	8.00	7.86	8.13	60.4	58.5	61.4
WS2b	7.83	7.79	7.86	7.97	7.82	8.17	60.6	58.9	61.9
MS3a	7.91	7.82	8.05	7.77	7.64	7.89	44.5	43.2	45.5
MS3b	7.84	7.76	7.96	7.80	7.68	7.92	44.7	43.1	46.1
MS4a	8.17	8.09	8.24	8.19	8.05	8.36	47.7	46.4	48.9
MS4b	8.02	7.94	8.10	8.21	8.02	8.36	47.5	46.1	49.0

*n.m. not measured

**The pH, DOC, and CSMR in the synthetic waters were adjusted after week 4 to better simulate the real waters

***The DOC was increased by about 1.45x in the synthetic waters during weeks 20 and 21

Table D.11 Chemistry of Synthetic Waters Following Stagnation in the Test Pieces

	DOC (mg/L) (weeks 1-4)	DOC (mg/L) (weeks 5-19)			DOC (mg/L) (weeks 20-21)
Sample	average	average	min	max	average
Wa	1.70	1.29	1.18	1.40	1.09
Wb	1.65	1.28	1.08	1.38	1.01
Ma	3.51	3.03	2.03	3.75	3.29
Mb	3.43	2.94	2.10	3.43	3.44
WS1a	n.m.	0.18	-	-	n.m.
WS1b	n.m.	0.11	-	-	n.m.
WS2a	1.35	1.40	1.38	1.44	2.19
WS2b	1.36	1.51	1.45	1.57	2.18
MS3a	n.m.	n.m.	n.m.	n.m.	n.m.
MS3b	n.m.	n.m.	n.m.	n.m.	n.m.
MS4a	3.14	3.33	3.11	3.53	4.65
MS4b	3.43	3.15	3.02	3.25	4.54

*n.m. not measured

**The pH, DOC, and CSMR in the synthetic waters were adjusted after week 4 to better simulate the real waters

***The DOC was increased by about 1.45x in the synthetic waters during weeks 20 and 21

Table D.11 Chemistry of Synthetic Waters Following Stagnation in the Test Pieces

	Turbidity (NTU)			SUVA (L/mg-C/m)		
Sample	average	min	max	average	min	max
Wa	0.25	0.11	0.57	3.31	2.75	4.06
Wb	0.15	0.11	0.19	3.12	2.09	4.33
Ma	0.28	0.15	0.63	2.44	2.18	2.62
Mb	0.32	0.14	0.79	2.48	2.28	2.62
WS1a	0.30	0.15	1.15	3.58	-	-
WS1b	0.23	0.11	0.60	4.73	-	-
WS2a	0.61	0.20	3.25	5.13	4.95	5.33
WS2b	0.40	0.17	1.25	4.81	4.57	4.98
MS3a	0.27	0.12	1.54	n.m.	n.m.	n.m.
MS3b	0.39	0.16	1.37	n.m.	n.m.	n.m.
MS4a	0.50	0.18	1.34	4.94	4.70	5.12
MS4b	0.47	0.29	0.89	4.97	4.76	5.05

*n.m. not measured

**The pH, DOC, and CSMR in the synthetic waters were adjusted after week 4 to better simulate the real waters

***The DOC was increased by about 1.45x in the synthetic waters during weeks 20 and 21

Table D.12 Changes to the Chemistry of the Synthetic Waters During Stagnation

	pH (weeks 1-4)			pH (weeks 5-21)			DIC (mg/L)		
Sample	initial	final	change	initial	final	change	initial	final	change
Wa		7.59	0.30		7.76	0.58		66.1	-4.9
Wb	7.30	7.66	0.36	7.19	7.74	0.56	71.0	67.0	-4.0
Ma		7.76	0.20		7.77	0.32		40.9	-2.2
Mb	7.56	7.84	0.28	7.45	7.87	0.42	43.1	40.5	-2.6
WS1a		7.65	0.53		7.67	0.50		59.7	-7.5
WS1b	7.12	7.64	0.52	7.16	7.65	0.49	67.2	60.5	-6.7
WS2a		7.81	0.65		8.00	0.81		60.4	-6.6
WS2b	7.16	7.83	0.67	7.19	7.97	0.78	67.0	60.6	-6.4
MS3a		7.91	0.40		7.77	0.22		44.5	-5.2
MS3b	7.51	7.84	0.33	7.55	7.80	0.24	49.7	44.7	-4.9
MS4a		8.17	0.66		8.19	0.60		47.7	-1.8
MS4b	7.51	8.02	0.50	7.59	8.21	0.61	49.5	47.5	-2.1

*n.m. not measured

**The pH, DOC, and CSMR in the synthetic waters were adjusted after week 4 to better simulate the real waters

***The DOC was increased by about 1.45x in the synthetic waters during weeks 20 and 21

Table D.12 Changes to the Chemistry of the Synthetic Waters During Stagnation

	DOC (mg/L) (weeks 1-4)			DOC (mg/L) (weeks 5-19)			DOC (mg/L) (weeks 20-21)		
Sample	initial	final	change	initial	final	change	initial	final	change
Wa	1.77	1.70	-0.07	1.35	1.29	-0.06	1.08	1.09	0.01
Wb		1.65	-0.12		1.28	-0.07		1.01	-0.07
Ma	3.65	3.51	-0.14	3.40	3.03	-0.37	3.93	3.29	-0.64
Mb		3.43	-0.22		2.94	-0.47		3.44	-0.49
WS1a	n.m.	n.m.	-	0.07	0.18	0.11	n.m.	n.m.	-
WS1b		n.m.	-		0.11	0.04		n.m.	-
WS2a	n.m.	1.35	-	1.76	1.40	-0.36	2.45	2.19	-0.27
WS2b		1.36	-		1.51	-0.25		2.18	-0.28
MS3a	n.m.	n.m.	-	n.m.	n.m.	-	0.20	n.m.	-
MS3b		n.m.	-		n.m.	-		n.m.	-
MS4a	n.m.	3.14	-	3.49	3.33	-0.17	5.18	4.65	-0.54
MS4b		3.43	-		3.15	-0.34		4.54	-0.64

*n.m. not measured

**The pH, DOC, and CSMR in the synthetic waters were adjusted after week 4 to better simulate the real waters

***The DOC was increased by about 1.45x in the synthetic waters during weeks 20 and 21

Table D.12 Changes to the Chemistry of the Synthetic Waters During Stagnation

	Turbidity (NTU)			SUVA (L/mg-C/m)		
Sample	initial	final	change	initial	final	change
Wa		0.25	0.08		3.31	0.45
Wb	0.16	0.15	-0.01	2.86	3.12	0.26
Ma		0.28	0.15		2.44	0.25
Mb	0.13	0.32	0.19	2.19	2.48	0.30
WS1a		0.30	-0.18		3.58	-6.65
WS1b	0.48	0.23	-0.25	10.23	4.73	-5.50
WS2a		0.61	0.00		5.13	0.30
WS2b	0.61	0.40	-0.20	4.83	4.81	-0.02
MS3a		0.27	0.07		n.m.	-
MS3b	0.20	0.39	0.19	3.48	n.m.	-
MS4a		0.50	-0.16		4.94	0.11
MS4b	0.66	0.47	-0.19	4.83	4.97	0.14

*n.m. not measured

**The pH, DOC, and CSMR in the synthetic waters were adjusted after week 4 to better simulate the real waters

***The DOC was increased by about 1.45x in the synthetic waters during weeks 20 and 21

Table D.13 Metals Concentrations Before Stagnation Measured Using CRC ICP-MS

Sample	Date	Hardness (mg $CaCO_3$/L)	Al	Sb	As	Ba	B	Cd
W	Oct. 22 2019	322	n.d.	n.d.	0.00014	0.0755	0.031	0.0000385
	Nov. 19 2019	302	n.d.	n.d.	0.00011	0.0754	0.026	0.0000340
	Average	312	n.d.	n.d.	0.00013	0.0755	0.029	0.0000363
M	Oct. 22 2019	249	0.0578	0.00012	0.00034	0.0376	0.023	0.0000066
	Nov. 19 2019	278	0.0431	n.d.	0.00028	0.0272	0.018	0.0000080
	Average	264	0.0505	0.00009	0.00031	0.0324	0.021	0.0000073
WS1	Oct. 22 2019	331	n.d.	n.d.	n.d.	0.00116	n.d.	n.d.
	Nov. 19 2019	312	n.d.	n.d.	n.d.	0.00106	n.d.	0.0000050
	Average	322	n.d.	n.d.	n.d.	0.00111	n.d.	0.0000038
WS2	Oct. 22 2019	335	0.0065	n.d.	n.d.	0.00103	n.d.	n.d.
	Nov. 19 2019	315	0.0061	n.d.	n.d.	0.00109	n.d.	0.0000131
	Average	325	0.0063	n.d.	n.d.	0.00106	n.d.	0.0000078
MS3	Oct. 22 2019	277	n.d.	n.d.	n.d.	0.00089	n.d.	n.d.
	Nov. 19 2019	254	n.d.	n.d.	n.d.	0.00086	n.d.	n.d.
	Average	266	n.d.	n.d.	n.d.	0.00088	n.d.	n.d.
MS4	Oct. 22 2019	274	0.0099	n.d.	n.d.	0.00096	n.d.	n.d.
	Nov. 19 2019	266	0.0111	n.d.	n.d.	0.00092	n.d.	0.0000129
	Average	270	0.0105	n.d.	n.d.	0.00094	n.d.	0.0000077

* Concentrations in mg/L

** n.d. = below detection limit

Table D.13 Metals Concentrations Before Stagnation Measured Using CRC ICP-MS

Sample	Date	Ca	Cr	Co	Cu	Fe	Pb	Li	Mg
W	Oct. 22 2019	82.4	0.00153	n.d.	0.0013	n.d.	0.00034	0.0016	28.1
	Nov. 19 2019	78.6	n.d.	n.d.	0.0011	n.d.	n.d.	0.0010	25.7
	Average	80.5	0.00089	n.d.	0.0012	n.d.	0.00018	0.0013	26.9
M	Oct. 22 2019	63.2	0.00135	n.d.	n.d.	n.d.	n.d.	0.0015	22.1
	Nov. 19 2019	75.1	n.d.	0.00011	0.0010	n.d.	n.d.	n.d.	21.9
	Average	69.2	0.00080	0.00008	0.0008	n.d.	n.d.	0.0010	22.0
WS1	Oct. 22 2019	82.4	0.00215	n.d.	n.d.	n.d.	0.000058	n.d.	30.5
	Nov. 19 2019	78.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	28.1
	Average	80.5	0.00120	n.d.	n.d.	n.d.	0.000042	n.d.	29.3
WS2	Oct. 22 2019	83.1	0.00124	n.d.	n.d.	n.d.	0.000087	n.d.	30.9
	Nov. 19 2019	79.6	n.d.	n.d.	n.d.	0.010	0.000111	n.d.	28.2
	Average	81.4	0.00075	n.d.	n.d.	0.008	0.000099	n.d.	29.6
MS3	Oct. 22 2019	71.6	0.00102	n.d.	n.d.	n.d.	n.d.	n.d.	23.9
	Nov. 19 2019	66.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	21.5
	Average	69.0	0.00064	n.d.	n.d.	n.d.	n.d.	n.d.	22.7
MS4	Oct. 22 2019	69.9	0.00129	n.d.	n.d.	0.013	0.000137	n.d.	24.1
	Nov. 19 2019	69.8	0.00082	n.d.	0.0012	0.025	0.000194	n.d.	22.4
	Average	69.9	0.00106	n.d.	0.0009	0.019	0.000166	n.d.	23.3

* Concentrations in mg/L

** n.d. = below detection limit

Table D.13 Metals Concentrations Before Stagnation Measured Using CRC ICP-MS

Sample	Date	Mn	Mo	Ni	K	Rb	Se	Si	Na
W	Oct. 22 2019	n.d.	0.000537	n.d.	1.42	0.00076	0.000112	4.66	37.4
	Nov. 19 2019	n.d.	0.000457	n.d.	1.42	0.00072	0.000103	4.54	34.5
	Average	n.d.	0.000497	n.d.	1.42	0.00074	0.000108	4.60	36.0
M	Oct. 22 2019	0.00159	0.000773	n.d.	2.95	0.00103	0.000083	1.9	40.8
	Nov. 19 2019	0.00451	0.001000	0.00053	3.60	0.00108	0.000124	1.92	46.1
	Average	0.00305	0.000887	0.00039	3.28	0.00106	0.000104	1.91	43.5
WS1	Oct. 22 2019	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	247
	Nov. 19 2019	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	241
	Average	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	244
WS2	Oct. 22 2019	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	247
	Nov. 19 2019	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	240
	Average	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	244
MS3	Oct. 22 2019	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	149
	Nov. 19 2019	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	143
	Average	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	146
MS4	Oct. 22 2019	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	154
	Nov. 19 2019	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.11	141
	Average	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.08	148

* Concentrations in mg/L

** n.d. = below detection limit

Table D.13 Metals Concentrations Before Stagnation Measured Using CRC ICP-MS

Sample	Date	Sr	S	Sn	U	Zn
W	Oct. 22 2019	0.225	10.6	n.d.	0.000526	0.0091
	Nov. 19 2019	0.233	10.4	0.00011	0.000489	0.0080
	Average	0.229	10.5	0.00008	0.000508	0.00855
M	Oct. 22 2019	0.302	12.9	n.d.	0.00029	n.d.
	Nov. 19 2019	0.346	15.3	0.00011	0.000425	n.d.
	Average	0.324	14.1	0.00008	0.000358	n.d.
WS1	Oct. 22 2019	0.0386	44.7	n.d.	n.d.	n.d.
	Nov. 19 2019	0.0376	39.8	0.00020	n.d.	n.d.
	Average	0.0381	42.3	0.00015	n.d.	n.d.
WS2	Oct. 22 2019	0.0383	44.1	n.d.	n.d.	n.d.
	Nov. 19 2019	0.0380	41.2	0.00022	n.d.	n.d.
	Average	0.0382	42.7	0.00014	n.d.	n.d.
MS3	Oct. 22 2019	0.0324	34.5	n.d.	n.d.	n.d.
	Nov. 19 2019	0.0320	31.2	0.00012	n.d.	n.d.
	Average	0.0322	32.9	0.00009	n.d.	n.d.
MS4	Oct. 22 2019	0.0327	34.9	0.00016	n.d.	n.d.
	Nov. 19 2019	0.0334	32.7	0.00036	n.d.	n.d.
	Average	0.0331	33.8	0.00026	n.d.	n.d.

* Concentrations in mg/L

** n.d. = below detection limit

Appendix E

Raw Data for Chapter 4

Description of Samples

Sample	Description
W	Raw water from municipal well in Cambridge Ontario (Region of Waterloo)
M	Post-UV treated water from the Mannheim Water Treatment Plant (Region of Waterloo), sourced from the Grand River
WS1	Synthetic water modelling well water without any NOM
WS2	Synthetic water modelling well water with Suwannee River NOM
MS3	Synthetic water modelling river water without any NOM
MS4	Synthetic water modelling river water with Suwannee River NOM
FB	Field Blank (MilliQ water)
FIL	Filter Blank (MilliQ water)
MQ End	MilliQ water
Wa/Wb	Duplicates using W water
Ma/Ma	Duplicates using M water
WS1a/WS1b	Duplicates using WS1 water
WS2a/WS2b	Duplicates using WS2 water
MS3a/MS3b	Duplicates using MS3 water
MS4a/MS4b	Duplicates using MS4 water

Galvanic Current (µA)

Sample	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6*	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12	Week 13
Wa	38.6	38.9	40.9	48.2	64.0	67.6	56.6	34.4	34.6	37.7	55.2	82.5	44.7
Wb	43.9	40.6	43.5	42.3	44.7	35.3	50.7	40.8	36.4	41.8	39.1	37.6	44.2
Ma	43.6	42.6	46.4	46.4	45.3	39.9	44.8	47.3	45.0	42.2	40.7	43.1	40.0
Mb	45.0	45.0	44.9	47.4	44.2	42.1	49.8	49.3	47.0	46.2	42.9	43.6	43.1
WS1a	58.5	46.4	45.1	42.8	43.9	47.7	47.8	53.5	48.3	49.0	45.9	47.6	49.4
WS1b	52.3	50.2	44.6	42.0	46.0	44.7	41.8	49.1	44.7	46.0	47.1	45.7	n.m.
WS2a	59.9	60.5	61.3	61.7	73.6	56.3	73.1	64.8	74.7	56.5	57.5	69.2	n.m.
WS2b	66.2	60.1	65.2	68.8	73.2	58.1	69.2	74.6	71.2	70.6	57.2	67.8	n.m.
MS3a	48.8	44.6	41.9	39.5	37.5	35.2	34.0	36.0	33.5	31.5	32.8	31.4	n.m.
MS3b	42.9	38.9	34.1	32.1	32.5	32.2	30.8	34.2	38.8	36.0	36.1	35.8	n.m.
MS4a	46.3	44.5	44.9	48.4	39.4	37.3	43.6	46.7	40.1	45.1	41.0	40.4	44.0
MS4b	45.7	45.1	45.4	45.4	42.7	40.7	46.3	53.7	46.0	46.5	46.1	54.1	46.7

🟦 Duplicated measurement

*Measured after a 3 day stagnation event

**n.m. Not measured

Galvanic Current (μA)

Sample	Week 14	Week 15	Week 16	Week 17	Week 18	Week 19	Week 20	Week 21
Wa	63.0	60.4	70.7	74.1	76.2	67.2	64.1	53.1
Wb	46.9	48.4	49.0	49.5	49.4	47.1	47.4	55.0
Ma	43.1	41.8	48.9	45.7	44.7	42.8	46.3	50.6
Mb	48.3	46.2	49.1	50.7	51.5	46.6	53.4	54.6
WS1a	45.0	49.5	49.3	45.1	45.1	48.7	49.4	45.3
WS1b	45.1	47.8	49.6	44.4	45.0	46.1	47.2	48.1
WS2a	62.5	75.5	70.6	72.0	74.9	78.2	72.5	78.1
WS2b	69.0	69.4	72.6	72.1	77.6	76.2	68.8	72.8
MS3a	36.2	37.6	35.3	33.3	33.5	33.7	33.6	33.0
MS3b	38.7	40.1	39.7	38.6	38.3	39.0	38.0	39.7
MS4a	39.1	42.6	42.5	55.0	39.5	46.9	38.5	42.8
MS4b	43.8	47.0	47.9	46.1	44.4	48.6	49.5	48.5

🟦 Duplicated measurement

*Measured after a 3 day stagnation event

**n.m. Not measured

Lead (µg/L) - Weekly Composite Samples

Sample	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6*	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12
Wa	3052	3195	1617	1456	1555	624.1	3352	6222	3175	2552	9047	6452
Wb	3224	1947	1529	961.6	877.1	609.6	1785	617.3	817.7	616.6	477.0	516.5
Ma	931.5	799.8	546.2	551.9	560.8	532.0	554.3	595.4	575.8	498.7	494.2	434.2
Mb	1858	1628	1488	1320	1239	1082	2122	1394	1304	1282	2451	1355
WS1a	4136	5768	1896	1750	1363	594.4	2112	4921	1333	4617	1766	1744
WS1b	3442	2256	1961	873.2	754.7	513.2	2013	1399	383.2	580.8	371.5	333.4
WS2a	2888	4100	14040	4756	17110	2952	38220	11140	17560	12960	7463	14390
WS2b	3925	4584	4610	3110	3223	3470	3263	2739	2815	4092	9449	4511
MS3a	5962	3516	2430	2273	1237	774.2	1282	922.8	860.7	519.4	710.2	337.6
MS3b	4933	2279	10420	1452	1660	869.0	1292	2395	3787	4028	1969	1070
MS4a	3721	4692	6500	3665	3528	2413	2312	2200	2305	2297	2205	2003
MS4b	4044	2356	2913	5314	3349	2673	3018	3107	4090	2542	3373	2944
FB	1.884	0.652	0.424	0.428	3.484	0.134	0.328	0.489	0.101	0.493	0.111	0.304

🟦 Duplicated measurement

*Included one 48 hour stagnation followed by two 72 hour stagnations

Lead (µg/L) - Weekly Composite Samples

Sample	Week 13	Week 14	Week 15	Week 16	Week 17	Week 18	Week 19	Week 20	Week 21
Wa	1942	1127	🟦 1279	2078	3141	3004	1286	755.0	2428
Wb	471.8	437.9	663.3	472.9	491.0	803.0	459.6	414.6	680.9
Ma	425.9	🟦 395.5	377.8	🟦 407.4	351.0	353.2	326.8	361.1	376.1
Mb	🟦 3039	2755	2315	3232	2672	2520	2097	1796	2532
WS1a	732.6	642.5	632.5	702.3	532.8	853.4	433.6	425.3	640.3
WS1b	199.8	184.5	508.1	968.3	262.0	1027	253.6	259.4	297.4
WS2a	4878	2426	2849	16860	2261	6084	2280	2837	3851
WS2b	3517	2473	7820	3178	2389	5943	1219	1728	6481
MS3a	242.8	208.9	172.6	254.3	🟦 224.6	283.0	207.8	174.8	🟦 189.7
MS3b	2358	1655	1830	4571	4895	10390	3955	2411	25990
MS4a	2944	1640	1689	1905	2337	2128	🟦 2119	1796	2358
MS4b	2708	2580	2596	3831	3133	🟦 3710	2888	3268	7490
FB	0.822	0.109	0.090	0.087	0.063	0.078	0.069	-0.008	0.149

🟦 Duplicated measurement

*Included one 48 hour stagnation followed by two 72 hour stagnations

Lead (µg/L) - Samples from Individual 48 hour Stagnation Events

	Week 1			Week 3			Week 5			Week 7		
Sample	Dissolved	Particulate	Total	Dissolved	Particulate	Total	Dissolved	Particulate	Total	Dissolved	Particulate	Total
Wa	414.8	1739	2154	501.3	1817	2318	427.6	1420	1848	500.8	3905	4406
Wb	498.8	2517	3016	476.6	752	1229	507.3	716.7	1224	512.1	2938	3450
Ma	700.0	431	1131	430.2	86.2	516.4	475.3	127.8	603.1	516.9	155.8	672.7
Mb	942.9	691.1	1634	846.1	936.9	1783	745.1	334.9	1080	843.1	2439	3282
WS1a	127.9	3363	3491	128.1	2855	2983	151.1	1087	1238	138.3	632.2	770.5
WS1b	105.6	2586	2692	49.84	3140	3190	66.97	1189	1256	40.76	1303	1344
WS2a	1238	741.0	1979	1382	27218	28600	2184	22931	25115	2209	49131	51340
WS2b	2150	1490	3640	2099	3557	5656	2094	1620	3714	2225	1732	3957
MS3a	86.49	3527	3613	121.8	1961	2083	167.2	1142	1309	109.9	1226	1336
MS3b	80.18	2305	2385	89.66	6558	6648	67.13	3037	3104	59.89	872.7	932.6
MS4a	2561	1938	4499	2328	2684	5012	2277	1062	3339	1492	1916	3408
MS4b	1703	1583	3286	1171	3020	4191	1457	2318	3775	2094	2176.5	4270
FB	0.147	-0.105	0.042	-0.004	0.365	0.361	0.067	0.066	0.133	0.077	0.011	0.088
FIL	-0.067	-	-	-0.095	-	-	0.030	-	-	0.027	-	-

🟦 Duplicated measurement

Lead (µg/L) - Samples from Individual 48 hour Stagnation Events

	Week 9			Week 11			Week 13			Week 16		
Sample	Dissolved	Particulate	Total	Dissolved	Particulate	Total	Dissolved	Particulate	Total	Dissolved	Particulate	Total
Wa	399.2	2884	3283	414.5	7234	7648	396.5	1832	2228	478.3	2101	2579
Wb	470.6	118	588.6	340.7	167	507.3	422.0	110.0	532.0	436.5	137.4	573.9
Ma	450.5	78.8	529.3	430.5	69.9	500.4	385.3	81.60	466.9	338.9	181.9	520.8
Mb	667.4	751	1418	1739	1724	3463	2144	1732	3876	1748	3582	5330
WS1a	161.6	1099.4	1261	111.8	3385.2	3497	219.2	602.7	821.9	148.7	642.9	791.6
WS1b	41.78	220	262.0	159.3	301	460.6	42.97	160.2	203.2	205.0	816.0	1021
WS2a	2983	35037	38020	1911	4448	6359	1622	6663	8285	1732	43168	44900
WS2b	1744	675	2419	3088	19082	22170	1689	1413	3102	1408	3774	5182
MS3a	103.6	1453	1557	47.77	274	321.7	62.39	165.1	227.5	53.33	205.4	258.7
MS3b	79.26	4398.7	4478	53.10	2190.9	2244	75.37	2016	2091	91.36	2250	2341
MS4a	1691	608	2299	1251	1466	2717	1408	3764	5172	1305	878.0	2183
MS4b	2112	1143	3255	2000	1788.5	3789	1843	1228	3071	2103	4382	6485
FB	0.067	0.116	0.183	0.049	0.111	0.160	0.074	0.072	0.146	0.215	1.041	1.256
FIL	0.041	-	-	0.006	-	-	0.027	-	-	0.078	-	-

🟦 Duplicated measurement

Lead (µg/L) - Samples from Individual 48 hour Stagnation Events

	Week 17			Week 20			Week 21		
Sample	Dissolved	Particulate	Total	Dissolved	Particulate	Total	Dissolved	Particulate	Total
Wa	432.6	6728	7161	297.8	585.3	883.1	290.8	3750	4041
Wb	429.5	161.7	591.2	333.8	70.40	404.2	522.6	533.4	1056
Ma	297.6	26.00	323.6	324.5	9.300	333.8	324.1	64.70	388.8
Mb	1634	1467	3101	999.1	1349	2348	1249	2914	4163
WS1a	78.18	291.8	370	107.6	286.8	394.4	90.45	958.6	1049
WS1b	69.63	172.9	242.5	66.64	250.8	317.4	41.24	300.2	341.4
WS2a	1595	948.0	2543	1574	1771	3345	1329	4198	5527
WS2b	1214	397.0	1611	945.2	369.8	1315	2415	6991	9406
MS3a	51.13	133.3	184.4	71.47	156.9	228.4	35.71	92.39	128.1
MS3b	84.57	4422	4507	72.90	2924	2997	102.7	65127	65230
MS4a	1801	981.0	2782	1305	524.0	1829	1508	1878	3386
MS4b	2036	903.0	2939	1834	2333	4167	2391	12639	15030
FB	0.096	-0.002	0.094	0.808	-0.835	-0.027	0.233	0.375	0.608
FIL	0.080	-	-	-0.040	-	-	0.047	-	-

🟦 Duplicated measurement

Copper (µg/L) - Weekly Composite Samples

Sample	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6*	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12	Week 13
Wa	417.8	470.9	566.8	867.1	1003	970.3	857.7	557.5	662.9	575.8	524.4	625.5	847.8
Wb	352.7	467.1	424.4	527.2	1065	1012	1077	874.0	680.9	655.6	711.0	687.7	801.9
Ma	282.8	311.8	321.8	329.0	330.9	328.1	383.3	403.0	365.3	355.4	347.4	419.7	346.2
Mb	309.9	329.9	358.1	365.2	385.4	350.1	335.0	348.9	382.4	328.1	362.1	407.4	344.4
WS1a	69.35	47.81	39.22	43.49	36.72	33.90	32.80	33.64	32.70	26.71	27.31	28.92	25.98
WS1b	41.29	42.93	27.86	31.37	29.51	32.88	35.29	40.42	20.03	21.37	20.39	32.58	22.33
WS2a	161.3	125.8	121.7	128.9	127.7	91.39	69.03	99.86	120.6	84.42	75.56	71.09	69.25
WS2b	210.3	145.5	342.6	144.6	170.9	155.6	147.1	186.0	205.0	113.6	106.0	60.89	72.93
MS3a	41.29	38.77	23.04	23.09	22.39	20.62	20.14	15.82	13.46	16.40	11.55	19.21	13.31
MS3b	55.14	29.11	26.32	25.12	19.53	21.30	19.49	20.29	18.13	19.33	14.16	13.46	15.70
MS4a	269.9	168.2	157.7	143.2	110.4	78.04	72.72	105.5	69.52	105.7	67.96	51.24	42.11
MS4b	170.5	152.4	155.5	132.7	133.6	115.8	83.84	131.2	67.80	82.30	79.20	76.30	70.34
FB	0.404	0.227	6.862	0.550	0.133	0.200	0.785	0.955	0.394	1.362	0.263	0.693	0.922

🟦 Duplicated measurement

*Included one 48 hour stagnation followed by two 72 hour stagnations

Copper (µg/L) - Weekly Composite Samples

Sample	Week 14	Week 15	Week 16	Week 17	Week 18	Week 19	Week 20	Week 21
Wa	864.7	1016	1001	1155	1020	1077	999.0	1022
Wb	772.3	843.9	813.3	891.4	842.2	861.3	860.4	880.4
Ma	305.7	355.1	551.6	541.4	528.5	622.9	544.9	558.5
Mb	314.4	320.4	470.2	471.0	437.5	477.1	578.5	551.1
WS1a	26.12	27.97	33.12	32.31	36.29	42.18	22.93	35.32
WS1b	25.14	92.74	45.03	27.99	49.12	41.32	19.83	29.34
WS2a	74.21	136.7	209.4	204.0	191.2	211.4	171.8	186.9
WS2b	123.8	174.1	286.0	215.0	237.0	380.7	179.4	182.9
MS3a	10.73	18.11	19.74	21.07	22.40	26.11	13.57	16.78
MS3b	16.83	20.62	18.53	24.38	18.90	23.85	15.03	13.90
MS4a	40.61	89.82	139.7	257.3	183.1	146.0	50.64	72.69
MS4b	139.1	112.4	165.4	175.9	169.3	167.7	104.7	105.4
FB	0.389	0.486	0.348	0.452	0.553	0.383	0.379	0.711

🟦 Duplicated measurement

*Included one 48 hour stagnation followed by two 72 hour stagnations

Copper (µg/L) - Samples from Individual Stagnation Events

	Week 1			Week 3			Week 5			Week 7		
Sample	Dissolved	Particulate	Total	Dissolved	Particulate	Total	Dissolved	Particulate	Total	Dissolved	Particulate	Total
Wa	451.6	58.90	510.5	588.1	119.3	707.4	859.4	121.4	980.8	901.8	112.2	1014
Wb	390.4	50.00	440.4	366.3	84.20	450.5	1130	128.0	1258	1054	214.0	1268
Ma	234.8	52.00	286.8	281.1	77.60	358.7	274.3	56.30	330.6	386.5	129.7	516.2
Mb	292.2	63.90	356.1	276.5	106.9	383.4	328.8	73.50	402.3	276.9	101.3	378.2
WS1a	45.26	26.20	71.46	20.40	23.23	43.63	25.36	13.74	39.10	19.60	16.77	36.37
WS1b	13.15	23.59	🟦 36.74	18.11	10.77	🟦 28.88	19.84	11.95	31.79	25.12	19.98	45.10
WS2a	136.1	54.80	190.9	🟦 72.71	58.20	130.9	65.08	29.35	🟦 94.43	47.41	26.11	🟦 73.52
WS2b	147.4	56.50	203.9	97.45	77.25	174.7	99.03	37.47	136.5	105.5	57.70	163.2
MS3a	🟦 17.77	35.63	53.39	11.82	11.29	23.11	🟦 11.51	9.250	20.76	7.279	7.151	14.43
MS3b	18.21	19.31	37.52	11.31	15.07	26.38	8.207	12.54	20.75	9.155	13.60	22.75
MS4a	126.0	70.90	196.9	96.46	47.64	144.1	79.19	25.61	104.8	52.29	32.64	84.93
MS4b	106.1	44.80	150.9	99.00	64.70	163.7	104.9	30.90	135.8	🟦 63.66	40.95	104.6
FB	0.027	0.352	0.379	5.671	2.194	7.865	0.066	0.043	0.109	0.222	0.160	0.382
FIL	0.011	-	-	0.011	-	-	-0.025	-	-	0.034	-	-

🟦 Duplicated measurement

Copper (µg/L) - Samples from Individual Stagnation Events

	Week 9			Week 11			Week 13			Week 16		
Sample	Dissolved	Particulate	Total	Dissolved	Particulate	Total	Dissolved	Particulate	Total	Dissolved	Particulate	Total
Wa	683.0	59.90	742.9	470.6	78.90	549.5	873.4	59.20	932.6	1189	101.0	1290
Wb	577.7	71.70	649.4	638.6	105.8	744.4	801.9	87.80	889.7	808.1	126.3	934.4
Ma	360.9	51.10	412.0	376.6	65.10	441.7	336.1	35.00	371.1	496.5	74.40	570.9
Mb	357.7	53.70	411.4	364.0	70.50	434.5	413.9	-40.40	373.5	441.5	63.70	505.2
WS1a	13.88	13.90	27.78	16.73	19.05	35.78	15.96	13.29	29.25	16.45	17.71	34.16
WS1b	10.42	7.370	17.79	11.12	8.780	19.90	14.36	8.290	22.65	15.94	23.58	39.52
WS2a	53.01	102.5	155.5	56.13	21.06	77.19	47.34	13.75	61.09	104.0	113.9	217.9
WS2b	70.13	41.27	111.4	46.64	35.64	82.28	57.59	13.21	70.80	119.0	125.9	244.9
MS3a	6.201	5.519	11.72	5.887	6.013	11.90	6.599	5.581	12.18	8.898	12.94	21.84
MS3b	5.969	12.22	18.19	7.394	10.15	17.54	3.813	6.337	10.15	3.699	11.77	15.47
MS4a	50.09	10.01	60.10	44.78	20.43	65.21	35.57	3.700	39.27	49.46	95.34	144.8
MS4b	56.87	9.85	66.72	71.10	41.90	113.0	57.15	7.92	65.07	66.15	100.3	166.4
FB	0.368	0.029	0.397	0.059	0.353	0.412	0.151	0.290	0.441	0.913	7.193	8.106
FIL	0.143	-	-	0.010	-	-	0.163	-	-	0.846	-	-

🟦 Duplicated measurement

Copper (µg/L) - Samples from Individual Stagnation Events

	Week 17			Week 20			Week 21		
Sample	Dissolved	Particulate	Total	Dissolved	Particulate	Total	Dissolved	Particulate	Total
Wa	1194	106.0	1300	1006	79.00	1085	920.9	101.1	1022
Wb	878.5	130.5	1009	900.7	102.8	1004	862.2	177.8	1040
Ma	496.1	64.50	560.6	553.6	30.20	583.8	549.0	95.40	644.4
Mb	404.7	53.30	458.0	527.0	48.80	575.8	522.4	106.9	629.3
WS1a	16.71	17.61	34.32	11.28	7.650	18.93	15.55	17.41	32.96
WS1b	12.85	16.75	29.60	11.26	11.30	22.56	18.05	10.60	28.65
WS2a	83.85	101.7	185.5	141.7	36.60	178.3	110.6	65.60	176.2
WS2b	89.15	107.8	196.9	136.1	33.90	170.0	110.6	56.00	166.6
MS3a	7.709	12.36	20.07	11.67	3.330	15.00	8.564	7.317	15.88
MS3b	4.294	11.55	15.84	3.718	10.29	14.01	3.786	19.42	23.21
MS4a	187.3	110.3	297.6	49.72	1.60	51.32	47.72	58.58	106.3
MS4b	78.98	100.0	179.0	77.68	69.62	147.3	78.98	37.72	116.7
FB	0.869	-0.043	0.826	0.387	-0.306	0.081	0.270	0.400	0.670
FIL	0.836	-	-	0.095	-	-	0.169	-	-

▨ Duplicated measurement

pH

	Week 1					Week 2					Week 3				
Sample	U1	U2	U3	S3	Change	U1	U2	U3	S3	Change	U1	U2	U3	S3	Change
Wa				7.75	0.56				7.49	0.18				7.43	0.14
Wb	7.48	7.49	7.19	7.92	0.72	7.45	7.21	7.31	7.54	0.23	7.05	7.38	7.29	7.53	0.24
Ma				7.94	0.36				7.67	0.10				7.66	0.05
Mb	7.61	7.77	7.58	7.93	0.35	7.58	7.61	7.57	7.75	0.18	7.31	7.65	7.61	7.77	0.16
WS1a				7.68	0.71				7.58	0.43				7.61	0.41
WS1b	7.17	7.14	6.97	7.68	0.71	7.23	7.08	7.16	7.63	0.48	6.90	7.17	7.21	7.61	0.41
WS2a				7.75	0.68				7.77	0.60				7.83	0.56
WS2b	7.27	7.21	7.07	7.83	0.76	7.21	7.17	7.17	7.79	0.62	6.92	7.16	7.27	7.86	0.59
MS3a				8.05	0.65				7.86	0.30				7.82	0.27
MS3b	7.59	7.56	7.41	7.96	0.56	7.52	7.47	7.56	7.76	0.20	7.26	7.52	7.55	7.79	0.24
MS4a				8.24	0.80				8.09	0.56				8.21	0.59
MS4b	7.58	7.56	7.44	8.10	0.66	7.60	7.47	7.53	7.94	0.41	7.30	7.54	7.62	8.00	0.38
FB	8.82	-	6.71	6.87	0.16	-	-	6.47	5.90	-0.57	-	-	6.89	6.44	-0.45

🟦 Duplicated measurement
U Unstagnated
S Stagnated
*Calculated over a three day stagnation

pH

	Week 4					Week 5					Week 6				
Sample	U1	U2	U3	S3	Change	U1	U2	U3	S3	Change	U1	U2	U3	S3*	Change*
Wa				7.70	0.41				7.68	0.54				7.65	0.35
Wb	7.13	7.29	7.29	7.65	0.36	7.27	7.37	7.14	7.62	0.48	7.26	7.21	7.30	7.73	0.43
Ma				7.78	0.24				7.75	0.31				7.78	0.22
Mb	7.38	7.56	7.54	7.92	0.38	7.56	7.66	7.45	7.84	0.40	7.45	7.40	7.56	7.89	0.33
WS1a				7.71	0.54				7.61	0.56				7.67	0.45
WS1b	7.03	7.18	7.17	7.64	0.47	7.20	7.22	7.05	7.62	0.57	7.16	7.06	7.22	7.63	0.41
WS2a				7.87	0.65				7.98	0.88				8.13	0.82
WS2b	7.05	7.19	7.22	7.84	0.62	7.21	7.23	7.10	7.97	0.87	7.15	7.05	7.32	8.05	0.74
MS3a				7.92	0.29				7.81	0.35				7.77	0.11
MS3b	7.45	7.58	7.63	7.84	0.21	7.58	7.59	7.46	7.81	0.35	7.53	7.39	7.66	7.76	0.10
MS4a				8.16	0.61				8.19	0.73				8.28	0.61
MS4b	7.43	7.55	7.56	8.02	0.47	7.60	7.60	7.46	8.02	0.56	7.53	7.46	7.67	8.19	0.52
FB	-	-	6.47	6.77	0.30	-	-	6.48	6.07	-0.41	-	-	6.17	6.04	-0.13

🟦 Duplicated measurement
U Unstagnated
S Stagnated
*Calculated over a three day stagnation

pH

	Week 7					Week 8					Week 9				
Sample	U1	U2	U3	S3	Change	U1	U2	U3	S3	Change	U1	U2	U3	S3	Change
Wa				7.83	0.65				7.80	0.53				7.79	0.62
Wb	7.14	7.23	7.18	7.84	0.66	7.15	7.20	7.27	7.81	0.54	7.19	7.25	7.17	7.80	0.63
Ma				7.86	0.39				7.89	0.27				7.82	0.38
Mb	7.41	7.48	7.47	7.94	0.47	7.40	7.51	7.62	7.99	0.37	7.46	7.57	7.44	7.91	0.47
WS1a				7.76	0.63				7.78	0.53				7.84	0.68
WS1b	7.12	7.08	7.13	7.72	0.59	7.10	7.04	7.25	7.76	0.51	7.17	7.25	7.16	7.76	0.60
WS2a				8.13	0.94				8.08	0.84				8.04	0.92
WS2b	7.12	7.08	7.19	8.02	0.83	7.10	7.05	7.24	7.96	0.72	7.11	7.20	7.12	8.02	0.90
MS3a				7.88	0.34				7.88	0.26				7.87	0.38
MS3b	7.50	7.50	7.54	7.85	0.31	7.46	7.44	7.62	7.89	0.27	7.47	7.54	7.49	7.90	0.41
MS4a				8.22	0.66				8.26	0.61				8.25	0.75
MS4b	7.71	7.51	7.56	8.23	0.67	7.51	7.45	7.65	8.21	0.56	7.51	7.61	7.50	8.27	0.77
FB	-	-	6.50	6.45	-0.05	-	-	6.27	6.29	0.02	-	-	6.16	6.52	0.36

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated

*Calculated over a three day stagnation

pH

	Week 10					Week 11					Week 12				
Sample	U1	U2	U3	S3	Change	U1	U2	U3	S3	Change	U1	U2	U3	S3	Change
Wa				7.84	0.71				7.74	0.52				7.69	0.52
Wb	7.17	7.15	7.13	7.85	0.72	7.15	7.18	7.22	7.65	0.43	7.16	7.15	7.17	7.59	0.42
Ma				7.85	0.44				7.78	0.26				7.64	0.29
Mb	7.43	7.42	7.42	8.01	0.59	7.43	7.46	7.52	7.78	0.26	7.36	7.34	7.35	7.67	0.32
WS1a				7.79	0.72				7.57	0.38				7.56	0.41
WS1b	7.10	7.09	7.07	7.75	0.68	7.08	7.10	7.19	7.57	0.38	7.14	7.11	7.15	7.55	0.40
WS2a				8.08	0.96				7.86	0.57				7.91	0.72
WS2b	7.09	7.07	7.12	8.06	0.94	7.08	7.10	7.29	7.93	0.64	7.17	7.12	7.19	7.88	0.69
MS3a				7.89	0.46				7.70	0.10				7.66	0.15
MS3b	7.46	7.43	7.43	7.92	0.49	7.48	7.52	7.60	7.75	0.15	7.51	7.49	7.51	7.68	0.17
MS4a				8.26	0.81				8.10	0.44				8.12	0.54
MS4b	7.66	7.50	7.45	8.30	0.85	7.51	7.52	7.66	8.07	0.41	7.55	7.51	7.58	8.09	0.51
FB	-	-	6.10	6.30	0.20	-	-	6.13	6.11	-0.02	-	-	5.91	6.02	0.11

🟦 Duplicated measurement
U Unstagnated
S Stagnated
*Calculated over a three day stagnation

pH

	Week 13					Week 14					Week 15				
Sample	U1	U2	U3	S3	Change	U1	U2	U3	S3	Change	U1	U2	U3	S3	Change
Wa				7.77	0.60				7.82	0.60				7.66	0.39
Wb	7.16	7.15	7.17	7.82	0.65	7.19	7.16	7.22	7.80	0.58	7.17	7.19	7.27	7.65	0.38
Ma				7.81	0.37				7.90	0.35				7.66	0.12
Mb	7.44	7.40	7.44	7.95	0.51	7.63	7.51	7.55	8.01	0.46	7.45	7.51	7.54	7.82	0.28
WS1a				7.82	0.60				7.72	0.45				7.55	0.31
WS1b	7.16	7.14	7.23	7.73	0.51	7.36	7.15	7.27	7.72	0.45	7.13	7.19	7.24	7.56	0.32
WS2a				8.13	0.83				8.07	0.70				7.98	0.55
WS2b	7.18	7.12	7.30	8.12	0.82	7.39	7.16	7.37	8.17	0.80	7.15	7.23	7.43	8.00	0.57
MS3a				7.85	0.27				7.88	0.12				7.72	-0.11
MS3b	7.56	7.52	7.58	7.89	0.31	7.78	7.68	7.76	7.88	0.12	7.49	7.71	7.83	7.76	-0.07
MS4a				8.36	0.67				8.28	0.59				8.12	0.39
MS4b	7.63	7.61	7.69	8.36	0.67	7.84	7.63	7.69	8.31	0.62	7.59	7.61	7.73	8.20	0.47
FB	-	-	6.00	6.10	0.10	-	-	6.25	6.06	-0.19	-	-	6.15	6.03	-0.12

🟦 Duplicated measurement
U Unstagnated
S Stagnated
*Calculated over a three day stagnation

pH

	Week 16					Week 17					Week 18				
Sample	U1	U2	U3	S3	Change	U1	U2	U3	S3	Change	U1	U2	U3	S3	Change
Wa				7.76	0.60				7.78	0.59				🟦 7.90	0.74
Wb	7.18	7.18	7.16	7.78	0.62	7.15	7.14	7.19	7.80	0.61	7.17	7.17	7.15	7.77	0.62
Ma				7.75	0.45				7.78	0.30			🟦	7.73	0.34
Mb	7.30	7.32	7.30	7.75	0.45	7.42	7.43	7.48	7.83	0.35	7.35	7.38	🟦 7.40	7.88	0.49
WS1a				7.65	0.50				7.59	0.38				7.64	0.48
WS1b	7.17	7.16	7.15	7.64	0.49	7.15	7.14	7.21	🟦 7.64	0.43	7.17	7.18	7.16	7.63	0.47
WS2a				7.90	0.69				7.90	0.56				7.93	0.74
WS2b	7.17	7.17	7.21	7.94	0.73	7.16	7.16	7.34	7.89	0.55	7.19	7.19	7.19	7.88	0.69
MS3a			🟦	7.73	0.18				7.64	0.07				7.74	0.21
MS3b	7.54	7.54	🟦 7.56	7.79	0.24	7.52	7.52	7.57	7.70	0.13	7.54	7.58	7.53	7.75	0.22
MS4a				🟦 8.18	0.58			🟦	8.14	0.50				8.20	0.60
MS4b	7.59	7.59	7.60	8.25	0.65	7.57	7.54	🟦 7.65	8.09	0.45	7.59	7.62	7.60	8.32	0.72
FB	-	-	5.94	6.10	0.16	-	-	6.03	6.26	0.23	-	-	6.13	6.26	0.13

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated

*Calculated over a three day stagnation

pH

	Week 19					Week 20					Week 21				
Sample	U1	U2	U3	S3	Change	U1	U2	U3	S3	Change	U1	U2	U3	S3	Change
Wa				7.71	0.52				7.84	0.66				7.72	0.51
Wb	7.17	7.20	7.19	7.65	0.46	7.16	7.18	7.18	7.71	0.53	7.15	7.18	7.21	7.78	0.57
Ma				7.61	0.24				7.69	0.21				7.80	0.33
Mb	7.34	7.38	7.37	7.80	0.43	7.45	7.49	7.48	7.83	0.35	7.41	7.45	7.47	7.91	0.44
WS1a				7.58	0.33				7.56	0.33				7.63	0.44
WS1b	7.16	7.19	7.25	7.58	0.33	7.18	7.23	7.24	7.55	0.32	7.13	7.14	7.19	7.62	0.43
WS2a				7.93	0.60				7.87	0.60				8.00	0.68
WS2b	7.19	7.21	7.33	7.85	0.52	7.18	7.26	7.27	7.82	0.55	7.15	7.15	7.33	7.94	0.62
MS3a				7.66	0.05				7.68	0.06				7.74	0.11
MS3b	7.56	7.57	7.61	7.72	0.11	7.55	7.61	7.62	7.72	0.10	7.48	7.52	7.63	7.77	0.14
MS4a				8.12	0.42				8.05	0.42				8.07	0.43
MS4b	7.59	7.65	7.70	8.22	0.52	7.58	7.67	7.63	8.22	0.59	7.55	7.58	7.64	8.17	0.53
FB	-	-	6.32	6.33	0.01	-	-	6.03	6.26	0.23	-	-	6.20	5.98	-0.22

🟦 Duplicated measurement
U Unstagnated
S Stagnated
*Calculated over a three day stagnation

DOC (mg C/L) - Measured using LC-OCD

	Week 1	Week 2	Week 3	Week 4	Week 5	Week 7			Week 8	Week 9	Week 10
Sample	U	U	S	U	U	U	S	Change	U	U	U
Wa			1.696				1.303	-0.072			
Wb	2.026	1.767	1.646	1.503	1.709	1.375	1.380	0.005	1.676	1.393	1.436
Ma			3.508				3.323	-0.255			
Mb	3.613	3.707	3.433	3.638	3.924	3.577	3.282	-0.295	3.755	3.654	3.728
WS1a			-				-	-			
WS1b	-	-	-	-	-	0.066	-	-	-	-	-
WS2a			1.351				1.384	-0.491			
WS2b	-	-	1.355	-	-	1.875	1.496	-0.379	-	-	-
MS3a			-				-	-			
MS3b	-	-	-	-	-	-	-	-	-	-	-
MS4a			3.141				3.112	-0.267			
MS4b	-	-	3.429	-	-	3.379	3.017	-0.362	-	-	-
FB	-	-	0.166	-	-	0.094	0.130	0.036	-	-	-
FIL	-	0.072	0.030	0.195	0.091	0.237	0.043	-0.194	0.334	0.048	0.006

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated

DOC (mg C/L) - Measured using LC-OCD

	Week 11			Week 12	Week 13	Week 14	Week 15	Week 16			Week 17	Week 18	Week 19	Week 20
Sample	U	S	Change	U	U	U	U	U	S	Change	U	U	U	U
Wa		1.400	0.099						1.176	-0.060				
Wb	1.301	1.382	0.081	1.346	1.441	1.342	1.197	1.236	1.075	-0.161	1.303	1.095	1.096	1.078
Ma		3.746	0.121						2.026	-0.347				
Mb	3.625	3.426	-0.199	2.729	3.520	3.643	3.717	2.373	2.097	-0.276	3.529	2.668	3.197	3.868
WS1a		0.180	-						-	-				
WS1b	-	-	-	-	-	-	-	-	0.105	-	-	-	-	-
WS2a		1.380	-0.357						1.441	-0.230				
WS2b	1.737	1.570	-0.167	-	-	-	-	1.671	1.453	-0.218	-	-	-	-
MS3a		-	-						-	-				
MS3b	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MS4a		3.533	-0.035						3.336	-0.194				
MS4b	3.568	3.245	-0.323	-	-	-	-	3.530	3.188	-0.342	-	-	-	-
FB	0.116	0.089	-0.027	-	-	-	-	0.054	0.101	0.047	-	-	-	-
FIL	-	0.049	-	0.145	-	0.080	0.313	0.036	0.045	0.009	0.027	-	0.051	0.057

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated

DOC (mg C/L) - Measured using LC-OCD

	Week 21		
Sample	U	S	Change
Wa	1.078	1.086	0.008
Wb		1.005	-0.073
Ma	3.983	3.289	-0.694
Mb		3.437	-0.546
WS1a	-	-	-
WS1b		-	-
WS2a	2.453	2.187	-0.266
WS2b		2.175	-0.278
MS3a	0.195	-	-
MS3b		-	-
MS4a	5.185	4.647	-0.538
MS4b		4.542	-0.643
FB	0.060	0.083	0.023
FIL	0.031	0.057	0.026

▨	Duplicated measurement
U	Unstagnated
S	Stagnated

DOC (mg/L) - Measured by ALS Labs

	Week 21	% Higher than
Sample	U	LC-OCD
Wa		
Wb	1.36	26.2
Ma		
Mb	4.20	5.4
WS1a		
WS1b	-	-
WS2a		
WS2b	3.01	22.7
MS3a		
MS3b	n.d.	-
MS4a		
MS4b	5.59	7.82

TOC (mg/L) - Measured by ALS Labs

	Week 21		
Sample	U	S	Change
Wa		3.43	1.60
Wb	1.83	3.44	1.61
Ma		4.77	0.31
Mb	4.46	4.68	0.22
WS1a		-	-
WS1b	-	-	-
WS2a		3.30	0.10
WS2b	3.20	3.14	-0.06
MS3a		-	-
MS3b	0.68	1.29	0.61
MS4a		6.14	-0.01
MS4b	6.15	6.11	-0.04

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated

*n.d. = not detected, detection limit of 0.5 mg/L

DIC (mg C/L) - Calculated Based on pH and Alkalinity

Sample	Week 1 - U	Week 2 - U	Week 3 - U	Week 4 - U	Week 4 - S	Week 4 Change	Week 5 - U	Week 6 - U	Week 7 - U
Wa					63.72	-7.86			
Wb	63.35	63.13	70.06	71.58	64.72	-6.86	69.55	67.58	69.17
Ma					42.02	-2.64			
Mb	42.21	44.87	46.32	44.66	41.03	-3.62	41.95	41.06	38.23
WS1a					61.67	-8.32			
WS1b	-	-	-	69.99	62.17	-7.82	-	-	-
WS2a					61.38	-8.68			
WS2b	-	-	-	70.06	61.88	-8.19	-	-	-
MS3a					43.56	-5.20			
MS3b	-	-	-	48.76	44.54	-4.22	-	-	-
MS4a					46.38	-2.02			
MS4b	-	-	-	48.40	46.14	-2.26	-	-	-
FB	-	-	-	-	0.64	-	-	-	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated

DIC (mg C/L) - Calculated Based on pH and Alkalinity

Sample	Week 8 - U	Week 8 - S	Week 8 Change	Week 9 - U	Week 10 - U	Week 11 - U	Week 12 - U	Week 12 - S
Wa		65.15	-7.10					67.02
Wb	72.26	65.10	-7.15	70.92	71.31	71.71	71.51	68.49
Ma		36.29	-3.55					43.07
Mb	39.84	36.07	-3.78	39.97	38.10	40.16	45.34	42.94
WS1a		59.82	-7.42					59.64
WS1b	67.24	60.91	-6.33	-	-	-	66.98	60.22
WS2a		60.63	-6.05					60.73
WS2b	66.68	60.54	-6.14	-	-	-	66.41	59.87
MS3a		45.15	-4.05					45.48
MS3b	49.19	44.63	-4.57	-	-	-	49.35	45.39
MS4a		47.13	-2.73					48.89
MS4b	49.86	47.48	-2.38	-	-	-	50.10	48.96
FB	-	0.97	-	-	-	-	-	1.39

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated

DIC (mg C/L) - Calculated Based on pH and Alkalinity

Sample	Week 12 Change	Week 13 - U	Week 14 - U	Week 15 - U	Week 15 - S	Week 15 Change	Week 16 - U	Week 17 - U
Wa	-4.48				67.97	-4.42		
Wb	-3.01	72.60	72.55	72.40	68.54	-3.85	72.74	74.45
Ma	-2.27				38.98	-1.05		
Mb	-2.40	39.07	38.60	40.03	37.95	-2.08	49.05	42.80
WS1a	-7.33				57.94	-7.58		
WS1b	-6.75	-	-	65.52	58.63	-6.89	-	-
WS2a	-5.68				58.52	-6.07		
WS2b	-6.54	-	-	64.59	58.94	-5.65	-	-
MS3a	-3.87				43.23	-6.77		
MS3b	-3.96	-	-	50.00	43.08	-6.92	-	-
MS4a	-1.21				47.92	-0.93		
MS4b	-1.14	-	-	48.85	46.78	-2.08	-	-
FB	-	-	-	-	1.37	-	-	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated

DIC (mg C/L) - Calculated Based on pH and Alkalinity

Sample	Week 18 - U	Week 18 - S	Week 18 Change	Week 19 - U	Week 20 - U	Week 21 - U
Wa		66.67	-7.35			
Wb	74.03	68.28	-5.75	72.94	72.05	76.09
Ma		44.19	-3.59			
Mb	47.78	44.66	-3.12	40.28	52.35	52.69
WS1a		59.60	-6.81			
WS1b	66.41	60.66	-5.74	-	-	-
WS2a		60.65	-6.48			
WS2b	67.13	61.83	-5.30	-	-	-
MS3a		45.14	-6.04			
MS3b	51.18	46.09	-5.09	-	-	-
MS4a		48.22	-2.14			
MS4b	50.36	47.96	-2.40	-	-	-
FB	-	1.01	-	-	-	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated

Alkalinity (mg $CaCO_3$/L)

	Week 1	Week 2	Week 3	Week 4			Week 5	Week 6	Week 7	Week 8			Week 9	Week 10	Week 11
Sample	U	U	U	U	S	Change	U	U	U	U	S	Change	U	U	U
Wa					256	-4					264	0			
Wb	248	246	248	260	260	0	262	254	252	264	264	0	262	262	262
Ma					170	-2					148	-6			
Mb	168	178	176	172	166	-6	166	160	148	154	148	-6	156	148	156
WS1a					248	2					242	0			
WS1b	-	-	-	246	250	4	-	-	-	242	246	4	-	-	-
WS2a					250	2					250	10			
WS2b	-	-	-	248	252	4	-	-	-	240	248	8	-	-	-
MS3a					178	-12					184	-8			
MS3b	-	-	-	190	182	-8	-	-	-	192	182	-10	-	-	-
MS4a					192	4					196	0			
MS4b	-	-	-	188	191	3	-	-	-	196	197	1	-	-	-
FB	-	-	-	2	2	0	-	-	-	2	2	0	-	-	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated

Alkalinity (mg $CaCO_3$/L)

	Week 12			Week 13	Week 14	Week 15			Week 16	Week 17	Week 18			Week 19	Week 20
Sample	U	S	Change	U	U	U	S	Change	U	U	U	S	Change	U	U
Wa		269	7				272	6				272	0		
Wb	262	272	10	266	268	266	274	8	268	272	272	276	4	268	264
Ma		172	-2				156	0				178	-5		
Mb	174	172	-2	152	154	156	154	-2	186	166	183	182	-1	154	204
WS1a		236	-8				229	-9				238	-6		
WS1b	244	238	-6	-	-	238	232	-6	-	-	244	242	-2	-	-
WS2a		248	4				240	4				248	0		
WS2b	244	244	0	-	-	236	242	6	-	-	248	252	4	-	-
MS3a		182	-12				174	-22				182	-20		
MS3b	194	182	-12	-	-	196	174	-22	-	-	202	186	-16	-	-
MS4a		202	4				198	4				200	0		
MS4b	198	202	4	-	-	194	194	0	-	-	200	200	0	-	-
FB	2	2	0	-	-	2	2	0	-	-	2	2	0	-	-

▨ Duplicated measurement
U Unstagnated
S Stagnated

Alkalinity (mg $CaCO_3$/L)

	Week 21
Sample	U
Wa	
Wb	278
Ma	
Mb	204
WS1a	
WS1b	-
WS2a	
WS2b	-
MS3a	
MS3b	-
MS4a	
MS4b	-
FB	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated

Specific Conductance (µS/cm)

	Week 1	Week 2	Week 3	Week 4			Week 5	Week 6	Week 7	Week 8	Week 9	Week 10	Week 11
Sample	U	U	U	U	S	Change	U	U	U	U	U	U	U
Wa					665	-71							
Wb	721	653	711	736	367	-370	720	653	742	763	760	750	766
Ma					688	33							
Mb	693	685	650	655	614	-41	644	624	614	630	617	599	621
WS1a	-	-	-		793	-548	-	-	-		-	-	-
WS1b	-	-	-	1341	1371	30	-	-	-	1695	-	-	-
WS2a	-	-	-		1339	-9	-	-	-		-	-	-
WS2b	-	-	-	1348	1336	-12	-	-	-	1669	-	-	-
MS3a	-	-	-		1102	445	-	-	-		-	-	-
MS3b	-	-	-	657	1109	452	-	-	-	1153	-	-	-
MS4a	-	-	-		1129	240	-	-	-		-	-	-
MS4b	-	-	-	890	1106	217	-	-	-	1159	-	-	-
FB	-	-	-	10.7	6.4	-4.3	-	-	-	5.7	-	-	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated

Specific Conductance (µS/cm)

	Week 12			Week 13	Week 14	Week 15			Week 16	Week 17	Week 18			Week 19
Sample	U	S	Change	U	U	U	S	Change	U	U	U	S	Change	U
Wa		720	-56				734	-12				735	-19	
Wb	776	725	-51	764	746	746	747	1	737	753	754	742	-12	752
Ma		619	-58				621	-7				664	9	
Mb	677	625	-52	636	629	628	630	2	669	623	655	663	8	612
WS1a		1637	-95	-	-		1690	24	-	-		1656	-8	-
WS1b	1732	1632	-100	-	-	1666	1670	4	-	-	1664	1661	-3	-
WS2a		1628	-101	-	-		1684	25	-	-		1685	13	-
WS2b	1729	1618	-111	-	-	1659	1698	39	-	-	1672	1687	15	-
MS3a		1101	-94	-	-		1143	8	-	-		1142	-10	-
MS3b	1195	1096	-99	-	-	1135	1134	-1	-	-	1152	1114	-38	-
MS4a		1121	-68	-	-		1166	16	-	-		1153	-22	-
MS4b	1189	1113	-76	-	-	1150	1145	-5	-	-	1174	1154	-20	-
FB	7.5	4.6	-2.9	-	-	3.9	5.0	1.1	-	-	13.4	8.1	-5.3	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated

Specific Conductance (µS/cm)

	Week 20	Week 21
Sample	U	U
Wa		
Wb	720	752
Ma		
Mb	726	767.0
WS1a	-	-
WS1b	-	-
WS2a	-	-
WS2b	-	-
MS3a	-	-
MS3b	-	-
MS4a	-	-
MS4b	-	-
FB	-	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated

Turbidity (NTU)

	Week 1				Week 2	Week 3				Week 4	Week 5				Week 6
Sample	U	S	A	Change	U	U	S	A	Change	U	U	S	A	Change	U
Wa		0.18	▨ 0.16	0.02			0.31	▨ 0.20	0.10		▨	▨ 0.20	0.14	-0.23	
Wb	0.16	0.18	0.13	0.02	0.23	0.21	0.16	0.20	-0.05	0.20	▨ 0.43	0.13	▨ 0.13	-0.30	0.13
Ma		0.37	0.27	0.25			0.29	0.22	0.15			0.63	0.24	0.45	
Mb	0.12	0.40	0.27	0.28	0.20	0.14	0.39	0.25	0.25	0.12	0.18	0.79	0.24	0.61	0.12
WS1a		1.15	0.21	0.99			0.22	0.15	-0.17			0.18	0.12	-0.74	
WS1b	0.16	▨ 0.60	0.19	0.44	-	0.39	0.20	0.15	-0.19	-	0.92	0.14	0.11	-0.78	-
WS2a	▨	0.49	0.36	0.14			▨ 0.38	0.29	0.25			0.43	0.83	0.01	
WS2b	▨ 0.35	0.56	0.35	0.21	-	0.13	0.26	0.22	0.13	-	0.42	0.30	0.29	-0.12	-
MS3a		1.54	0.19	1.21			0.17	0.14	-0.10			0.14	0.11	-0.12	
MS3b	0.33	0.33	0.16	0.00	-	0.27	0.17	0.13	-0.10	-	0.26	0.47	0.11	0.21	-
MS4a		1.34	0.55	1.17		▨	0.54	0.49	0.32			0.48	0.37	-0.49	
MS4b	0.17	0.60	0.52	0.43	-	▨ 0.22	0.48	0.33	0.26	-	0.97	0.45	0.43	-0.52	-
FB	0.13	0.08	0.10	-0.05	-	0.11	0.08	0.09	-0.03	-	0.08	0.09	0.09	0.01	-

▨	Duplicated measurement
U	Unstagnated
S	Stagnated
A	Acidified with nitric acid to pH < 2 for at least 16 hours
Change	S-U

Turbidity (NTU)

	Week 7				Week 8	Week 9				Week 10	Week 11				Week 12
Sample	U	S	A	Change	U	U	S	A	Change	U	U	S	A	Change	U
Wa		0.16	0.16	-0.07			0.57	0.15	0.44			0.50	0.17	0.34	
Wb	0.23	0.17	0.13	-0.06	0.14	0.13	0.13	0.15	0.00	0.18	0.16	0.13	0.16	-0.03	0.15
Ma		0.38	0.21	0.25			0.35	0.22	0.25			0.24	0.21	0.10	
Mb	0.13	0.38	0.19	0.25	0.19	0.10	0.37	0.17	0.27	0.13	0.14	0.29	0.18	0.15	0.08
WS1a		0.35	0.12	-2.07			0.23	0.16	-0.22			0.22	0.12	-0.19	
WS1b	2.42	0.31	0.11	-2.11	-	0.45	0.27	0.13	-0.18	-	0.41	0.16	0.14	-0.25	-
WS2a		0.63	0.38	-1.92			3.25	0.78	1.59			0.36	0.21	0.01	
WS2b	2.55	0.52	0.26	-2.03	-	1.67	0.41	0.27	-1.26	-	0.35	1.25	0.27	0.90	-
MS3a		0.16	0.13	-0.15			0.18	0.10	0.01			0.14	0.12	-0.04	
MS3b	0.30	0.16	0.11	-0.14	-	0.17	1.37	0.11	1.20	-	0.18	0.33	0.09	0.15	-
MS4a		0.93	0.43	-1.01			0.46	0.51	-1.22			0.35	0.33	-0.85	
MS4b	1.94	0.89	0.47	-1.05	-	1.68	0.73	0.41	-0.95	-	1.20	0.38	0.25	-0.82	-
FB	0.20	0.10	0.12	-0.10	-	0.08	0.09	0.09	0.01	-	0.08	0.09	0.10	0.01	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
A	Acidified with nitric acid to pH < 2 for at least 16 hours
Change	S-U

Turbidity (NTU)

	Week 13				Week 14	Week 15	Week 16				Week 17				Week 18
Sample	U	S	A	Change	U	U	U	S	A	Change	U	S	A	Change	U
Wa		0.16	0.18	0.04				0.14	0.15	0.05		0.23	0.12	0.07	
Wb	0.12	0.11	0.13	-0.01	0.12	0.09	0.09	0.19	0.16	0.10	0.16	0.13	0.16	-0.03	0.09
Ma		0.18	0.17	0.08				0.17	0.17	0.02		0.16	0.15	0.05	
Mb	0.10	0.18	0.16	0.08	0.09	0.12	0.15	0.23	0.16	0.08	0.11	0.19	0.14	0.08	0.16
WS1a		0.15	0.12	0.03				0.24	0.11	0.12		0.16	0.13	0.03	
WS1b	0.12	0.11	0.10	-0.01	-	-	0.12	0.16	0.11	0.04	0.13	0.21	0.11	0.08	-
WS2a		0.23	0.29	-0.14				0.27	0.26	0.04		0.24	0.22	-0.01	
WS2b	0.37	0.17	0.21	-0.20	-	-	0.23	0.18	0.19	-0.05	0.25	0.21	0.28	-0.05	-
MS3a		0.12	0.12	-0.08				0.13	0.14	0.02		0.12	0.11	0.00	
MS3b	0.20	0.18	0.11	-0.02	-	-	0.11	0.28	0.11	0.17	0.12	0.56	0.09	0.44	-
MS4a		0.31	0.41	-0.05				0.18	0.39	-0.03		0.36	0.46	0.16	
MS4b	0.36	0.37	0.31	0.02	-	-	0.21	0.33	0.31	0.12	0.20	0.30	0.34	0.10	-
FB	0.08	0.10	0.08	0.02	-	-	0.12	0.08	0.10	-0.04	0.08	0.08	0.07	0.00	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
A	Acidified with nitric acid to pH < 2 for at least 16 hours
Change	S-U

Turbidity (NTU)

	Week 19	Week 20				Week 21			
Sample	U	U	S	A	Change	U	S	A	Change
Wa			0.11	0.13	0.01		0.16	0.13	-0.06
Wb	0.11	0.10	0.15	0.12	0.05	0.22	0.18	0.13	-0.04
Ma			0.15	0.19	0.05		0.20	0.21	-0.03
Mb	0.10	0.10	0.14	0.14	0.04	0.23	0.20	0.14	-0.03
WS1a			0.17	0.10	0.09		0.23	0.10	0.12
WS1b	-	0.09	0.19	0.11	0.11	0.12	0.20	0.10	0.09
WS2a			0.20	0.26	0.05		0.23	0.30	0.04
WS2b	-	0.15	0.21	0.25	0.06	0.19	0.36	0.28	0.17
MS3a			0.12	0.11	0.02		0.17	0.15	0.01
MS3b	-	0.10	0.20	0.11	0.10	0.16	0.22	0.15	0.06
MS4a			0.25	0.50	0.05		0.32	0.46	0.17
MS4b	-	0.20	0.29	0.37	0.09	0.15	0.36	0.40	0.21
FB	-	0.07	0.09	0.07	0.02	0.10	0.07	0.10	-0.03

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
A	Acidified with nitric acid to pH < 2 for at least 16 hours
Change	S-U

Anions (mg/L) - Chloride and Sulfate

	Week 1 - U			Week 2 - U			Week 3 - U			Week 4 - U		
Sample	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR
Wa	63.0	19.6	3.22	65.4	20.6	3.18	67.2	21.6	3.12	69.0	22.5	3.07
Wb												
Ma	82.0	29.8	2.75	85.1	27.9	3.04	76.1	27.8	2.73	82.8	30.1	2.75
Mb												
WS1a	-	-	-	-	-	-	-	-	-	264.9	111.3	2.38
WS1b												
WS2a	-	-	-	-	-	-	-	-	-	249.7	111.6	2.24
WS2b												
MS3a	-	-	-	-	-	-	-	-	-	217.2	85.5	2.54
MS3b												
MS4a	-	-	-	-	-	-	-	-	-	216.1	85.0	2.54
MS4b												
FB	-	-	-	-	-	-	-	-	-	0.0077	0.026	0.30

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
n.d.	Not detected

Anions (mg/L) - Chloride and Sulfate

	Week 4 - S Jul. 10 19			Week 4 Change			Week 5 - U Jul. 9 19			Week 6 - U Jul. 16 19		
Sample	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR
Wa	64.1	20.7	3.09	-4.9	-1.7	0.02						
Wb	64.6	21.0	3.08	-4.5	-1.5	0.01	64.1	20.7	3.10	61.8	18.0	3.43
Ma	77.6	28.2	2.75	-5.2	-1.9	0.00						
Mb	77.7	28.2	2.75	-5.0	-1.9	0.00	78.5	29.8	2.64	80.2	30.8	2.60
WS1a	248.9	103.9	2.40	-16.0	-7.4	0.02						
WS1b	249.3	105.1	2.37	-15.6	-6.2	-0.01	-	-	-	-	-	-
WS2a	234.3	103.3	2.27	-15.4	-8.3	0.03						
WS2b	233.8	103.2	2.26	-16.0	-8.4	0.03	-	-	-	-	-	-
MS3a	203.0	79.8	2.54	-14.3	-5.7	0.00						
MS3b	203.9	80.5	2.53	-13.4	-5.0	-0.01	-	-	-	-	-	-
MS4a	204.4	79.6	2.57	-11.8	-5.4	0.02						
MS4b	202.9	79.9	2.54	-13.3	-5.1	0.00	-	-	-	-	-	-
FB	0.0084	n.d.	-	0.0007	-	-	-	-	-	-	-	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
n.d.	Not detected

Anions (mg/L) - Chloride and Sulfate

	Week 7 - U Aug. 6 19			Week 8 - U Aug. 13 19			Week 9 - U Aug. 20 19			Week 10 - U Aug. 27 19		
Sample	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR
Wa												
Wb	66.4	23.6	2.82	68.4	24.0	2.85	69.3	24.2	2.87	68.0	24.7	2.76
Ma												
Mb	77.3	30.8	2.51	78.4	31.2	2.52	75.8	29.2	2.60	76.9	29.1	2.64
WS1a												
WS1b	-	-	-	-	-	-	-	-	-	-	-	-
WS2a												
WS2b	-	-	-	-	-	-	-	-	-	-	-	-
MS3a												
MS3b	-	-	-	-	-	-	-	-	-	-	-	-
MS4a												
MS4b	-	-	-	-	-	-	-	-	-	-	-	-
FB	-	-	-	-	-	-	-	-	-	-	-	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
n.d.	Not detected

Anions (mg/L) - Chloride and Sulfate

	Week 11 - U Sept. 3 19			Week 12 - U Sept. 10 19			Week 12 - S Sept. 18 19			Week 12 Change		
Sample	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR
Wa							64.9	24.3	2.67	-2.5	-1.1	0.02
Wb	67.6	24.8	2.73	67.4	25.5	2.65	65.2	24.6	2.65	-2.3	-0.9	0.00
Ma							76.6	30.2	2.54	-2.4	-0.8	-0.01
Mb	75.4	30.6	2.47	79.0	31.1	2.54	76.9	30.2	2.55	-2.1	-0.9	0.01
WS1a							336.5	104.4	3.22	-3.2	-0.8	-0.01
WS1b	-	-	-	339.7	105.2	3.23	334.3	103.7	3.22	-5.4	-1.5	-0.01
WS2a							336.9	103.3	3.26	-4.2	-2.2	0.03
WS2b	-	-	-	341.1	105.4	3.24	336.4	103.8	3.24	-4.7	-1.6	0.01
MS3a							207.4	83.3	2.49	-3.3	-1.5	0.00
MS3b	-	-	-	210.7	84.8	2.48	211.9	84.4	2.51	1.2	-0.4	0.02
MS4a							210.5	84.2	2.50	-2.7	-1.2	0.01
MS4b	-	-	-	213.2	85.4	2.50	211.3	84.1	2.51	-1.9	-1.4	0.02
FB	-	-	-	0.0050	n.d.	-	0.0122	0.02	-	0.0072	-	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
n.d.	Not detected

Anions (mg/L) - Chloride and Sulfate

	Week 13 - U Sept. 17 19			Week 14 - U Sept. 24 19			Week 15 - U Oct. 1 19			Week 16 - U Oct. 8 19		
Sample	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR
Wa												
Wb	65.2	25.6	2.55	65.3	25.6	2.55	65.6	26.4	2.49	66.0	26.5	2.49
Ma												
Mb	81.0	30.8	2.63	79.8	33.2	2.40	80.3	34.2	2.35	84.9	32.8	2.59
WS1a												
WS1b	-	-	-	-	-	-	-	-	-	-	-	-
WS2a												
WS2b	-	-	-	-	-	-	-	-	-	-	-	-
MS3a												
MS3b	-	-	-	-	-	-	-	-	-	-	-	-
MS4a												
MS4b	-	-	-	-	-	-	-	-	-	-	-	-
FB	-	-	-	-	-	-	-	-	-	-	-	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
n.d.	Not detected

Anions (mg/L) - Chloride and Sulfate

	Week 17 - U Oct. 15 19			Week 18 - U Oct. 22 19			Week 18 - S Oct. 30 19			Week 18 Change		
Sample	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR
Wa							61.8	25.6	2.41	-4.5	-1.7	-0.02
Wb	66.2	26.9	2.46	66.3	27.3	2.43	62.2	25.7	2.43	-4.1	-1.7	0.00
Ma							79.1	32.2	2.45	-4.2	-1.5	-0.01
Mb	83.2	37.2	2.24	83.3	33.8	2.47	79.2	32.1	2.47	-4.0	-1.7	0.01
WS1a							327.7	101.5	3.23	-18.2	-5.6	0.00
WS1b	-	-	-	346.0	107.2	3.23	329.6	101.8	3.24	-16.3	-5.4	0.01
WS2a							326.9	100.4	3.25	-18.7	-6.8	0.03
WS2b	-	-	-	345.6	107.3	3.22	327.5	101.7	3.22	-18.1	-5.6	0.00
MS3a							204.3	81.6	2.50	-11.8	-4.6	0.00
MS3b	-	-	-	216.1	86.2	2.51	203.6	81.2	2.51	-12.5	-5.1	0.00
MS4a							201.1	80.5	2.50	-14.1	-5.5	0.00
MS4b	-	-	-	215.2	86.0	2.50	202.4	80.7	2.51	-12.8	-5.3	0.01
FB	-	-	-	n.d.	n.d.	-	0.1419	n.d.	-	-	-	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
n.d.	Not detected

Anions (mg/L) - Chloride and Sulfate

	Week 19 - U Oct. 29 19			Week 20 - U Nov. 12 19			Week 21 - U Nov. 19 19		
Sample	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR	Chloride	Sulfate	CSMR
Wa									
Wb	66.6	29.7	2.24	63.1	28.0	2.25	61.7	29.1	2.12
Ma									
Mb	87.9	34.5	2.55	82.7	41.5	1.99	95.8	44.8	2.14
WS1a									
WS1b	-	-	-	-	-	-	-	-	-
WS2a									
WS2b	-	-	-	-	-	-	-	-	-
MS3a									
MS3b	-	-	-	-	-	-	-	-	-
MS4a									
MS4b	-	-	-	-	-	-	-	-	-
FB	-	-	-	-	-	-	-	-	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
n.d.	Not detected

Anions (mg/L) - Nitrate

	Week 1	Week 2	Week 3	Week 4			Week 5	Week 6	Week 7	Week 8	Week 9	Week 10	Week 11
Sample	U	U	U	U	S	Change	U	U	U	U	U	U	U
Wa					1.89	-0.20							
Wb	2.51	2.37	2.23	2.09	1.97	-0.13	1.89	1.95	1.77	1.93	1.99	1.82	1.83
Ma					12.21	-0.29							
Mb	13.09	12.76	14.21	12.50	12.35	-0.15	11.72	10.40	9.84	9.95	9.05	7.65	8.69
WS1a				🟦	n.d.	-							
WS1b	-	-	-	🟦 n.d.	n.d.	-	-	-	-	-	-	-	-
WS2a					n.d.	-							
WS2b	-	-	-	n.d.	n.d.	-	-	-	-	-	-	-	-
MS3a					n.d.	-							
MS3b	-	-	-	n.d.	n.d.	-	-	-	-	-	-	-	-
MS4a					n.d.	-							
MS4b	-	-	-	n.d.	n.d.	-	-	-	-	-	-	-	-
FB	-	-	-	0.013	0.018	0.02	-	-	-	-	-	-	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
n.d.	Not detected

Anions (mg/L) - Nitrate

	Week 12			Week 13	Week 14	Week 15	Week 16	Week 17	Week 18			Week 19	Week 20	Week 21
Sample	U	S	Change	U	U	U	U	U	U	S	Change	U	U	U
Wa		1.64	-0.23							1.50	-0.20			
Wb	1.87	1.67	-0.20	1.66	1.68	1.71	1.54	1.45	1.71	1.46	-0.24	1.38	2.09	2.11
Ma		10.26	-0.40							8.73	-0.55			
Mb	10.66	10.39	-0.27	9.47	8.80	9.26	10.92	8.77	9.28	8.80	-0.48	8.62	21.58	21.05
WS1a		n.d.	-							n.d.	-			
WS1b	n.d.	n.d.	-	-	-	-	-	-	n.d.	n.d.	-	-	-	-
WS2a		n.d.	-							n.d.	-			
WS2b	n.d.	n.d.	-	-	-	-	-	-	n.d.	n.d.	-	-	-	-
MS3a		n.d.	-							n.d.	-			
MS3b	n.d.	n.d.	-	-	-	-	-	-	n.d.	n.d.	-	-	-	-
MS4a		n.d.	-							n.d.	-			
MS4b	n.d.	n.d.	-	-	-	-	-	-	n.d.	n.d.	-	-	-	-
FB	n.d.	0.030	-	-	-	-	-	-	n.d.	n.d.	-	-	-	-

▨	Duplicated measurement
U	Unstagnated
S	Stagnated
n.d.	Not detected

SUVA (L/mg-C/m) - Measured on LC-OCD

	Week 1	Week 2	Week 3	Week 4	Week 5	Week 7			Week 8	Week 9	Week 10	Week 11			Week 12
Sample	U	U	S	U	U	U	S	Change	U	U	U	U	S	Change	U
Wa			3.58				2.75	-0.09					3.07	-0.72	
Wb	2.09	2.71	3.01	2.73	2.82	2.84	2.76	-0.08	2.34	2.60	2.64	3.79	2.09	-1.70	3.38
Ma			2.25			🟦	🟦 2.62	0.32					2.18	0.00	
Mb	2.73	2.57	2.46	2.29	2.16	🟦 2.30	2.56	0.27	2.29	2.07	2.54	2.18	2.62	0.44	2.52
WS1a			-				-	-					3.58	-	
WS1b	-	-	-	-	-	10.23	-	-	-	-	-	-	-	-	-
WS2a			4.38				5.12	1.14				🟦	4.95	0.17	
WS2b	-	-	4.27	-	-	3.98	4.89	0.91	-	-	-	🟦 4.78	4.57	-0.21	-
MS3a			-				-	-					-	-	
MS3b	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MS4a			5.00				5.12	0.08					🟦 4.70	-0.04	
MS4b	-	-	🟦 4.76	-	-	5.04	5.05	0.01	-	-	-	4.74	5.05	0.31	-
FB	-	-	6.05	-	-	7.64	4.39	-	-	-	-	8.74	8.00	-	-
FIL	-	11.22	13.47	4.16	11.49	4.44	4.99	-	1.28	4.18	n.d.	-	13.25	-	4.73

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated

SUVA (L/mg-C/m) - Measured on LC-OCD

	Week 13	Week 14	Week 15	Week 16			Week 17	Week 18	Week 19	Week 20	Week 21		
Sample	U	U	U	U	S	Change	U	U	U	U	U	S	Change
Wa					3.10	0.36						4.06	1.02
Wb	2.96	2.59	3.09	2.74	3.42	0.68	2.95	3.15	3.04	2.91	3.04	4.33	1.29
Ma					2.61	0.76						2.52	0.46
Mb	2.04	2.18	2.00	1.85	2.28	0.43	1.86	1.93	1.70	2.31	2.06	2.50	0.44
WS1a					-	-						-	-
WS1b	-	-	-	-	4.73	-	-	-	-	-	-	-	-
WS2a					5.33	-0.26						5.22	0.24
WS2b	-	-	-	5.59	4.98	-0.61	-	-	-	-	4.98	5.10	0.12
MS3a					-	-						-	-
MS3b	-	-	-	-	-	-	-	-	-	-	3.48	-	-
MS4a					4.94	0.12						5.14	0.42
MS4b	-	-	-	4.82	5.03	0.21	-	-	-	-	4.73	4.85	0.13
FB	-	-	-	14.75	5.65	-	-	-	-	-	13.80	11.93	-1.87
FIL	-	16.72	2.97	16.10	21.15	-	26.24	-	11.15	19.35	18.24	11.11	-7.13

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated

Hydrophobic (mg C/L) - LC-OCD

	Week 1	Week 2	Week 3	Week 4	Week 5	Week 7			Week 8	Week 9	Week 10	Week 11		
Sample	U	U	S	U	U	U	S	Change	U	U	U	U	S	Change
Wa			0.266				0.118	0.060					0.231	0.112
Wb	0.395	0.227	0.218	0.123	0.208	0.058	0.149	0.091	0.248	0.136	0.192	0.119	0.268	0.149
Ma			0.416				0.335	-0.033					0.714	0.271
Mb	0.283	0.356	0.401	0.382	0.389	0.368	0.296	-0.072	0.461	0.420	0.600	0.443	0.386	-0.057
WS1a			-				-	-					0.106	-
WS1b	-	-	-	-	-	0.024	-	-	-	-	-	-	-	-
WS2a			0.108				n.d.	-					n.d.	-
WS2b	-	-	0.164	-	-	0.205	0.157	-0.048	-	-	-	0.221	0.132	-0.089
MS3a			-				-	-					-	-
MS3b	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MS4a			0.242				0.065	-0.063					0.381	-0.001
MS4b	-	-	0.359	-	-	0.128	0.039	-0.089	-	-	-	0.382	0.243	-0.139
FB	-	-	0.080	-	-	0.037	0.034	-0.003	-	-	-	0.066	0.040	-
FIL	-	0.039	0.013	0.054	0.032	0.075	0.002	-0.073	0.072	0.013	n.d.	-	0.023	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
n.d.	Not detected

Hydrophobic (mg C/L) - LC-OCD

	Week 12	Week 13	Week 14	Week 15	Week 16			Week 17	Week 18	Week 19	Week 20
Sample	U	U	U	U	U	S	Change	U	U	U	U
Wa						0.183	0.016				
Wb	0.133	0.231	0.162	0.055	0.167	0.102	-0.065	0.099	0.042	0.086	0.116
Ma						0.142	-0.198				
Mb	0.249	0.496	0.421	0.538	0.340	0.237	-0.103	0.338	0.204	0.317	0.488
WS1a						-	-				
WS1b	-	-	-	-	-	0.060	-	-	-	-	-
WS2a						0.019	-0.073				
WS2b	-	-	-	-	0.092	n.d.	-	-	-	-	-
MS3a						-	-				
MS3b	-	-	-	-	-	-	-	-	-	-	-
MS4a						0.151	0.008				
MS4b	-	-	-	-	0.143	0.081	-0.062	-	-	-	-
FB	-	-	-	-	0.016	0.049	-	-	-	-	-
FIL	0.083	-	0.020	0.235	0.016	0.021	-	0.007	-	0.015	0.017

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
n.d.	Not detected

Hydrophobic (mg C/L) - LC-OCD

	Week 21		
Sample	U	S	Change
Wa		0.176	0.010
Wb	0.166	0.112	-0.054
Ma		0.222	-0.474
Mb	0.696	0.354	-0.342
WS1a		-	-
WS1b	-	-	-
WS2a		0.096	-0.181
WS2b	0.277	0.171	-0.106
MS3a		-	-
MS3b	0.076	-	-
MS4a		0.221	-0.244
MS4b	0.465	0.166	-0.299
FB	0.026	0.041	0.015
FIL	0.008	0.026	0.018

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
n.d.	Not detected

Biopolymers (mg C/L) - LC-OCD

	Week 1	Week 2	Week 3	Week 4	Week 5	Week 7			Week 8	Week 9	Week 10	Week 11		
Sample	U	U	S	U	U	U	S	Change	U	U	U	U	S	Change
Wa			0.019				0.012	0.011					0.012	0.011
Wb	0.002	0.004	0.009	0.002	0.004	0.001	0.032	0.031	n.d.	0.002	0.002	0.001	0.014	0.013
Ma			0.203				0.171	-0.027					0.179	-0.044
Mb	0.236	0.182	0.195	0.193	0.203	0.198	0.165	-0.033	0.181	0.188	0.184	0.223	0.197	-0.026
WS1a			-				-	-					0.006	-
WS1b	-	-	-	-	-	0.002	-	-	-	-	-	-	-	-
WS2a			n.d.				0.006	-					0.004	0.002
WS2b	-	-	0.001	-	-	n.d.	0.003	-	-	-	-	0.002	0.020	0.018
MS3a			n.d.				-	-					-	-
MS3b	-	-	n.d.	-	-	-	-	-	-	-	-	-	-	-
MS4a			n.d.				0.002	-					0.011	0.0085
MS4b	-	-	n.d.	-	-	n.d.	n.d.	-	-	-	-	0.002	0.014	0.012
FB	-	-	n.d.	-	-	0.003	0.002	-0.001	-	-	-	0.002	n.d.	-
FIL	-	0.002	n.d.	0.003	n.d.	0.007	n.d.	-	n.d.	n.d.	0.002	-	0.002	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
n.d.	Not detected

Biopolymers (mg C/L) - LC-OCD

	Week 12	Week 13	Week 14	Week 15	Week 16			Week 17	Week 18	Week 19	Week 20
Sample	U	U	U	U	U	S	Change	U	U	U	U
Wa						0.011	-				
Wb	0.004	0.001	0.002	0.010	n.d.	0.006	-	n.d.	n.d.	0.002	0.001
Ma						0.112	-0.010				
Mb	0.147	0.207	0.255	0.228	0.122	0.112	-0.01	0.301	0.215	0.218	0.147
WS1a						-	-				
WS1b	-	-	-	-	-	0.003	-	-	-	-	-
WS2a						0.004	-				
WS2b	-	-	-	-	n.d.	0.002	-	-	-	-	-
MS3a						-	-				
MS3b	-	-	-	-	-	-	-	-	-	-	-
MS4a						0.001	-0.002				
MS4b	-	-	-	-	0.003	0.003	0.000	-	-	-	-
FB	-	-	-	-	0.002	n.d.	-	-	-	-	-
FIL	n.d.	-	n.d.	n.d.	n.d.	n.d.	-	0.003	-	0.009	0.009

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
n.d.	Not detected

Biopolymers (mg C/L) - LC-OCD

	Week 21		
Sample	U	S	Change
Wa	n.d.	0.016	-
Wb		0.016	-
Ma	0.140	0.132	-0.008
Mb		0.135	-0.005
WS1a	-	-	-
WS1b		-	-
WS2a	0.001	0.006	0.005
WS2b		0.004	0.003
MS3a	n.d.	-	-
MS3b		-	-
MS4a	🟦 0.003	0.010	0.007
MS4b		0.009	0.006
FB	0.005	0.001	-0.004
FIL	0.002	n.d.	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
n.d.	Not detected

Humic Substances (mg C/L) - LC-OCD

	Week 1	Week 2	Week 3	Week 4	Week 5	Week 7			Week 8	Week 9	Week 10	Week 11		
Sample	U	U	S	U	U	U	S	Change	U	U	U	U	S	Change
Wa			0.920				0.696	-0.145					0.698	-0.092
Wb	1.031	1.028	0.925	0.953	0.948	0.841	0.706	-0.135	0.856	0.794	0.817	0.790	0.677	-0.113
Ma			2.030				1.897	-0.075					1.808	-0.103
Mb	2.145	2.160	2.027	2.221	2.137	1.972	1.907	-0.065	2.065	2.016	1.938	1.911	1.799	-0.112
WS1a			-				-	-					n.d.	-
WS1b	-	-	-	-	-	n.d.	-	-	-	-	-	-	-	-
WS2a			1.006				1.115	-0.191					1.144	-0.104
WS2b	-	-	0.925	-	-	1.306	1.102	-0.204	-	-	-	1.248	1.133	-0.115
MS3a			-				-	-					-	-
MS3b	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MS4a			2.445				2.508	-0.192					2.627	-0.0805
MS4b	-	-	2.583	-	-	2.700	2.440	-0.260	-	-	-	2.707	2.560	-0.147
FB	-	-	n.d.	-	-	n.d.	n.d.	-	-	-	-	n.d.	n.d.	-
FIL	-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-	n.d.	n.d.	n.d.	-	n.d.	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
n.d.	Not detected

Humic Substances (mg C/L) - LC-OCD

	Week 12	Week 13	Week 14	Week 15	Week 16			Week 17	Week 18	Week 19	Week 20
Sample	U	U	U	U	U	S	Change	U	U	U	U
Wa						0.584	-0.117				
Wb	0.808	0.788	0.766	0.721	0.701	0.569	-0.132	0.726	0.700	0.641	0.585
Ma						1.111	-0.162				
Mb	1.466	1.878	2.063	1.953	1.273	1.061	-0.212	1.890	1.531	1.768	1.979
WS1a						n.d.	-				
WS1b	-	-	-	-	-	-	-	-	-	-	-
WS2a						1.169	-0.102				
WS2b	-	-	-	-	1.271	1.189	-0.082	-	-	-	-
MS3a						-	-				
MS3b	-	-	-	-	-	-	-	-	-	-	-
MS4a						2.650	-0.134				
MS4b	-	-	-	-	2.784	2.600	-0.184	-	-	-	-
FB	-	-	-	-	n.d.	n.d.	-	-	-	-	-
FIL	n.d.	-	n.d.	n.d.	n.d.	n.d.	-	n.d.	-	n.d.	n.d.

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
n.d.	Not detected

Humic Substances (mg C/L) - LC-OCD

	Week 21		
Sample	U	S	Change
Wa		0.547	0.009
Wb	0.538	0.500	-0.038
Ma		1.846	-0.159
Mb	2.005	1.795	-0.210
WS1a		-	-
WS1b	-	-	-
WS2a		1.669	-0.122
WS2b	1.791	1.634	-0.157
MS3a		-	-
MS3b	n.d.	-	-
MS4a		3.688	-0.208
MS4b	3.896	3.612	-0.284
FB	n.d.	n.d.	-
FIL	n.d.	n.d.	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
n.d.	Not detected

Building Blocks (mg C/L) - LC-OCD

	Week 1	Week 2	Week 3	Week 4	Week 5	Week 7			Week 8	Week 9	Week 10	Week 11		
Sample	U	U	S	U	U	U	S	Change	U	U	U	U	S	Change
Wa			0.255				0.242	-0.026					0.220	-0.008
Wb	0.280	0.227	0.263	0.223	0.282	0.268	0.244	-0.024	0.258	0.273	0.230	0.228	0.221	-0.007
Ma			0.400				0.457	-0.097					0.534	-0.035
Mb	0.503	0.519	0.392	0.385	0.647	0.554	0.465	-0.089	0.529	0.486	0.508	0.569	0.555	-0.014
WS1a			-				-	-					0.019	-
WS1b	-	-	-	-	-	0.012	-	-	-	-	-	-	-	-
WS2a			0.139				0.149	-0.01					0.131	-0.015
WS2b	-	-	0.128	-	-	0.159	0.146	-0.013	-	-	-	0.146	0.115	-0.031
MS3a			-				-	-					-	-
MS3b	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MS4a			0.304				0.306	-0.008					0.275	-0.016
MS4b	-	-	0.301	-	-	0.314	0.315	0.001	-	-	-	0.290	0.269	-0.021
FB	-	-	0.032	-	-	0.024	0.022	-0.002	-	-	-	0.018	0.013	-
FIL	-	0.008	0.003	0.043	0.013	0.017	0.002	-0.015	0.019	0.002	0.002	-	0.004	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
n.d.	Not detected

Building Blocks (mg C/L) - LC-OCD

	Week 12	Week 13	Week 14	Week 15	Week 16			Week 17	Week 18	Week 19	Week 20
Sample	U	U	U	U	U	S	Change	U	U	U	U
Wa						0.235	0.009				
Wb	0.216	0.233	0.229	0.235	0.226	0.252	0.026	0.250	0.202	0.219	0.218
Ma						0.360	0.057				
Mb	0.467	0.441	0.389	0.493	0.304	0.392	0.089	0.494	0.344	0.383	0.713
WS1a						0.010	-				
WS1b	-	-	-	-	-	-	-	-	-	-	-
WS2a						0.135	-0.025				
WS2b	-	-	-	-	0.160	0.140	-0.02	-	-	-	-
MS3a						-	-				
MS3b	-	-	-	-	-	-	-	-	-	-	-
MS4a						0.316	-0.017				
MS4b	-	-	-	-	0.333	0.286	-0.047	-	-	-	-
FB	-	-	-	-	0.009	0.011	-	-	-	-	-
FIL	0.004	-	0.013	0.004	0.002	0.003	-	0.002	-	0.009	0.010

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
n.d.	Not detected

Building Blocks (mg C/L) - LC-OCD

	Week 21		
Sample	U	S	Change
Wa		0.194	-0.042
Wb	0.236	0.206	-0.03
Ma		0.615	-0.032
Mb	0.647	0.635	-0.012
WS1a		-	-
WS1b	-	-	-
WS2a		0.208	-0.006
WS2b	0.214	0.182	-0.032
MS3a		-	-
MS3b	0.017	-	-
MS4a		0.436	-0.019
MS4b	0.455	0.441	-0.014
FB	0.007	0.012	0.005
FIL	0.003	0.004	0.001

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
n.d.	Not detected

LMW Neutrals (mg C/L) - LC-OCD

	Week 1	Week 2	Week 3	Week 4	Week 5	Week 7			Week 8	Week 9	Week 10	Week 11		
Sample	U	U	S	U	U	U	S	Change	U	U	U	U	S	Change
Wa			0.190				0.196	0.036					0.197	0.072
Wb	0.170	0.205	0.185	0.156	0.203	0.160	0.210	0.05	0.267	0.144	0.156	0.125	0.155	0.03
Ma			0.341				0.344	-0.008					0.368	0.014
Mb	0.312	0.372	0.302	0.330	0.391	0.352	0.326	-0.026	0.389	0.401	0.360	0.354	0.349	-0.005
WS1a			-				-	-					0.030	-
WS1b	-	-	-	-	-	0.019	-	-	-	-	-	-	-	-
WS2a			0.091				0.108	-0.066					0.148	0.034
WS2b	-	-	0.130	-	-	0.174	0.080	-0.094	-	-	-	0.115	0.164	0.050
MS3a			-				-	-					-	-
MS3b	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MS4a			0.129				0.206	-0.006					0.218	0.047
MS4b	-	-	0.174	-	-	0.212	0.201	-0.011	-	-	-	0.171	0.148	-0.023
FB	-	-	0.028	-	-	0.015	0.052	0.037	-	-	-	0.013	0.018	-
FIL	-	0.018	0.012	0.067	0.022	0.072	0.037	-0.035	0.220	0.029	0.004	-	0.010	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
n.d.	Not detected

LMW Neutrals (mg C/L) - LC-OCD

	Week 12	Week 13	Week 14	Week 15	Week 16			Week 17	Week 18	Week 19	Week 20
Sample	U	U	U	U	U	S	Change	U	U	U	U
Wa						0.131	0.027				
Wb	0.144	0.136	0.146	0.143	0.104	0.113	0.009	0.192	0.118	0.112	0.126
Ma						0.220	-0.029				
Mb	0.305	0.355	0.374	0.358	0.249	0.215	-0.0335	0.373	0.283	0.368	0.401
WS1a						0.023	-				
WS1b	-	-	-	-	-	-	-	-	-	-	-
WS2a						0.107	-0.030				
WS2b	-	-	-	-	0.137	0.121	-0.016	-	-	-	-
MS3a						-	-				
MS3b	-	-	-	-	-	-	-	-	-	-	-
MS4a						0.208	-0.049				
MS4b	-	-	-	-	0.257	0.209	-0.048	-	-	-	-
FB	-	-	-	-	0.018	0.025	-	-	-	-	-
FIL	0.037	-	0.014	0.020	0.012	0.013	-	0.013	-	0.012	0.013

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
n.d.	Not detected

LMW Neutrals (mg C/L) - LC-OCD

	Week 21		
Sample	U	S	Change
Wa		0.122	0.014
Wb	0.108	0.140	0.032
Ma		0.366	-0.003
Mb	0.369	0.405	0.036
WS1a		-	-
WS1b	-	-	-
WS2a		0.201	0.045
WS2b	0.156	0.177	0.021
MS3a		-	-
MS3b	0.074	-	-
MS4a		0.305	-0.044
MS4b	0.349	0.300	-0.049
FB	0.011	0.017	0.006
FIL	0.014	0.023	0.009

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
n.d.	Not detected

LMW Acids (mg C/L) - LC-OCD

	Week 1	Week 2	Week 3	Week 4	Week 5	Week 7			Week 8	Week 9	Week 10	Week 11		
Sample	U	U	S	U	U	U	S	Change	U	U	U	U	S	Change
Wa			0.046				0.038	-0.009					0.043	0.005
Wb	0.148	0.074	0.046	0.045	0.063	0.047	0.039	-0.008	0.046	0.044	0.038	0.038	0.047	0.009
Ma			0.117				0.120	-0.015					0.141	0.016
Mb	0.135	0.118	0.117	0.127	0.157	0.135	0.122	-0.013	0.131	0.143	0.137	0.125	0.140	0.015
WS1a			-				-	-					0.018	-
WS1b	-	-	-	-	-	0.009	-	-	-	-	-	-	-	-
WS2a			0.006				0.006	-0.025					0.006	0
WS2b	-	-	0.007	-	-	0.031	0.007	-0.024	-	-	-	0.006	0.006	0
MS3a			-				-	-					-	-
MS3b	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MS4a			0.021				0.025	-0.001					0.022	0.006
MS4b	-	-	0.022	-	-	0.026	0.022	-0.004	-	-	-	0.016	0.011	-0.005
FB	-	-	0.026	-	-	0.014	0.020	0.006	-	-	-	0.017	0.018	-
FIL	-	0.005	0.002	0.028	0.023	0.066	0.001	-0.065	0.022	0.004	n.d.	-	0.010	-

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
n.d.	Not detected

LMW Acids (mg C/L) - LC-OCD

	Week 12	Week 13	Week 14	Week 15	Week 16			Week 17	Week 18	Week 19	Week 20
Sample	U	U	U	U	U	S	Change	U	U	U	U
Wa						0.032	-0.006				
Wb	0.040	0.051	0.037	0.033	0.038	0.032	-0.006	0.035	0.031	0.035	0.032
Ma						0.081	-0.005				
Mb	0.094	0.143	0.142	0.147	0.086	0.079	-0.007	0.134	0.092	0.143	0.140
WS1a						0.008	-				
WS1b	-	-	-	-	-	-	-	-	-	-	
WS2a						0.007	-0.003				
WS2b	-	-	-	-	0.010	0.006	-0.004	-	-	-	-
MS3a						-	-				
MS3b	-	-	-	-	-	-	-	-	-	-	-
MS4a						0.010	-0.001				
MS4b	-	-	-	-	0.011	0.010	-0.001	-	-	-	-
FB	-	-	-	-	0.009	0.017	-	-	-	-	-
FIL	0.020	-	0.033	0.054	0.004	0.008	-	0.002	-	0.007	0.008

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
n.d.	Not detected

LMW Acids (mg C/L) - LC-OCD

	Week 21		
Sample	U	S	Change
Wa		0.030	0.000
Wb	0.030	0.030	0.000
Ma		0.109	-0.017
Mb	0.126	0.113	-0.013
WS1a		-	-
WS1b	-	-	-
WS2a		0.008	-0.004
WS2b	0.012	0.008	-0.004
MS3a		-	-
MS3b	0.028	-	-
MS4a		0.014	-0.004
MS4b	0.018	0.015	-0.003
FB	0.010	0.011	0.001
FIL	0.003	0.004	0.001

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated
n.d.	Not detected

Humic Acids (au) - FEEM

	Week 1	Week 2	Week 3			Week 4	Week 5	Week 6	Week 7		
Sample	U	U	U	S	Change	U	U	U	U	S	Change
Wa				91.7015	-29.056					74.1333	-35.2418
Wb	142.9612	125.3994	120.7575	99.5025	-21.255	114.6982	131.2575	114.3803	109.3751	73.2305	-36.1446
Ma				132.5196	-20.7056					134.0747	-31.0670
Mb	183.6110	169.8299	153.2252	129.6322	-23.593	156.7366	163.1275	144.8114	165.1416	138.2655	-26.8761
WS1a	-	-		3.0356	-	-	-	-		-	-
WS1b	-	-	-	-	-	-	-	-	0.5349	20.0348	19.4999
WS2a	-	-		102.5015	-17.1264	-	-	-		115.5619	-19.7166
WS2b	-	-	119.6279	111.2610	-8.3669	-	-	-	135.2785	113.7846	-21.4939
MS3a	-	-		-	-	-	-	-		-	-
MS3b	-	-	2.2089	-	-	-	-	-	-	-	-
MS4a	-	-		224.1886	-39.1058	-	-	-		233.8646	-21.0345
MS4b	-	-	263.2944	226.9426	-36.3518	-	-	-	254.8991	230.8058	-24.0933
FB	-	-	11.9573	11.1118	-0.8455	-	-	-	7.2249	10.2019	2.9770
FIL	0.3071	1.6082	0.6747	0.4415	-0.2332	2.3383	0.3492	0.2112	0.7565	0.6023	-0.1542
MQ End	-0.0726	-0.0633	0.1816	0.3505	0.1689	-0.2439	-0.1249	0.0655	-0.0011	0.3449	0.3460

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated

Humic Acids (au) - FEEM

	Week 8	Week 9	Week 10	Week 11			Week 12	Week 13	Week 14	Week 15
Sample	U	U	U	U	S	Change	U	U	U	U
Wa					73.7577	-32.1719				
Wb	105.8243	110.0257	102.1767	105.9296	71.3384	-34.5912	97.5406	97.6130	93.9249	88.3098
Ma					122.5952	-31.0063				
Mb	171.1740	162.4695	169.8118	153.6015	122.1677	-31.4338	108.3992	139.7129	144.2866	138.4436
WS1a	-	-	-		2.2520	1.8309	-	-	-	-
WS1b	-	-	-	0.4211	-	-	-	-	-	-
WS2a	-	-	-		115.3214	-12.2756	-	-	-	-
WS2b	-	-	-	127.5970	116.5871	-11.0099	-	-	-	-
MS3a	-	-	-		-	-	-	-	-	-
MS3b	-	-	-	-	-	-	-	-	-	-
MS4a	-	-	-		233.2952	-18.5070	-	-	-	-
MS4b	-	-	-	251.8022	219.1630	-32.6392	-	-	-	-
FB	-	-	-	7.8414	5.2021	-2.6393	-	-	-	-
FIL	0.7194	0.3783	0.6952	3.1650	0.1872	-2.9778	0.3537	7.2575	1.3716	-0.1560
MQ End	0.3797	0.0536	-0.1519	0.4966	0.0919	-0.4047	-0.1059	-0.3831	-0.2013	0.1008

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated

Humic Acids (au) - FEEM

	Week 16			Week 17	Week 18	Week 19	Week 20	Week 21		
Sample	U	S	Change	U	U	U	U	U	S	Change
Wa		59.2221	-30.5235						56.4877	-17.2764
Wb	89.7456	63.4756	-26.2700	89.9564	85.9958	89.6950	77.3558	73.7641	54.1756	-19.5885
Ma	62.1456	63.3461	1.2006						106.0276	-19.8051
Mb		61.8234	-0.3222	105.4105	69.2237	94.3514	141.4118	125.8327	107.3670	-18.4657
WS1a		-	-	-	-	-	-		-	-
WS1b	0.4997	1.6950	1.1953	-	-	-	-	-	-	-
WS2a		114.0699	-21.2016	-	-	-	-		157.4425	-26.3008
WS2b	135.2715	113.2545	-22.0170	-	-	-	-	183.7433	155.2039	-28.5394
MS3a		-	-	-	-	-	-		-	-
MS3b	-	-	-	-	-	-	-	2.5973	2.8564	0.2591
MS4a		236.4423	-21.0260	-	-	-	-	343.8190	311.4736	-32.3454
MS4b	257.4683	230.7136	-26.7547	-	-	-	-		297.4213	-46.3977
FB	2.6762	3.6818	1.0056	-	-	-	-	2.0795	3.5549	1.4754
FIL	0.2782	-0.0097	-0.2879	-0.2960	-0.4871	-0.0788	0.4317	-0.1053	0.3795	0.4848
MQ End	-0.1212	-0.3890	-0.2678	-0.0952	-0.2628	-0.2953	0.1138	-0.0303	0.0270	0.0573

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated

Fulvic Acids (au) - FEEM

	Week 1	Week 2	Week 3			Week 4	Week 5	Week 6	Week 7		
Sample	U	U	U	S	Change	U	U	U	U	S	Change
Wa				84.1531	-22.976					68.4504	-28.2174
Wb	138.5085	117.2005	107.1291	89.4554	-17.6737	105.2994	116.7169	103.9016	96.6678	67.8860	-28.7818
Ma				117.9605	-11.3087					120.5226	-27.6782
Mb	157.9402	153.3023	129.2692	114.3226	-14.9466	139.4470	143.3930	126.7047	148.2007	123.5326	-24.6681
WS1a	-	-		4.3507	-	-	-	-		-	-
WS1b	-	-	-	-	-	-	-	-	0.5792	35.6572	35.0780
WS2a	-	-		75.4459	-6.9867	-	-	-		81.7074	-15.6750
WS2b	-	-	82.4326	83.4117	0.9791	-	-	-	97.3824	82.3177	-15.0647
MS3a	-	-		-	-	-	-	-		-	-
MS3b	-	-	3.4571	-	-	-	-	-	-	-	-
MS4a	-	-		164.9709	-18.4654	-	-	-		167.0163	-5.0006
MS4b	-	-	183.4363	165.0639	-18.3725	-	-	-	172.0169	165.0230	-6.9939
FB	-	-	11.0498	10.6223	-0.4275	-	-	-	7.2872	13.7799	6.4927
FIL	0.2383	2.1632	0.8015	0.7885	-0.013	2.8371	0.2984	0.2408	0.8881	0.5419	-0.3462
MQ End	0.0848	0.3198	0.3847	0.3337	-0.051	-0.1645	-0.1647	-0.1792	0.1136	0.1725	0.0589

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated

Fulvic Acids (au) - FEEM

	Week 8	Week 9	Week 10	Week 11			Week 12	Week 13	Week 14	Week 15
Sample	U	U	U	U	S	Change	U	U	U	U
Wa					68.9565	-25.7495				
Wb	96.1786	96.6686	93.4774	94.7060	65.5620	-29.1440	88.5778	89.2029	86.6005	79.0930
Ma					107.0157	-28.3210				
Mb	150.6139	139.0850	147.4596	135.3367	105.7563	-29.5804	95.9145	124.9429	128.7532	121.5154
WS1a	-	-	-		3.6225	2.9791	-	-	-	-
WS1b	-	-	-	0.6434	-	-	-	-	-	-
WS2a	-	-	-	90.3228	82.6609	-7.6619	-	-	-	-
WS2b	-	-	-		82.7300	-7.5928	-	-	-	-
MS3a	-	-	-		-	-	-	-	-	-
MS3b	-	-	-	-	-	-	-	-	-	-
MS4a	-	-	-		164.8201	-15.8465	-	-	-	-
MS4b	-	-	-	180.6665	158.5076	-22.1589	-	-	-	-
FB	-	-	-	9.8362	8.0619	-1.7743	-	-	-	-
FIL	0.3235	-2.7818	0.8866	2.4977	0.2928	-2.2049	0.8024	7.1042	0.8099	-0.4101
MQ End	0.1178	-3.3754	-0.0554	-0.0882	0.0763	0.1645	0.0196	-0.3762	-0.2865	0.0384

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated

Fulvic Acids (au) - FEEM

	Week 16			Week 17	Week 18	Week 19	Week 20	Week 21		
Sample	U	S	Change	U	U	U	U	U	S	Change
Wa		57.4402	-24.5032						53.9908	-15.0216
Wb	81.9434	60.6965	-21.2469	80.4057	77.6261	104.8220	69.6877	69.0124	50.6772	-18.3352
Ma	57.2193	58.3708	1.1515						91.6355	-12.7113
Mb		59.1003	1.8810	90.2967	57.4987	78.6114	122.8289	104.3468	91.2272	-13.1196
WS1a		-	-	-	-	-	-		-	-
WS1b	0.7807	2.5903	1.8096	-	-	-	-	-	-	-
WS2a		81.4605	-17.0083	-	-	-	-		108.1305	-25.7488
WS2b	98.4688	80.1706	-18.2982	-	-	-	-	133.8793	107.4748	-26.4045
MS3a		-	-	-	-	-	-		-	-
MS3b	-	-	-	-	-	-	-	5.5925	4.4948	-1.0977
MS4a		169.2538	-17.9508	-	-	-	-	246.5127	223.4408	-23.0719
MS4b	187.2046	165.9766	-21.2280	-	-	-	-		215.4420	-31.0707
FB	5.3264	6.7344	1.4080	-	-	-	-	4.2200	5.0244	0.8044
FIL	0.2008	0.1299	-0.0709	-0.2680	-0.4280	0.0567	0.2335	-0.0878	0.2653	0.3531
MQ End	0.0668	-0.2520	-0.3188	-0.1888	-0.0386	-0.2807	-0.0881	-0.2749	0.0066	0.2815

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated

Protein Like Materials (au) - FEEM

	Week 1	Week 2	Week 3			Week 4	Week 5	Week 6	Week 7		
Sample	U	U	U	S	Change	U	U	U	U	S	Change
Wa				13.3971	-0.0198					10.7482	-0.8040
Wb	19.7243	15.4442	13.4169	17.1647	3.7478	11.7544	14.6880	12.5311	11.5522	13.5896	2.0374
Ma				25.5098	5.2639					26.5342	2.9944
Mb	24.6218	23.1314	20.2459	24.3170	4.0711	22.1135	21.1136	20.5761	23.5397	25.1089	1.5692
WS1a	-	-		7.5354	-	-	-	-		-	-
WS1b	-	-	-	-	-	-	-	-	1.1477	21.7399	20.5922
WS2a	-	-		10.3107	3.9174	-	-	-		9.5956	-1.1031
WS2b	-	-	6.3933	14.4169	8.0236	-	-	-	10.6987	9.0155	-1.6832
MS3a	-	-		-	-	-	-	-		-	-
MS3b	-	-	2.3858	-	-	-	-	-	-	-	-
MS4a	-	-		13.9572	2.0243	-	-	-		12.5924	2.5658
MS4b	-	-	11.9329	14.3285	2.3956	-	-	-	10.0266	12.9784	2.9518
FB	-	-	4.0536	5.1705	1.1169	-	-	-	2.9483	5.0445	2.0962
FIL	1.4911	2.3531	3.9526	1.8416	-2.111	2.4632	1.7982	1.4640	4.6128	0.9406	-3.6722
MQ End	-0.1489	0.1283	0.3949	0.4394	0.0445	-0.0153	-0.1845	0.1554	-0.0493	0.2859	0.3352

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated

Protein Like Materials (au) - FEEM

	Week 8	Week 9	Week 10	Week 11			Week 12	Week 13	Week 14	Week 15
Sample	U	U	U	U	S	Change	U	U	U	U
Wa					12.3295	1.3824				
Wb	11.8599	17.0668	11.0736	10.9471	12.9865	2.0394	11.5402	14.4806	9.1087	10.2266
Ma					24.2708	1.9446				
Mb	25.0499	24.3310	25.5713	22.3262	23.3787	1.0525	16.9598	24.4249	25.0800	23.1487
WS1a	-	-	-		3.9661	2.6541	-	-	-	-
WS1b	-	-	-	1.3120	-	-	-	-	-	-
WS2a	-	-	-	6.1900	8.4566	2.2667	-	-	-	-
WS2b	-	-	-		8.6541	2.4642	-	-	-	-
MS3a	-	-	-		-	-	-	-	-	-
MS3b	-	-	-	-	-	-	-	-	-	-
MS4a	-	-	-		12.7761	1.5617	-	-	-	-
MS4b	-	-	-	11.2144	12.3283	1.1139	-	-	-	-
FB	-	-	-	2.9175	3.1826	0.2651	-	-	-	-
FIL	1.9831	0.5062	0.9294	1.1462	1.3625	0.2163	6.5885	2.4329	3.1568	0.8555
MQ End	0.6252	-0.1370	0.0517	0.6570	0.1928	-0.4642	0.0944	-0.2457	-0.2410	0.1204

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated

Protein Like Materials (au) - FEEM

	Week 16			Week 17	Week 18	Week 19	Week 20	Week 21		
Sample	U	S	Change	U	U	U	U	U	S	Change
Wa		10.5001	1.9652						10.8196	3.1155
Wb	8.5349	11.0141	2.4792	10.6649	6.6938	6.9172	8.3975	7.7041	11.8171	4.1130
Ma		14.9914	4.3539						17.6887	1.1039
Mb	10.6375	14.8847	4.2472	16.2680	9.6055	14.8317	18.7318	16.5848	19.107	2.5222
WS1a		-	-	-	-	-	-		-	-
WS1b	1.1643	3.9962	2.8319	-	-	-	-	-	-	-
WS2a		7.3557	-0.6666	-	-	-	-		9.8010	-1.3298
WS2b	8.0223	7.4808	-0.5415	-	-	-	-	11.1308	9.0443	-2.0865
MS3a		-	-	-	-	-	-		-	-
MS3b	-	-	-	-	-	-	-	4.2605	3.4060	-0.8545
MS4a		12.4341	1.9139	-	-	-	-		14.5757	-1.1150
MS4b	10.5202	10.8687	0.3485	-	-	-	-	15.6907	13.4948	-2.1959
FB	1.3874	5.2232	3.8358	-	-	-	-	1.8869	2.8056	0.9187
FIL	1.5170	0.8951	-0.6219	1.7851	-0.5016	-0.5833	1.0882	0.4594	1.0492	0.5898
MQ End	0.3715	-0.3410	-0.7125	0.1786	-0.2431	-0.7775	0.3112	-0.2420	0.0974	0.3394

🟦	Duplicated measurement
U	Unstagnated
S	Stagnated