# EVALUATION OF ARSENIC AND IRON TRANSPORT FROM SEDIMENTS OF A POTABLE WATER TREATMENT PLANT WASTEWATER STABILIZATION POND SYSTEM

by

ALI EKHLASI NIA

A Thesis Submitted to the College of Graduate and Postdoctoral Studies In Partial Fulfillment of the Requirements For the Degree of Master of Science In the Department of Civil, Geological and Environmental Engineering University of Saskatchewan Saskatoon, Saskatchewan, Canada

Unless otherwise noted, copyright of the material in this thesis belongs to the author. © March 2021 Ali Ekhlasi Nia

## PERMISSION TO USE

In presenting this thesis/dissertation in partial fulfillment of the requirements for a Postgraduate degree from the University of Saskatchewan, I agree that the Libraries of this University may make it freely available for inspection. I further agree that permission for copying of this thesis/dissertation in any manner, in whole or in part, for scholarly purposes may be granted by the professor or professors who supervised my thesis/dissertation work or, in their absence, by the Head of the Department or the Dean of the College in which my thesis work was done. It is understood that any copying or publication or use of this thesis/dissertation or parts thereof for financial gain shall not be allowed without my written permission. It is also understood that due recognition shall be given to me and to the University of Saskatchewan in any scholarly use which may be made of any material in my thesis/dissertation.

## DISCLAIMER

Reference in this thesis/dissertation to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not constitute or imply its endorsement, recommendation, or favoring by the University of Saskatchewan. The views and opinions of the author expressed herein do not state or reflect those of the University of Saskatchewan and shall not be used for advertising or product endorsement purposes.

Requests for permission to copy or to make other uses of materials in this thesis/dissertation in whole or part should be addressed to:

Head of the Department of Civil, Geological and Environmental Engineering 3B48 Engineering
Building,
57 Campus Drive
University of Saskatchewan Saskatoon, Saskatchewan S7N 5A9

Canada OR

Dean

College of Graduate and Postdoctoral Studies University of Saskatchewan 116 Thorvaldson Building, 110 Science Place Saskatoon, Saskatchewan S7N 5C9 Canada

## ABSTRACT

The creation of clean drinking water within Drinking Water Treatment Plants (DWTP) leads to residual wastewaters which need to be properly treated before being released into the environment. Treated wastewater effluents must meet effluent guidelines which can be difficult for DWTPs that use groundwater as their sole source of raw water, since their wastewaters typically contain elevated concentrations of metal(loid)s, such as arsenic (As) and iron (Fe). A treatment strategy for DWTP wastewaters is the use of Wastewater Stabilization Ponds (WSP), in which most of the metal(loid)s are either settled in the sedimentation process by adsorption to the suspended particles or precipitated by producing insoluble compounds. However, these metal(loid)s are not perpetually fixed in the sediments and can become resuspended and released back into the residual wastewater over time. This potential for release shows the importance of evaluation of metal(loid)s in sediments.

The studied pond system has been in use for more than 50 years and consists of five sequential ponds currently designated as Ponds 1 through 5. The pond system receives wastewaters from a DWTP that has been recently upgraded from treating a mixture of surface and groundwater with electro-dialysis reversal (EDR) technology to treating only groundwater with reverse osmosis (RO) technology with an increased production capacity to meet the growing needs of the municipality. The pond system effluent was found to have frequently elevated concentrations of As and Fe and exceeded guideline values for As prior to the start of this study. This study monitored both the overlying water and sediment As and Fe concentrations, among other parameters, in each of the individual ponds over the spring and summer of 2019 (before the new DWTP commissioning) and spring and summer of 2020 (after the January 2020 commissioning of the new DWTP). The collected pond sediments on one sampling occasion in 2020 were also used in laboratory experiments used to better understand the fate and transport potential of As and Fe between sediments and water. These laboratory experiments included determination of solid-water partitioning coefficients (K<sub>d</sub>) and leaching rates for both As and Fe using a 16 day duration to mimic the overall WSP hydraulic retention time.

The results from this study indicate that the individual ponds and the pond system effluents had elevated As and Fe concentrations. These concentrations did not meet the guidelines for As concentrations, while were close to exceeding new Fe guidelines currently under consideration. It is interesting to note that the historic Fe guidelines were often exceeded but were more stringent than the new guidelines which vary based on organic carbon concentrations and pH of the water. Release of polluted effluent has resulted in As contamination in sediments downstream of the pond system outlet causing the sediments to exceed As guidelines. The pond system sediments were found to contain elevated As and Fe contents in the ranges of about 25 to 400 and 10,000 to 45,000 mg/kg, respectively, and with variations more significant between the ponds than in each individual pond over time. Thus far, the ponds sediment As and Fe concentrations in 2019 and 2020 suggest that the change in the DWTP treatment process did not affect the ponds' sediments significantly.

Results from the sediment leaching experiments indicated that each of the ponds can potentially release leachable As and Fe contents over their individual retention times, as well as during the overall WSP retention times. The As concentrations resulted in sediment log K<sub>d</sub> values ranging widely from 2.21 to 4.31 L/kg among the ponds with K<sub>d</sub> values of Pond 1  $\gg$  Pond 3 > Pond 4 > Pond 5  $\gg$  Pond 2. The Fe concentrations resulted in sediment log K<sub>d</sub> values having a range of 3.32 to 5.53 L/kg with the values being in the following order: Pond 5  $\gg$  Pond 1 > Pond 4 > Pond 3  $\gg$  Pond 2. For the leaching rate experiments, As concentrations increased from Day 0 to Day 9 for all ponds with a range of concentrations from ~0.005 to 0.015 mg/L. From Day 9 to Day 16 the water concentrations stabilized resulting in the highest concentrations in the Day 0 sampling with Pond 2 being the highest at ~0.18 mg/L followed by Pond 1 at ~0.15 mg/L and Pond 4 at ~0.14 mg/L. Unlike As, the Fe concentrations reduced after initial peaks until approximately Day 6 or Day 9 when the concentrations reached a steady state of under 0.05 mg/L for all ponds.

The conclusion of this research is that the DWTP WSP system has elevated concentrations of As and Fe in pond sediments that can potentially impact the treatment process via leaching of these pollutants into the overlying waters. Clearly the sediments are already shown to be releasing into the overlying waters given the increasing concentrations found for both As and Fe through the WSP system on numerous sampling occasions. These results may be useful to inform potential updates to the WSP system in the future.

## ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my supervisor, Dr. Kerry McPhedran, for giving me the opportunity to do research and for his support, guidance, and patience throughout this entire process. I could not have imagined having a better advisor and mentor for my MSc study.

I would like to thank Harrison Bull, Ali Motalebi Damuchali, and Kathryn Lindsay for their invaluable contribution to this research.

I would also like to acknowledge funding through the Mitacs Accelerate program and SaskWater. In addition, research support has been provided by SaskWater personnel, including Sumith Kahanda, Enisa Zanacic, Dale Hreshka, and Timo Jansen.

I also thank Helen Yin, Khaled Zoroufchi Benis and Mohammad Behravan, for their assist in my research.

# TABLE OF CONTENTS

PERMISSION TO USE	i
DISCLAIMER	ii
ABSTRACT	<b></b> iii
ACKNOWLEDGEMENTS	v
TABLE OF CONTENTS	vi
LIST OF FIGURES	ix
LIST OF TABLES	<b></b> xi
LIST OF ABBREVIATIONS	xiii
Chapter 1: General Introduction	1
1.1 Overview	1
1.2 As and Fe in the Environment	3
1.2.1 As Speciation, Behavior, and Toxicity	3
1.2.2 Fe Speciation, Behavior, and Toxicity	5
1.2.3 Metal(loid)S Ecological Impacts	6
1.2.4 Sources of As and Fe in the Environment	6
1.3 DWTP and their Wastewaters	7
1.3.1 DWTP – General Overview	7
1.3.2 DWTP Wastewater, Regulations and Treatment	. 11
1.4 Wastewater Stabilization Ponds	. 12
1.4.1 As and Fe Overview in the Context of WSPs	. 12
1.4.2 Sediments	. 16
1.5 Melville potable water supply system (MEPOWSS)	. 21
1.6 Thesis Partner	. 23
1.7 Thesis Overview	. 23
1.7.1 Thesis Objectives	. 23
1.7.2 Chapter 2 Overview	. 24
1.7.3 Chapter 3 Overview	. 25
1.7.4 Chapter 4 Overview	. 26
References	. 27
Chapter 2: Evaluation of Arsenic and Iron Transport from Sediments of a Potable Water Treatment Wastewater Pond System	. 37

Abstract	37
2.1 Introduction	38
2.2 Methodology	40
2.2.1 DWTP and WSP System	40
2.2.2 Sampling and analysis	42
2.3 Results and Discussion	43
2.3.1 As Sediment and Wastewater Concentrations	43
2.3.2 Fe Sediment and Wastewater Concentrations	45
2.3.3 As and Fe variations in ponds sediment	45
2.4 Conclusions	48
Acknowledgements	49
References	49
Chapter 3: Assessment of Arsenic and Iron Occurrence and Leaching Potential for The	
Sediments of a Potable Water Treatment Wastewater Stabilization Pond System	52
Abstract	52
3.1 Introduction	53
3.2 Methodology	56
3.2.1 DWTP and the Pond System	56
3.2.2 Sampling and Analysis	58
3.2.3 Modeling and Statistics	59
3.2.4 Leaching Experiments	59
3.3 Results and Discussion	62
3.3.1 As Sediment and Overlying Water Concentrations	62
3.3.2 Fe Sediment and Overlying Water Concentrations	65
3.3.3 As and Fe Relationships in Pond Sediments	68
3.3.4 As and Fe Correlation with Other Parameters	72
3.3.5 Pond DO and Eh conditions and As and Fe speciation	73
3.3.6 As and Fe Leaching Experiments Result	76
3.4 Conclusions	81
Acknowledgements	81
References	82
Chapter 4: Discussion and Recommendations for Future Work	88
4.1 General Discussion	88

4.2 Engineering Significance	
4.3 Future Work	
Appendix: Chapter 3 Supplementary Information	
A.1 2019 and 2020 sediments chemistry	
A.1.1 2019 July sediments chemistry	
A.1.2 2019 August sediments chemistry	
A.1.3 2019 October sediments chemistry	
A.1.4 2020 May sediments chemistry	101
A.1.5 2020 June sediments chemistry	103
A.1.6 2020 July sediments chemistry	105
A.2 ANOVA Test Results for the Ponds Sediment As and Fe Concentrations	107
A.3 ANOVA Test Results for the Ponds Redox Potential and DO Concentration	109
A.4 Sediment As and Fe Correlation With Other Elements	111
A.5 PHREEQC Modeling Data	112
A.6 Leaching Rate Experiment Individual Reactors As And Fe Concentrations	115

# LIST OF FIGURES

<u>Chapter 1:</u>
Figure 1.1: Main As transformation pathways in WSPs14
Figure 1.2: Main Fe transformation pathways in WSPs
Figure 1.3: WSP system in 2019 and 2020 with five main ponds labelled 1 through 522
<u>Chapter 2:</u>
Figure 2.1: 2019 WSP system with five ponds (labelled 1 through 5) that sequentially treat the         DWTP effluents
<b>Figure 2.2:</b> As concentrations in wastewater (mg/L on left y-axis) and sediments (mg/kg on right y-axis) for each of the five ponds as determined for three sampling events in 201944
<b>Figure 2.3:</b> Fe concentrations in wastewater (mg/L on left y-axis) and sediments (mg/kg on right y-axis) for each of the five ponds as determined for three sampling events in 201946
Figure 2.4: As and Fe concentrations in sediments for each pond (including Pond 0) over time with samples collected in July, August, and October 2019
<u>Chapter 3:</u>
Figure 3.1: The 2020 WSP system consisting of five settling ponds (labelled 1 through 5) receiving DWTP wastewaters
<b>Figure 3.2:</b> A) Leaching rate experiment reactor setup; and B) Schematic of an individual reactor setup
<b>Figure 3.3:</b> The As concentrations in overlying waters and sediments for each of the five ponds during six sampling events in 2019 and 2020
<b>Figure 3.4:</b> The Fe concentrations in overlying waters and sediments for each of the five ponds during six sampling events in 2019 and 2020
Figure 3.5: As and Fe concentrations in sediments for each pond in 2019 and 202070
<b>Figure 3.6:</b> 2019 and 2020 sediment concentration box-and-whisker plots for each individual pond for: A) As; and B) Fe

Figure 3.7: A) DO concentrations and B) redox potentials in each pond measured over five months
in 2020
Figure 3.8: Average As and Fe concentrations (n=4) in overlying water of each individual pond
reactor over 16 days
Appendix A:
Figure A.1: 2020 Pond 1 PHREEQC modeling data
Figure A.2: 2020 Pond 2 PHREEQC modeling data
Figure A.3: 2020 Pond 3 PHREEQC modeling data
Figure A.4: 2020 Pond 4 PHREEQC modeling data
Figure A.5: 2020 Pond 5 PHREEQC modeling data
Figure A.6: As and Fe concentrations in overlying water of each individual pond reactors (n=4)
over 45 days 115

# LIST OF TABLES

## Chapter 1:

<b>Table 1.1:</b> Advantages and disadvantages of selected DWTP water treatment technologies8
Table 1.2: Advantages and disadvantages of in-situ and ex-situ sediment remediation strategies
<u>Chapter 3:</u>
<b>Table 3.1:</b> The As concentration trends in the WSP system sediments and overlying waters in 2019 and 2020 sampling periods.
<b>Table 3.2:</b> The Fe concentration trends in the WSP system sediments and overlying waters in 2019       and 2020 sampling periods
<b>Table 3.3:</b> Aqueous and sediment As concentrations correlations with various elements
<b>Table 3.4:</b> As and Fe solid-water distribution coefficients and corresponding leached concentrations measured in the distilled water
Appendix A:
Table A.1: 2019 July sediments chemistry    94
<b>Table A.2:</b> 2019 August sediments chemistry
Table A.3: 2019 October sediments chemistry    98
Table A.4: 2020 May sediments chemistry
Table A.5: 2020 June sediments chemistry
Table A.6: 2020 July sediments chemistry    105
<b>Table A.7:</b> A) ANOVA test and B) Tukey's post hoc test results on 2019 and 2020 ponds Asconcentrations indicating significant (p<0.05) differences between ponds
<b>Table A.8:</b> A) ANOVA test and B) Tukey's post hoc test results on 2019 and 2020 ponds Feconcentrations indicating significant (p<0.05) differences between ponds

Table A.9: A) ANOVA test and B) Tukey's post hoc test results on 2020 ponds redox condit	ion
indicating significant (p<0.05) differences between ponds	109
Table A.10: A) ANOVA test and B) Tukey's post hoc test results on 2020 ponds b	DO
concentrations indicating significant (p<0.05) differences between ponds	110
Table A.11: Sediment As and Fe concentrations correlations with various elements	111

# LIST OF ABBREVIATIONS

AAS: Atomic Absorption Spectroscopy CCME : Canadian Council of Ministers of the Environment CRC ICP-MS: Inductively Coupled Plasma Mass Spectrometer Using Collision/Reaction Cell DI: Deionized DNA: Deoxyribonucleic Acid DO: Dissolved Oxygen DOC: Dissolved Organic Carbon **DWTP: Drinking Water Treatment Plant** EDR: Electro-Dialysis Reversal EPA: Environmental Protection Agency HDPE: High-Density Polyethylene HPLC: High Performance Liquid Chromatography Spectrometer HPLC-ICP-MS: High performance liquid chromatography inductively coupled mass spectrometer ICP-MS: Inductively Coupled Plasma Mass Spectrometer ISQG: Freshwater Interim Sediment Quality Guidelines **OM:** Organic Matter PEL: Probable Effect Levels **RO:** Reverse Osmosis **ROS:** Reactive Oxygen Species SOM : Sediment Organic Matter SRB: Sulphate Reducing Bacteria USask: University of Saskatchewan US-EPA: The United States Environmental Protection Agency **USGS: United States Geological Surveys** WSP: Wastewater Stabilization Pond WHO: World Health Organization

## Chapter 1: General Introduction

### **1.1 Overview**

Drinking water quality plays a major role in human health, yet more than two billion people around the world do not have access to safe drinking water (World Health Organization 2019). Drinking water contaminated with toxic heavy metals can adversely affect human health and cause various types of cancer (Oyem et al. 2015). The contamination level depends on the quality of source water and the treatment system used in water treatment plants. Surface water and groundwater are two major sources of raw water and can become contaminated with heavy metals through both natural and anthropogenic processes. However, groundwater is often more polluted with heavy metals and metalloids as compared to surface waters (Oyem et al. 2015). Raw water requires treatment to decrease heavy metals and metalloids concentration, in addition to other parameters, in order to meet water quality guidelines prior to consumption and drinking water treatment plants (DWTP) are employed for this purpose (Chowdhury et al. 2016).

Drinking water treatment plants produce various wastes and wastewaters containing elevated metal(loid)s concentrations that cannot be disposed of into the environment without meeting the related guidelines. Therefore, the generated wastewaters are required to be treated, and wastewater stabilization ponds (WSPs) are widely used for this purpose (Clancy et al. 2013). In these ponds, metal(loid)s are removed through sedimentation and precipitation processes, which ideally will result in the effluent meeting the required guidelines prior to release to the environment (Peng et al., 2009). However, metal(loid)s can accumulate in the ponds' sediments over time, making them a potential source of contamination, releasing the metal(loid)s back into the overlying water under various conditions (Mulligan et al. 2001, Peng et al., 2009).

The Melville Potable Water Treatment Plant's (MEPOWSS) WSP system has been in use for more than 50 years but has not been thoroughly evaluated since its installation, and its performance for treating residual wastewaters is not well understood. SaskWater, the owner and operator of the MEPOWSS, has recently built a new DWTP, changing the source of raw water from a mixture of surface water and groundwater to only groundwater, and the treatment technology from electrodialysis reversal (EDR) to reverse osmosis (RO) with a higher production capacity required to meet the growing needs of the municipality. Groundwater has higher metal(loid) concentrations than surface water, thus, using only groundwater as source water, and treating a higher volume of water, is expected to result in a higher metal(loid) loading rate to the WSP system (Oyem et al. 2015). The WSP system's efficiency for treating this new wastewater stream and how the individual ponds will be affected by the increased loading rates are unknown.

The WSP system outflow has been monitored monthly since 2017 and contains elevated arsenic (As) and iron (Fe) concentrations. However, only As effluent concentrations exceed the current guidelines with Fe exceeding previous guidelines, but not updated guidelines currently being assessed. Arsenic is an extremely toxic metalloid capable of causing various types of cancer such as cancer of skin, bladder, kidney, lungs, liver, and prostate (Xu et al., 2019). Iron can also impose significant risks to human health at high concentrations causing diseases such as hereditary hemochromatosis (Dev and Babitt 2017). Both As and Fe concentrations were also found to often be higher in the pond system outlet as compared to the inlet, suggesting As and Fe release from the pond system sediments into the effluent as the probable source for this increase in concentrations) and evaluating their potential to pollute the effluent (i.e., resuspension or dissolution from sediments) are necessary to better understand the WSP system.

This research's primary objective is to evaluate As and Fe concentrations and leaching potential from the sediments of the WSP system before and after implementing changes in the DWTP system. Pond sediments were sampled during the spring and summer of 2019 (before the new DWTP commissioning) and spring and summer of 2020 (after January 2020 commissioning of the new DWTP). This sampling allowed for the assessment of As and Fe seasonal variations and helped determine the impacts of the DWTP changes on the ponds' sediments. The sediments were also used in laboratory leaching experiments to acquire a better understanding of As and Fe fate and transport potential between sediments and water. It is also worth mentioning here that both As and Fe were investigated in this study, however, more attention was given to As since only As exceeded the Canadian Council of Ministers of the Environment guidelines for effluent waters (CCME 2001).

This Chapter 1 includes a literature review focusing on sections including: As and Fe in the Environment (Section 1.2); DWTPs and their Wastewaters (Section 1.3); Wastewater Stabilization Ponds (Section 1.4); and a description of the MEPOWSS site (Section 1.5). First chemistry, fate and toxicity of As and Fe in the Environment are described. Then DWTPs and their wastewaters,

including disposal regulations and wastewater treatment technologies are explained. The next section further describes the wastewater stabilization ponds, their sediments and As and Fe chemistry and fate in the context of these WSPs. Lastly, an in-depth description of the MEPOWSS site, including the plant history and the upgrades in the plant system. The final two sections include a brief overview of the industrial partner (Section 1.6) and of the thesis structure (Section 1.7).

### 1.2 As and Fe in the Environment

Arsenic (As), a widely distributed environmental contaminant metalloid, is located in group 15 on the periodic table and has atomic weight and numbers of 74.92 and 33, respectively (Tchounwou et al. 2015). Arsenic is the 20<sup>th</sup> most abundant element in the earth's crust with typical concentrations of 1.5–3 mg kg<sup>-1</sup> (Mandal and Suzuki 2002). Arsenic can be derived from both natural sources such as volcanogenic rocks and anthropogenic sources such as mining and smelting of nonferrous metals (Wang and Mulligan 2006). Arsenic is usually found in natural waters at concentrations lower than 10  $\mu$ g L<sup>-1</sup> but can also exists at concentrations as high as 5,000  $\mu$ g l<sup>-1</sup> (Smedley and Kinniburgh 2002).

Iron (Fe) has an atomic weight and number of 55.85 and 26, respectively. Iron is one of the essential nutrients for most living creatures, primarily because it is the cofactor for numerous necessary proteins and enzymes and is a crucial element in hemoglobin and myoglobin. It also takes part in energy metabolism maintenance (Jaishankar et al. 2014, Khatri et al. 2017, Manahan 2002). Iron enters groundwater when the water passes through Fe-containing rocks and sediments which then dissolves the Fe (Ityel 2011). Iron also exists in surface water at concentrations ranging from 0.5 to 50 mg L<sup>-1</sup> (World Health Organization 2011).

#### 1.2.1 As Speciation, Behavior, and Toxicity

Arsenic is found throughout the environment in four oxidation states ( $As^{3-}$ ,  $As^{0}$ ,  $As^{3+}$ ,  $As^{5+}$ ) as both inorganic and organic compounds depending on sorbents' characteristics and quantities, pH, redox conditions, and microbiological activity (Wang and Mulligan 2006). In natural waters, trivalent arsenite and pentavalent arsenate are the predominant oxidation states under anaerobic and aerobic conditions, respectively (Brandt et al. 2017). Around pH values equal to 8, temperature of 25 °C and pressure of 1 bar, arsenite and arsenate mostly appear as arsenious acid, H<sub>3</sub>AsO<sub>3</sub>, and HAsO<sub>4</sub><sup>-2</sup> (Wolthers et al. 2005).

Arsenic mostly coprecipitates with (hydro)oxides of iron (Fe), aluminum (Al), and manganese (Mn), but can also sorb to clays and minerals. The particles' size also affects As mobility and distribution; finer particles can adsorb more As due to their larger surface areas (Wang and Mulligan 2006). Arsenic chemistry and its transformation pathways are determined by the water's chemistry. For example, changes in redox potential, pH values and dissolved oxygen concentrations can cause the release of As from sediments to overlying waters. This release can occur due to the dissolution of As-associated Fe and Mn and/or As reduction from arsenate to arsenite, a more mobile species (Smedley and Kinniburgh 2002). In general, arsenate settles through adsorption/coprecipitation by manganese dioxide (MnO<sub>2(s)</sub>) or precipitation as minerals along with calcium (Ca), magnesium (Mg), aluminum (Al) and Fe, while arsenite is removed by adsorption/coprecipitation to iron sulphide (FeS) or precipitation as sulphide/iron minerals (Lizama, Fletcher 2011).

Arsenic is a toxic substance and a carcinogen that exists in different forms of organic and inorganic compounds. The toxicity level of As depends on its speciation. For example, arsenite is reported to be 25 to 60 times more toxic than arsenate (Zhang et al. 2008). Exposure to As and its compounds occurs through inhalation, dermal contact, and ingestion of drinking water (Ratnaike 2003). For the general population, 92-98% of the total daily As intake comes from consuming drinking water and food. Soil/dust ingestion accounts for approximately 2% of the total daily As intake; however, it can be as high as 4 and 9% for infants and young children, respectively (CCME 1997). In Canada, exposure to As is mostly through ingestion of As contaminated drinking water or food, and people living near As releasing industrial and geological sites (Wang and Mulligan 2006). Severe poisoning by As through ingestion can cause coma and death within 30 minutes of exposure (Alam and McPhedran 2019). Chronic exposure to As can seriously damage the skin and ultimately cause skin cancer as well as cancers of the bladder, kidney, lungs, liver, and prostate (Xu et al., 2019). A lifetime of consuming contaminated water with a minimum As concentration of 50 µg/L can lead to a cancer death rate as high as 1 person in 100 (National Research Council 1999). Guidelines for As in effluent waters have been set to 5  $\mu$ g/L by the Canadian Council of Ministers of the Environment (CCME 2001).

#### 1.2.2 Fe Speciation, Behavior, and Toxicity

Iron exists in two oxidation states of soluble ferrous iron (Fe<sup>2+</sup>) and insoluble ferric iron (Fe<sup>3+</sup>) depending on oxygen availability, redox conditions, and microbial activities (Pehkonen 1995). Iron in groundwater can exist as ferrous iron under anaerobic conditions at concentrations as high as several milligrams per litre. However, the ferrous iron oxidizes to ferric iron upon exposure to oxygen (World Health Organization 2008).

Iron and its minerals play an important role in contaminant cycling and stabilisation in sediments. Iron oxides and oxy-hydroxides, which are highly insoluble, are the predominant forms of Fe under oxic conditions, and can adsorb contaminants, including both As and Fe, at levels depending on their hydroxyl groups chemistry, reactivity, and structure as well as the pH condition (Bjorn and Roychoudhury 2015). However, ferric oxides can become reduced to ferrous species under subtoxic conditions resulting in release of Fe and adsorbed and co-precipitated contaminants into aqueous phase (Bjorn and Roychoudhury 2015). Iron compounds in sediments can also react with dissolved sulfides to form Fe monosulfide and pyrite (FeS<sub>2</sub>) with further reactions with dissolved sulfide. This process results in formation of solid-phase iron sulfides that can permanently immobilize Fe when buried in sediments (Wijsman et al. 2001).

Excessive ingestion of Fe can result in vomiting, diarrhea, abdominal pain, and gastrointestinal bleeding (Banner and Tong 1986). However, it can result in more adverse health effects in people with hemochromatosis (Fe overload disorder), Fe overloading anemias, transfusional Fe overloaded, and other secondary forms hemochromatosis (Dev and Babitt 2017). Hereditary hemochromatosis arises due to a defect in genes. This disorder causes the body to absorb too much dietary Fe and accumulates extra Fe in the body's tissue and organs. Hereditary hemochromatosis symptoms include joint pain, extreme tiredness, weight loss, abdominal pain, and loss of sex drive. As hemochromatosis progresses, the symptoms may include arthritis, heart abnormalities, liver disease, diabetes, skin discoloration, cancers, kidney disease, and neurodegenerative disease (such as Parkinson and Alzheimer) (Drakesmith et al. 2005, Wessling-Resnick 2016). Current guidelines under consideration for Fe in effluent waters varies depending on the pH and dissolved organic carbon (DOC) concentrations in the final effluent (Environment and Climate Change Canada 2019). Previous guidelines for Fe were 300  $\mu$ g/L (CCME, 2001)

#### **1.2.3 Metal(loid)s Ecological Impacts**

Some plants can absorb high levels of metal(loid)s from contaminated soil around them. Thus, metal(loid)s can be accumulated in plants and transported to human or animal bodies through consumption. However, the possibility of exposure to metal(loid)s contamination is higher from the soil that sticks to the plant than the plant itself as the soils might not be washed off thoroughly (Martin and Griswold 2009). Root crops, leafy vegetables, and parts of the plant growing nearby the polluted soil are more likely to be contaminated. Accumulation can also happen in animals consuming the contaminated plants or bottom feeders. Fish species living in polluted water and consuming contaminated plants and organisms experience high exposure to contaminates (Martin and Griswold 2009).

Arsenic is toxic to plants at lower concentrations as compared to humans or animals (Finnegan and Chen 2012). It can significantly slow the growth, fertility, and fruit production of plants and cause death at high concentrations (Finnegan and Chen 2012). In mammals and aquatic animals, As can damage DNA and cause oxidative stress, which is the inadequacy of antioxidants to neutralize free radicals in the body. Arsenate and arsenite species can cause different damage, such as mitochondrial impairment and enzymes' inactivation, respectively (Fattorini and Regoli 2004, Ventura-Lima et al. 2011).

Iron ions at high concentrations can result in toxic effects in plants, such as damaging cell structures, reducing plant growth, preventing biosynthesis of chlorophyll, and causing excessive production of reactive oxygen species (ROS) via the Fenton reaction (Saaltink et al. 2017, Zaid et al. 2020). In animals, exceeding Fe guidelines can result in lipid peroxidation, causing a defect in the liver's mitochondria and lysosome functions. Iron overload is also reported to cause DNA damage, thus contributing to the possibility of a malignant transformation (Britton et al. 2002).

#### 1.2.4 Sources of As and Fe in the Environment

In many countries, including Canada, As is deposited as arsenide compounds in geological bedrock and As-rich aquifers (Jang et al. 2016). The As can then become mobilised in the environment through natural processes such as weathering, volcanic emissions, and geochemical reactions. Anthropogenic activities such as mining and smelting and the use of arsenical insecticides and pesticides also contribute to the release of As into the environment (Jang et al. 2016). Freshwater As concentrations have been found to vary by more than four orders of

magnitude; however, groundwaters are expected to contain higher levels of As due to mobilization during water-rock contacts (Smedley and Kinniburgh 2002). Surface and ground waters in Canada typically contain low As concentrations in the range 0.001 to 0.002 mg/ L, however, elevated As concentrations have been found mainly due to anthropogenic activities (Wang and Mulligan 2006).

Iron naturally exists in underground rock matrices and enters natural waters through weathering processes of Fe-containing rocks, sediments, and Fe-rich minerals. Water bodies also receive Fe contamination from anthropogenic sources such as wastewaters generated by Fe and other metallurgical activities (Sarkar and Shekhar 2018). Iron can be found in concentrations as high as 15 mg/L in groundwaters and surface waters through natural and anthropogenic activities (Khatri et al 2017). However, dissolved Fe species in surface waters can later form insoluble species through reaction with the available oxygen and form insoluble compounds (Ityel 2011).

### **1.3 DWTP and their Wastewaters**

Raw sources of drinking water, including both surface water and groundwater, are often contaminated with various impurities such as heavy metals and metalloids, thus are required to be treated in DWTPs (Chowdhury et al. 2016). DWTPs employ a series of treatment processes to eliminate impurities from the raw sources of water and produce safe drinking water. However, these treatment processes also produce various types of waste and wastewaters depending on the raw water source (Ippolito et al 2011). The generated wastewaters are often disposed of into nearby water bodies. However, within Canada, they must meet regulated guidelines prior to being released into the environment. Therefore, these wastewaters must undergo a treatment process to decrease their contaminants concentration to acceptable levels meeting regulatory guidelines (Clancy et al. 2013).

### 1.3.1 DWTP – General Overview

There are many drinking water treatment technologies for the removal of contaminants, with a current focus on As and Fe, from water sources, including coagulation, adsorption, ion exchange, oxidation, and membrane filtration including EDR and RO (Choong et al. 2007, Khatri et al. 2017). Table 1.1 provides an overview of the advantages and disadvantages of selected water treatment technologies. Each of these technologies will be discussed in this section; however, more attention will be given to the EDR and RO treatment technologies as the studied DWTP has employed

7

Technology	Advantages	Disadvantages	References
Oxidation/filtration	<ul> <li>Simple operation</li> <li>No hazardous wastes products</li> <li>Oxidizes the As and Fe to less harmful species</li> <li>Kills bacteria capable of causing disease</li> </ul>	<ul> <li>Oxidant can cause corrosion in system parts</li> <li>Difficulty in oxidant transportation and storage</li> <li>Requires control of the pH</li> </ul>	Khatri et al. 2017, Chaturvedi and Dave 2012, Mohan and Pittman 2007
Coagulation/filtration	<ul> <li>Process simplicity</li> <li>Highly effective</li> <li>Possibility of sludge reuse</li> <li>Low implementation cost</li> </ul>	<ul> <li>High cost of chemicals</li> <li>Rapid filter clog for treating groundwater with excessive Fe</li> <li>High sludge production</li> <li>Possibility of As leaching</li> </ul>	Shan et al 2019, Mohan and Pittman 2007
Adsorption	<ul> <li>Highly effective</li> <li>Low cost and practical</li> <li>No use of toxic chemicals</li> <li>Little to no leaching</li> </ul>	<ul> <li>Less effective at high pH</li> <li>Produces sludge</li> <li>Access to material may be limited</li> <li>Possible toxic by-products</li> </ul>	Khatri et al. 2017, Shan et al 2019
Ion exchange	<ul> <li>Highly effective</li> <li>Operation under various pH and alkalinity conditions</li> <li>Able to remove organic bound As and Fe</li> <li>Possibility of reusing material</li> </ul>	<ul> <li>Highly technical operation and maintenance</li> <li>High cost</li> <li>Access to material may be limited</li> <li>Difficulty in arsenite removal</li> </ul>	Thirunavukkarasu et al. 2002, Chaturvedi and Dave 2012, Shan et al 2019

**Table 1.1:** Advantages and disadvantages of selected DWTP water treatment technologies.

Biological	<ul> <li>Highly effective</li> <li>low cost implementation and operation</li> <li>Removes other impurities</li> <li>No chemical addition required</li> </ul>	<ul> <li>Requires specific pH condition</li> <li>Requires research on accessibility and commercialization</li> <li>Long start-up time</li> </ul>	Khatri et al. 2017, Shan et al 2019
Electro-dialysis reversal	<ul> <li>High As and Fe removal efficiency</li> <li>High water recovery rates</li> <li>Long useful life of membranes</li> <li>Operation at elevated temperatures up to 50 °C</li> <li>Less membrane fouling</li> <li>No chemical addition required</li> </ul>	<ul> <li>Not capable of removing viruses, bacteria, microorganisms, organic contaminants, and other neutral components</li> <li>Typically requires pretreatment of the feed water</li> <li>Generates concentrated reject that requires further treatment</li> </ul>	De Esparza 2006, Strathmann 2010, USEPA 2013
Reverse osmosis	<ul> <li>Very high As and Fe removal efficiency</li> <li>No chemical addition required</li> <li>Low solid waste generation</li> <li>Eliminates all types of dyes, salts, minerals, suspended solids, microorganisms, volatile and non-volatile organics</li> </ul>	<ul> <li>Membrane fouling</li> <li>High maintenance and operation costs</li> <li>High energy requirements</li> <li>Generates concentrated reject that requires further treatment</li> <li>High Investment costs for small and medium industries</li> </ul>	Crini and Lichtfouse 2019, Malaeb and Ayoub 2011, Schmidt et al. 2016

these two technologies both prior to being updated up to 2019 (EDR) and after updates (RO) completed in 2020.

The oxidation/filtration process is used to oxidize ferrous iron to ferric iron, which forms an insoluble iron complex, and trivalent As to pentavalent As species, which can later be adsorbed onto ferric oxides and co-precipitated out of solution or become trapped through filtration (Chaturvedi and Dave 2012, Shan et al. 2019). The coagulation process causes colloid particles to collide and form larger particles (flocs) by neutralizing the repulsive forces between colloid particles. The flocs can then be removed through sedimentation and/or filtration (Choong et al. 2007). Adsorption is a process in which compounds from a gaseous or liquid solution accumulate on the adsorbent surface due to physical forces or by chemical bonds between the adsorbent and adsorbate surface structures (Choong et al. 2007). Ion exchange is a physiochemical reaction that involves the exchange of unwanted ions in the solution phase with pre saturated ions on the solid resin phase (Chaturvedi and Dave 2012). Biological treatment is a strategy that employs natural biological techniques such as microbial oxidation by microorganisms to remove contaminants such as As and Fe from water (Choong et al. 2007, Khatri et al. 2017).

Electro-dialysis reversal (EDR) has been shown to be useful for treatment in DWTPs for As removal from source waters with an efficiency of up to 80% (De Esparza 2006). The EDR process uses a driving force of direct current power to transfer ionic species from the source water through cation and anion exchange membranes to a concentrate waste stream, producing a more diluted water stream. The EDR periodically need to employ the electrodes in a reverse polarity to clean the fouled membrane surfaces (Gabarrón et al. 2016). However, EDR cannot remove viruses, bacteria, microorganisms, organic contaminants, and other neutral components, and typically needs a pretreatment process for feed waters having Fe concentrated wastewaters that require further treatment before discharge to the environment (USEPA 2013). However, creation of residual wastes and wastewaters is always an issue for any DWTP process.

Reverse osmosis (RO) is widely used in drinking water treatment applications and has been shown to have an As removal efficiency of over 95% (Schmidt et al. 2016). The RO is a separation process that uses high hydrostatic pressure to pass water through a path full of 'twists and turns' through semipermeable membranes to filter the source water's dissolved components. This RO recovery rates vary from 35% to 85%, depending on the composition of the source water and its salinity, use of pretreatment technologies, and optimization of the system energy consumption (Greenlee et al. 2009). A drawback of RO is membrane fouling, which happens when water constituents are deposited on the membrane surface through the treatment process (Malaeb and Ayoub 2011). In addition, RO also rejects 15 to 25% of the source water as a waste stream, which is also subsequently. two to five times more concentrated than the source water (Corroto et al. 2019). As with EDR, this RO wastewater stream needs to be treated prior to safe release into the receiving environment.

#### **1.3.2 DWTP Wastewater, Regulations and Treatment**

There are various types of wastes and wastewaters generated from domestic, industrial, commercial, and agricultural activities. Events such as surface runoff or stormwater can also produce contaminated waters, which are often treated as wastewaters (Sonune and Ghate 2004). In the case of DWTPs, the level of contamination in wastewaters depends on the source of water and treatment process; while surface waters contain a variety of contaminants with high levels of organic materials, groundwaters contain higher concentrations of metal(loid)s including As and Fe (Oyem et al. 2015, Splane 2002). DWTPs using membrane technologies such as EDR and RO generate residual wastewaters in the forms of backwash and concentrate waters. These wastewaters are usually discharged either directly to a nearby surface water body or to a sanitary sewer system connected to a publicly owned treatment works. The residuals can also be disposed of through underground injection using a deep injection well (this was done previously for the currently studied DWTP). However, there are regulations and guidelines that are required to be met prior to any wastewater disposal (Cornwell et al. 2004).

To discharge As and Fe (and other parameters of) contaminated wastewaters into the environment, there are guidelines set forth by the Canadian Council of Ministers of the Environment (CCME) and Environment and Climate Change Canada (ECCC) to assure that the required standards for wastewater disposal are fulfilled. Although the limit for As in effluent waters is set to a constant number of 5  $\mu$ g/L, the Fe limit is required to be calculated based on the effluent pH and dissolved organic carbon (DOC) concentration of the water being assessed. In the case of effluent from the water treatment plant studied for this thesis, the calculated Fe limit is approximately 5 mg/L depending on the effluent variability (CCME 2001, Environment and Climate Change Canada 2019). Although there is no specific guideline for the discharge of As and

Fe contaminated wastewaters into the sewer connected to publicly owned treatment systems, the quantity and concentration limits are typically determined by the sewer control authority based on the treatment system size and efficiency, as well as the amount of As and Fe entering the system from other sources (Sorg 2000). Overall, all of the wastewaters must undergo a treatment process to meet the regulated guidelines for safe disposal into the environment.

The treatment intensity and final quality of the treated wastewater depend on whether the purpose of the treatment is to reuse the treated wastewater or to dispose of it in the environment (Salgot and Folch 2018). Although many treatment strategies used for drinking water treatment can also be used for the treatment of the residuals, waste stabilization ponds (WSPs) are often the preferred method as these ponds reduce suspended solids and typically can provide a treated effluent that is within the required guidelines if the WSP is properly maintained (Cornwell et al. 2004, Walsh et al. 2008). These ponds also help to keep discharge flow rates constant by prohibiting batch discharges and limiting discharges of solid residuals by allowing for solids settling during the treatment process (USEPA 2011).

### **1.4 Wastewater Stabilization Ponds**

Wastewater stabilization ponds are commonly used earlier form of constructed wetlands for the treatment of DWTP residuals having elevated concentrations of metal(loid)s. These systems are shallow water bodies that have low implementation costs and are easy and cheap to operate. In these systems, metal(loid)s are mostly adsorbed to the suspended solids and settled in the process of sedimentation. Metal(loid)s removal can also happen by forming insoluble salts and precipitating, or in an uptake process by microorganisms and plants. These removal processes are interdependent, making the overall removal process complicated, and therefore it is difficult to identify specific removal processes and functions (Kayombo et al. 2004, Üstün 2009).

#### 1.4.1 As and Fe Overview in the Context of WSPs

Of current interest is the ecological impacts of As and Fe on water bodies such as WSPs. However, a proper evaluation of the ecological impacts requires an understanding of As and Fe distribution and transformation pathways. Figures 1.1 and 1.2 provide more in-depth insight into the main processes responsible for the transformation of As and Fe in the presence of other chemical species in WSPs. Figure 1.1 shows the main As transformation pathways in WSPs with the most important removal processes highlighted in bold. Arsenate and arsenite species are in the center with blue arrows indicating the possibility of oxidation and reduction processes. While bacteria can both oxidize and reduce the As species, manganese oxides  $(MnO2_{(s)})$  and organic matter (OM) can mediate only the oxidation process and reduction process, respectively. The top section of Figure 1.1 shows sorption and coprecipitation of both arsenate and arsenite species by iron oxyhydroxides  $(Fe(OH)_{3(s)})$ , sorption by OM, and the uptake process by plants. The right section of Figure 1.1 shows arsenate sorption and coprecipitation by  $MnO_{2(s)}$ , sorption by the media, and precipitation as minerals where Fe, calcium (Ca), magnesium (Mg), and aluminum (Al) are present. The bottom section of Figure 1.1 indicates that arsenite can be removed by both adsorption and/or coprecipitation to iron sulphide (FeS) or precipitation as sulphide/iron minerals such as realgar (AsS) and arsenopyrite (AsFeS). Pyrite (FeS2) can also sorb both arsenate and arsenite species (Lizama et al. 2011).

Figure 1.2 shows the main Fe transformation pathways in WSPs. Ferric and ferrous species are in the center with blue arrows indicating the possibility of oxidation and reduction processes. Presence and absence of oxygen significantly affect the Fe species through the oxidation processes and reduction processes, respectively (World Health Organization 2008). Bacteria can also play a major role in both oxidization and reduction of the Fe species (Pronk and Johnson 1992). The left section of Figure 1.2 shows the uptake of ferrous species by plants and the sorption of ferrous species by clay minerals and hydrous metal oxides (Nano and Strathmann 2006, Tsai and Schmidt 2017, Van Groeningen et al. 2020). The right section of Figure 1.2 shows ferric coprecipitation with organic matter and alum, MgCl2 and PACl through coagulation (Pang et al. 2011, Sodano et al. 2017). The bottom section indicates precipitation of ferrous species as FeCO<sub>3</sub>, FeS and FeS<sub>2</sub> and precipitation of ferric species as Fe (oxy-hydr)oxides (Bjorn and Roychoudhury 2015, Wu et al. 2019).



Figure 1.1: Main As transformation pathways in WSPs with the most important removal processes highlighted in bold (Adapted from Lizama et al. 2011).



Figure 1.2: Main Fe transformation pathways in WSPs.

#### 1.4.2 Sediments

Sediments are deposited solid particles that were suspended in moving water prior to the sedimentation process. These particles consist of rock fragments and minerals generated through soil weathering and erosion processes as well as the residual organic matter from decay of plants and animals. These solid particles are mainly transported by wind and water.

#### 1.4.2.1 Process of sedimentation

Sedimentation is a physical separation process used in water treatment plants to remove suspended particles using the force of gravity driven by the density difference between particles and the fluid (Carlsson 1998). Sedimentation can also be a more complex process that requires precipitation, coprecipitation and flocculation of particles to form larger particles capable of settling. Sediments can trap and accumulate a variety of contaminants, including heavy metals and metalloids at concentrations determined by environmental physicochemical properties such as pH and redox potentials, as well as properties of the metal(loid)s themselves such as concentration and speciation (Matagi et al. 1998).

#### 1.4.2.2 Diel and Seasonal Impacts on Metal(Loid) Distributions

Metal(loid) mass transfer between water and sediments is a function of a variety of physicochemical parameters. For example, diel (over 24 hours) effects such as variation in water pH and temperature have been shown to cause changes in metal(loid)s concentrations in streams. These changes were considered significant in streams with neutral to alkaline pH over 24 hours regardless of changes in the water flow rate and the significance of the concentration (Nimick et al. 2003). For example, changes in the aqueous As concentration in neutral to alkaline conditions have been reported to be up to 51-55 percent with maximum and minimum concentrations in the late afternoon and early morning, respectively (Gammons et al. 2007, Nimick et al. 2003, Nimick et al. 2005).

In addition to diel variations, seasonal metal(loid)s concentration variations can occur in waters and sediments because of changes in wastewater flow rates, nutrients, dissolved oxygen concentrations, and other physicochemical parameters (Adeyemo et al. 2008). For example, aqueous As concentrations have been found to vary by as much as 290% on a seasonal timeline with higher concentrations in summer due to various seasonal causes such as evapotranspiration,

surface runoff formed from melting snow, and channel ice formation, which can each take away a considerable volume of water from winter streamflow (Nimick et al. 2005). In addition, Fe concentrations and As speciation have also been found to impact water and sediment As concentrations on a seasonal timeline (La Force et al. 2000, Yan et al. 2016). In sediments, heavy metal seasonal variations occur as a part of a one-year cycle with the highest concentrations in summer and autumn and lowest concentrations around April and May (Sakai et al. 1986). This cycling is mainly due to events such as freshet water flow and water shortage, which cause a decrease and increase in sediment heavy metal contents, respectively. Also, a decrease in particle size leads to increased heavy metals concentration with a more significant change on seasonal timelines (Sakai et al. 1986).

#### 1.4.2.3 Leaching of Heavy Metals from Sediments

Arsenic and iron in sediment increase over time when precipitation of heavy metals and metalloids from overlying wastewater occurs, as in the current study WSP system. The finer the sediment particles, the more concentrated they can become by being in contact with the wastewater (Ma et al. 2019, Sakai et al. 1986, Trefry and Presley 1976). The sediment can then become a source of contamination itself, releasing metal(loid)s at a rate dependent on the overlying water characteristics such as pH and salinity (Duncan et al. 2018, Li et al. 2013).

For As, speciation is an important factor in the leaching rate from sediment, especially in the short term in which the  $As^{3+}$  species are more mobile as compared to  $As^{5+}$  species (Brannon and Patrick 1987, Ruokolainen et al. 2000). Therefore, the determination of As speciation in the system will give a better understanding of the leaching phenomenon. There are also compounds competing with As and Fe for adsorption sites in sediments such as phosphorus, selenium, and molybdate. Therefore, these compounds can cause a high rate of As leaching from sediments by replacing As in the available adsorption sites. Sediment adsorption capacity also plays a role itself, given leaching of As will be increased when most of the adsorption sites are occupied (CCME 1997).

Along with physicochemical parameters, microbial activity in sediments has been shown to increase As mobilization by reducing arsenate to arsenite, which is a more soluble As species. Through this process, As is liberated by altering sorbed arsenate to arsenite compounds, which are uncharged and will be released to the aqueous phase (Drewniak and Sklodowska 2013). In addition to the release of As by microbial arsenate reduction, Fe-reducing bacteria have been found to cause

a release of co-precipitated As from Fe compounds by reducing the Fe in the minerals (Gounou et al. 2010, Quantin et al. 2001, Saup et al. 2017). On the other hand, there are As oxidizing microbes and sulfate reducing bacteria (SRB) that can meditate As removal under specific conditions. While As oxidization by microbes is found at a nearly neutral pH and aerobic conditions, As removal by SRB is more possible at anoxic, neutral to acidic environment with redox potential (Eh) of less than a reported range of -100 mV to -200 mV (Lizama et al. 2011). SRB metabolism increases the pH and decreases the redox potential, and therefore, these two parameters can be monitored to evaluate SRB activity (De Matos et al. 2018).

#### 1.4.2.4 Assessing Leaching Potential

Many leaching tests have been developed to assess the leaching potential of sediments. However, each test varies in terms of leaching liquid, liquid/solid ratio, contact time, etc. (Obe et al. 2016). These tests enable acquiring a proper understanding of the contaminant's fate and transport potential between different phases which is necessary for contamination assessment and characterization (Wilhelm 2004). The distribution (or partition) coefficient ( $K_d$ ) is an important parameter for estimating contaminant migration possibilities between aqueous and solid phases. The  $K_d$  can be estimated using leaching experiments that measures the ratio of an element concentration in the solid phase to the equilibrium concentration in the surrounding aqueous phase. The higher the ratio the greater the resistance will be for leaching of the element (Wilhelm 2004). Another important leaching test is to determine the leaching rate of an element from solid phase into the aqueous phase. This test provides insight into the potential release of an element and enables calculation and comparison of the leaching rates over different ponds/locations and under various conditions (D'Silva 2017).

#### **1.4.2.5 Sediment Treatment Strategies**

Heavy metals and metalloids can be removed from wastewaters, at rates of more than 99% in some cases, through the sedimentation process (Peng et al. 2009). However, this process can lead to pollution of the sediments over time and make them a potential source of metal(loid)s contamination in the future. Metal(loid) are not permanently fixed in the sediments, and changes in the overlying water's physicochemical condition can resuspend some of these metal(loid)s and cause them to re-enter the water (Mulligan et al. 2001, Peng et al. 2009). The sedimentation process

also creates a sludge layer in the bottom of the WSP individual ponds, which can become more thickened due to algal and bacterial growth. The sludge buildup is more intense in preliminary ponds of a WSP system and can make these ponds less efficient by changing their characteristics, such as decreasing the effective volume (Nelson et al. 2004, Oakley et al. 2012). Therefore, the polluted sediments should be treated or removed on a regular basis to help to prevent the release of metal(loid)s to the waters and increase the efficiency of the WSP system.

For metal(loid)s treatment in sediments, in-situ and ex-situ remediation strategies are used based on the sediment characteristics. Table 1.2 provides an overview of the advantages and disadvantages of in-situ and ex-situ remediation strategies. In-situ techniques, such as capping and adsorption, with lower ecological risk and operation cost, can stabilize metal(loid)s in the sediment. However, leaching is always a chance as the sediments' metal(loid) content will not be reduced (Ma et al. 2019). Ex-situ techniques such as washing, flotation and immobilization are usually considered for heavily polluted sediments and are more expensive because of the excavation process (Peng et al. 2009). Sediments can also be disposed of as solid wastes if they meet the related guidelines (USEPA 2009). The use of a sediment treatment strategy or a disposing option is determined based on the sediment characteristics such as metal(loid) loads, particle size, and metal(loid) species, which requires sediment characterization and assessment (Peng et al. 2009).

Strategy	Examples	Advantages	Disadvantages	References
In-situ	Capping, adsorption, and microbial degradation	<ul> <li>Increases metal(loid) stabilization in sediment</li> <li>Low ecological risk</li> <li>Low cost and simple operation</li> <li>Does not disrupt the natural hydrological conditions</li> <li>Fast remediation effects</li> </ul>	<ul> <li>Sediments become a potential secondary pollution source</li> <li>Not effective to heavily polluted sediments</li> </ul>	Ma et al. 2019, Peng et al. 2009, Cai et al. 2019, Liu et al. 2018
Ex-situ	Washing, flotation and immobilization	<ul> <li>Possibility of significantly reducing sediments metal(loid)</li> <li>Effective to heavily polluted sediments</li> </ul>	<ul> <li>Requires dredging of the polluted sediments</li> <li>Causes deterioration in the sediment structure</li> <li>High cost of operation</li> </ul>	Ma et al. 2019, Peng et al. 2009, Cai et al. 2019, Liu et al. 2018

 Table 1.2: Advantages and disadvantages of in-situ and ex-situ sediment remediation strategies.

### **1.5** Melville potable water supply system (MEPOWSS)

The DWTP for the City of Melville has been serving the community since 1959 and was originally constructed to treat surface water from the Crescent Creek Reservoir. It underwent two major upgrades in 1984 and 1989, in which a groundwater treatment system was added to the plant. Until early 2020, the Melville Potable Water Supply System (MEPOWSS) site treated drinking water using EDR technology and a mixture of groundwater and surface water pretreated by greensand filters. This system generated wastewater with elevated metal(loid)s concentrations (including As and Fe) and ammonium, along with high electrical conductivity. The MEPOWSS wastewater is discharged into a 50-year-old WSP system (Figure 1.3) used for oxidization and sedimentation treatment of the produced wastewaters. A deep injection well had been used to dispose of EDR wastewater until 2017 after which both EDR and backwash wastewaters were released into the WSP system. The wastewater flows through the ponds and is discharged into a low-flow creek named Crescent Creek, which has fish species in spring and summer and is frozen over in winter. Historically, the outflow water from the WSP system contained high concentrations of several species, notably As and Fe, which exceed the CCME guidelines (CCME 2001).

SaskWater has recently built a new treatment system to treat only groundwater using RO treatment. The new RO system has been designed to produce 34.5 L/s of treated water, which is higher than the previous capacity of 25 L/s. Using only groundwater as source water, and treating a higher volume of water, is expected to result in a much higher metal(loid) loading rate to the WSP. Figure 1.3 shows the WSP system in 2019 and 2020. The ponds were covered by various vegetation species such as cattails, bulrushes, and algae during the spring and summer. The ponds were also habitat to bird and animal species, including two beavers inhabiting Pond 2 over the 2020 sampling season. In general, the DWTP wastewater enters the pond system through a pipe to Pond 1, passing all ponds to the end of Pond 5, where a second pipe discharges the effluent to the creek. In 2019, Pond 1 was considered as two ponds due to the inactivity of half of it, which was named Pond 0 for recording purposes. However, the system underwent changes in the Pond 1 layout in 2020 to include the inactive portion. Pond 1 now includes Pond 0 and has a longer flow path resulting in an increase in its retention time.



**Figure 1.3:** WSP system in 2019 and 2020 with five main ponds labelled 1 through 5. The flow path is indicated via the red line starting at Pond 1 inlet and exiting through Pond 5. Note: 2019 Pond 0 is a part of Pond 1 that was not in the flow path.
## **1.6 Thesis Partner**

#### **SaskWater**

SaskWater is a Government of Saskatchewan Crown corporation water utility that provides drinking water treatment, wastewater treatment, and related services to Saskatchewan's communities and industries. SaskWater entered into an agreement with the City of Melville to acquire the MEPOWSS making SaskWater the owner and operator of the Melville DWTP. The DWTP wastewater, which is treated by a pond system, does not typically meet the As environmental guidelines set forth by the Canadian Council of Ministers of the Environment. Therefore, the pond system was evaluated as part of this thesis for determination of its treatment efficiency and the potential need for upgrades. As well, SaskWater built a new DWTP with an updated drinking water treatment technology, while increasing the volumetric capacity, necessitating a study on the effects of the new loading of wastewater on the WSP system. SaskWater provided access to the plant and its laboratory for the current thesis research project, the staff gave valuable advice and technical support, and partnered in funding through Mitacs Accelerate. In addition, part of this thesis research was accomplished during the author's internship at SaskWater from July 2019 through October 2020.

## **1.7 Thesis Overview**

#### 1.7.1 Thesis Objectives

Given this DWTP WSP system and the provided introduction background information, the research questions for this thesis include:

- Do the As and Fe concentrations in the WSP system sediments change over time and between ponds/along the flow path?
- What are the effects of the new load of wastewater on the ponds? And how efficient is the WSP system in treating this new wastewater?
- What is the potential for As and Fe to leach from the sediments of each individual pond back into the overlying waters?

Based on these research questions, this thesis's primary goal was to characterize the sediment in the pond system and assess the ponds' performance in removing Fe and As. Therefore, the following objectives were devised to meet this goal:

1. To analyze the sediments of the ponds system, with focus on As and Fe, on a monthly timeframe over two seasons. This objective fulfills a lack of information about the chemistry of the sediment of each pond of the system and determines the effects of changes in the DWTP system on the As and Fe concentrations in ponds' sediments.

2. To conduct laboratory experiments on the sediments of each pond in the WSP system to study As and Fe leaching from the ponds' sediments and find a leaching rate for As and Fe. This objective fulfils the gap in As and Fe leaching potential of the ponds' sediment.

3. To model the ponds using PHREEQC software to determine As and Fe speciation and analyse the individual ponds of the WSP system using SPSS software to find correlations between As, Fe and other parameters such as DO and redox conditions.

#### 1.7.2 Chapter 2 Overview

This chapter focuses on monitoring and understanding the chemistry of the sediments of a WSP system used to treat residual wastewaters of a DWTP located in Saskatchewan. The pond system, which consists of five sequential ponds, has been in use for more than 50 years, but its performance for treating wastewaters has not been thoroughly investigated since its installation. To fulfill this lack of information, the sediments and overlying waters of the pond system were sampled on three occasions during 2019 during the months of July, August, and October. Although the water and sediment samples were analyzed for a variety of elements, more attention was given to As and Fe as the pond system effluent was found to exceed the existing guidelines for these two metal(loid)s concentrations before the start of this study. The DWTP underwent a significant upgrade in its treatment technology, raw source of water, and production capacity in early 2020; thus, the results from this chapter were also used in Chapter 3 to help determine whether the upgrades have significantly affected the ponds performance and the chemistry of the sediment.

A version of this Chapter will be published as a conference paper for the 2021 CSCE Annual Conference with the following details:

Ekhlasi Nia, A., Bull, H., Motalebi Damuchali, A., and McPhedran K. (2021). Evaluation of arsenic and iron transport from sediments of a potable water treatment wastewater stabilization pond system. *Proceedings of the Canadian Society of Civil Engineers Annual Conference* to be held virtually May 26-29, 2021.

#### 1.7.3 Chapter 3 Overview

Chapter 3 includes the results from both the initial 2019 monitoring and the 2020 monitoring after commissioning of the new DWTP in early 2020. In addition, this chapter includes laboratory leaching experiments and extensive statistical analysis of experimental results. During the 2020 monitoring, sediments in upstream and downstream of the pond system outlet were sampled to determine whether pond system effluent has polluted the downstream sediments, and if the sediments As and Fe exceed the guidelines. Using the monitoring results over two years of sampling also helped determine variations between the ponds and within each pond over time and whether the wastewater from the new DWTP has significantly affected the pond's sediment. Sediment leaching tests were performed in the UofS laboratory to determine the distribution (or partition) coefficients ( $K_d$ ) for As and Fe, the potential for sediment to pollute the overlying water and the rate of the leaching over time for each pond. The results helped to develop a better understanding of As and Fe fate and transport potential between sediments and water and to determine how changes in pond retention times may impact the As and Fe mobility. The pond overlying waters were then modeled using PHREEQC software to determine As and Fe speciation. Also, ponds water and sediment were analysed using SPSS software to find potential correlations between As, Fe and other metals and ponds temp, pH, DO and redox condition.

A version of this Chapter will be submitted to the *Canadian Journal of Civil Engineering* with the following details:

Ekhlasi Nia, A., Bull, H., and McPhedran K. (2021). Assessment of Arsenic and Iron Occurrence and Leaching Potential for the Sediments of a Potable Water Treatment Wastewater Stabilization Pond System. To be submitted to the *Canadian Journal of Civil Engineering*.

#### **1.7.4 Chapter 4 Overview**

Chapter 4 includes a summary of the research findings in the previous chapters, the engineering significance of the thesis and provides direction for future work in this research area.

## References

Adeyemo, O. K., Adedokun, O. A., Yusuf, R. K., and Adeleye, E. A. (2008). Seasonal changes in physico-chemical parameters and nutrient load of river sediments in Ibadan City, Nigeria. Global Nest Journal, 10(3), 326–336.

Alam, R., and McPhedran, K. (2019). Applications of biological sulfate reduction for remediation of arsenic – A review. Chemosphere, 222(1), 932–944.

Bjorn, P., & Roychoudhury, A. N. (2015). Application, chemical interaction and fate of iron minerals in polluted sediment and soils. Current Pollution Reports, 1(4), 265-279.

Brandt, M. J., Johnson, K. M., Elphinston, A. J., and Ratnayaka, D. D. (2017). Specialized and advanced water treatment processes. Twort's Water Supply, 407-473.

Brannon, J. M., and Patrick, W. H. (1987). Fixation, transformation, and mobilization of arsenic in sediments. Environmental Science and Technology, 21(5), 450–459.

Britton, R. S., Leicester, K. L., & Bacon, B. R. (2002). Iron toxicity and chelation therapy. International journal of hematology, 76(3), 219-228.

Cai, C., Zhao, M., Yu, Z., Rong, H., and Zhang, C. (2019). Utilization of nanomaterials for in-situ remediation of heavy metal (loid) contaminated sediments: a review. Science of the Total Environment, 662, 205-217.

Canadian Council of Ministers of the Environment (CCME). (1997). Canadian soil quality guidelines for the protection of environmental and human health - Arsenic (inorganic). Canadian Council of Ministers of the Environment, 7. ISBN 1-896997-34-1

Canadian Council of Ministers of the Environment. (2001). Canadian water quality guidelines for the protection of aquatic life: Arsenic. Updated. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg. Canadian Council of Ministers of the Environment, 7. ISBN 1-896997-34-1

Carlsson, B. (1998). An introduction to sedimentation theory in wastewater treatment. Systems and Control Group, Uppsala University.

Chaturvedi, S., and Dave, P. N. (2012). Removal of iron for safe drinking water. Desalination, 303, 1-11.

Choong, T. S. Y., Chuah, T. G., Robiah, Y., Gregory Koay, F. L., and Azni, I. (2007). Arsenic toxicity, health hazards and removal techniques from water: An overview. Desalination, 217(1), 139–166.

Chowdhury, S., Mazumder, M. J., Al-Attas, O., & Husain, T. (2016). Heavy metals in drinking water: occurrences, implications, and future needs in developing countries. Science of the Total Environment, 569, 476-488.

Clancy, T. M., Hayes, K. F., and Raskin, L. (2013). Arsenic waste management: a critical review of testing and disposal of arsenic-bearing solid wastes generated during arsenic removal from drinking water. Environmental Science and Technology, 47(19), 10799-10812.

Cornwell, D., MacPhee, M., Mutter, R., Novak, J. T., & Edwards, M. (2004). Disposal of waste resulting from arsenic removal processes (pp. 9-12). IWA Publishing.

Corroto, C., Iriel, A., Cirelli, A. F., and Carrera, A. P. (2019). Constructed wetlands as an alternative for arsenic removal from reverse osmosis effluent. Science of The Total Environment, 691, 1242-1250.

Crini, G., and Lichtfouse, E. (2019). Advantages and disadvantages of techniques used for wastewater treatment. Environmental Chemistry Letters, 17(1), 145-155.

De Esparza, M. C. (2006, Jun 20–24). Removal of arsenic from drinking water and soil bioremediation. In Natural Arsenic in Groundwater of Latin America International Congress, Mexico City, Mexico.

De Matos, L. P., Costa, P. F., Moreira, M., Gomes, P. C. S., de Queiroz Silva, S., Gurgel, L. V. A., and Teixeira, M. C. (2018). Simultaneous removal of sulfate and arsenic using immobilized non-traditional SRB mixed culture and alternative low-cost carbon sources. Chemical Engineering Journal, 334, 1630-1641.

Dev, S., and Babitt, J. L. (2017). Overview of iron metabolism in health and disease. Hemodialysis International, 21, S6–S20.

Drakesmith, H., Schimanski, L. M., Ormerod, E., Merryweather-Clarke, A. T., Viprakasit, V., Edwards, J. P., ... and Robson, K. J. (2005). Resistance to hepcidin is conferred by hemochromatosis-associated mutations of ferroportin. Blood, 106(3), 1092-1097.

Drewniak, L., and Sklodowska, A. (2013). Arsenic-transforming microbes and their role in biomining processes. Environmental Science and Pollution Research, 20(11), 7728–7739.

D'Silva, L. P. (2017). Biological and physicochemical mechanisms affecting phosphorus and arsenic efflux from prairie reservoir sediment, Buffalo Pound Lake, SK, Canada (Doctoral dissertation, University of Saskatchewan).

Duncan, A. E., de Vries, N., and Nyarko, K. B. (2018). Assessment of heavy metal pollution in the sediments of the river pra and its tributaries. Water, Air, and Soil Pollution, 229(8).

Environment and Climate Change Canada (ECCC). (2019). Canadian environmental protection act, 1999. Federal environmental quality guidelines - iron. Environment and Climate Change Canada.

Fattorini, D., and Regoli, F. (2004). Arsenic speciation in tissues of the mediterranean polychaete Sabella Spallanzani. Environmental Toxicology and Chemistry, 23(8), 1881.

Finnegan, P. M., and Chen, W. (2012). Arsenic toxicity: the effects on plant metabolism. Frontiers in Physiology, 3, 182.

Gabarrón, S., Gernjak, W., Valero, F., Barceló, A., Petrovic, M., and Rodríguez-Roda, I. (2016). Evaluation of emerging contaminants in a drinking water treatment plant using electrodialysis reversal technology. Journal of hazardous materials, 309, 192-201.

Gammons, C. H., Grant, T. M., Nimick, D. A., Parker, S. R., and DeGrandpre, M. D. (2007). Diel changes in water chemistry in an arsenic-rich stream and treatment-pond system. Science of the Total Environment, 384(1–3), 433–451.

Gounou, C., Bousserrhine, N., Varrault, G., and Mouchel, J. M. (2010). Influence of the ironreducing bacteria on the release of heavy metals in anaerobic river sediment. Water, Air, and Soil Pollution, 212(1–4), 123–139.

Greenlee, L. F., Lawler, D. F., Freeman, B. D., Marrot, B., and Moulin, P. (2009). Reverse osmosis desalination: water sources, technology, and today's challenges. Water research, 43(9), 2317-2348.

Ippolito, J. A., Barbarick, K. A., & Elliott, H. A. (2011). Drinking water treatment residuals: a review of recent uses. Journal of environmental quality, 40(1), 1-12.

Ityel, D. (2011). Ground water: Dealing with iron contamination. Filtration and Separation, 48(1), 26-28.

Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B. B., and Beeregowda, K. N. (2014). Toxicity, mechanism and health effects of some heavy metals. Interdisciplinary Toxicology, 7(2), 60–72.

Jang, Y. C., Somanna, Y., & Kim, H. (2016). Source, distribution, toxicity and remediation of arsenic in the environment–a review. International Journal of Applied Environmental Sciences, 11(2), 559-581.

Kayombo, S. T. S. A., Mbwette, T. S. A., Katima, J. H. Y., Ladegaard, N., and Jrgensen, S. E. (2004). Waste stabilization ponds and constructed wetlands: design manual.

Khatri, N., Tyagi, S., and Rawtani, D. (2017). Recent strategies for the removal of iron from water: A review. Journal of Water Process Engineering, 19(13), 291–304.

La Force, M. J., Hansel, C. M., and Fendorf, S. (2000). Arsenic speciation, seasonal transformations and co-distribution with iron in a mine waste-influenced palustrine emergent wetland. Environmental Science and Technology, 34(18), 3937–3943.

Li, H., Shi, A., Li, M., and Zhang, X. (2013). Effect of pH, temperature, dissolved oxygen, and flow rate of overlying water on heavy metals release from storm sewer sediments. Journal of Chemistry, 2013, 1-11.

Liu, L., Li, W., Song, W., and Guo, M. (2018). Remediation techniques for heavy metalcontaminated soils: principles and applicability. Science of the Total Environment, 633, 206-219.

Lizama, K., Fletcher, T. D., and Sun, G. (2011). Removal processes for arsenic in constructed wetlands. Chemosphere, 84(8), 1032-1043.

Ma, T., Sheng, Y., Meng, Y., and Sun, J. (2019). Multistage remediation of heavy metal contaminated river sediments in a mining region based on particle size. Chemosphere, 225, 83–92.

Malaeb, L., and Ayoub, G. M. (2011). Reverse osmosis technology for water treatment: state of the art review. Desalination, 267(1), 1-8.

Manahan, S. E. (2002). Toxicological chemistry and biochemistry (pp. 194-195). CRC Press.

Mandal, B. K., and Suzuki, K. T. (2002). Arsenic round the world: a review. Talanta, 58(1), 201-235.

Martin, S., and Griswold, W. (2009). Human health effects of heavy metals. Environmental Science and Technology Briefs for Citizens, 15, 1-6. <u>www.engg.ksu.edu/CHSR/</u>

Matagi, S. V., Swai, D., & Mugabe, R. (1998). A review of heavy metal removal mechanisms in wetlands. African Journal of Tropical Hydrobiology and Fisheries, 8(1), 13-25.

Mohan, D., & Pittman Jr, C. U. (2007). Arsenic removal from water/wastewater using adsorbents—a critical review. Journal of Hazardous Materials, 142(1-2), 1-53.

Mulligan, C. N., Yong, R. N., and Gibbs, B. F. (2001). An evaluation of technologies for the heavy metal remediation of dredged sediments. Journal of Hazardous Materials, 85(1-2), 145-163.

Nano, G. V., & Strathmann, T. J. (2006). Ferrous iron sorption by hydrous metal oxides. Journal of Colloid and Interface Science, 297(2), 443-454.

National Research Council 1999. Arsenic in drinking water. Washington, DC: The National Academies Press.

Nelson, K. L., Cisneros, B. J., Tchobanoglous, G., and Darby, J. L. (2004). Sludge accumulation, characteristics, and pathogen inactivation in four primary waste stabilization ponds in central Mexico. Water Research, 38(1), 111-127.

Nimick, D. A., Cleasby, T. E., and McCleskey, R. B. (2005). Seasonality of diel cycles of dissolved trace-metal concentrations in a Rocky mountain stream. Environmental Geology, 47(5), 603–614.

Nimick, D. A., Gammons, C. H., Cleasby, T. E., Madison, J. P., Skaar, D., and Brick, C. M. (2003). Diel cycles in dissolved metal concentrations in streams: occurrence and possible causes. Water Resources Research, 39(9).

Oakley, S. M., Mendonça, L. C., and Mendonça, S. R. (2012). Sludge removal from primary wastewater stabilization ponds with excessive accumulation: a sustainable method for developing regions. Journal of Water, Sanitation and Hygiene for Development, 2(2), 68-78.

Obe, R. K. D., De Brito, J., Mangabhai, R., & Lye, C. Q. (2016). Sustainable construction materials: copper slag (pp. 27-86). Woodhead Publishing.

Pang, F. M., Kumar, P., Teng, T. T., Omar, A. M., & Wasewar, K. L. (2011). Removal of lead, zinc and iron by coagulation–flocculation. Journal of the Taiwan Institute of Chemical Engineers, 42(5), 809-815.

Pehkonen, S. (1995). Determination of the oxidation states of iron in natural waters. A review. Analyst, 120(11), 2655-2663.

Peng, J. feng, Song, Y. hui, Yuan, P., Cui, X. yu, and Qiu, G. lei. (2009). The remediation of heavy metals contaminated sediment. Journal of Hazardous Materials, 161(2–3), 633–640.

Pronk, J. T., & Johnson, D. B. (1992). Oxidation and reduction of iron by acidophilic bacteria. Geomicrobiology Journal, 10(3-4), 153-171.

Quantin, C., Becquer, T., Rouiller, J. H., and Berthelin, J. (2001). Oxide weathering and trace metal release by bacterial reduction in a New Caledonia Ferralsol. Biogeochemistry, 53(3), 323–340.

Ratnaike, R. N. (2003). Acute and chronic arsenic toxicity. Postgraduate Medical Journal, 79(933), 391-396.

Ruokolainen, M., Pantsar-Kallio, M., Haapa, A., and Kairesalo, T. (2000). Leaching, runoff and speciation of arsenic in a laboratory mesocosm. Science of the Total Environment, 258(3), 139–147.

Saaltink, R. M., Dekker, S. C., Eppinga, M. B., Griffioen, J., & Wassen, M. J. (2017). Plant-specific effects of iron-toxicity in wetlands. Plant and Soil, 416(1-2), 83-96.

Sakai, H., Kojima, Y., and Saito, K. (1986). Distribution of heavy metals in water and sieved sediments in the Toyohira river. Water Research, 20(5), 559–567.

Salgot, M., & Folch, M. (2018). Wastewater treatment and water reuse. Current Opinion in Environmental Science & Health, 2, 64-74.

Sarkar, A., & Shekhar, S. (2018). Iron contamination in the waters of Upper Yamuna basin. Groundwater for Sustainable Development, 7, 421-429.

Saup, C. M., Williams, K. H., Rodríguez-Freire, L., Cerrato, J. M., Johnston, M. D., and Wilkins,
M. J. (2017). Anoxia stimulates microbially catalyzed metal release from Animas river sediments.
Environmental Science: Processes and Impacts, 19(4), 578–585.

Schmidt, S. A., Gukelberger, E., Hermann, M., Fiedler, F., Großmann, B., Hoinkis, J., ... and Bundschuh, J. (2016). Pilot study on arsenic removal from groundwater using a small-scale reverse osmosis system—Towards sustainable drinking water production. Journal of Hazardous Materials, 318, 671-678.

Shan, Y., Mehta, P., Perera, D., and Varela, Y. (2019). Cost and efficiency of arsenic removal from groundwater: A review. United Nations University-Institute for Water, Environment and Health. ISBN: 978-92-808-6093-1.

Smedley, P. L., and Kinniburgh, D. G. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. Applied Geochemistry, 17(5), 517-568.

Sodano, M., Lerda, C., Nisticò, R., Martin, M., Magnacca, G., Celi, L., & Said-Pullicino, D. (2017). Dissolved organic carbon retention by coprecipitation during the oxidation of ferrous iron. Geoderma, 307, 19-29.

Sonune, A., & Ghate, R. (2004). Developments in wastewater treatment methods. Desalination, 167, 55-63.

Sorg, T. J. (2000). Regulations on the disposal of arsenic residuals from drinking water treatment plants. EPA Contract 68-C7-0011. Work Assignment 0-38, EPA/600/R-00/025.

Splane, L. (2002). Nutritional Self-Defense: Better Health in a Polluted, Over-Processed, and Stressful World (pp. 45-46). Anaphase II Publishing.

Strathmann, H. (2010). Electrodialysis, a mature technology with a multitude of new applications. Desalination, 264(3), 268–288.

Tchounwou, P. B., Udensi, U. K., Isokpehi, R. D., Yedjou, C. G., and Kumar, S. (2015). Arsenic and cancer. In Handbook of Arsenic Toxicology (pp. 533-555). Academic Press.

Thirunavukkarasu, O. S., Viraraghavan, T., Subramanian, K. S., & Tanjore, S. (2002). Organic arsenic removal from drinking water. Urban Water, 4(4), 415-421.

Trefry, J. H., and Presley, B. J. (1976). Heavy metals in sediments from San Antonio Bay and the northwest Gulf of Mexico. Environmental Geology, 1(5), 283–294.

Tsai, H. H., & Schmidt, W. (2017). One way. Or another? Iron uptake in plants. New Phytologist, 214(2), 500-505.

USEPA (United States Environmental Protection Agency). (2009). Hazardous waste characteristics: A user-friendly reference document. http://www.epa.gov/epawaste/wyl/stateprograms.htm

USEPA (United States Environmental Protection Agency). (2011). Drinking Water Treatment Plant Residuals Management Technical Report. EPA 820-R-11-003

USEPA (United States Environmental Protection Agency). (2013). Technologies to improve efficiency of waste management and cleanup after a radiological dispersal device incident standard operational guideline. EPA 600/R-13/124.

USGS (United States Geological Survey). (2020). Sediment and Suspended Sediment. https://www.usgs.gov/special-topic/water-science-school/science/sediment-and-suspended-sediment

Üstün, G. E. (2009). Occurrence and removal of metals in urban wastewater treatment plants. Journal of Hazardous Materials, 172(2-3), 833-838.

Van Groeningen, N., ThomasArrigo, L. K., Byrne, J. M., Kappler, A., Christl, I., & Kretzschmar,R. (2020). Interactions of ferrous iron with clay mineral surfaces during sorption and subsequent oxidation. Environmental Science: Processes & Impacts, 22, 1355-1367.

Ventura-Lima, J., Bogo, M. R., and Monserrat, J. M. (2011). Arsenic toxicity in mammals and aquatic animals: A comparative biochemical approach. Ecotoxicology and Environmental Safety, 74(3), 211–218.

Walsh, M. E., Lake, C. B., & Gagnon, G. A. (2008). Strategic pathways for the sustainable management of water treatment plant residuals. Journal of Environmental Engineering and Science, 7(1), 45-52.

Wang, S., and Mulligan, C. N. (2006). Occurrence of arsenic contamination in Canada: sources, behavior and distribution. Science of the Total Environment, 366(2-3), 701-721.

Wessling-Resnick, M. (2016). Iron: basic nutritional aspects. In Molecular, genetic, and nutritional aspects of major and trace minerals (pp. 161–173). Elsevier.

Wijsman, J. W., Middelburg, J. J., Herman, P. M., Böttcher, M. E., & Heip, C. H. (2001). Sulfur and iron speciation in surface sediments along the northwestern margin of the Black Sea. Marine Chemistry, 74(4), 261-278.

Wilhelm, R. G. (2004). 'Understanding variation in partition coefficient,  $K_d$ , values volume iii: review of geochemistry and available  $K_d$  values for americium, arsenic, curium, iodine, neptunium, radium, and technetium. Washington DC: EPA.

Wolthers, M., Charlet, L., van Der Weijden, C. H., Van der Linde, P. R., and Rickard, D. (2005). Arsenic mobility in the ambient sulfidic environment: Sorption of arsenic (V) and arsenic (III) onto disordered mackinawite. Geochimica et Cosmochimica Acta, 69(14), 3483-3492.

World Health Organization. (2008). Guidelines for drinking-water quality [electronic resource]: incorporating 1st and 2nd addenda, Vol.1, recommendations, 3rd ed. World Health Organization.

World Health Organization. (2011). Guidelines for drinking-water quality. WHO chronicle, 38(4), 104-8.

World Health Organization. (2019). Water, sanitation, hygiene and health: a primer for health professionals (No. WHO/CED/PHE/WSH/19.149). World Health Organization.

Wu, B., Amelung, W., Xing, Y., Bol, R., & Berns, A. E. (2019). Iron cycling and isotope fractionation in terrestrial ecosystems. Earth-Science Reviews, 190, 323-352.

Xu, Y., Fu, J., Wang, H., Hou, Y., and Pi, J. (2019). Arsenic exposure and lifestyle-related diseases. In Arsenic Contamination in Asia: Biological Effects and Preventive Measures (pp. 83–118). Springer Singapore.

Yan, C., Che, F., Zeng, L., Wang, Z., Du, M., Wei, Q., Wang, Z., Wang, D., and Zhen, Z. (2016). Spatial and seasonal changes of arsenic species in Lake Taihu in relation to eutrophication. Science of the Total Environment, 563–564, 496–505.

Zaid, A., Ahmad, B., Jaleel, H., Wani, S. H., & Hasanuzzaman, M. (2020). A critical review on iron toxicity and tolerance in plants: Role of exogenous Phytoprotectants. Plant Micronutrients, 83-99.

Zhang, X., Yongfeng, J. I. A., Xin, W. A. N. G., and Liying, X. U. (2008). Phylogenetic analysis and arsenate reduction effect of the arsenic-reducing bacteria enriched from contaminated soils at an abandoned smelter site. Journal of Environmental Sciences, 20(12), 1501-1507.

## Chapter 2: Evaluation of Arsenic and Iron Transport from Sediments of a Potable Water Treatment Wastewater Pond System

## **Overview**

A version of this Chapter will be published as a conference paper for the 2021 CSCE Annual Conference with the following details:

Ekhlasi Nia, A., Bull, H., Motalebi Damuchali, A., and McPhedran K. (2021). Evaluation of arsenic and iron transport from sediments of a potable water treatment wastewater stabilization pond system. *Proceedings of the Canadian Society of Civil Engineers Annual Conference* to be held virtually May 26-29, 2021.

## Abstract

High concentrations of metal(loid)s, such as arsenic (As) and iron (Fe), in wastewater streams are of environmental concern for drinking water treatment plants (DWTP), especially those which use groundwater as their source water. Metal(loid)s can be present in residual wastewaters, sludges, and sediments that make it necessary for them to be treated before release into receiving environments. The present study evaluated As and Fe sediment concentrations for wastewater treatment ponds of a municipal DWTP in Saskatchewan which used both surface and groundwater raw water sources until 2019. The residual wastewater stabilization pond (WSP) system consists of five ponds used for contaminant treatment and/or settling. The evaluation of metal(loid)s in these pond sediments is of importance due to the possibility of their leaching from sediments into groundwater and/or to be released back into the residual wastewater over time. In 2019, As and Fe, among other parameters, were monitored in sediments collected from each of the ponds on three occasions (July, August, and October). Results showed As and Fe in sediments ranged from 46.5 to 580 and 10,000 to 51,800 mg/kg, respectively. Both As and Fe concentrations varied among the ponds and over time. Further assessment of these ponds was completed in 2020 when a new DWTP was commissioned using the same pond system while including only groundwaters as a raw water source.

## **2.1 Introduction**

Drinking water treatment plants (DWTPs) create various types of wastes and wastewaters such as sludges, backwash waters, and concentrate waters, which have varying physicochemical characteristics depending on the raw source water. Groundwater is the primary source of drinking water for at least 50% of the world's population and is often the only source of raw water in many small communities (Nouri et al. 2008). The concentration of metal(loid)s, such as arsenic (As) and iron (Fe), are usually higher in groundwaters than in surface waters due to both anthropogenic and geogenic inputs (Chakravarty et al. 2002, Stollenwerk 2003). Arsenic is a widely recognized human carcinogen and exists in a variety of species of organic and inorganic compounds. However, inorganic species of trivalent arsenite and pentavalent arsenate are dominant in water due to their relatively high solubilities (Jain and Ali, 2000). Iron is one of the essential nutrients for most living organisms; however, excessive Fe ingestion can result in significant health effects such as hereditary hemochromatosis (causing joint pain, extreme tiredness, weight loss, abdominal pain, and loss of sex drive), Fe overloading anemias, and trans-fusional Fe overloaded or other secondary forms of hemochromatosis (Dev and Babitt 2017, Drakesmith et al. 2011, Wessling-Resnick 2016). Both As and Fe are typically found in elevated concentrations in many Canadian groundwaters used as raw water sources for DWTPs, especially for small communities in Saskatchewan and the other prairie provinces.

Residual wastewaters resulting from DWTP facilities with groundwater as their raw source water often contain high concentrations of As and Fe, thus, they must be treated prior to discharging into recipient water bodies. According to the Canadian Council of Ministers of the Environment (CCME 1997), the limit for As in effluent waters is  $5 \mu g/L$ . For Fe, the new Federal Water Quality Guideline is about 4.91 mg/L for the current pond system but varies based on the pH and the DOC (dissolved organic carbon) levels in the final effluents. Wastewater stabilization ponds (WSPs), or a series of these ponds, can be effective treatment processes for residual wastewaters coming from DWTP facilities, especially for smaller facilities such as those found in many small communities. However, the effectiveness of these systems in treating residual wastewaters should be monitored over time as it could be reduced considerably due to the variety of reasons. One of the important parameters that could cause treatment effectiveness reduction in the WSPs is their sediments' contamination. Sediments exposed to wastewaters containing

metal(loid)s become concentrated with these pollutants over time by particulate settling from the overlying wastewater as part of the treatment process. The sediments can then become a source of contamination to the future pond wastewaters, releasing metal(loid)s through desorption with a rate depending on the overlying effluent characteristics such as pH, temperature, and salinity, among others (Duncan, de Vries, and Nyarko 2018, Li et al. 2013).

Generally, the metal(loid) mass transfer between water and sediments (and vice versa) is a function of various physicochemical parameters. For example, diel (over 24 hour) effects such as variation in water pH and temperature have been shown to cause changes in the concentrations of metal(loid)s in streams. These changes were considered to be significant in streams with neutral to alkaline pH over 24 hours regardless of changes in flow rate and the significance of the concentration (Nimick et al. 2003). In addition to daily variations, seasonal metal(loid)s concentration variations occur in sediments because of changes in wastewater flow rates, nutrients, dissolved oxygen (DO), and other physicochemical parameters (Adeyemo et al. 2008). For example, As concentrations have been found to vary by as much as 290% on a seasonal timeline with higher concentrations in summer vs. winter months (Nimick et al. 2005). In addition, Fe concentrations and As speciation have also been found to impact As concentrations on a seasonal timeline (La Force et al. 2000, Yan et al. 2016).

Along with physicochemical parameters, the microbial activities in sediments have been shown to increase As mobilization by the reduction of arsenate to arsenite, which is a more soluble As species. Through this process, As is liberated by altering sorbed arsenate to arsenite compounds, which are uncharged and will be released to the aqueous phase (Drewniak and Sklodowska 2013). In addition to the release of As by microbial arsenate reduction, Fe-reducing bacteria have been found to cause a release of co-precipitated As from Fe compounds by reducing the Fe in the minerals (Gounou et al. 2010, Quantin et al. 2001, Saup et al. 2017). There are also compounds competing with As and Fe for adsorption sites in sediments such as phosphorus, selenium, and molybdate. Therefore, these compounds can cause a high rate of As leaching from sediments by replacing As in the available adsorption sites. Sediment adsorption capacity also plays a role itself given leaching of As will be increased when most of the adsorption sites are occupied (Canadian Council of Ministers of the Environment (CCME) 1997). Thus, metal(loid) concentrations in sediments and wastewaters of WSPs used for treatment of residuals from DWTPs should be monitored regularly to monitor treatment effectiveness over time.

To the best of the authors knowledge, As and Fe fate and transport potential between sediments and water in DWTP WSP systems has not been a research focus and, thus, no data is available for this application for As and Fe in the literature. Although, there are results available from WSPs treating mining wastewaters they are not applicable to this study. The objective of this study was to monitor As and Fe concentrations in the sediments of a WSP system consisting of five sequential ponds used to treat residual wastewaters of a DWTP (Figure 2.1). This facility is located in Saskatchewan and was using a combination of groundwater and surface water as its raw source water until the end of 2019. Samples from the effluents of the WSPs have been shown to exceed guidelines previous to the start of this study which necessitated the need to better assess the individual ponds to evaluate their effectiveness including both the wastewater (as part of a parallel study; Bull, 2021) and the sediments (current study). In early 2020, a new treatment system using reverse osmosis was being commissioned that will be using 100% groundwater as the raw water source. It is expected that this new system will produce higher concentrations of both As and Fe contaminated residual wastewaters that could affect the WSP system treatment efficiency. In this study, As and Fe concentrations were measured in the sediments of the five ponds of the WSP system in on three occasions during 2019 (July, August, and October) and the variations among the ponds and over time are presented and discussed.

#### 2.2 Methodology

#### 2.2.1 DWTP and WSP System

The studied DWTP has been in use since 1959 when it was first constructed to treat only surface water contained in a nearby reservoir. In 1989, an electro-dialysis reversal (EDR) system using groundwater as the raw source water was added to the DWTP and both systems remained active until the end of 2019. Prior to 2017, the EDR backwash waters were sent to a deep injection well; after this time, the EDR residuals were released into the WSP system. This combined DWTP system generated wastewater that was concentrated in metals such as As and Fe which was discharged into the WSP system consisting of a series of five ponds (Figure 2.1). This pond system has been in use for more than 50 years receiving wastewaters from the DWTP during which there have been a number of unrecorded changes in pond configuration. This includes impacts of heavy rainfall in the area in the early 2010's that flooded all ponds and a large portion of the DWTP municipality.



**Figure 2.1:** 2019 WSP system with five ponds (labelled 1 through 5) that sequentially treat the DWTP effluents. The flow path is indicated via the red line starting from the bottom middle of the figure and exiting through Pond 5. **Note**: Pond 0 is a part of Pond 1 that is no longer in the flow path due to sedimentation and short circuiting of the pond

These ponds allow for oxidation and sedimentation of wastewater contaminants before releasing the effluents into a nearby waterbody. This receiving waterbody is a low-flow creek that contains fish species during the spring and summer, while the creek is largely frozen over in winter months. Historic monitoring by the DWTP operator of the WSP system effluents shows that the As concentrations were often exceeding the CCME guidelines of  $5 \mu g/L$  (CCME 2001). As Figure 2.1 shows, the system consists of five dissimilar ponds that largely covered by cattails and bulrushes and are habitat to both bird and animal species in the spring and summer months. The residual wastewater enters the pond system through a pipe to Pond 1, and it passes all the ponds to the end of Pond 5 where a pipe discharges the effluent to the creek. Currently, Pond 1 has been considered as consisting of two separate ponds due to the inactivity of half of the Pond 1 occurring over time due to sedimentation and short-circuiting of the pond into Pond 1. Thus, the inactive portion of this Pond 1 has been designated Pond 0 for recording purposes.

#### 2.2.2 Sampling and analysis

Sampling of the five ponds was completed on three occasions during 2019 during the months of July, August, and October (the ponds sediment was not sampled in the winter months as the ponds were frozen over in these months and also due to the budgetary limitations). Random sediment sampling was performed for surficial (0 to 15 cm) sediment samples. Initially, the ponds were each divided into grids with intersected nodes sequentially numbered. The ponds were to be randomly sampled via the grid pattern with three samples for Ponds 1, 3, and 4 and five samples for Pond 3 and 5 based on pond sizes. Unfortunately, access to pond locations was limited due to vegetation, so the ponds were each sampled in random, accessible locations determined at the site. In addition, due to pond vegetation, the use of typical sampling apparatus such as a Ponar sampler was not feasible (although it was attempted). Instead, at each site, a sampling scoop was used to collect the surficial sediments to a volume of 2 L per sampling location (6 to 10 L of the total sample for each pond). This comprehensive sample was mixed thoroughly in a container and 2 - 2 L ziplock bags (average of 3.2 kg each) were filled with sediments from each pond. One bag was processed for shipping to ALS Environmental (Saskatoon, SK, Canada) for analysis, while the second was transported in a cooler to the Environmental Engineering laboratory at USask and stored at 4 °C for use in future research experiments. All samples were transported at <10 °C in under 72 hours to ALS labs for analysis as per guidelines (actual 4 °C and 48 h). Samples transported to USask also followed the temperature guideline prior to long-term storage as they were not analyzed immediately.

In addition to sediment samples, wastewater samples were also taken from each of the ponds as part of a parallel study on the wastewater characterization (Bull, 2021). These samples were taken from the outlets of each pond at 8 AM of the same day as the sediment samples. The ALS Environmental Laboratory provided the necessary sample containers and cooler for wastewater samples and all procedures they provided were followed as for the sediment samples. Metal(loid) analysis of wastewaters and sediments at ALS Environmental was conducted using collision/reaction inductively coupled plasma mass spectrometry (CRC ICP-MS) according to the Method 6020A of U.S. Environmental Protection Agency (EPA, 1998). All wastewater samples were filtered using a 0.45  $\mu$ m glass-fibre filter prior to analysis. All sediment samples were dried, disaggregated, and sieved using a 2 mm mesh. Then, they were digested with nitric and hydrochloric acids and analyzed using the CRC ICP-MS method. Although a suite of metal(loid)s were examined for all of the wastewater and sediment samples, only As and Fe are presented in this Chapter as they are considered to be contaminants of interest based on the historic DWTP monitoring indicating they could be present at concentrations that exceed CCME guidelines.

The temperature of the pond system wastewater was also measured and found to be in the ranges of 12.8 to 26.3 °C, 9.7 to 17.5 °C and 1.8 to 7.9 °C for the months of July, August and October, respectively. In 2019, the DO concentrations were also measured in the month of August, however, the instruments used to collect these data was found to be operating incorrectly so the 2019 data were discarded. However, the wastewater DO concentrations were measured in the second stage of this study in 2020 as included in Chapter 3 of this thesis.

## 2.3 Results and Discussion

#### 2.3.1 As Sediment and Wastewater Concentrations

Figure 2.2 shows the concentrations of As in the wastewater (mg/L on left y-axis) and sediment (mg/kg on right y-axis) samples for each of the ponds in July, August, and October, respectively. In general, the sediment As concentrations decreased from Pond 1 to Pond 5 on each sampling occasion at about 300 to 450 mg/kg and about 50 mg/kg, respectively. Interestingly, the sediments in Pond 2 had lower concentrations than Pond 1, however, the concentrations then increased in for both Ponds 3 and 4 before decreasing again in Pond 5. The only outlier was the

July Pond 3 sample that was lower than the Pond 3 concentration. This low As concentration in the sediments of Pond 3 could be explained by development of vegetation including cattails and



**Figure 2.2:** As concentrations in wastewater (mg/L on left y-axis) and sediments (mg/kg on right y-axis) for each of the five ponds as determined for three sampling events in 2019.

bulrushes that covered a large area of the pond which impeded sample collection from the centre of the ponds (a safety issue for sampling access). Despite the ponds being sampled in multiple locations, the concentrations of metal(loid)s would be expected to be higher in the deeper, centre sections of each pond where more settling may have occurred over time (Andreas et al. 2019). In general, sampling the entire ponds' sediments is not an option and the sub-sampling and mixing protocol used currently should provide for a representative sample for each pond.

For comparative purposes, the sediment concentrations may also be compared to the aqueous concentrations. For July and August, the aqueous concentrations generally increased from Pond 1 to Pond 5, while in October the concentrations were largely the same throughout the pond system. The higher As concentrations in the months of July and August as compared to the October levels could be due to the higher temperature of the wastewater in the ponds which can cause As redissolution and also increase the microbial activity which results in As mobilization (Drewniak and Sklodowska 2013). Furthermore, higher bird and animal activities during warmer months of summer could have disturbed the pond system sediments and caused As mobilization. Also, the increase of As concentrations from Pond 1 to Pond 5 may be the result of leaching of As from sediments into the wastewater in July and August. The determination of this leaching, including calculation of desorption rates, is assessed in Chapter 3 of this thesis.

#### 2.3.2 Fe Sediment and Wastewater Concentrations

Figure 2.3 shows the concentrations of Fe in the wastewater (mg/L on left y-axis) and sediment (mg/kg on right y-axis) samples for each of the ponds in July, August, and October, respectively. Similar to As, the general trend for Fe concentrations is a decrease from Pond 1 to Pond 5 with 25,000 to 45,000 mg/kg and about 20,000 mg/kg, respectively. In addition, the same trends for Ponds 2, 3, and 4 are also apparent for Fe. In general, this would appear to indicate that As and Fe concentrations in sediments are correlated to each other. The Fe wastewater aqueous concentrations show a similar trend as As for July and August; however, unlike As, the Fe concentration also increasing from Pond 1 through Pond 5 in October.

#### 2.3.3 As and Fe variations in ponds sediment

Figure 2.4 shows the sediments As and Fe concentration variations in the individual ponds (including Pond 0) from July, August, and October, respectively. In general, variations in As and



Figure 2.3: Fe concentrations in wastewater and sediments for each of the five ponds as determined for three sampling events in 2019.



**Figure 2.4:** As and Fe concentrations in sediments for each pond (including Pond 0) over time with samples collected in July, August, and October 2019.

Fe concentrations in the sediments of each pond over time were much lower than their variations from pond to pond. The As concentration increased from July to August and then decreased in October in all ponds except Pond 4, where As decreased over time. The lowest As concentrations were observed in the sediments of Pond 5 where As fluctuated from 40 to 60 mg/kg. In contrast, the highest As contaminations were observed in the Pond 0 where As ranged from 400 to 600 mg/kg; while the Pond 1 was also high at about 350 to 450 mg/kg. The Fe concentrations had similar trends to As in Ponds 2, 3, and 4 but increased over time in Ponds 1 and 5. Pond 5 that had the lowest As-contaminated sediments, also had the lowest sediment Fe concentrations (although they were similar to Pond 2). The Fe concentrations ranged from 17,000 to 22,000 mg/kg and from 18,000 to 22,000 mg/kg in the sediments of Ponds 5 and 2, respectively. Similar to As, the Pond 0 had the highest Fe concentrations that ranged from 34,000 to 52,000 mg/kg.

## **2.4 Conclusions**

In general, DWTPs that use groundwater as a raw source water produce wastewaters that are elevated in metal(loid)s, such as As and Fe. The As and Fe in the current study often exceed regulatory guidelines, thus, these wastewaters need to be treated before releasing to the environment. The DWTP WSP systems are typically designed to treat such wastewaters; however, the efficiency of these ponds needs to be monitored as the ponds can accumulate contaminants within their sediments and, therefore, become a source of wastewater contamination over time rather than a sink. This study monitored As and Fe concentrations in the wastewaters and sediments of a WSP system containing five sequential ponds for a Saskatchewan DWTP over three sampling events. The sediments contained As and Fe concentrations in the range of about 45 to 600 and 10,000 to 52,000 mg/kg, respectively. The concentrations varied among the ponds and over time, however, the variations between the ponds were greater than in each of the individual ponds over time. Of most interest are Ponds 3 and 4 that appear to have a potential for release of sediment bound As and Fe back into the wastewater stream. This release can then impact the pond system effluents and potentially leading to exceedances of CCME guidelines. This year 2019 research was preliminary research prior to the more intensive assessment of these ponds in 2020 as presented in Chapter 3 of this thesis.

## Acknowledgements

The authors would like to acknowledge funding through the Mitacs Accelerate program and SaskWater. In addition, research support has been provided by SaskWater personnel including Sumith Kahanda, Enisa Zanacic, Dale Hreshka, and Timo Jansen.

## References

Adeyemo, O.K., Adedokun, O.A., Yusuf, R.K., and Adeleye, E.A. 2008. Seasonal changes in physico-chemical parameters and nutrient load of river sediments in Ibadan City, Nigeria. Global Nest Journal, 10(3): 326-336.

Andreas, V., Irvine, K., Jindal, R., Thongdara, R., Chatterji, N. N., & Sheng, W. B. 2019. Spatial Patterns of Heavy Metals in the Sediments of a Municipal Wastewater Treatment Pond System and Receiving Waterbody, Cha am, Thailand. Journal of Water Management Modeling, 27: 465-465.

CCME (Canadian Council of Ministers of the Environment). 1997. Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health - Arsenic (Inorganic). ISBN 1-896997-34-1.

Chakravarty, S., Dureja, V., Bhattacharyya, G., Maity, S., and Bhattacharjee, S. 2002. Removal of arsenic from groundwater using low cost ferruginous manganese ore. Water Research, 36(3): 625-632.

Dev, S., and Babitt, J.L. 2017. Overview of iron metabolism in health and disease. Hemodialysis International, 21: S6-S20.

Drakesmith, H., Schimanski, L.M., Ormerod, E., Merryweather-Clarke, A.T., Viprakasit, V., Edwards, J.P., Sweetland, E., Bastin, J.M., Cowley, D., Chinthammitr, Y. and Robson, K.J., 2005. Resistance to hepcidin is conferred by hemochromatosis-associated mutations of ferroportin. Blood, 106(3): 1092-1097.

Drewniak, L., and Sklodowska, A. 2013. Arsenic-transforming microbes and their role in biomining processes. Environmental Science and Pollution Research, 20(11): 7728-7739.

Duncan, A.E., de Vries, N., and Nyarko, K.B. 2018. Assessment of Heavy Metal Pollution in the Sediments of the River Pra and Its Tributaries. Water, Air, and Soil Pollution, 229(8): 272.

La Force, M.J., Hansel, C.M., and Fendorf, S. 2000. Arsenic speciation, seasonal transformations and co-distribution with iron in a mine waste-influenced palustrine emergent wetland. Environmental Science and Technology, 34(18): 3937-3943.

Gounou, C., Bousserrhine, N., Varrault, G., and Mouchel, J.M. 2010. Influence of the ironreducing bacteria on the release of heavy metals in anaerobic river sediment. Water, Air, and Soil Pollution 212(1-4): 123-139.

Jain, C.K. and Ali, I. 2000. Arsenic: occurrence, toxicity and speciation techniques. Water research, 34(17): 4304-4312.

Li, H., Shi, A., Li, M., and Zhang, X. 2013. Effect of pH, temperature, dissolved oxygen, and flow rate of overlying water on heavy metals release from storm sewer sediments. Journal of Chemistry, 1-11.

National Research Council. 2001. Arsenic in Drinking Water: 2001 Update. The National Academies Press, Washington, DC, USA.

Nimick, D.A., Cleasby, T.E., and McCleskey, R.B. 2005. Seasonality of diel cycles of dissolved trace-metal concentrations in a Rocky Mountain stream. Environmental Geology, 47(5): 603-614.

Nimick, D.A., Gammons, C.H., Cleasby, T.E., Madison, J.P., Skaar, D., and Brick, C.M. 2003. Diel cycles in dissolved metal concentrations in streams: Occurrence and possible causes. Water Resources Research, 39(9): 1247-1264.

Nouri, J., Mahvi, A.H., Jahed, G.R., and Babaei, A.A. 2008. Regional distribution pattern of groundwater heavy metals resulting from agricultural activities. Environmental Geology, 55(6): 1337-1343.

Quantin, C., Becquer, T., Rouiller, J.H., and Berthelin, J. 2001. Oxide weathering and trace metal release by bacterial reduction in a New Caledonia Ferralsol. Biogeochemistry, 53(3): 323-340.

Saup, C.M., Williams, K.H., Rodríguez-Freire, L., Cerrato, J.M., Johnston, M.D., and Wilkins, M.J. 2017. Anoxia stimulates microbially catalyzed metal release from Animas River sediments. Environmental Science: Processes and Impacts, 19(4): 578-585.

US EPA (United States Environmental Protection Agency). 2011. Drinking Water Treatment Plant Residuals Management Technical Report: Summary of Residuals Generation, Treatment, and Disposal at Large Community Water Systems. EPA 820-R-11-003.

US EPA (United States Environmental Protection Agency). 1998. Inductively coupled plasma - mass spectrometry. EPA 6020A (SW-846).

US EPA (United States Environmental Protection Agency). 2013. Technologies to improve efficiency of waste management and cleanup after a radiological dispersal device incident standard operational guideline. EPA/600/R-13/124.

Wessling-Resnick, M. 2017. Iron: Basic Nutritional Aspects. In Molecular, Genetic, and Nutritional Aspects of Major and Trace Minerals, pp. 161-173. Academic Press, Cambridge, MA, USA.

Xu, Y., Fu, J., Wang, H., Hou, Y., and Pi, J. 2019. Arsenic Exposure and Lifestyle-Related Diseases. In Arsenic Contamination in Asia: Biological Effects and Preventive Measures, pp. 83-118. Springer, Singapore, Singapore.

Yan, C., Che, F., Zeng, L., Wang, Z., Du, M., Wei, Q., Wang, Z., Wang, D., and Zhen, Z. 2016. Spatial and seasonal changes of arsenic species in Lake Taihu in relation to eutrophication. Science of the Total Environment, 563: 496-505.

Zhang, X., Jia, Y., Wang, X., and Xu, L. 2008. Phylogenetic analysis and arsenate reduction effect of the arsenic-reducing bacteria enriched from contaminated soils at an abandoned smelter site. Journal of Environmental Sciences, 20(12): 1501-1507.

# Chapter 3: Assessment of Arsenic and Iron Occurrence and Leaching Potential for the Sediments of a Potable Water Treatment Wastewater Stabilization Pond System

## Overview

A version of this Chapter has been submitted to the *Canadian Journal of Civil Engineering* with the following details:

Ekhlasi Nia, A., Bull, H., and McPhedran K. (2021). Assessment of Arsenic and Iron Occurrence and Leaching Potential for the Sediments of a Potable Water Treatment Wastewater Stabilization Pond System. Submitted in March, 2021 to the *Canadian Journal of Civil Engineering*.

## Abstract

Drinking water treatment plants (DWTPs) may have residual wastes and wastewaters with elevated levels of heavy metals and metalloids that need to be treated in order to effluent guidelines before being discharged into receiving waterbodies. Wastewater stabilization ponds (WSPs) are commonly used to reduce residual wastewater metal(loid) concentrations mainly through sedimentation processes. However, this process results in an increase in the sediment metal(loid)s concentration over time, creating the possibility of sediments releasing metal(loid)s back into the overlying water under various conditions. In this study, the overlying water and sediments of a WSP system for a Saskatchewan based DWTP were investigated given historically elevated As and Fe concentrations of effluents which were often higher than the influent pond concentrations. Further, the elevated effluent As concentrations resulted in exceedance of guideline values for sediments collected from a stream downstream of the pond system outlet. The WSP system, consists of five ponds in series that were individually sampled (both water and sediments) on six occasions. Three sampling events occurred in 2019 prior to a DWTP plant upgrade, and three sampling events in 2020 after the DWTP was upgraded to a new treatment technology and higher volumetric capacity. In addition to field monitoring, the sediments collected on one occasion were used in laboratory-based experiments to determine their leaching potential. Overall, the sediments

were found to contain elevated concentrations of As and Fe in the ranges of approximately 25 to 400 and 10,000 to 45,000 mg/kg, respectively. Results from the sediment leaching experiments indicated that each of the ponds can potentially release leachable As and Fe contents over their individual retention times, as well as during the overall WSP retention times. The As concentrations resulted in sediment log K<sub>d</sub> values ranging widely from 2.21 to 4.31 L/kg among the ponds with K<sub>d</sub> values of Pond 1  $\gg$  Pond 3 > Pond 4 > Pond 5  $\gg$  Pond 2. The Fe concentrations resulted in sediment log K<sub>d</sub> values having a range of 3.32 to 5.53 L/kg with the values being in the following order: Pond 5  $\gg$  Pond 1 > Pond 4 > Pond 3  $\gg$  Pond 2.

#### **3.1 Introduction**

Raw water sources for drinking water treatment plants (DWTPs) include both surface waters and groundwaters which may contain elevated concentrations of heavy metals and metalloids, such as arsenic (As) and iron (Fe). Metal(loid) species are widely distributed in the environment and are found to be naturally occurring in rocks, soils, sediments, and waters. However, elevated As and Fe levels above naturally occurring background concentrations can be the result of releases due to anthropogenic, and sometimes natural, activities leading to the contamination of natural waterbodies (Khatri, Tyagi and Rawtani 2017, Wang and Mulligan 2006). Metal(loid)s present in these waterbodies can be toxic to biota including plants and animals. For example, plants can bioaccumulate many of the various metal(loid)s from surrounding contaminated soils and waters which can then be consumed by, and have toxic impacts on, animals including humans. In addition, fish species are at high risk of toxicity affects caused by metal(loid) pollution as they might be living in polluted water and consuming contaminated plants and other organisms (Martin and Griswold, 2009). As with plants, animal and human ingestion of fish species containing elevated metal(loid) concentrations can lead to both acute and chronic negative impacts.

Of most interest in the current study are compounds including species of the metalloid As and the heavy metal Fe. For example, groundwaters used as DWTP sources are frequently found to be contaminated with high concentrations of various As species (Oyem, Oyem, and Usese 2015). Arsenic, with an atomic number of 33, exists throughout the environment in four oxidation states of As<sup>3-</sup>, As<sup>0</sup>, As<sup>3+</sup>, and As<sup>5+</sup>, with trivalent As and pentavalent As being the most common species (Wang and Mulligan 2006, Tchounwou et al. 2015). Chronic exposure to As and its compounds through inhalation, dermal contact, and drinking water ingestion can cause cancers of the skin, bladder, kidney, lungs, liver, and prostate (Ratnaike 2003, Xu et al. 2019). Iron, the fourth most common element on Earth with an atomic number of 26, exists in two oxidation states of ferrous iron (Fe<sup>2+</sup>) and ferric iron (Fe<sup>3+</sup>) (Khatri et al. 2017). Excessive Fe ingestion can be toxic and cause vomiting, diarrhea, abdominal pain, and gastrointestinal bleeding (Banner and Tong 1986). Speciation is the most important factor in As and Fe toxicity and mobility assessment. For example, arsenite is known to be more toxic and soluble than arsenate (Zhang et al. 2008), while ferric iron is insoluble and ferrous iron is soluble and can be toxic as well (Fraga and Oteiza 2002). Generally, the speciation and mobility of both As and Fe can be predicted using models, such as PHREEQC, based upon redox and other physicochemical parameters (Parkhurst and Appelo 1999). Overall, As and Fe are found to co-exist in a variety of species and may be potentially problematic contaminants within DWTP processes.

Generally, DWTPs employ a variety of technologies to treat raw waters for the creation of safe potable water. For example, many DWTPs have employed membrane technologies such as electrodialysis reversal (EDR) and reverse osmosis (RO). The inclusion of RO is especially common in smaller, rural community DWTPs throughout Canada including the plant being assessed in the current study. Through the treatment process, membranes generate backwash waters with concentrated contaminants including metal(loid)s, salts, and other impurities that are present in much lower concentrations in the raw water sources (Greenlee et al. 2009). These backwash waters can be treated via 'natural' methods such as a series of wastewater stabilization ponds (WSPs) which are widely used, simple, and cost-effective technologies for the treatment of a variety of wastewaters (Clancy et al. 2013). In these systems, metal(loid) removals can occur by formation of insoluble salts followed by precipitation, or through uptake in microorganisms and plants (Kayombo et al. 2004, Üstün 2009). These processes result in the concentration of metal(loid)s in sediments which can become a potential contamination source if not managed appropriately over time.

The release of metal(loid)s from sediment is principally controlled by the temperature, pH, redox conditions, salinity, and dissolved oxygen (DO) concentration of the overlying water. In addition, physical and biological disturbances have also been shown to result in the release of metal(loid)s from sediments (Duncan et al. 2018, Li et al. 2013). For WSPs, the sedimentation process results in increased sediment buildup within initial ponds which can decrease their

effectiveness due to factors such as reducing their effective volume (Agunwamba 2001). The sediment accumulation can also negatively impact both overlying water and groundwater quality via the potential for metal(loid) resuspension and/or leaching from sediments; thus, sediments should be removed regularly and appropriately disposed of. However, sediment removal frequency and handling differ from pond to pond in a WSP system necessitating a better understanding of each pond's individual physiochemical characteristics including metal(loid) content (Clozel et al. 2006). In addition to individual pond variability, sediment metal(loid) release and sorption processes can vary diurnally and seasonally. For example, significant diel changes of up to 54% for As have been found to be caused by variation in water pH and temperature (Nimick et al. 2003). Further, seasonal As concentrations have been shown to range up to 290% due to evapotranspiration, surface runoff, and channel ice formation (Nimick et al. 2005). Clearly, metal(loid) fate and transport within systems such as WSPs is complex and needs further investigation. For example, leaching experiments may be useful for an improved understanding of a contaminant's movement between different phases of a WSP system (Wilhelm 2004).

The first objective of this research was to investigate As and Fe concentrations in the sediments of a DWTP WSP system over two field seasons (2019 and 2020) (Figure 3.1). This DWTP was updated (see Materials and Methods for further details) with the initial treatment process occurring until 2019 and the new treatment process being commissioned in January 2020. To determine the impacts of this new DWTP on the WSP pond system, As and Fe concentrations in sediments (along with other metal(loid)s) were measured on six occasions in each of five ponds within the system including three events in 2019 and three events in 2020. The second objective was to perform laboratory leaching experiments to determine As and Fe distribution (or partition) coefficients (K<sub>d</sub>) and determine their potential leaching rates from sediments into the overlying water. The distribution coefficient is defined as the ratio of an element concentration in the solid phase to the equilibrium concentration in the surrounding aqueous phase and is of most importance when estimating the potential for contaminant transport between aqueous and solid phases (Wilhelm 2004). These experiments enable the calculation and comparison of As and Fe flux rates over each of the individual pond's retention time. In addition, these experiments may be useful in determining correlations between As and Fe and other factors such as pH, DO, and redox potential (D'Silva 2017).

#### 3.2 Methodology

#### 3.2.1 DWTP and the Pond System

The studied DWTP was constructed in 1959 to treat surface water from a creek reservoir which was upgraded in 1984, and 1989, to simultaneously treat surface water and groundwater with an EDR technology. In early 2020, the plant underwent a major upgrade in both treatment strategy and production capacity using RO technology to treat groundwater as its sole source of raw water. The generated wastewaters from both previous and current systems have elevated metal(loid) concentrations, such as As and Fe, which need to be treated before safe release into the environment. Note that the 2020 pond system inlet As and Fe concentrations were expected to be higher than in 2019 since groundwaters typically contain higher metal(loid) concentrations than surface waters, thus, using only groundwater as a source water should lead to a higher metal(loid) loading rate to the WSP system (Oyem et al. 2015). The DWTP has used a WSP system, consisting of five sequential ponds, to treat wastewaters through oxidization and sedimentation processes for more than fifty years (Figure 3.1). The treated wastewater is released into a low-flow creek with fish species in the spring and summer, while being frozen over in the winter. The WSP system outflow has been monitored monthly since 2017 and, most notably, has been shown to regularly exceeding the CCME guidelines for As of 5 µg/L (CCME, 2001). It should be noted that the WSP outflow Fe concentrations also regularly exceeded historic CCME guidelines; however, updated variable guidelines that include pH and DOC parameters resulted in Fe concentrations being well below the newer guideline calculations (Environment and Climate Change Canada 2019).

Figure 3.1 shows the pond system after undergoing changes in the Pond 1 layout in 2020 to include previously inactive areas (see Chapter 2) resulting in a longer flow path and increased retention times. The approximate retention times of one day for Ponds 1, 3 and 4 and three days for Ponds 2 and 5 were determined through a parallel study on the ponds using drone imaging and in-field flow measurements (Bull, 2020). The ponds are covered by various vegetation such as cattails, bulrushes, and algae during the spring and summer and are also habitat to a variety of bird and animal species including two beavers which inhabited Pond 2 over the 2020 sampling season. The WSP wastewater enters Pond 1 and flows through all the ponds to the end of Pond 5 where it is directed into a creek through a discharge pipe that was equipped with a flow meter in 2019.



**Figure 3.1:** The 2020 WSP system consisting of five settling ponds (labelled 1 through 5) receiving DWTP wastewaters. The flow path is indicated via the red line starting from the southwest area of Pond 1 and exiting through a discharge pipe on the west side of Pond 5.

#### **3.2.2 Sampling and Analysis**

Pond sediments and their overlying waters were sampled on six occasions, with three events occurring in 2019 during July, August, and October and another three events in 2020 during May, June, and July (the ponds sediment was not sampled in the winter months as the ponds were frozen over in these months and also due to the budgetary limitations). Upstream and downstream sediments of the WSP system outlet were also sampled in an effort to evaluate the potential impacts of the discharges on the receiving creek. Surficial sediment samples (0 to 15 cm) were taken using a random sampling method by dividing each pond into grids, numbering the cells, and generating a random number indicating the correspondent cell to be sampled. Pond locations that were not accessible due to vegetation or depth were excluded and replaced with alternative locations based on the same methodology. Based on the pond sizes, three samples from Ponds 1, 3, and 4 and five samples from Pond 3 and 5 were taken using a sampling scoop to a volume of 2 L. Each pond's individual samples (6 to 10 L) were thoroughly mixed in a 20 L container to create a composite sample for each pond (n=5) and then placed into two ziplock bags with an average weight of 3.2 kg each. Two bags per pond were transported in a cooler at 4 °C in under 48 hours, one to ALS Environmental (Saskatoon, SK, Canada) for analysis and one to the Environmental Engineering laboratory at University of Saskatchewan (USask) for long-term storage at 4 °C (Cavanagh et al. 1994, CCME 2011) prior to analysis and use in experiments. The overlying waters from each pond's outlets were sampled and stored in containers provided by ALS and kept in a cooler following the procedures provided by ALS.

Metal(loid) concentrations in the pond sediments and waters were analyzed at ALS Environmental using collision/reaction inductively coupled plasma mass spectrometry (CRC ICP-MS) referenced as Method 6020A of U.S. Environmental Protection Agency (EPA 1998). Sediments were dried, disaggregated, and sieved using a 2 mm mesh. Then, they were digested with nitric and hydrochloric acids and analyzed using the CRC ICP-MS method. Water samples were filtered using a 0.45  $\mu$ m filter prior to analysis using the same method. Other than As and Fe, a wide range of other metal(loid)s were also measured in both sediment and water samples to allow for the evaluation of potential correlation between other metal(loid)s and As and Fe (see Results).

Five physicochemical parameters of pH, conductivity, dissolved oxygen, temperature, and redox potential were measured both *in situ* and in the laboratory experiments with a Hanna Instruments® HI 98194 multiparameter probe. The temperature of the pond system overlying
water was found to be in the ranges of 12.8 to 26.3 °C, 9.7 to 17.5 °C and 1.8 to 7.9 °C for the 2019 months of July, August and October, respectively, and in the ranges of 7.7 to 14.3 °C, 11 to 19.7 °C and 13.1 to 25.8 °C for the 2020 months of May, June and July, respectively.

#### **3.2.3 Modeling and Statistics**

In this study, PHREEQC version 3 with the included MINTEQ.v4 database (EPA 1998) was used to determine As and Fe speciation, among other elements. PHREEQC is a modelling program developed by the United States Geological Survey (USGS). PHREEQC is designed to model a wide variety of aqueous geochemical processes including models to determine element speciation and saturation index for soluble minerals (Parkhurst and Appelo 1999).

SPSS software was used to perform one-way analysis of variance (ANOVA) and determine Pearson correlation coefficients (r). An ANOVA compares the variation between groups to variation within each of the groups to determine whether there is a statistically significant difference between the groups. In this study the ANOVA test followed by Tukey's post hoc test was performed with a confidence level of 95%. Correlation analysis is a statistical method used to measure of the strength of the association between two quantitative variables. In this study Pearson correlation coefficient (r) were determined with confidence level of at least 95%, 2-tailed.

### **3.2.4 Leaching Experiments**

Two different sets of leaching experiments were performed to determine the potential for the WSP sediments to release sorbed As and Fe into overlying waters including determination of the solid-water distribution coefficients ( $K_d$ ) and leaching rates. The  $K_d$  values can be used to estimate the mobility and distribution of As and Fe in the environment resulting from sediments. The second leaching experiment was performed to calculate the leaching rate of As and Fe over time for each pond and investigate changes in the rates over time to determine how pond retention times may impact metalloid mobility.

#### **3.2.4.1 Solid-Water Distribution Coefficient Experiments**

The K<sub>d</sub> experiments were conducted using a method described previously by Sheppard et al. (2007). Briefly, five replicates of sediments (n=5) were centrifuged in 50 mL centrifuge tubes at 5,000 rpm for 20 minutes to drain the sediment pore water. The pore water was replaced by an equal amount of deionized water (approximately 20 mL water per 50 g of dried sediment) so that

the moisture content of the sediment approximated the *in situ* field capacity moisture content. The sediments were then transferred to another centrifuge tube, and the system was left undisturbed for eight days at room temperature (~20 °C) to allow for equilibration between the sediments and the deionized water. Following this equilibration, the pore waters were extracted again through centrifugation, filtered through a 0.45  $\mu$ m filter, and measured for Fe and As concentrations (mg/L). As the sediment Fe and As concentrations (mg/kg) were already determined through the field sample analysis, the solid-water distribution coefficients (K<sub>d</sub>) were calculated by dividing the concentration of metal(loid)s in sediment by concentrations in water (units of L/kg) (Sheppard et al. 2007, Sullivan and Aller 1996).

#### **3.2.4.2 Leaching Rate Experiments**

The design of these experiments was adopted from a setup previously used by D'Silva (2017) and modified as shown in Figure 3.2. Twenty 2-L high-density polyethylene (HDPE) bottles were developed with four replicates (n=4) for each of the five ponds running simultaneously in a glove box chamber filled with nitrogen at room temperature. The bottles had a height of 22 cm, a diameter of 11 cm, and provided a surface area of 91 cm<sup>2</sup> between the sediments and overlying water. To develop the reactors, 750 g (about 450 mL) of saturated sediment (at saturation levels approximately equal to the *in situ* levels) was poured into the individual bottles and filled with 1.5 L deionized water. The reactors were saturated with nitrogen sparging until the water DO concentration was < 0.5 mg/L. This nitrogen sparging was done as field measurements indicated DO concentrations < 0.5 mg/L at the water-sediment surface for all ponds; thus, the sediments were anoxic. The reactors were sampled six times at 0.5, 1, 3, 6, 9, and 16 days to exceed the approximate total WSP retention time (~9 days) and to determine the necessary equilibration time needed for the experiments. Prior to each sampling event the reactors were initially bubbled with nitrogen gas to ensure that the column of water was well-mixed (D'Silva 2017), then, 10 mL of the overlying water was pipetted, filtered with 0.45 µm filter, and acidified with 2% nitric acid, and then analyzed using atomic adsorption spectroscopy (AAS) for As and Fe. In addition, the sample temperature, DO concentration, and redox potential (Eh) of the overlying water were monitored directly after the sample collection. After each sampling, the system was topped up with 10 mL deionized water so that the total water volume remained constant throughout the experimental duration. The total volume of sampled water was 60 mL or 4 % of the reactor water volume.



**(B)** 



**Figure 3.2:** A) Leaching rate experiment reactor setup; and B) Schematic of an individual reactor setup. The reactors were running simultaneously in a glove box chamber filled with nitrogen gas to eliminate oxygen and maintain an anaerobic condition similar to the *in situ* pond sediments.

# **3.3 Results and Discussion**

#### 3.3.1 As Sediment and Overlying Water Concentrations

Figure 3.3 shows the As concentrations in the overlying water (mg/L on primary y-axis) and sediment (mg/kg secondary y-axis) of each pond over three months for the years of 2019 (left side panels) and 2020 (right side panels). These years represent the 'before' and 'after' years for the commissioning of the new DWTP system. The 2019 sediment As concentrations generally decreased from Pond 1 (with a maximum ~450 mg/kg in August) to Pond 5 (~50 mg/kg for all months). In comparison, the water total As concentrations increased from Pond 1 to Pond 5 for the months of July (~0.007 to 0.020 mg/L) and August (~0.010 to 0.020 mg/L) while remaining stable for October (~0.005 to 0.007 mg/L), respectively. The 2020 sediments had analogous decreases through the WSP system as for 2019 with similar As concentrations in Ponds 1 to 4 ranging from 150 to 400 mg/kg and lower As concentrations in Pond 5 at approximately 50 mg/kg for all months (similar to 2019). In contrast to 2019, the 2020 water total As concentrations were found to decrease marginally from Pond 1 to Pond 5 for all months starting from 0.010 to 0.030 mg/L in Pond 1 to 0.010 to 0.015 mg/L for Pond 5, respectively. The higher As concentrations for the months of July and August (as compared to the October levels in 2019) and in the months of June and July (as compared to the May levels in 2020) could be due to the higher temperature of the wastewater in the ponds during these months. The higher temperature has been suggested to result in As re-dissolution of secondary minerals and the increase of microbial activity leading to As mobilization by reducing arsenate species to arsenite species (Drewniak and Sklodowska 2013). Furthermore, the pond system sediments are more likely to be disturbed during warmer months of summer as result of higher bird and animal activities in the pond system, and release back As into the overlying water.

Table 3.1 displays the As concentration trend in WSP pond sediments and overlying waters in 2019 and 2020. For sediments, the As concentration trend between ponds was the same in both 2019 and 2020 with As concentrations decreasing markedly from Pond 1 to Pond 2 and then increasing in both Ponds 3 and 4, before declining markedly again in Pond 5 to the lowest concentrations. The only exception was the 2019 July Pond 3 sample that showed lower sediment As concentrations as compared to all other Pond 3 sediment samples. It is hypothesized that this low concentration can be attributed to extensive vegetation growth in 2019 over a large area of



Arsenic (As)- Total concentration in water \_\_\_\_ Arsenic (As)- Dissolved concentration in water \_\_\_\_ Arsenic (As)- concentration in sediment

**Figure 3.3:** The As concentrations in overlying waters and sediments for each of the five ponds during six sampling events in 2019 and 2020.

Year	Month	Sediment As concentration			Total As concentration in water				
		P1 to P2	P2 to P3	P3 to P4	P4 to P5	P1 to P2	P2 to P3	P3 to P4	P4 to P5
2019	July	$\downarrow \downarrow \downarrow$	$\downarrow\downarrow$	$\uparrow\uparrow\uparrow\uparrow$	$\downarrow \downarrow \downarrow \downarrow \downarrow$	$\uparrow \uparrow$	<b>†</b> †	$\downarrow$	$\uparrow\uparrow$
	August	$\downarrow \downarrow \downarrow \downarrow \downarrow$	$\uparrow \uparrow \uparrow$	$\downarrow$	$\downarrow \downarrow \downarrow \downarrow \downarrow$	$\downarrow$	$\uparrow \uparrow$	$\uparrow \uparrow \uparrow$	1
	October	$\downarrow \downarrow \downarrow \downarrow \downarrow$	$\uparrow\uparrow\uparrow$	$\downarrow$	$\downarrow \downarrow \downarrow$	$\downarrow$	$\uparrow\uparrow$	$\downarrow$	$\downarrow$
2020	May	$\downarrow$	$\uparrow\uparrow$	$\downarrow$	$\downarrow \downarrow \downarrow \downarrow \downarrow$	↑	1	$\downarrow\downarrow$	$\downarrow$
	June	$\downarrow$	$\uparrow\uparrow$	1	$\downarrow \downarrow \downarrow \downarrow \downarrow$	$\downarrow$	$\downarrow$	$\downarrow$	<b>↑</b>
	July	$\downarrow \downarrow \downarrow \downarrow \downarrow$	$\uparrow\uparrow$	1	$\downarrow \downarrow \downarrow$	$\downarrow$	$\downarrow \downarrow \downarrow \downarrow \downarrow$	1	<b>↑</b>

**Table 3.1:** The As concentration trends in the WSP system sediments and overlying waters in 2019 and 2020 sampling periods.

Pond 3 which prevented the center of the pond from being safely sampled. The center section of the ponds would be expected to be richer in As (and Fe) as increased settling can occur in water pathways over time. All WSP sediments exceeded CCME freshwater Interim Sediment Quality Guidelines (ISQGs) and Probable Effect Levels (PELs) with limits of 5.9 and 17 mg/kg, respectively (CCME, 1997). In contrast to the sediments, the water total As concentration trends were sporadic with concentration changes being less drastic between ponds. Despite the mixed trends of As in the WSP system in 2019 and 2020, the pond effluents exceeded CCME freshwater guidelines of 5  $\mu$ g/L (CCME, 1997) for 5 of the 6 months sampled in this study.

#### 3.3.2 Fe Sediment and Overlying Water Concentrations

Figure 3.4 shows the Fe concentrations in the overlying water (mg/L primary y-axis) and sediment (mg/kg secondary y-axis) of each pond for three months in 2019 (left side panels) and 2020 (right side panels). Similar to the sediment As concentration trends, the 2019 sediment Fe concentrations decreased from Pond 1 (range of ~25,000 to 40,000 mg/kg) to Pond 5 (~20,000 mg/kg), respectively. In comparison, the water total Fe concentrations increased from Pond 1 to Pond 5 for all months ranging from ~0.2 to 0.4 mg/L in Pond 1 up to ~0.6 to 0.8 mg/L for Pond 5. The 2020 sediments had similar decreases for May and July at 20,000 to 15,000 mg/kg and 35,000 to 20,000 mg/kg, respectively. However, the June sample had consistent concentrations for all ponds in the 20,000 to 25,000 mg/kg range. In contrast to 2019, the 2020 water total Fe concentrations decreased for June (0.7 to 0.4 mg/L) and July (1.5 to 0.4 mg/L) while increasing as they did in 2019 for the May 2020 sample from 0.5 to 0.8 mg/L, for Ponds 1 and 5, respectively.

Similar to Table 3.1 for As, Table 3.2 presents the Fe concentration trends for the WSP system sediment and overlying water in 2019 and 2020. For sediments, the Fe sediment concentrations trends were typically similar to As across all ponds in 2019 and 2020 with decreasing (or unchanged) concentrations from Pond 1 to Pond 2, increasing concentrations from Pond 2 to 3 and Pond 3 to 4, and large decreases for Pond 5. Unlike As, there are no existing Canadian sediment guidelines for Fe concentrations. The water total Fe concentration trends (Table 3.2) were more consistent than total As concentrations (Table 3.1) with generally decreasing concentrations from Pond 1 to 2 and continuing from Pond 2 to 3, then increasing from Pond 3 to 4 and once again from Pond 4 to 5 (Table 3.2). For Fe, the new Federal Water Quality Guideline is about 4.91 mg/L



Figure 3.4: The Fe concentrations in overlying waters and sediments for each of the five ponds during six sampling events in 2019 and 2020.

Year	Month	Sediment Fe concentration			Total Fe concentration in water				
		P1 to P2	P2 to P3	P3 to P4	P4 to P5	P1 to P2	P2 to P3	P3 to P4	P4 to P5
2019	July	$\downarrow$	$\downarrow \downarrow \downarrow$	$\uparrow\uparrow\uparrow\uparrow$	$\downarrow \downarrow \downarrow \downarrow \downarrow$	$\downarrow$	$\downarrow$	<b>†</b> †	1
	August	$\downarrow \downarrow \downarrow \downarrow \downarrow$	$\uparrow \uparrow$	1	$\downarrow \downarrow \downarrow$	$\downarrow$	$\downarrow$	$\uparrow\uparrow\uparrow\uparrow$	$\downarrow$
	October	$\downarrow \downarrow \downarrow \downarrow \downarrow$	$\uparrow \uparrow$	1	$\downarrow\downarrow$	$\downarrow$	$\downarrow$	ſ	$\uparrow \uparrow$
2020	May	↑	$\uparrow \uparrow$	$\downarrow$	$\downarrow \downarrow \downarrow$	$\downarrow$	$\downarrow\downarrow$	$\downarrow$	$\uparrow \uparrow \uparrow$
	June	<b>↑</b>	1	$\uparrow\uparrow$	$\downarrow$	$\downarrow\downarrow$	$\downarrow\downarrow$	1	$\uparrow\uparrow$
	July	$\downarrow \downarrow \downarrow \downarrow \downarrow$	1	$\uparrow \uparrow$	$\downarrow\downarrow$	$\downarrow \downarrow \downarrow \downarrow \downarrow$	$\downarrow \downarrow$	1	1

**Table 3.2:** The Fe concentration trends in the WSP system sediments and overlying waters in 2019 and 2020 sampling periods.

for the current pond system but varies based on the pH and the DOC (dissolved organic carbon) levels in the final effluents (Environment and Climate Change Canada 2019).

Clearly, the water total Fe concentrations for effluents easily met this guideline on all sampling occasions. In addition, no concentrations within the WSP system exceeded this guideline for any samples taken during the study period of 2019 and 2020. Interestingly, the previous Fe Water Quality for the Protection of Aquatic Life guideline for freshwaters of 300  $\mu$ g/L (CCME, 2007) would have been exceeded for all Pond 5 effluent samples collected during this study. The Fe contamination was considered to be an issue at the start of this research; however, the new guidelines result in Fe water concentrations that are safe for release into the receiving creek from the WSP system.

#### **3.3.3** As and Fe Relationships in Pond Sediments

Figure 3.5 presents both As (primary y-axis on left) and Fe (secondary y-axis on right) concentrations in each of the individual pond's sediments for the three month sampling periods for 2019 (left side panels) and 2020 (right side panels). Generally, the similar monthly trends in As and Fe concentrations for all sampling events indicates that these two metal(loid)s are typically correlated to each other within the WSP system. This correlation can be explained by the distinct affinity of iron hydroxides for As and their significant role in As uptake mechanisms (Fritzsche, Dienemann and Dudel 2006). Interestingly, while Ponds 1 and 3 showed similar relationships between As and Fe, Ponds 2, 4, and 5 showed lower relative Fe concentrations as compared to As. This variation is most notable in Pond 5 for both 2019 and 2020 seasons. Reasons for this discrepancy are unknown but may be due to differences in the individual pond physical structures and resultant treatment capabilities. For example, the Pond 5 is much deeper than the other four ponds which could potentially lead to differences in metal(loid) mass transfer between overlying waters and sediments. In addition, the amount of vegetation covering the pond surfaces was variable between all of the WSP system both on a seasonal and yearly basis.

In addition to having similar overall monthly trends, the As and Fe concentrations for each of the individual DWTP ponds were similar on a yearly basis with general concentrations being comparable in 2019 and 2020 for each of the three-month sampling periods. This result indicates that the significant changes in the DWTP treatment process occurring between 2019 and 2020 did not immediately have a significant impact on the sediment concentrations of either As or Fe. The



Figure 3.5: As and Fe concentrations in sediments for each pond in 2019 and 2020

only exception was Pond 1 where the As and Fe concentrations were markedly lower in 2020 versus 2019 sampling periods. However, this change is likely the result of the changes to the Pond 1 layout and routing which was completed in 2020 in an effort to improve the DWTP effluent flow. At the onset of this study, these changes in the WSP system were not yet being considered by the DWTP operator. Thus, further subsequent monitoring of this WSP system would be useful to determine if there are potentially longer-term impacts due of the new DWTP process and changes in wastewater effluents.

Figure 3.6 presents the overall 2019 and 2020 sediment As (Panel A) and Fe (Panel B) concentrations in the form of box-and-whisker plots for each of the individual ponds in the WSP system. One-way ANOVA was used to determine whether the differences in the mean concentrations of As and Fe for each of the ponds were statistically significantly with results indicated within Figure 3.6 (see caption for details).

In contrast to the relatively stable monthly and yearly concentrations presented in Figure 3.5, the inter-pond variations for both As and Fe concentrations were markedly higher. Both As and Fe concentrations were highest in Pond 1 ranging from 205 to 455 mg/kg and 21,800 to 44,200 mg/kg, respectively. Pond 1 also showed the highest variability in sample concentrations throughout the sampling period as indicated by larger range between 25% and 75% percentiles. Both As and Fe exhibited significant declines in sediment concentrations for Pond 2 in conjunction with a much lower variability in sample concentrations throughout the two-year sampling period. Concentrations of As and Fe increased in Pond 3 with similar concentrations in Pond 4 for As only. In contrast, Fe concentrations continued to significantly increase from Pond 3 to Pond 4 with a resultant mean concentration being similar to the initial value of Pond 1. By Pond 5 both As and Fe concentrations decreased to minimum values overall ranging from 25 to 60 mg/kg and 15,000 to 25,000 mg/kg, respectively. As indicated in the previous section, July 2019 samples were outliers for both As and Fe given the inability to sample the pond due to dense vegetation and resulting sampling safety concerns.

The WSP system discharges through a pipe exiting from Pond 5 (Figure 3.1) into a nearby low-flow creek which supports a seasonal fish population. In order to understand the potential impacts of the WSP effluents on this receiving waterbody, creek sediments were collected both upstream and downstream of the WSP outlet. The upstream and downstream sediments were found to have As concentrations of 3.39 and 34.8 mg/kg, respectively, and Fe concentrations of 16,000



**Figure 3.6:** 2019 and 2020 sediment concentration box-and-whisker plots for each individual pond for: A) As; and B) Fe. Results of ANOVA are show above each plot with results having different letters indicating significant (p<0.05) differences between ponds (July 2019 Pond 3 results were excluded since they were outliers).

and 15,100 mg/kg, respectively. Clearly, these results indicate that the WSP system effluents have polluted the creek's downstream sediments with As concentrations exceeding both CCME freshwater Interim Sediment Quality Guidelines (ISQGs) and Probable Effect Levels (PELs) with limits of 5.9 and 17 mg/kg, respectively. As indicated previously, Fe sediment Canadian guidelines are not available.

#### **3.3.4** As and Fe Correlation with Other Parameters

Sediment and water chemistry data from the six sampling events (total of 30 samples; Appendix A Table A.1) were analyzed using SPSS software to determine possible correlations between As, Fe, and other parameters. However, only As correlations were investigated herein since Fe compounds are known to associate with other metals in sediments (Benjamin et al. 1996, Yin et al. 2016) and initial review of correlations for this study showed similar results. Table 3.3 shows the sediment and water chemistry parameters with As correlations at either 95% or 99% of both the overlying waters (six with three at 95% and three at 99%) and sediments (12 with one at 95% and 11 at 99%).

The positive correlation between As and organic carbon (both in water and sediment) is expected given sediment organic matter (SOM) has been shown to improve As adsorption (Anawar et al. 2002, Gu et al. 2020). Arsenic was also found to positively correlate with Fe and aluminum (Al), both in water and sediment; however, the correlation is more significant in sediment since As has been shown to coprecipitate with both Fe and Al (Vasques 2018, Wang and Mulligan 2006). Although As can also coprecipitate with cadmium (Cd), it is released more easily than when forming coprecipitates with Fe minerals and therefore is more mobile. This increased mobility may explain the positive correlation between Cd and As in water and a negative correlation between them in sediment (Jiang et al. 2013). The correlation between As and barium (Ba) in both water and sediment can be explained as they have been found to behave similarly in the environment (Vink et al. 2017). Manganese (Mn), magnesium (Mg), sodium (Na), and calcium (Ca) were also found to enhance As adsorption by increasing the sediment electropositivity and the electrostatic force between As and the sediment (Meers et al. 2009; Smith, Naidu and Alston 2002; Zhang et al. 2017).

Although Mn and Na were found to correlate positively with As in the studied sediments, Ca and Mg correlated negatively. The As desorption in these cases could result from Ca or Mg adsorption with bicarbonate saturating Fe mineral surfaces (Saalfield and Bostick 2010). Also, the PHREEQC modelling indicates that Ca and Mg coprecipitated with sulfate and therefore reduced the chance of As and Fe sulfate complex formation. The Na concentration in sediments were found to be correlated with overlying water As concentrations, and the correlation was surprisingly positive. Although As showed no correlation with competing elements of phosphate (P) and selenium (Se) in water, As correlated positively with both of them in the sediment indicating adequate sorption sites for all of them (CCME 1997; Smith, Naidu and Alston 2002). Ammonium-N was found to correlate negatively with As in sediment. Ammonium-N has been shown to improve microbial activity, which causes more oxygen to be consumed, which in turn results in lower Eh in the ponds. Reducing conditions in the ponds causes a release of As from sediment to the water (Kurosawa et al. 2008). In general, metal cations can cause precipitation of As species, but the formed metal-As complexes require specific conditions to remain stable (Wuana and Okieimen 2011).

#### 3.3.5 Pond DO and Eh conditions and As and Fe speciation

Figure 3.7 shows the individual pond summarized overlying water DO and Eh box-andwhisker plots based on data collected in 2020 over five months (June through October). In general, DO decreased significantly from Pond 1 to Pond 4 (mean of ~6 mg/L to ~1 mg/L), and then increased in Pond 5 which also exhibited that highest variability. Ponds Eh followed a similar decreasing trend to DO with Pond 2 redox potentials were in the same range as Pond 1 (mean of  $\sim$ 350 mV) and decreasing further decreasing for Ponds 3 and 4 (means of  $\sim$ 200 mV). Overall, both DO and redox potentials were lowest in Ponds 3 and 4 indicating more reductive conditions in these two ponds that could lead to the release of As and Fe from sediments due to change in their speciation (Smedley and Kinniburgh, 2002). In general, As solubility increases when Eh values decrease since arsenate is efficiently adsorbed in oxic sediments with Eh values of 200 to 500 mV, and can partially dissolve under relatively reducing conditions of 0 to 100 mV as observed in some areas of Ponds 3 and 4 (Gorny et al. 2015). Although pond DO and Eh were found to be correlated (R=0.696), they did not show a correlation with As and Fe changes in the sediments or overlying waters. These measured data were also used to determine As and Fe speciation using PHREEQC software. PHREEQC thermodynamic modelling showed that pond As was predicted to be mostly in the form of  $HAsO_4^{2-}$  (above 95%) and less as  $H_2AsO^{4-}$  (about 3%) at all measured redox

	Element	Pearson's
		Correlation
Aqueous As	Dissolved Organic Carbon	$0.410^{*}$
	Aluminum in water	<b>0.491</b> **
	Barium in water	0.463**
	Iron in water	0.585**
	Sodium in sediment	$0.454^*$
	Cadmium in sediment	$0.450^{*}$
Sediment As	Total Organic Carbon	0.623**
	Ammonium-N	-0.516**
	Aluminum	0.885**
	Barium	0.848**
	Cadmium	-0.451*
	Calcium	-0.674**
	Iron	0.844**
	Phosphorus	0.877**
	Manganese	0.767**
	Sodium	0.463**
	Magnesium	-0.642**
	Selenium	0.754**

**Table 3.3:** Aqueous and sediment As concentrations correlations with various elements.

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



**Figure 3.7:** A) DO concentrations and B) redox potentials in each pond measured over five months in 2020. Results of ANOVA are show above each plot with results having different letters indicating significant (p<0.05) differences between ponds.

potentials. However, ponds Fe species were more susceptible to redox potentials and were found in forms of Fe<sup>+2</sup> (0 to 56%), Fe(OH)<sub>2</sub><sup>+</sup> (15 to 50%), Fe(OH)<sub>3</sub> (14 to 44%), FeSO<sub>4</sub> (0 to 9%), FeHCO<sub>3</sub><sup>+</sup> (0 to 3%), Fe(OH)<sub>4</sub><sup>-</sup> (0 to 5%). At Eh values of about 110 mv, ferrous Fe and ferric Fe species concentrations were found to be equal, meaning at Eh values of above 110 mv, ferric Fe species concentrations exceeded ferrous Fe species concentrations. At Eh values of above 200 mV, more than 95% of Fe species appeared as ferric Fe species.

#### 3.3.6 As and Fe Leaching Experiments Result

The significant increase of As and Fe concentrations in overlying waters from Pond 1 to Pond 5 in 2019 and slight increases at some points in 2020 suggest a possibility that As and Fe are leaching from sediments into the overlying water. To assess this leaching potential, As and Fe leaching experiments were conducted to determine both the solid-water distribution coefficients and the leaching rates. The July 2020 sediments were selected for these experiments to minimize the storage time before the start of the experiments in July 2020. Given the extent of these experiments, only one set of sediments were used as representative samples for the five WSP system ponds.

#### 3.3.7.1 Solid-Water Distribution Coefficient Experiment

Table 3.4 shows the results from the solid-water distribution coefficient experiments for both As and Fe. For As, the measured As concentrations were highest for Pond 2 (0.860 mg/L) followed by Pond 4 (0.195 mg/L), and Pond 3 (0.089 mg/L). The remaining two ponds had markedly lower concentrations with Pond 1 and Pond 5 values of 0.029 mg/L and 0.057 mg/L, respectively. These concentrations resulted in sediment log K<sub>d</sub> values ranging widely from 2.21 to 4.31 L/kg among the ponds with log K<sub>d</sub> values of Pond 1  $\gg$  Pond 3 > Pond 4 > Pond 5  $\gg$  Pond 2. Note that the higher K<sub>d</sub> values indicate greater resistance to leaching (higher sorption to solids), so it would be expected that sediments in Ponds 2 and 5 are more likely to release As. One of the reasons for low K<sub>d</sub> values in Pond 1 at 11% organic carbon content. It has been shown that sediment organic matter (SOM) can stimulate As adsorption (Gu et al. 2020); thus, this would likely limit the sediment desorption potential for the Pond 1 sample.

The current As  $\log K_d$  values fall within the range of literature review values of 1.6 to 4.3 L/kg with median, mean, and standard deviation of 2.2, 2.4 and 0.7, respectively. The  $K_d$  values can vary over many orders of magnitude due to the variability in sediment and porewater compositions (Allison and Allison 2005). While all As log K<sub>d</sub> values fall within two standard deviations from the mean, Pond 1 values are significantly higher and out of this range. Also, Pond 2 log Kd values, although the lowest values as compared to other ponds, are between the literature values median and mean. Although not WSP sediments, Cornett et al. (1992) found average values of 3.3 L/kg for As log K<sub>d</sub> values in surficial sediments which are similar to this study's finding for Ponds 3,4 and 5. Similarly, Mok and Wai (1990) found a range of 2.6 to 3.3 L/kg for As log Kd values in sediments. The average As log K<sub>d</sub> for all of the current WSPs of 3.19 may also be compared to a creek's average sediment As log K<sub>d</sub> result of 2.92 as reported by Routh and Ikramuddin (1996), indicating that the pond system has a greater resistance to leaching than this studied creek. The As log K<sub>d</sub> values from this study may also be compared to soil As log K<sub>d</sub> values found in the literature. For example, Allison and Allison (2005) found a wide soil As log K<sub>d</sub> range of 0.3 to 4.3 L/kg. In addition, Sheppard et al. (2009) provided a geometric mean of 2.99 L/kg for As  $\log K_d$  in Canadian agricultural soils. Lastly, a study by Yang et al. (2012) found an As log Kd range of 2.3 to 5.7 L/kg for As in paddy soil.

For Fe, the measured Fe concentrations followed a similar pattern as the As results with the highest value for Pond 2 (9.07 mg/) followed by Pond 3 (2.53 mg/L) and Pond 4 (1.37 mg/L) (Table 3.4). The same two lowest concentrations as As were found for Fe in Pond 1 and Pond 5 with values of 0.501 mg/L and 0.100 mg/L, respectively. These concentrations resulted in sediment Fe log K<sub>d</sub> values having a wide range of 3.32 to 5.53 L/kg with the values being in the following order: Pond 5  $\gg$  Pond 1 > Pond 4 > Pond 3  $\gg$  Pond 2. Generally, the current results are within a similar reported literature range of 4.0 to 5.7 L/kg (Marcussen et al. 2008). However, the Pond 2 value of 3.32 L/kg falls outside of this range, while this pond also had the lowest log K<sub>d</sub> value for As at 2.21. Similarly, Pertsemli and Voutsa (2007) found a log K<sub>d</sub> range of 4.8 to 5.8 for Fe in sediments which is in the range of Ponds 1 and 5 log K<sub>d</sub> values. The average Fe log K<sub>d</sub> across all of the current ponds of 4.38 is comparable to a creek average sediment Fe log K<sub>d</sub> result of 4.50 reported by Routh and Ikramuddin (1996). Sheppard et al. (2009) provided a geometric mean of 4.46 L/kg for Fe log K<sub>d</sub> in Canadian agricultural soils, and only Ponds 1 and 5 (log Kd) values with geometric means of 4.90 and 5.35 L/kg fall above the literature value.

Dand	Tuba	As	As	Fe	Fe
PONA	number	Concentration	(log Kd)	Concentration	(log Kd)
number		(mg/L)	values (L/kg)	( <b>mg/L</b> )	values (L/kg)
	p11	0.019	4.31	0.153	5.35
	p12	0.024	4.22	0.672	4.71
Pond 1	p13	0.042	3.97	0.719	4.68
	p14	0.029	4.13	0.459	4.87
	AVG	0.029(0.010)	4.16(0.15)	0.501(0.258)	4.90(0.31)
	p21	0.881	2.22	9.221	3.32
	p22	0.895	2.21	9.207	3.32
Pond 2	p23	0.803	2.26	9.189	3.32
	p24	0.862	2.23	8.671	3.35
	AVG	0.860(0.040)	2.23(0.02)	9.07(0.27)	3.33(0.01)
	p31	0.071	3.53	2.896	3.90
	p32	0.058	3.61	1.743	4.12
Pond 3	p33	0.165	3.16	3.234	3.86
	p34	0.062	3.58	2.252	4.01
	AVG	0.089(0.051)	3.47(0.21)	2.53(0.66)	3.97(0.12)
	p41	0.195	3.11	1.574	4.28
	p42	0.242	3.02	1.588	4.28
Pond 4	p43	0.190	3.12	1.286	4.37
	p44	0.153	3.21	1.031	4.47
	AVG	0.195(0.037)	3.12(0.08)	1.37(0.27)	4.35(0.09)
	p51	0.042	3.08	0.092	5.36
Dond 5	p52	0.052	2.98	0.063	5.53
Pona 5	p53	0.086	2.76	0.161	5.12
	p54	0.046	3.04	0.083	5.41
	AVG	0.057(0.020)	2.97(0.14)	0.100(0.043)	5.36(0.17)

**Table 3.4:** As and Fe solid-water distribution coefficients (log  $K_d$ ) and corresponding leached concentrations measured in the distilled water. Note values in parentheses are standard deviations.

#### **3.3.7.2** As and Fe Leaching Rate Experiment

Figure 3.8 shows the average As and Fe concentrations in overlying water for each set of four reactors for Ponds 1 to 5. Initially after the experiment setup, both of the As and Fe concentrations spiked due to the sediment disturbance, and then became relatively constant over time. However, the initial expectation was that As and Fe concentrations would increase over time and then reach the peak values after equilibration between the sediments and overlying water. In general, As concentrations increased from Day 0 (first sample) to Day 9 for all ponds with a range of concentrations from ~0.005 to 0.015 mg/L. From Day 9 to Day 16 the water concentrations stabilized resulting in the highest concentration for Pond 2 at ~0.02 mg/L followed by Ponds 3 and 4 at ~0.015 mg/L. Ponds 1 and 5 had the lowest concentrations at ~0.01 mg/L. For Fe, the initial leaching rate was high reaching the highest levels in the Day 0 sampling with Pond 2 being the highest at ~0.18 mg/L followed by Pond 1 at ~0.15 mg/L and Pond 4 at ~0.14 mg/L. The lowest concentrations were found in Ponds 3 and 5 at ~0.08 mg/L. Unlike As, the Fe concentrations reduced after initial peaks until approximately Day 6 or Day 9 when the concentrations reached a steady state of under 0.05 mg/L.

Statistical analysis indicated that the reactor As concentrations correlated with the individual pond pH, Eh and DO concentrations with R values of 0.423, -0.377 and -0.313, respectively. However, no correlations were found between measured pond parameters and reactor Fe concentrations. On the other hand, both As and Fe concentrations correlated significantly for the overlying pond water and the porewater from the solid-water distribution coefficient experiments with R values of 0.585 and 0.963, respectively. This indicates release of As-Fe compounds while As and Fe were not correlated in the leaching rate experiments indicating an As only releasing mechanism. The hypothesis here is that in the lack of disturbance, As was released in the reactors due to the biological and chemical processes interfering with Eh and DO levels. While in the ponds at field conditions, As was also released due to disturbance to the ponds caused by animals, wind and changes in the flows (Arnold and Oldham 1997). This hypothesis can be further supported as the experimental As concentrations from Ponds 3, 4 and 5 were found to be in the range of concentrations indicating that a major part of Fe release in the ponds is probably due to physical disturbances to the pond's sediment or changes in the inlet water's physiochemical characteristics.



**Figure 3.8:** Average As and Fe concentrations (n=4) in overlying water of each individual pond reactor over 16 days. Error bars represent one standard deviation of uncertainty.

## **3.4 Conclusions**

Drinking water treatment plants (DWTPs) generate wastewaters with elevated metal(loid)s concentrations that cannot be disposed of into the environment without treatment to meet jurisdictional guidelines. The current DWTP treats residual wastewaters using a series of wastewater stabilization ponds (WSPs). The WSP treatment process results in the contamination of the pond sediments over time leading to the possibility of release of metal(loid)s back into the overlying waters. This study investigated a Saskatchewan DWTP WSP system, consisting of five ponds, with an effluent that has historically had elevated As and Fe concentrations that have not met guidelines. In fact, the effluents often had higher As and Fe concentrations than the wastewater entering the pond system. The WSP system individual pond sediments and overlying waters were monitored over six occasions, three in 2019 and three in 2020. The sediments were found to contain As and Fe concentrations in the range of 25 to 400 mg/kg and 10,000 to 45,000 mg/kg, respectively. The sediment As and Fe concentration variations were also found to be greater between the ponds than in each pond over time. In addition, by comparing each ponds sediment As and Fe levels in 2019 and 2020, change in the DWTP treatment process was found not to affect the ponds' sediments significantly. Ponds water was measured for redox potentials and DO concentrations, and the results indicated that Ponds 3 and 4 with the lowest DO contents and redox potentials can reduce As and Fe species to more mobile species resulting in an easier release of As and Fe from sediment to the overlying water. Results from sediment leaching experiments indicated that physical disturbances could potentially cause significant release of As in Ponds 2 and 5 and Fe in Ponds 2 and 3.

## Acknowledgements

The authors would like to thank Kathryn Lindsay for her contributions to the writing of this manuscript. The authors would also like to acknowledge funding through the Mitacs Accelerate program and SaskWater. In addition, research support has been provided by SaskWater personnel including Sumith Kahanda, Enisa Zanacic, Dale Hreshka, and Timo Jansen.

# References

Agunwamba, J. C. (2001). Analysis of socioeconomic and environmental impacts of waste stabilization pond and unrestricted wastewater irrigation: interface with maintenance. Environmental Management, 27(3), 463-476.

Allison, J. D., & Allison, T. L. (2005). Partition coefficients for metals in surface water, soil, and waste. Rep. EPA/600/R-05, 74.

Anawar, H., Komaki, K., Akai, J., Takada, J., Ishizuka, T., Takahashi, T., ... & Kato, K. (2002). Diagenetic control on arsenic partitioning in sediments of the Meghna River delta, Bangladesh. Environmental Geology, 41(7), 816-825.

Arnold, T. N., & Oldham, C. E. (1997). Trace-element contamination of a shallow wetland in Western Australia. Marine and freshwater research, 48(6), 531-539.

Banner Jr, W., & Tong, T. G. (1986). Iron poisoning. Pediatric Clinics of North America, 33(2), 393-409.

Benjamin, M. M., Sletten, R. S., Bailey, R. P., & Bennett, T. (1996). Sorption and filtration of metals using iron-oxide-coated sand. Water research, 30(11), 2609-2620.

Canadian Council of Ministers of the Environment (CCME). (1997). Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health - Arsenic (Inorganic). ISBN 1-896997-34-1.

Canadian Council of Ministers of the Environment (CCME). (1999). Canadian sediment quality guidelines for the protection of aquatic life: Arsenic. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg. ISBN 1-896997-34-1

Canadian Council of Ministers of the Environment (CCME). (2001). Canadian water quality guidelines for the protection of aquatic life: Arsenic. Updated. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg. Canadian Council of Ministers of the Environment, 7. ISBN 1-896997-34-1

Canadian Council of Ministers of the Environment (CCME). (2007). Canadian water quality guidelines for the protection of aquatic life: Summary table. Updated September, 2007. In:

Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

Canadian Council of Ministers of the Environment (CCME). (2011). Protocols manual for water quality sampling in Canada. Canadian Council of Ministers of the Environment. ISBN 978-1-896997-7-0

Cavanagh, N., Swain, L. G., Nordin, R. N., & Pommen, L. W. (1994). Lake and stream bottom: sediment sampling manual. BC Ministry of Environment, Lands and Parks, Water Quality Branch.

Clancy, T. M., Hayes, K. F., & Raskin, L. (2013). Arsenic waste management: a critical review of testing and disposal of arsenic-bearing solid wastes generated during arsenic removal from drinking water. Environmental Science & Technology, 47(19), 10799-10812.

Clozel, B., Ruban, V., Durand, C., & Conil, P. (2006). Origin and mobility of heavy metals in contaminated sediments from retention and infiltration ponds. Applied Geochemistry, 21(10), 1781-1798.

Cornett, J., Chant, L., & Risto, B. (1992). Arsenic transport between water and sediments. In Sediment/Water Interactions (pp. 533-544). Springer, Dordrecht.

Drewniak, L., and Sklodowska, A. (2013). Arsenic-transforming microbes and their role in biomining processes. Environmental Science and Pollution Research, 20(11): 7728-7739.

D'Silva, L. P. (2017). Biological and physicochemical mechanisms affecting phosphorus and arsenic efflux from prairie reservoir sediment, Buffalo Pound Lake, SK, Canada (Doctoral dissertation, University of Saskatchewan).

Duncan, A.E., de Vries, N., and Nyarko, K.B. (2018). Assessment of Heavy Metal Pollution in the Sediments of the River Pra and Its Tributaries. Water, Air, and Soil Pollution, 229(8), 272.

Environment and Climate Change Canada (ECCC). (2019). Canadian environmental protection act, 1999. Federal environmental quality guidelines - iron. Environment and Climate Change Canada.

Fraga, C. G., & Oteiza, P. I. (2002). Iron toxicity and antioxidant nutrients. Toxicology, 180(1), 23-32.

Fritzsche, A., Dienemann, H., & Dudel, E. G. (2006). Arsenic fixation on iron-hydroxide-rich and

plant litter-containing sediments in natural environments. Environmental Geology, 51(1), 133-142.

Gorny, J., Billon, G., Lesven, L., Dumoulin, D., Madé, B., & Noiriel, C. (2015). Arsenic behavior in river sediments under redox gradient: a review. Science of the Total Environment, 505, 423-434.

Greenlee, L. F., Lawler, D. F., Freeman, B. D., Marrot, B., & Moulin, P. (2009). Reverse osmosis desalination: water sources, technology, and today's challenges. Water research, 43(9), 2317-2348.

Gu, X., Ouyang, W., Xu, L., Tysklind, M., Lin, C., He, M., ... & Xin, M. (2020). Occurrence, migration, and allocation of arsenic in multiple media of a typical semi-enclosed bay. Journal of Hazardous Materials, 384, 121313.

Jiang, W., Lv, J., Luo, L., Yang, K., Lin, Y., Hu, F., ... & Zhang, S. (2013). Arsenate and cadmium co-adsorption and co-precipitation on goethite. Journal of Hazardous Materials, 262, 55-63.

Kayombo, S. T. S. A., Mbwette, T. S. A., Katima, J. H. Y., Ladegaard, N., & Jrgensen, S. E. (2004). Waste stabilization ponds and constructed wetlands: Design manual.

Khatri, N., Tyagi, S., & Rawtani, D. (2017). Recent strategies for the removal of iron from water: A review. Journal of water process engineering, 19, 291-304.

Kurosawa, K., Egashira, K., Tani, M., Jahiruddin, M., Moslehuddin, A. Z. M., & Zulfikar Rahman, M. (2008). Variation in arsenic concentration relative to ammonium nitrogen and oxidation reduction potential in surface and groundwater. Communications in Soil Science and Plant Analysis, 39(9-10), 1467-1475.

Li, H., Shi, A., Li, M., and Zhang, X. 2013. Effect of pH, temperature, dissolved oxygen, and flow rate of overlying water on heavy metals release from storm sewer sediments. Journal of Chemistry, 1-11.

Marcussen, H., Dalsgaard, A., & Holm, P. E. (2008). Content, distribution and fate of 33 elements in sediments of rivers receiving wastewater in Hanoi, Vietnam. Environmental Pollution, 155(1), 41-51.

Martin, S., & Griswold, W. (2009). Human health effects of heavy metals. Environmental Science and Technology briefs for citizens, 15, 1-6. www.engg.ksu.edu/CHSR/

Meers, E., Du Laing, G., Tack, F. M., & Verloo, M. G. (2009). Heavy metal displacement by exchangeable bases (Ca, Mg, K, Na) in soils and sediments. Soil Science, 174(4), 202-209.

Mok, W. M., & Wai, C. M. (1990). Distribution and mobilization of arsenic and antimony species in the Coeur D'Alene River, Idaho. Environmental Science & Technology, 24(1), 102-108.

Nimick, D.A., Cleasby, T.E., and McCleskey, R.B. 2005. Seasonality of diel cycles of dissolved trace-metal concentrations in a Rocky Mountain stream. Environmental Geology, 47(5): 603-614.

Nimick, D.A., Gammons, C.H., Cleasby, T.E., Madison, J.P., Skaar, D., and Brick, C.M. 2003. Diel cycles in dissolved metal concentrations in streams: Occurrence and possible causes. Water Resources Research, 39(9): 1247-1264.

Oyem, H. H., Oyem, I. M., & Usese, A. I. (2015). Iron, manganese, cadmium, chromium, zinc and arsenic groundwater contents of Agbor and Owa communities of Nigeria. SpringerPlus, 4(1), 104.

Parkhurst, D. L., & Appelo, C. A. J. (1999). User's guide to PHREEQC (Version 2): A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. Water-resources Investigations Report, 99(4259), 312.

Pertsemli, E., & Voutsa, D. (2007). Distribution of heavy metals in lakes doirani and kerkini, northern Greece. Journal of Hazardous Materials, 148(3), 529-537.

Ratnaike, R. N. (2003). Acute and chronic arsenic toxicity. Postgraduate Medical Journal, 79(933), 391-396.

Routh, J., & Ikramuddin, M. (1996). Trace-element geochemistry of Onion Creek near Van Stone lead-zinc mine (Washington, USA)—chemical analysis and geochemical modeling. Chemical Geology, 133(1-4), 211-224.

Saalfield, S. L., & Bostick, B. C. (2010). Synergistic effect of calcium and bicarbonate in enhancing arsenate release from ferrihydrite. Geochimica et Cosmochimica Acta, 74(18), 5171-5186.

Sheppard, M. I., Sheppard, S. C., & Grant, C. A. (2007). Solid/liquid partition coefficients to model trace element critical loads for agricultural soils in Canada. Canadian Journal of Soil Science, 87(Special Issue), 189-201.

Sheppard, S., Long, J., Sanipelli, B., & Sohlenius, G. (2009). Solid/liquid partition coefficients

(Kd) for selected soils and sediments at Forsmark and Laxemar-Simpevarp (No. SKB-R--09-27). Sweden.

Smith, E., Naidu, R., & Alston, A. M. (2002). Chemistry of inorganic arsenic in soils: II. Effect of phosphorus, sodium, and calcium on arsenic sorption. Journal of Environmental Quality, 31(2), 557-563.

Söderberg, T. U., Kleja, D. B., Åström, M., Jarsjö, J., Fröberg, M., Svensson, A., & Augustsson, A. (2019). Metal solubility and transport at a contaminated landfill site–From the source zone into the groundwater. Science of the total environment, 668, 1064-1076.

Sullivan, K. A., & Aller, R. C. (1996). Diagenetic cycling of arsenic in Amazon shelf sediments. Geochimica et Cosmochimica Acta, 60(9), 1465-1477.

Tchounwou, P. B., Udensi, U. K., Isokpehi, R. D., Yedjou, C. G., & Kumar, S. (2015). Arsenic and cancer. In Handbook of Arsenic Toxicology (pp. 533-555). Academic Press.

US EPA (United States Environmental Protection Agency). (1998). MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems—User Manual Supplement for Version 4.0: Athens, Georgia, National Exposure Research Laboratory, Ecosystems Research Division. Revised September 1999.

US EPA (United States Environmental Protection Agency). (1998). Inductively coupled plasma - mass spectrometry. EPA 6020A (SW-846).

Üstün, G. E. (2009). Occurrence and removal of metals in urban wastewater treatment plants. Journal of Hazardous Materials, 172(2-3), 833-838.

Vasques, I. C., de Mello, J. W., Veloso, R. W., Ferreira, V. D. P., & Abrahão, W. A. (2018). Effectiveness of ferric, ferrous, and aluminum (hydr) oxide coprecipitation to treat water contaminated with arsenate. Journal of Environmental Quality, 47(6), 1339-1346.

Vink, J. P., van Zomeren, A., Dijkstra, J. J., & Comans, R. N. (2017). When soils become sediments: Large-scale storage of soils in sandpits and lakes and the impact of reduction kinetics on heavy metals and arsenic release to groundwater. Environmental Pollution, 227, 146-156.

Wang, S., & Mulligan, C. N. (2006). Occurrence of arsenic contamination in Canada: sources, behavior and distribution. Science of the Total Environment, 366(2-3), 701-721.

Wilhelm, R. G. (2004). 'Understanding Variation in Partition Coefficient, K<sub>d</sub>, Values Volume iii: Review of Geochemistry and Available K<sub>d</sub> Values for Americium, Arsenic, Curium, Iodine, Neptunium, Radium, and Technetium. Washington DC: EPA.

Wuana, R. A., & Okieimen, F. E. (2011). Heavy metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation. ISRN Ecology, 2011, 1-20.

Xu, Y., Fu, J., Wang, H., Hou, Y., and Pi, J. 2019. Arsenic Exposure and Lifestyle-Related Diseases. In Arsenic Contamination in Asia: Biological Effects and Preventive Measures, pp. 83-118. Springer, Singapore, Singapore.

Yang, X., Hou, Q., Yang, Z., Zhang, X., & Hou, Y. (2012). Solid-solution partitioning of arsenic (As) in the paddy soil profiles in Chengdu Plain, Southwest China. Geoscience Frontiers, 3(6), 901-909.

Yin, H., Tan, N., Liu, C., Wang, J., Liang, X., Qu, M., Feng, X., Qiu, G., Tan, W. and Liu, F. (2016). The associations of heavy metals with crystalline iron oxides in the polluted soils around the mining areas in Guangdong Province, China. Chemosphere, 161, 181-189.

Zhang, L., Qin, X., Tang, J., Liu, W., & Yang, H. (2017). Review of arsenic geochemical characteristics and its significance on arsenic pollution studies in karst groundwater, Southwest China. Applied Geochemistry, 77, 80-88.

Zhang, X., Jia, Y., Wang, X., and Xu, L. (2008). Phylogenetic analysis and arsenate reduction effect of the arsenic-reducing bacteria enriched from contaminated soils at an abandoned smelter site. Journal of Environmental Sciences, 20(12): 1501-1507.

# Chapter 4: Discussion and Recommendations for Future Work

# **4.1 General Discussion**

Groundwater and surface water as major sources of drinking water can contain high concentrations of heavy metals and metalloids, including arsenic and iron, due to anthropogenic and natural activities. Chronic exposure to As and its compounds through inhalation, dermal contact, and drinking water ingestion can cause cancers of the skin, bladder, kidney, lungs, liver, and prostate, and excessive Fe ingestion can be toxic and cause vomiting, diarrhea, abdominal pain, and gastrointestinal bleeding. Therefore, the raw water must be treated in drinking water treatment plants (DWTP) prior to consumption. Many technologies have been developed for drinking water treatment, including coagulation, adsorption, ion exchange, oxidation, and membrane filtration as presented in Chapter 1 of this thesis. Among these treatments, membrane technologies such as electro-dialysis reversal (EDR) and reverse osmosis (RO) with high removal efficiencies are more commonly employed. However, they generate backwash waters with elevated concentrations of contaminants that often exceed the guidelines for direct disposal into the environment. In the case of membrane technologies, the wastewaters can be treated in wastewater stabilization ponds (WSPs) which reduce suspended solids and help to keep discharge flow rates constant. In these ponds, metal(loid)s are removed through the precipitation process and accumulate in sediments over time. However, these metalloids can resuspend and re-enter the overlying water due to changes in the physicochemical condition of the overlying water and result in seasonal variation. The sediment metal(loid) seasonal variation can affect the overlying water quality due to the mass transfer between water and sediments. Therefore, the sediments were monitored and investigated for their leaching potential. It should also be mentioned here that as of 2020, the WSP pond system receives new wastewater due to the upgrades in the water treatment plant and the impacts were investigated.

Chapter 2 and Chapter 3 include the results from the WSP pond system overlying waters and sediments monitoring over three events in 2019 and three events in 2020. Surficial sediment samples were collected using a random sampling method by dividing each pond into grids, numbering the cells, and generating a random number indicating the correspondent cell to be sampled. Considering the pond sizes, three locations from Ponds 1, 3, and 4 and five locations

from Pond 3 and 5 were sampled. Each pond's samples were thoroughly mixed in a container, placed into two ziplock bags, and transported in a cooler at 4 °C in under 48 hours, one to ALS Environmental (Saskatoon, SK, Canada) for analysis and one to the Environmental Engineering laboratory at University of Saskatchewan (USask) for long-term storage at 4 °C. The overlying waters were sampled from each pond's outlets, stored in ALS containers, and transported following the same procedure as sediments.

Results indicated that the pond system effluent exceeded the guidelines for As concentrations and contained elevated Fe concentrations. The sediments were also found to contain elevated As and Fe concentrations ranging from about 25 to 400 and 10,000 to 45,000 mg/kg, respectively, with variations found greater between the ponds than in each of the ponds over time. The pond sediment results from 2019 and 2020 also indicated that the new wastewater did not significantly affect the pond sediment As and Fe contents. These findings fulfilled the first objective of this study which was to analyze the sediments of the ponds system, with focus on As and Fe, on a monthly timeframe over two seasons. In addition to WSP sediments, sediments from upstream and downstream of the pond system outlet were found to contain As and Fe concentrations of 3.39 and 16,000 mg/kg in the upstream sediments and 34.8 and 15,100 mg/kg in downstream sediments, respectively. The creek's downstream sediments As concentrations were found to exceed both CCME freshwater ISQGs and PELs limits, implying that the pond system effluents have polluted the downstream sediments.

Laboratory leaching experiments were performed to fulfill the second objective of this study which was to conduct laboratory experiments on the sediments of each pond in the WSP system to study As and Fe leaching from the ponds' sediments and find a leaching rate for As and Fe. Chapter 3 contains the leaching experiments results including As and Fe distribution (or partition) coefficients ( $K_d$ ) and As and Fe leaching rates from each pond sediments to the overlying water. The  $K_d$  experiments were performed in five replicates for each of the ponds; sediments were centrifuged to drain the sediment pore water, and then the pore water was replaced by an equal amount of deionized water. The system was then left undisturbed for eight days so that the sediments and the deionized water reach equilibrium. Subsequently, the pore waters were extracted again, filtered, and measured for Fe and As contents. The solid-water distribution coefficients ( $K_d$ ) were then calculated by dividing the concentration of metal(loid)s in sediment by concentrations in the pore water. The experiment resulted in finding sediment log  $K_d$  values for As and Fe ranging from 2.21 to 4.31 L/kg and from 3.32 to 5.53 L/kg, respectively, with the order of Pond 1  $\gg$  Pond 3 > Pond 4 > Pond 5  $\gg$  Pond 2 for As and order of Pond 5  $\gg$  Pond 1 > Pond 4 > Pond 3  $\gg$  Pond 2 for Fe. Since higher K<sub>d</sub> values indicate greater resistance to leaching, the release of As in Ponds 2 and 5 and Fe in Ponds 2 and 3 is more likely to occur.

The leaching rate experiments were performed in four replicates for each of the ponds; Twenty 2-L HDPE bottles were developed by pouring 750 g of sediment into the individual bottles and filling them with 1.5 L deionized water. The reactors were then saturated with nitrogen to achieve anoxic conditions measured at the *in situ* water-sediment surface for all ponds. The reactors were sampled six times at 0.5, 1, 3, 6, 9, and 16 days to exceed the approximate total WSP retention time (~9 days). In each sampling, 10 mL of the overlying water was pipetted, filtered, and acidified before being measuring As and Fe using AAS. After each sampling, the reactor's temperature, DO concentration, and redox potential (Eh) were monitored, and then 10 mL deionized water was added to the system to keep the total water volume constant. Through this experiment, it was found that the overlying water As concentrations generally increased from Day 0 to Day 9 and then stabilized from Day 9 to Day 16. As concentrations ranged widely from 0.005 to 0.02 mg/L with the order of Pond 2 > Pond 4 > Pond 3 > Pond 5 > Pond 1. For Fe, the initial leaching rate was high and resulted in the highest Fe levels in Day 0, ranging from 0.08 to 0.18 mg/L with the order of Pond 2 > Pond 4 >>Pond 5 > Pond 3. However, unlike As, the Fe concentrations decreased over time, reaching levels under 0.05 mg/L.

To fulfill the third objective of this study, statistical analysis on results from leaching experiments and field samplings was performed in Chapter 3 of this study and the results indicated that the reactor As concentrations correlated with the individual pond pH, Eh and DO concentrations with R values of 0.423, -0.377 and -0.313, respectively, while Fe did not correlate with any of these parameters or with As. However, As and Fe were found to correlate significantly in the ponds overlying water and the porewater from the K<sub>d</sub> experiments with R values of 0.585 and 0.963, respectively. The results suggested that As release in the reactors was mainly due to the biological and chemical processes interfering with Eh and DO levels, while in the ponds at field conditions, physical disturbance to the ponds caused by animals, wind and changes in the flows played a major rule in As release. The ponds were also modeled using PHREEQC software and the As and Fe speciation in the pond system were found to be as follow: For As, the species are predicted to be mainly found in two forms of HAsO<sub>4</sub><sup>2-</sup> (above 95%) and H<sub>2</sub>AsO<sup>4-</sup> (about 3%),

while for Fe, the species were found in forms of  $Fe^{+2}$  (0 to 56%),  $Fe(OH)_{2^{+}}$  (15 to 50%),  $Fe(OH)_{3^{-}}$  (14 to 44%),  $FeSO_{4}$  (0 to 9%),  $FeHCO_{3^{+}}$  (0 to 3%),  $Fe(OH)_{4^{-}}$  (0 to 5%).

## 4.2 Engineering Significance

This study investigated a WSP system that treats wastewaters of DWTP in Saskatchewan. The WSP system has been in use for more than 50 years without its performance for treating the wastewaters being thoroughly evaluated. The WSP system had received new wastewater since early 2020 when the DWTP was upgraded in its treatment technology, source of raw water, and production capacity, which required investigation of the pond system's efficiency for treating the new wastewater as well as the effects of the new wastewater on the pond system. In general, there has been limited or no previous research that has characterized and assessed sediments of a WSP system. In this study, sediments of each individual pond of the WSP system were monitored on six occasions, with three events in 2019 (before the upgrade) and three events in 2020 (after the upgrade). The monitoring results fulfilled a lack of information about the sediments' chemistry and determined effects of DWTP upgrade on the ponds sediment As and Fe concentrations.

WSP ponds remove metal(loid)s mostly through the sedimentation and precipitation processes which increase As and Fe concentrations in the sediments over time. The polluted sediments can then act as a source of contamination and release metal(loid)s at a rate dependent on the overlying water characteristics such as pH, DO and redox condition. This study provided a better understanding of As and Fe fate and transport potential between sediment and water by performing leaching tests to determine solid-water distribution coefficients (K<sub>d</sub>) and leaching rates. The result helped determine ponds that are more likely to release As and Fe and provided insights on potential causes of As and Fe release from sediments to the overlying waters.

Speciation is an important factor in As and Fe toxicity and mobility assessment. For instance, arsenite has been reported to be 25 to 60 times more toxic than arsenate and is also a more mobile species. This study employed the PHREEQC software to determine As and Fe speciation in the ponds and predicted forms of As and Fe under different redox conditions.

# 4.3 Recommendations and Future Work

Based on the findings from this study, the following suggestions would help to decrease As and Fe concentrations in the studied WSP:

- Increase the dissolved oxygen concentrations in the ponds water through an air injection system. This will help decrease As concentrations in two ways: (1) by oxidizing arsenite species to arsenate species, which are less mobile and less toxic; and (2) by providing more Fe oxide species, thus enhancing the As coprecipitation with Fe.
- Addition of iron-based adsorbents to increase As stabilization in the sediments by increasing the sediments' adsorption capacity.
- Dredging the WSP sediments on a regular basis to help prevent the release of As and Fe from sediments to the water and to increase the efficiency of the WSP system.
- To improve the fences around the ponds to prohibit animals from entering the pond system, such as the two beavers who inhabited Pond 2 in 2020.

This study suggests that several topics be further explored including:

- Monitoring the pond sediment As and Fe concentrations over the winter season to provide a variation on a one-year cycle.
- Sampling the sediments from different areas of a pond to determine how As and Fe concentrations change over a pond's length and width.
- Performing the leaching experiments at low temperatures to determine the sediment leaching potentials to release As and Fe in winter conditions.
- Performing the leaching experiments in the presence of adsorbents such as agricultural wastes to investigate how sediment As and Fe leaching is affected.
- Performing two more leaching rate experiments, one using autoclaved sediments to investigate how the absence of microbial activities can affect the leaching potentials, and one with sediments containing molasses.
- Performing the leaching rate experiment with sediments sampled via a core sampler to investigate how mixing of sediments can affect the leaching potential.

- Performing an experiment similar to the leaching rate experiment using overlying water concentrated with As and Fe to evaluate the sediments efficiency in removing high concentrations of As and Fe.
- Modeling the ponds using PHREEQC software that simulates As and Fe flow and transport in the pond system to understand the Fe and As transport in the pond system under varying scenarios such as flowrate, pollution load and temperature.
- Measuring the As and Fe species in the ponds to evaluate the efficiency of the PHREEQC software in predicting As and Fe speciation in DWTP wastewaters.

# Appendix: Chapter 3 Supplementary Information

# A.1 2019 and 2020 sediments chemistry

# A.1.1 2019 July sediments chemistry

Table A.1: 2019 July	sediments chemistry
----------------------	---------------------

Parameter	Units	P1	P2	P3	P4	P5
Organic / Inorganic Carbon (Soil)						
Total Organic Carbon	%	13.4	8.07	6.11	10.5	5
Saturated Paste Extractables (Soil)						
% Saturation	%	341	488	96.7	383	220
Ammonia, Total (as N)	mg/L	< 0.80	14.3	1.84	5.09	8.13
SAR	SAR	5.44	6.03	5.13	5.83	4.72
Calcium (Ca)	mg/L	367	317	308	382	222
Calcium (Ca)	mg/kg	1250	1550	298	1460	489
Chloride (Cl)	mg/L	155	172	152	146	121
Chloride (Cl)	mg/kg	527	840	147	559	267
Conductivity (EC)	dS m-1	4.24	4.58	3.92	4.61	3.47
Magnesium (Mg)	mg/L	199	236	195	232	160
Magnesium (Mg)	mg/kg	679	1150	189	888	352
pH	pН	7.26	7.30	7.49	7.20	7.24
Metals (Soil)						
Aluminum (Al)	mg/kg	123000	26800	18600	82000	21100
Antimony (Sb)	mg/kg	0.16	0.12	0.14	0.14	0.12
Arsenic (As)	mg/kg	317	164	60.8	349	46.5
Barium (Ba)	mg/kg	237	95.5	41.6	242	83.7
Beryllium (Be)	mg/kg	0.42	0.24	0.21	0.33	0.21
Bismuth (Bi)	mg/kg	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20
Boron (B)	mg/kg	95.0	22.0	17.6	52.6	16.9
Cadmium (Cd)	mg/kg	0.067	0.092	0.112	0.077	0.139
Calcium (Ca)	mg/kg	28900	121000	75600	81200	85400
-----------------	-------	---------	---------	---------	---------	--------
Chromium (Cr)	mg/kg	4.05	3.58	31.8	4.09	8.80
Cobalt (Co)	mg/kg	6.27	6.95	3.94	7.95	4.50
Copper (Cu)	mg/kg	22.3	7.17	7.21	14.0	11.7
Iron (Fe)	mg/kg	25900	21300	10000	35400	17600
Lead (Pb)	mg/kg	2.17	1.55	1.86	1.86	3.04
Lithium (Li)	mg/kg	66.1	14.2	14.7	26.6	18.7
Magnesium (Mg)	mg/kg	3800	10800	18900	5280	8360
Manganese (Mn)	mg/kg	13000	12700	3910	22200	6090
Molybdenum (Mo)	mg/kg	10.2	16.5	7.05	10.0	7.59
Nickel (Ni)	mg/kg	8.09	7.18	19.3	7.49	11.0
Phosphorus (P)	mg/kg	6840	3020	1560	8660	1990
Potassium (K)	mg/kg	380	500	450	310	670
Selenium (Se)	mg/kg	0.89	0.41	0.30	0.76	0.40
Silver (Ag)	mg/kg	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10
Sodium (Na)	mg/kg	2240	2930	778	3040	1390
Strontium (Sr)	mg/kg	1540	772	373	1230	483
Sulfur (S)	mg/kg	7800	16500	3500	21400	12800
Thallium (Tl)	mg/kg	< 0.050	< 0.050	< 0.050	< 0.050	0.093
Tin (Sn)	mg/kg	<1.0	<1.0	<1.0	<1.0	<1.0
Titanium (Ti)	mg/kg	37.1	48.4	98.4	32.9	74.9
Tungsten (W)	mg/kg	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50
Uranium (U)	mg/kg	13.3	5.55	1.82	10.7	3.67
Vanadium (V)	mg/kg	14.7	7.94	9.97	11.0	9.83
Zinc (Zn)	mg/kg	18.5	14.5	16.3	14.0	21.6
Zirconium (Zr)	mg/kg	5.3	2.5	2.3	4.3	2.7

## A.1.2 2019 August sediments chemistry

Table	A.2:	2019	August	sediments	chemistry
-------	------	------	--------	-----------	-----------

Parameter	Units	P1	P2	P3	P4	P5
Organic / Inorganic Carbon (Soil)						
Total Organic Carbon	%	7.99	6.5	18.6	8.28	5.3
Plant Available Nutrients (Soil)						
Available Ammonium-N	mg/kg	6.7	22.7	7.2	12.4	42.8
Saturated Paste Extractables (Soil)						
SAR	SAR	6.06	6	4.74	6.08	5.07
Calcium (Ca)	mg/L	386	302	260	412	262
Calcium (Ca)	mg/kg	1260	1020	952	1620	692
Chloride (Cl)	mg/L	185	191	125	173	157
Chloride (Cl)	mg/kg	600	640	460	680	410
Conductivity Sat. Paste	dS m-1	4.26	4.29	3.45	4.80	3.78
Magnesium (Mg)	mg/L	178	215	152	238	171
Magnesium (Mg)	mg/kg	581	724	556	941	451
pH in Saturated Paste	pН	7.56	7.46	7.47	7.26	7.40
Potassium (K)	mg/L	25	28	23	<25	24
Potassium (K)	mg/kg	82	93	83	<99	62
% Saturation	%	326	337	367	395	264
Sodium (Na)	mg/L	574	558	389	627	430
Sodium (Na)	mg/kg	1870	1880	1430	2470	1130
Sulfur (as SO4)	mg/L	2260	1880	1580	2370	1540
Sulfur (as SO4)	mg/kg	7370	6340	5800	9340	4060
TGR(sodic)	t/ha	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10
TGR(brine)	t/ha	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10
Metals (Soil)						
Aluminum (Al)	mg/kg	120000	30700	86400	71000	24400
Antimony (Sb)	mg/kg	0.20	0.13	0.17	0.19	0.13

Arsenic (As)	mg/kg	454	185	350	323	58.6
Barium (Ba)	mg/kg	273	99.6	237	264	181
Beryllium (Be)	mg/kg	0.21	0.28	0.76	0.35	0.22
Bismuth (Bi)	mg/kg	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20
Boron (B)	mg/kg	114	25.2	62.3	53.9	21.0
Cadmium (Cd)	mg/kg	0.078	0.098	0.071	0.088	0.209
Calcium (Ca)	mg/kg	35500	106000	42800	81800	88300
Chromium (Cr)	mg/kg	3.08	3.62	4.20	4.44	6.36
Cobalt (Co)	mg/kg	7.68	7.27	8.99	6.74	4.88
Copper (Cu)	mg/kg	17.8	7.31	12.4	13.3	9.20
Iron (Fe)	mg/kg	43500	21800	29500	33200	19400
Lead (Pb)	mg/kg	3.48	1.69	1.71	1.70	2.19
Lithium (Li)	mg/kg	46.3	15.5	28.1	24.2	17.8
Magnesium (Mg)	mg/kg	3820	9660	4660	5240	6800
Manganese (Mn)	mg/kg	9420	14800	19100	22300	7600
Molybdenum (Mo)	mg/kg	12.5	11.3	8.08	16.4	8.78
Nickel (Ni)	mg/kg	7.09	7.67	10.2	8.16	10.5
Phosphorus (P)	mg/kg	6060	2690	5910	8630	2180
Potassium (K)	mg/kg	360	480	390	310	610
Selenium (Se)	mg/kg	0.82	0.37	0.92	0.66	0.43
Silver (Ag)	mg/kg	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10
Sodium (Na)	mg/kg	2200	2550	2170	2680	1460
Strontium (Sr)	mg/kg	1530	695	1310	1130	582
Sulfur (S)	mg/kg	9800	14900	9900	19500	16000
Thallium (Tl)	mg/kg	< 0.050	< 0.050	< 0.050	< 0.050	0.098
Tin (Sn)	mg/kg	<1.0	<1.0	<1.0	<1.0	<1.0
Titanium (Ti)	mg/kg	27.8	66.8	61.0	40.4	90.7
Tungsten (W)	mg/kg	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50
Uranium (U)	mg/kg	15.8	6.04	11.0	8.33	4.13
Vanadium (V)	mg/kg	15.1	9.32	14.9	10.2	10.8
Zinc (Zn)	mg/kg	20.1	13.6	14.0	14.5	20.4
Zirconium (Zr)	mg/kg	3.9	2.7	8.1	4.1	2.1

### A.1.3 2019 October sediments chemistry

Table A.3: 2019 October sediments chemistry	
---------------------------------------------	--

Parameter	Units	P1	P2	P3	P4	P5
Organic / Inorganic Carbon (Soil)						
Inorganic Carbon	%	1.44	2.67	1.82	3.40	5.97
Inorganic Carbon (as CaCO3 Equivalent)	%	12	22.2	15.2	28.3	49.8
Total Carbon by Combustion	%	9.66	8.69	13.2	10.1	14.1
Total Organic Carbon	%	8.22	6.02	11.4	6.7	8.1
Plant Available Nutrients (Soil)						
Available Ammonium-N	mg/kg	7.6	16.3	5.8	26.7	105
Saturated Paste Extractables (Soil)						
SAR	SAR	6.63	7.13	6.18	5.83	5.6
Calcium (Ca)	mg/L	472	352	409	437	366
Calcium (Ca)	mg/kg	1820	942	1680	1560	1620
Chloride (Cl)	mg/L	270	190	192	225	187
Chloride (Cl)	mg/kg	1020	500	790	800	830
Conductivity Sat. Paste	dS m-1	5.16	5.14	4.89	4.95	4.41
Magnesium (Mg)	mg/L	236	260	226	241	226
Magnesium (Mg)	mg/kg	907	696	930	858	1000
pH in Saturated Paste	pH	7.28	7.30	7.25	7.16	7.23
Potassium (K)	mg/L	33	31	26	<25	26
Potassium (K)	mg/kg	128	83	100	<89	120
% Saturation	%	384	268	411	356	441
Sodium (Na)	mg/L	707	724	627	612	553
Sodium (Na)	mg/kg	2720	1940	2580	2180	2440
Sulfur (as SO4)	mg/L	2410	2340	2350	2260	1980
Sulfur (as SO4)	mg/kg	9260	6270	9680	8050	8750
TGR(sodic)	t/ha	< 0.10	1.14	< 0.10	< 0.10	< 0.10
TGR(brine)	t/ha	< 0.10	0.66	< 0.10	< 0.10	< 0.10

Metals (Soil)						
Aluminum (Al)	mg/kg	65800	23900	62400	56600	20700
Antimony (Sb)	mg/kg	0.19	0.17	0.16	0.15	0.10
Arsenic (As)	mg/kg	400	102	252	202	42.5
Barium (Ba)	mg/kg	209	79.9	202	127	92.6
Beryllium (Be)	mg/kg	0.42	0.26	0.65	0.21	0.17
Bismuth (Bi)	mg/kg	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20
Boron (B)	mg/kg	63.3	17.3	42.6	42.9	20.0
Cadmium (Cd)	mg/kg	0.084	0.104	0.055	0.130	0.090
Calcium (Ca)	mg/kg	37100	77900	39400	84700	164000
Chromium (Cr)	mg/kg	16.9	119	3.87	3.62	2.93
Cobalt (Co)	mg/kg	20.7	7.17	9.22	6.28	4.13
Copper (Cu)	mg/kg	11.3	9.44	11.0	12.5	8.76
Iron (Fe)	mg/kg	44200	17800	24400	27600	22100
Lead (Pb)	mg/kg	2.92	1.81	1.56	2.06	1.75
Lithium (Li)	mg/kg	43.9	14.7	26.9	38.2	23.4
Magnesium (Mg)	mg/kg	5800	12500	3450	5760	7390
Manganese (Mn)	mg/kg	21500	7810	17400	14100	8480
Molybdenum (Mo)	mg/kg	35.5	17.8	6.15	38.5	15.0
Nickel (Ni)	mg/kg	19.0	67.1	8.56	8.56	8.83
Phosphorus (P)	mg/kg	6890	2120	5950	5420	2660
Potassium (K)	mg/kg	1050	600	430	340	560
Selenium (Se)	mg/kg	0.55	0.34	0.63	0.49	0.46
Silver (Ag)	mg/kg	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10
Sodium (Na)	mg/kg	2670	1930	1910	2280	2470
Strontium (Sr)	mg/kg	814	430	880	840	747
Sulfur (S)	mg/kg	6400	10700	8400	20700	23000
Thallium (Tl)	mg/kg	0.133	0.054	< 0.050	0.055	0.074
Tin (Sn)	mg/kg	<1.0	<1.0	<1.0	<1.0	<1.0
Titanium (Ti)	mg/kg	58.5	146	48.9	37.4	41.8
Tungsten (W)	mg/kg	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50
Uranium (U)	mg/kg	7.13	4.62	7.48	7.91	4.71

Vanadium (V)	mg/kg	14.9	13.9	11.6	9.00	6.13
Zinc (Zn)	mg/kg	23.7	16.4	14.0	14.2	13.0
Zirconium (Zr)	mg/kg	4.9	3.2	6.7	3.2	1.6

## A.1.4 2020 May sediments chemistry

Table A.4: 2020 May	sediments chemistry
---------------------	---------------------

Parameter	Units	P1	P2	P3	P4	P5	Downstream
Organic /Inorganic Carbon (Soil)							
Total Organic	%	9.49	9.93	11.6	9.24	4.5	3.4
Carbon Plant Available							
Nutrients (Soil)							
Available	mg/kg	3.5	22.8	10.5	15.2	24.4	12.6
Ammonium-N Saturated Paste							
Extractables (Soil)							
SAR	SAR	13	13.3	15.3	13	7.47	6.44
Calcium (Ca)	mg/L	301	450	365	487	593	645
Calcium (Ca)	mg/kg	581	610	577	628	585	363
Chloride (Cl)	mg/L	390	1110	870	1530	870	750
Chloride (Cl)	mg/kg	740	1510	1370	1970	853	420
Conductivity Sat. Paste	dS m-1	5.48	7.34	6.70	7.18	6.89	6.47
Magnesium (Mg)	mg/L	86	167	101	146	321	308
Magnesium (Mg)	mg/kg	165	227	159	188	316	173
pH in Saturated Paste	pН	8.15	8.17	8.19	8.13	7.79	7.67
Potassium (K)	mg/L	52	52	61	55	57	67
Potassium (K)	mg/kg	100	71	97	71	56	38
% Saturation	%	193	136	158	129	98.6	56.2
Sodium (Na)	mg/L	993	1300	1280	1280	909	794
Sodium (Na)	mg/kg	1910	1760	2020	1640	896	447
Sulfur (as SO4)	mg/L	2450	3900	3380	4030	4150	4110
Sulfur (as SO4)	mg/kg	4720	5290	5360	5190	4090	2310
TGR(sodic)	t/ha	12.5	9.18	13.6	8.4	0.79	< 0.10
TGR(brine)	t/ha	17.4	21.4	26.3	19.3	1.29	< 0.10
Metals (Soil)							
Aluminum (Al)	mg/kg	66700	48800	75700	61900	12500	6390
Antimony (Sb)	mg/kg	0.19	0.14	0.17	0.14	0.15	0.13

Arsenic (As)	mg/kg	240	188	292	237	25.6	34.8
Barium (Ba)	mg/kg	144	141	218	168	79.6	77.1
Beryllium (Be)	mg/kg	0.32	0.33	0.41	0.24	0.18	0.17
Bismuth (Bi)	mg/kg	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20
Boron (B)	mg/kg	62.8	33.9	57.0	41.2	11.6	13.7
Cadmium (Cd)	mg/kg	0.078	0.119	0.083	0.074	0.185	0.188
Calcium (Ca)	mg/kg	28100	81800	58500	81700	86400	72900
Chromium (Cr)	mg/kg	4.67	5.97	3.27	5.14	9.09	47.6
Cobalt (Co)	mg/kg	7.11	6.86	7.58	5.77	4.96	5.16
Copper (Cu)	mg/kg	15.7	11.4	14.7	11.7	12.8	8.68
Iron (Fe)	mg/kg	21800	23600	29300	26400	15800	15100
Lead (Pb)	mg/kg	2.18	2.29	1.79	1.52	3.30	2.54
Lithium (Li)	mg/kg	28.2	21.5	31.2	21.6	14.1	7.3
Magnesium (Mg)	mg/kg	3250	7820	4130	6340	9280	19700
Manganese (Mn)	mg/kg	12800	14200	23400	20900	4060	4130
Molybdenum (Mo)	mg/kg	9.66	14.1	14.6	8.98	12.0	4.07
Nickel (Ni)	mg/kg	7.78	8.85	7.27	7.34	14.2	29.2
Phosphorus (P)	mg/kg	5740	5010	7470	6040	1220	997
Potassium (K)	mg/kg	580	550	380	380	820	760
Selenium (Se)	mg/kg	0.59	0.55	0.66	0.52	0.36	0.45
Silver (Ag)	mg/kg	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10
Sodium (Na)	mg/kg	2190	2500	2310	2120	1390	812
Strontium (Sr)	mg/kg	795	875	1130	954	332	157
Sulfur (S)	mg/kg	5300	14400	13800	14100	10300	4900
Thallium (Tl)	mg/kg	< 0.050	0.053	< 0.050	< 0.050	0.119	0.090
Tin (Sn)	mg/kg	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Titanium (Ti)	mg/kg	35.4	59.0	39.9	47.0	72.3	104
Tungsten (W)	mg/kg	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50
Uranium (U)	mg/kg	6.84	6.40	9.86	7.15	2.54	1.35
Vanadium (V)	mg/kg	10.6	9.93	11.0	9.35	11.0	11.4
Zinc (Zn)	mg/kg	18.0	17.6	14.5	12.8	23.7	31.7
Zirconium (Zr)	mg/kg	4.1	4.3	4.1	2.9	2.0	1.3

### A.1.5 2020 June sediments chemistry

TGR(brine)

Metals (Soil)

Aluminum (Al)

Antimony (Sb)

t/ha

mg/kg

mg/kg

25.9

59000

0.21

Parameter	Units	P1	P2	P3	P4	P5	Upstream
Organic/Inorganic							
Carbon (Soil)	<u> </u>	11.7	0.07	15.0	11.1	<u> </u>	1.05
Total Organic Carbon	%	11.7	9.27	15.2	11.1	6.4	4.25
Plant Available							
Nutrients (Soil)							
Available	mg/kg	4.4	15.3	4.5	13.8	31.3	12.1
Ammonium-N	0 0						
Saturated Paste							
<b>Extractables (Soil)</b>							
SAR	SAR	15.7	17.3	12.8	14.1	9.7	0.52
Calcium (Ca)	mg/L	326	580	359	400	599	655
Calcium (Ca)	mg/kg	509	807	731	728	874	512
Chloride (Cl)	mg/L	490	1800	380	920	1880	416
Chloride (Cl)	mg/kg	760	2500	780	1670	2740	325
Conductivity Sat. Paste	dS m-1	6.49	10.5	5.80	6.73	7.64	4.36
Magnesium (Mg)	mg/L	99	299	93	119	337	400
Magnesium (Mg)	mg/kg	154	416	190	217	491	313
pH in Saturated Paste	pH	8.16	8.09	8.10	8.09	7.85	7.26
Potassium (K)	mg/L	59	76	48	57	67	56
Potassium (K)	mg/kg	92	106	98	103	98	44
% Saturation	%	156	139	204	182	146	78.2
Sodium (Na)	mg/L	1260	2060	1060	1250	1200	68
Sodium (Na)	mg/kg	1980	2870	2150	2280	1740	53
Sulfur (as SO4)	mg/L	3030	6440	2970	3500	4900	3200
Sulfur (as SO4)	mg/kg	4740	8970	6050	6370	7140	2500
TGR(sodic)	t/ha	14.1	14.5	12.9	13.7	4.66	< 0.10

< 0.10

5130

0.18

Table A 5. 2020 June sediments chemistry

>50

32200

0.12

20.7

63600

0.16

27.8

60700

0.14

13

24200

0.19

Arsenic (As)	mg/kg	205	148	273	278	56.4	3.39
Barium (Ba)	mg/kg	215	121	153	192	103	99.7
Beryllium (Be)	mg/kg	0.42	0.31	0.50	0.33	0.20	0.27
Bismuth (Bi)	mg/kg	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20
Boron (B)	mg/kg	40.9	22.7	44.8	39.1	19.7	11.1
Cadmium (Cd)	mg/kg	0.180	0.112	0.062	0.067	0.175	0.298
Calcium (Ca)	mg/kg	40500	117000	41800	74000	127000	57600
Chromium (Cr)	mg/kg	7.28	6.79	2.44	2.69	3.70	14.1
Cobalt (Co)	mg/kg	7.54	6.73	6.52	6.07	8.47	4.48
Copper (Cu)	mg/kg	13.4	8.30	14.2	11.0	15.2	10.5
Iron (Fe)	mg/kg	20900	21600	22100	28800	25100	16000
Lead (Pb)	mg/kg	2.30	1.71	1.45	1.49	2.78	4.52
Lithium (Li)	mg/kg	29.8	18.4	19.9	21.6	23.1	7.2
Magnesium (Mg)	mg/kg	6500	7850	3010	3880	10200	13700
Manganese (Mn)	mg/kg	15400	11700	16500	19700	8320	1120
Molybdenum (Mo)	mg/kg	10.4	16.3	9.18	8.64	19.4	1.41
Nickel (Ni)	mg/kg	11.8	9.61	7.00	6.05	26.9	12.8
Phosphorus (P)	mg/kg	4360	3580	5300	7340	2640	935
Potassium (K)	mg/kg	590	540	320	340	680	1150
Selenium (Se)	mg/kg	0.66	0.54	0.71	0.59	0.65	0.85
Silver (Ag)	mg/kg	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10
Sodium (Na)	mg/kg	2240	3400	2400	2730	2330	165
Strontium (Sr)	mg/kg	948	818	1060	1030	649	69.7
Sulfur (S)	mg/kg	7700	17300	9900	16500	20500	4900
Thallium (Tl)	mg/kg	0.062	< 0.050	< 0.050	< 0.050	0.129	0.135
Tin (Sn)	mg/kg	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Titanium (Ti)	mg/kg	67.3	47.4	32.3	27.8	47.3	125
Tungsten (W)	mg/kg	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50
Uranium (U)	mg/kg	9.00	7.50	9.72	8.98	5.16	3.13

## A.1.6 2020 July sediments chemistry

Table A.6:	2020 Jul	y sediments	chemistry
------------	----------	-------------	-----------

Parameter	Units	P1	P2	P3	P4	P5
Organic / Inorganic Carbon (Soil)						
Total Organic Carbon	%	11	6.5	11.3	9.05	6.2
Plant Available Nutrients (Soil)						
Available Ammonium-N	mg/kg	3.2	18.1	7.9	22.8	36.7
Saturated Paste Extractables (Soil)						
SAR	SAR	19.7	19.6	16.5	14.2	8.44
Calcium(Ca)	mg/L	523	517	393	500	667
Calcium(Ca)	mg/kg	818	593	659	958	1130
Chloride (Cl)	mg/L	830	1040	820	1860	600
Chloride (Cl)	mg/kg	1310	1190	1380	3560	1010
Conductivity Sat. Paste	dS m <sup>-1</sup>	10	11	7.37	7.97	7.77
Magnesium (Mg)	mg/L	189	312	123	214	391
Magnesium (Mg)	mg/kg	296	358	207	410	662
pH in Saturated Paste	pН	8.12	8.02	8.11	7.96	7.79
Potassium (K)	mg/L	64	82	54	52	60
Potassium (K)	mg/kg	100	94	90	100	102
% Saturation	%	156	115	168	192	169
Sodium (Na)	mg/L	2070	2290	1470	1500	1110
Sodium (Na)	mg/kg	3230	2630	2460	2880	1880
Sulfur (as SO4)	mg/L	5220	6280	4020	5100	4900
Sulfur (as SO4)	mg/kg	8160	7210	6750	9790	8290
TGR(sodic)	t/ha	19.4	14.2	16.3	14.6	3.16
TGR(brine)	t/ha	>50	>50	38.3	42.3	8.43
Metals (Soil)						
Aluminum (Al)	mg/kg	69300	19600	73700	54800	21000
Antimony (Sb)	mg/kg	0.21	0.11	0.17	0.15	0.17

Arsenic (As)	mg/kg	393	145	239	251	50
Barium (Ba)	mg/kg	242	90	188	154	131
Beryllium (Be)	mg/kg	0.37	0.22	0.39	0.27	0.22
Bismuth (Bi)	mg/kg	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20
Boron (B)	mg/kg	63.9	19.3	56.9	44	23.3
Cadmium (Cd)	mg/kg	0.221	0.085	0.072	< 0.50	0.194
Calcium (Ca)	mg/kg	55600	137000	50400	82400	146000
Chromium (Cr)	mg/kg	7.67	6.87	4.19	2.96	5.43
Cobalt (Co)	mg/kg	12.4	5.93	6.94	5.44	5.38
Copper (Cu)	mg/kg	17.6	5.71	14	11.9	13.7
Iron (Fe)	mg/kg	34300	19200	23200	30300	21300
Lead (Pb)	mg/kg	3.04	1.47	1.69	1.6	3.48
Lithium (Li)	mg/kg	31	13.8	23.3	23.4	19.7
Magnesium (Mg)	mg/kg	6610	8290	3900	4950	8610
Manganese (Mn)	mg/kg	30500	12500	21100	17800	7960
Molybdenum (Mo)	mg/kg	15	12.6	19.8	66.6	12.9
Nickel (Ni)	mg/kg	13.2	7.44	7.72	6.76	12.6
Phosphorus (P)	mg/kg	7730	3520	7050	7200	2180
Potassium (K)	mg/kg	660	540	370	380	830
Selenium (Se)	mg/kg	0.71	0.31	0.69	0.65	0.45
Silver (Ag)	mg/kg	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10
Sodium (Na)	mg/kg	4310	3320	2710	3200	2250
Strontium (Sr)	mg/kg	1260	886	1170	1060	735
Sulfur (S)	mg/kg	10500	12200	12500	23200	16700
Thallium (Tl)	mg/kg	0.067	< 0.050	< 0.050	< 0.050	0.12
Tin (Sn)	mg/kg	<1.0	<1.0	<1.0	<1.0	<1.0
Titanium (Ti)	mg/kg	47.1	57	32.1	26.6	59.6
Tungsten (W)	mg/kg	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50
Uranium (U)	mg/kg	8.85	4.78	9.1	8.83	4.06
Vanadium (V)	mg/kg	12.1	7.29	9.65	8.17	9.62
Zinc (Zn)	mg/kg	30.5	14	11.9	11.2	22.1
Zirconium (Zr)	mg/kg	4.9	2.2	4.4	4	2.8

### A.2 ANOVA Test Results for the Ponds Sediment As and Fe Concentrations

**Table A.7:** A) ANOVA test and B) Tukey's post hoc test results on 2019 and 2020 ponds As concentrations indicating significant (p<0.05) differences between ponds (July 2019 Pond 3 results were excluded since they were outliers).

(A)					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	319966.627	4	79991.657	25.126	.000
Within Groups	76407.720	24	3183.655		
Total	396374.347	28			

#### **(B)**

		Mean Difference (h			95% Confide	ence Interval
Pond #	Pond #	J)	Std. Error	Sig.	Lower Bound	Upper Bound
1	2	179.5000	32.5763	.000	83.529	275.471
	3	53.6333	34.1664	.530	-47.022	154.288
	4	61.5000	32.5763	.350	-34.471	157.471
	5	288.2333	32.5763	.000	192.262	384.204
2	1	-179.5000	32.5763	.000	-275.471	-83.529
	3	-125.8667	34.1664	.009	-226.522	-25.212
	· 4	-118.0000	32.5763	.011	-213.971	-22.029
	5	108.7333	32.5763	.021	12.762	204.704
3	1	-53.6333	34.1664	.530	-154.288	47.022
	2	125.8667	34.1664	.009	25.212	226.522
	4	7.8667	34.1664	.999	-92.788	108.522
	5	234.6000	34.1664	.000	133.945	335.255
4	1	-61.5000	32.5763	.350	-157.471	34.471
	2	118.0000	32.5763	.011	22.029	213.971
	3	-7.8667	34.1664	.999	-108.522	92.788
	5	226.7333	32.5763	.000	130.762	322.704
5	1	-288.2333	32.5763	.000	-384.204	-192.262
	2	-108.7333	32.5763	.021	-204.704	-12.762
	3	-234.6000	34.1664	.000	-335.255	-133.945
	4	-226.7333	32.5763	.000	-322.704	-130.762

**Table A.8:** A) ANOVA test and B) Tukey's post hoc test results on 2019 and 2020 ponds Fe concentrations indicating significant (p<0.05) differences between ponds (July 2019 Pond 3 results were excluded since they were outliers).

	Sum of Squares	df	Mean Squ	iare	F	Sig.
n Groups	675473620.7	4	1688684	05.2 5.568		.003
roups	727885000.0	24	3032854	1.67		
	1403358621	28				
	Mean Difference (I-			9	5% Confide	ence Interval
Pond #	J)	Std. Error	Sig.	Low	er Bound	Upper Bound
2	10883.333	3179.546	.017		1516.30	20250.37
3	6066.667	3334.736	.386		-3757.56	15890.90
4	1316.667	3179.546	.993		-8050.37	10683.70
5	11550.000	3179.546	.011		2182.97	20917.03
ୀ	-10883.333	3179.546	.017	-1	20250.37	-1516.30
3	-4816.667	3334.736	.606	-1	14640.90	5007.56
4	-9566.667	3179.546	.044	-1	18933.70	-199.63
5	666.667	3179.546	1.000		-8700.37	10033.70
1	-6066.667	3334.736	.386	-1	15890.90	3757.56
2	4816.667	3334.736	.606		-5007.56	14640.90
4	-4750.000	3334.736	.619	-1	14574.23	5074.23
5	5483.333	3334.736	.485		-4340.90	15307.56
1	-1316.667	3179.546	.993	-1	10683.70	8050.37
2	9566.667	3179.546	.044		199.63	18933.70
3	4750.000	3334.736	.619		-5074.23	14574.23
5	10233.333	3179.546	.027		866.30	19600.37
1	-11550.000	3179.546	.011	-1	20917.03	-2182.97
2	-666.667	3179.546	1.000	-1	10033.70	8700.37
3	-5483.333	3334.736	.485	-1	15307.56	4340.90
4	-10233.333	3179.546	.027	-1	19600.37	-866.30
	Pond # 2 3 4 5 1 3 4 5 1 2 4 5 1 2 4 5 1 2 3 5 1 2 3 5 1 2 3 3 5 1 2 3 3 5 1 2 3 3 5 1 2 3 3 5 1 2 3 3 5 1 3 4 5 3 3 4 5 5 1 2 3 3 5 5 1 1 2 3 3 5 5 1 1 2 3 3 5 5 1 1 2 3 3 5 5 1 1 2 3 3 5 5 1 1 2 3 1 2 3 1 5 5 1 1 5 5 1 1 5 5 5 1 5 5 5 1 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	Sum of Squares       Groups     675473620.7       Froups     727885000.0       1403358621     1403358621       Pond #     J)       2     10883.333°       3     6066.667       4     1316.667       5     11550.000°       1     -10883.333°       3     -4816.667       4     -9566.667°       5     6666.667       1     -6066.667       2     4816.667       4     -4750.000       5     5483.333       1     -1316.667       2     9566.667°       3     4750.000       5     10233.333°       1     -11550.000°       2     -666.667       3     -5483.333       1     -11550.000°       2     -666.667       3     -5483.333	Sum of Squares     df       oroups     675473620.7     4       oroups     727885000.0     24       1403358621     28       Pond #     1403358621     28       Mean Difference (I- J)     Std. Error       2     10883.333 <sup>*</sup> 3179.546       3     6066.667     3334.736       4     1316.667     3179.546       5     11550.000 <sup>*</sup> 3179.546       1     -10883.333 <sup>*</sup> 3179.546       3     -4816.667     334.736       4     -9566.667 <sup>*</sup> 3179.546       5     6666.667     3179.546       1     -6066.667     3334.736       4     -9566.667 <sup>*</sup> 3179.546       5     5483.333     3334.736       4     -4750.000     3334.736       1     -1316.667     3179.546       3     4750.000     3334.736       4     -4750.000     3334.736       2     9566.667 <sup>*</sup> 3179.546       3     4750.000     3334.736 <td>Sum of Squares     df     Mean Squ 1688844       aroups     675473620.7     4     16886844       aroups     727885000.0     24     30328544       aroups     727885000.0     24     30328544       aroups     727885000.0     24     30328544       aroups     1403358621     28     28       Pond #     J)     Std. Error     Sig.       2     10883.333     3179.546     .017       3     6066.667     3334.736     .386       4     1316.667     3179.546     .011       1     -10883.333     3179.546     .011       1     -10883.333     3179.546     .0117       3     -4816.667     3334.736     .606       4     -9566.667*     3179.546     .044       5     6666.667     3334.736     .606       4     -4750.000     3334.736     .619       5     5483.333     3334.736     .044       3     4750.000     3334.736     .044</td> <td>Sum of Squares     df     Mean Square       Groups     675473620.7     4     168868405.2       iroups     727885000.0     24     30328541.67       1403358621     28     28       Mean Difference (I- J)     Std. Error     Sig.     Low       2     10883.333     3179.546     .017     2       3     6066.667     3334.736     .386     4       4     1316.667     3179.546     .011     -1       1     -10883.333     3179.546     .011     -1       3     -4816.667     3334.736     .6066        4     -9566.667*     3179.546     .014        3     -4816.667     3334.736     .606        4     -9566.667*     3179.546     .044        5     6666.667     3179.546     .044        2     4816.667     3334.736     .606        4     -9566.667*     3179.546     .044     -     -  <t< td=""><td>Sum of Squares     df     Mean Square     F       a Groups     675473620.7     4     168868405.2     5.568       aroups     727885000.0     24     30328541.67     1403358621     28       Pond #     1403358621     28    </td></t<></td>	Sum of Squares     df     Mean Squ 1688844       aroups     675473620.7     4     16886844       aroups     727885000.0     24     30328544       aroups     727885000.0     24     30328544       aroups     727885000.0     24     30328544       aroups     1403358621     28     28       Pond #     J)     Std. Error     Sig.       2     10883.333     3179.546     .017       3     6066.667     3334.736     .386       4     1316.667     3179.546     .011       1     -10883.333     3179.546     .011       1     -10883.333     3179.546     .0117       3     -4816.667     3334.736     .606       4     -9566.667*     3179.546     .044       5     6666.667     3334.736     .606       4     -4750.000     3334.736     .619       5     5483.333     3334.736     .044       3     4750.000     3334.736     .044	Sum of Squares     df     Mean Square       Groups     675473620.7     4     168868405.2       iroups     727885000.0     24     30328541.67       1403358621     28     28       Mean Difference (I- J)     Std. Error     Sig.     Low       2     10883.333     3179.546     .017     2       3     6066.667     3334.736     .386     4       4     1316.667     3179.546     .011     -1       1     -10883.333     3179.546     .011     -1       3     -4816.667     3334.736     .6066        4     -9566.667*     3179.546     .014        3     -4816.667     3334.736     .606        4     -9566.667*     3179.546     .044        5     6666.667     3179.546     .044        2     4816.667     3334.736     .606        4     -9566.667*     3179.546     .044     -     - <t< td=""><td>Sum of Squares     df     Mean Square     F       a Groups     675473620.7     4     168868405.2     5.568       aroups     727885000.0     24     30328541.67     1403358621     28       Pond #     1403358621     28    </td></t<>	Sum of Squares     df     Mean Square     F       a Groups     675473620.7     4     168868405.2     5.568       aroups     727885000.0     24     30328541.67     1403358621     28       Pond #     1403358621     28

(A)

### A.3 ANOVA Test Results for the Ponds Redox Potential and DO

### Concentration

**Table A.9:** A) ANOVA test and B) Tukey's post hoc test results on 2020 ponds redox condition indicating significant (p<0.05) differences between ponds.

(A)							
		Sum of Squares	df	Mean Square	F	Sig.	
Between Grou	ups	1064833.951	4	266208.488	30.695	.000	
Within Groups	s	1509042.380	174	8672.657			
Total		2573876.331	178				
( <b>B</b> )							
	_		Mean Difference (l-			95% Confid	ence Interval
Pond #	P	ond #	J)	Std. Error	Sig.	Lower Bound	Upper Bound
1	_2		-17.02157	7 22.27073	.940	-78.4129	44.3698
	3		125.65906	22.12407	.000	64.6720	186.6461
	4		174.31454	22.27073	.000	112.9232	235.7059
	5		7.54510	22.27073	.997	-53.8463	68.9365
2	1		17.02157	7 22.27073	.940	-44.3698	78.4129
	3		142.68063	21.80145	.000	82.5829	202.7784
	4		191.33611	21.95027	.000	130.8281	251.8441
	5		24.56667	7 21.95027	.796	-35.9413	85.0746
3	1		-125.65906	22.12407	.000	-186.6461	-64.6720
	2		-142.68063	21.80145	.000	-202.7784	-82.5829
	4		48.65548	3 21.80145	.173	-11.4423	108.7532
	5		-118.11396	21.80145	.000	-178.2117	-58.0162
4	1		-174.31454	22.27073	.000	-235.7059	-112.9232
	2		-191.33611	21.95027	.000	-251.8441	-130.8281
	3		-48.65548	3 21.80145	.173	-108.7532	11.4423
	5		-166.76944	21.95027	.000	-227.2774	-106.2615
5	1		-7.54510	22.27073	.997	-68.9365	53.8463
	2		-24.56667	7 21.95027	.796	-85.0746	35.9413
	3		118.11396	21.80145	.000	58.0162	178.2117
	4		166.76944	21.95027	.000	106.2615	227.2774

**Table A.10:** A) ANOVA test and B) Tukey's post hoc test results on 2020 ponds DO concentrations indicating significant (p<0.05) differences between ponds.

**(A)** 

	Sum of Squares	df	Mean Square	$\widehat{F}^{(1)}$	Sig.
Between Groups	650.080	4	162.520	20.535	.000
Within Groups	1123.831	142	7.914		
Total	1773.912	146			

**(B)** 

		Mean Difference (I-			95% Confide	ence Interval
Pond #	Pond #	J)	Std. Error	Sig.	Lower Bound	Upper Bound
1.00	2.00	2.29333	.72637	.016	.2863	4.3004
	3.00	4.60248	.74628	.000	2.5404	6.6646
	4.00	5.01267	.72637	.000	3.0056	7.0197
	5.00	.23033	.72637	.998	-1.7767	2.2374
2.00	1.00	-2.29333	.72637	.016	-4.3004	2863
	3.00	2.30915	.74628	.020	.2471	4.3712
	4.00	2.71933	.72637	.002	.7123	4.7264
	5.00	-2.06300	.72637	.041	-4.0701	0559
3.00	1.00	-4.60248	.74628	.000	-6.6646	-2.5404
	2.00	-2.30915	.74628	.020	-4.3712	2471
	4.00	.41019	.74628	.982	-1.6519	2.4723
	5.00	-4.37215	.74628	.000	-6.4342	-2.3101
4.00	1.00	-5.01267*	.72637	.000	-7.0197	-3.0056
	2.00	-2.71933	.72637	.002	-4.7264	7123
	3.00	41019	.74628	.982	-2.4723	1.6519
	5.00	-4.78233	.72637	.000	-6.7894	-2.7753
5.00	1.00	23033	.72637	.998	-2.2374	1.7767
	2.00	2.06300	.72637	.041	.0559	4.0701
	3.00	4.37215	.74628	.000	2.3101	6.4342
	4.00	4.78233	.72637	.000	2.7753	6.7894

### A.4 Sediment As and Fe Correlation With Other Elements

Element	<b>Pearson's Correlation</b>			
	As	Fe		
Total Organic Carbon	0.623**	-		
Aluminum	0.885**	0.700**		
Ammonium-N	-0.516**	-		
Antimony	0.521**	0.474**		
Arsenic	-	0.844**		
Barium	0.848**	$0.771^{**}$		
Beryllium	0.554**	-		
Boron	0.871**	0.737**		
Cadmium	-0.451*	-		
Calcium	-0.674**	-0.363*		
Cobalt	0.577**	0.659**		
Copper	0.510**	0.455*		
Iron	0.844**	-		
Lithium	0.629**	0.607**		
Magnesium	-0.642**	-0.581**		
Manganese	0.767**	0.632**		
Phosphorus	0.877**	0.754**		
Potassium	-0.362*	-		
Selenium	0.754**	0.631**		
Sodium	0.463**	0.478**		
Strontium	0.844**	0.690**		
Titanium	-0.523**	-0.528**		
Uranium	0.858**	0.710**		
Vanadium	0.566**	0.419*		
Zirconium	0.695**	0.435*		

Table A.11: Sediment As and Fe concentrations correlations with various elements.

\*\* Correlation is significant at the 0.01 level (2-tailed).

\* Correlation is significant at the 0.05 level (2-tailed).

## A.5 PHREEQC Modeling Data

Molality
1.653e-22
1.562e-22
9.104e-24
3.802e-07
3.678e-07
1.194e-08
6.083e-09
5.105e-09
6.837e-10
2.478e-10
2.694e-05
1.895e-05
4.949e-06
3.038e-06
0.000e+00
6.589e-03
4.289e-03
1.134e-03
8.770e-04
2.719e-04

Figure A.1: 2020 Pond 1 PHREEQC modeling data

Elements	
Species	Molality
As(3)	1.894e-26
H3AsO3	1.777e-26
H2AsO3-	1.169e-27
As(5)	3.535e-07
HAsO4-2	3.421e-07
H2AsO4-	1.086e-08
Fe(2)	2.251e-11
Fe+2	1.878e-11
FeSO4	2.541e-12
FeHCO3+	9.766e-13
Fe(3)	8.981e-06
Fe (OH) 2+	5.729e-06
Fe (OH) 3	2.334e-06
Fe (OH) 4-	9.184e-07
S(-2)	0.000e+00
S(6)	6.589e-03
SO4-2	4.275e-03
CaSO4	1.133e-03
MgSO4	8.788e-04
NaSO4-	2.870e-04

Figure A.2: 2020 Pond 2 PHREEQC modeling data

Elements	
As(3)	4.541e-18
H3AsO3	4.298e-18
H2AsO3-	2.430e-19
As(5)	1.607e-07
HAsO4-2	1.544e-07
H2AsO4-	6.093e-09
Fe(2)	1.725e-07
Fe+2	1.415e-07
FeSO4	2.177e-08
FeHCO3+	7.764e-09
Fe(3)	2.702e-06
Fe (OH) 2+	1.761e-06
Fe (OH) 3	7.628e-07
Fe (OH) 4-	1.781e-07
S(-2)	0.000e+00
S(6)	7.310e-03
SO4-2	4.791e-03
CaSO4	1.188e-03
MgSO4	9.808e-04
NaSO4-	3.213e-04



Elements	
As(3)	9.650e-17
H3AsO3	9.009e-17
H2AsO3-	6.408e-18
As(5)	2.008e-07
HAsO4-2	1.945e-07
H2AsO4-	6.109e-09
Fe(2)	9.538e-07
Fe+2	7.802e-07
FeSO4	1.208e-07
FeHCO3+	4.238e-08
Fe(3)	4.076e-06
Fe (OH) 2+	2.389e-06
Fe (OH) 3	1.304e-06
Fe (OH) 4-	3.830e-07
S(-2)	0.000e+00
S(6)	7.310e-03
SO4-2	4.800e-03
CaSO4	1.187e-03
MgSO4	9.821e-04
NaSO4-	3.222e-04



Elements	
As(3)	3.804e-26
H3AsO3	3.551e-26
H2AsO3-	2.524e-27
As(5)	2.276e-07
HAsO4-2	2.203e-07
H2AsO4-	6.940e-09
Fe(2)	3.309e-11
Fe+2	2.744e-11
FeSO4	3.930e-12
FeHCO3+	1.350e-12
Fe(3)	7.723e-06
Fe (OH) 2+	4.527e-06
Fe (OH) 3	2.471e-06
Fe (OH) 4-	7.257e-07
S(-2)	0.000e+00
S(6)	6.787e-03
SO4-2	4.416e-03
CaSO4	1.120e-03
MgSO4	9.218e-04
NaSO4-	3.127e-04

Figure A.5: 2020 Pond 5 PHREEQC modeling data

# A.6 Leaching Rate Experiment Individual Reactors As And Fe Concentrations



**Figure A.6:** As and Fe concentrations in overlying water of each individual pond reactors (n=4) over 45 days