Desorption of Trace Inorganic Contaminants from Solids in Drinking Water Distribution Systems

Tiana W. Hammer
Utah State University

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DESORPTION OF TRACE INORGANIC CONTAMINANTS FROM SOLIDS IN DRINKING WATER DISTRIBUTION SYSTEMS

by

Tiana W. Hammer

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in Civil & Environmental Engineering (Environmental Engineering)

Approved:

_______________________                   _______________
David K. Stevens, Ph.D.                   Laurie McNeill, Ph.D.
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UTAH STATE UNIVERSITY
Logan, Utah

2018
ABSTRACT

DESORPTION OF TRACE INORGANIC CONTAMINANTS FROM SOLIDS IN DRINKING WATER DISTRIBUTION SYSTEMS

By

Tiana W. Hammer, Master of Science

Utah State University, 2018

Major Professor: Dr. David Stevens
Department: Civil and Environmental Engineering

Providing safe drinking water to the public is crucial; however, maintaining high quality throughout the drinking water distribution system (DWDS) can be challenging. Low-level contaminants entering the DWDS accumulate onto the pipes and toxic concentrations can later be released into the drinking water. In this study two different solids collected from flushing pipes in Park City, Utah, were assessed to determine which chemical and physical factors influence the release of the contaminants antimony (Sb), arsenic (As), chromium (Cr), copper (Cu), lead (Pb), and thallium (Tl) (termed trace inorganic contaminants, TICs), and two matrix elements known to interact with many TICs, iron (Fe) and manganese (Mn). The experiment used a full factorial design at three levels: high, low, and midpoint. The factors and their ranges were temperature (7, 16, and 25 °C), pH (6.5, 7.5, and 8.5), chlorine (0, 1, and 2 mg/L), and two competitive sorption
factors: calcium sulfate (CaSO₄, at 0, 175, and 350 mg/L) and potassium phosphate (KH₂PO₄, at 0, 1, and 2 mg/L), which are within ranges typically seen in DWDS. Solids were shaken for 24 hours in dark glass jars using a solids:water ratio comparable to DWDS. Results showed released concentrations approaching or above the maximum contaminant level (MCL), as set by the EPA, of Sb, As, Tl, and Mn. The elements Cr, Cu, Pb, and Fe were released at concentrations below the MCL or method detection limits. An influential factor was pH, where 8.5 caused maximum release of As, and pH of 6.5 caused high release of Tl and Mn. Other noteworthy factors were that the temperature of 25 °C compounded with pH 8.5 resulted in a large release of Sb, the addition of chlorine decreased Tl and Mn concentrations, and the addition of CaSO₄ influenced Sb, As, Tl, and Mn release. Overall the most substantial result was the high release of Tl which reached up to 90 µg/L, compared to the MCL of 2 µg/L. This study demonstrates that small changes to the chemical and physical properties of DWDS can cause contaminants to be released into the drinking water from pipe surfaces.
In order to maintain high quality safe drinking water, we need to understand what happens after the water has been cleaned at the drinking water plant and before it gets to the consumer’s house. Even if low concentrations of toxic contaminants enter the drinking water distribution system (DWDS) there is potential for contaminants to accumulate and be released by changes in flow or water conditions in high concentrations at the tap. For this study, we collected solid material from Park City, Utah that accumulated within the DWDS, along with a year of monthly monitoring of the DWDS. These solids were tested under five chemical and physical changes to see what contaminants can be released into the drinking water, with focus on eight elements: antimony (Sb), arsenic (As), chromium (Cr), copper (Cu), lead (Pb), and thallium (Tl) termed inorganic contaminants (TICs), also pipe elements iron (Fe) and manganese (Mn). From this study it was found that high concentrations of Sb, As, and Tl could be released under some conditions. Fortunately, we saw that the release of Cr, Cu, and Pb was either unmeasurable or so low that the amount never approached drinking water standards. The factors that were the most influential in producing high concentrations were both high and low pH, high temperature, low Cl₂, and CaSO₄. The most surprising observation was the very high concentrations of Tl released, reaching up to 90 µg/L, where the safe limit in drinking water is 2 µg/L. This study showed the importance of monitoring changes within the DWDS and that small changes can cause harmful levels of some contaminants to be released into the drinking water. However, monthly monitoring showed under normal conditions no harmful levels were detected.
ACKNOWLEDGMENTS

I would like to thank the groups that funded this project, the Utah Water Research Laboratory and the Water Research Foundation, for allowing me to be a part of this important research. Thanks to the Park City Municipal Corporation and Michelle DeHaan for inspiring the project and for the opportunity to intern with them. This was a large project working with many people who all have been beneficial to the project: thanks to Paul Jerominski, Melinda Friedman, Andrew Hill, Tessa Guy, Jason Blankenagel, Nate Rogers, Christel Olsen, and Darwin Sorenson.

A major acknowledgement goes to my family, Jeff, Debbie and Shayla, for the continued support in everything I do. Thanks to all of the lifelong friends I gained—without them my sanity may have diminished. This is especially true for William Kent, who was not only an amazing scientist and colleague to work closely with, but an exceptional friend. Again, thanks to Utah State University for the opportunity to work with and learn from many great scientists, and for the years of experience I gained throughout my bachelors. This is most true for my committee members, Laurie McNeill, David Stevens and Joan McLean, who constantly worked to improve my scientific skills. I appreciate it greatly.

Finally, I am most grateful for Jake Nelson, who decided to continue his studies and motivated me to do the same. Thanks to him for all of his emotional and scientific support during the painful years as I continued to finish.

Tiana W. Hammer
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CHAPTER 1

INTRODUCTION

Currently, in the United States, drinking water quality is regulated at the entrance to drinking water distribution systems (DWDS) by the US Environmental Protection Agency (USEPA), with the exception of lead, copper, and disinfectant by-products (DBPs) which are controlled at the consumers’ tap. Water quality is regulated by the National Primary Drinking Water Standards (NPDWS) at the entry point of the DWDS. For most utilities, from the point of entry through the distribution system there is little knowledge of what actually enters a consumer’s tap. It is known that most potential contaminants behave non conservatively throughout the piping system, where low levels of contaminants enter the drinking water distribution system and accumulate onto the pipes’ surfaces, then later are released from those surfaces at higher concentrations than in the DWDS influent. Sometimes this leads to contaminant concentrations exceeding drinking water limits. Different communities have experienced release events, where high turbidity and colored water with potentially high levels of contaminants have reached consumers’ taps. These releases generally are not a large concern for public health because consumers usually avoid using the discolored water during these short-duration events. However there can be release events that do not cause the water to be discolored and still have high concentrations of contaminants; this can be more harmful to consumers.
These release events may be due, in part, to changes in water chemistry that can cause particles and dissolved species to be released from pipe surfaces. Throughout the distribution system, trace inorganic contaminants (TICs) can attach to the pipe materials, corrosion products, or biofilms in the pipes by sorption, settling, co-precipitation, and other mechanisms, and over time their concentrations could build up in the system. Major changes in the water chemistry can then destabilize the surfaces causing release of the TICs back into the distribution system at higher concentrations than those seen at the entry point (Hill et al. 2010). Causes of these accumulation and release events are not fully understood by the scientific community. However, by understanding the mechanisms that control the non-conservative behavior, utilities can better protect consumers from release events. As described below, this study investigated the laboratory-scale behavior of certain contaminants as they interact with the solids from a distribution system and changing water quality.

Park City Background

Park City, Utah has experienced discolored water events in their DWDS and there is little known of the cause(s) of the events. This community has unique potable water challenges due to its history as a mining town, and now as a tourist destination with downhill skiing and an independent film festival in the winter, as well as hiking, biking, and other activities in summer. It is located 50 kilometers east of Salt Lake City in northern Utah and had approximately 8,000 full time residents in 2012, but during the winter tourist season the
town’s population can reach up to 45,000. In the 1800s, the Park City mining industry produced metals such as silver, gold, and lead (John 1997) from drift mines primarily in the mountains to the west and south of the current town location. Park City’s potable water supply consists of eight different sources: one spring (Thiriot), one surface water source (the Weber River), three wells (Divide well, Middle School (MS) well, Park Meadows (PM) well), and three old mine tunnels (Judge Tunnel, Spiro, and Ontario No 2 Drain Tunnel). Of these eight sources (Table 1), three go through a conventional treatment process, and all sources are disinfected conventionally using Cl2, with the exception that the PM well uses UltraViolet (UV) radiation. Water supplied from the Spiro tunnel is treated at the Spiro Water Treatment Plant (SWTP) where the effluent is mixed with Thiriot spring, the Weber River source is treated at the new Quinn’s Junction Water Treatment Plant (QJWTP), and Ontario No 2 Drain Tunnel is treated by Jordanelle Special Service District (JSSD), where treatment is focused on the removal of arsenic, thallium, iron, and manganese. Because Park City also uses this potable water to make snow for two of the three ski resorts in the area, and because of the influx of tourists during ski and summer seasons, there is a highly variable water demand, especially in the winter months.

In the fall of both 2007 and 2010 the Park City water department received customer complaints about reddish brown water from the tap. Some of the discolored samples were found to have high concentrations of iron (Fe), manganese (Mn), arsenic
Table 1, three go through a conventional treatment process, and all sources are disinfected conventionally using Cl₂, with the exception that the PM well uses UltraViolet (UV) radiation. Water supplied from the Spiro tunnel is treated at the Spiro Water Treatment Plant (SWTP) where the effluent is mixed with Thiriot spring, the Weber River source is treated at the new Quinn’s Junction Water Treatment Plant (QJWTP), and Ontario No 2 Drain Tunnel is treated by Jordanelle Special Service District (JSSD), where treatment is focused on the removal of arsenic, thallium, iron, and manganese. Because Park City also uses this potable water to make snow for two of the three ski resorts in the area, and because of the influx of tourists during ski and summer seasons, there is a highly variable water demand, especially in the winter months.

In the fall of both 2007 and 2010 the Park City water department received customer complaints about reddish brown water from the tap. Some of the discolored samples were found to have high concentrations of iron (Fe), manganese (Mn), arsenic

Table 1 - Sources including type and if treated where GW = ground water and SW = surface water

<table>
<thead>
<tr>
<th>Sources</th>
<th>Type</th>
<th>Treatment</th>
<th>Mine Tunnel</th>
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</thead>
<tbody>
<tr>
<td>Divide Well</td>
<td>GW</td>
<td>Cl₂</td>
<td>No</td>
</tr>
<tr>
<td>JSSD</td>
<td>GW</td>
<td>Coagulation/Flocculation</td>
<td>Yes</td>
</tr>
<tr>
<td>Judge Tunnel</td>
<td>GW</td>
<td>Cl₂</td>
<td>Yes</td>
</tr>
<tr>
<td>MS Well</td>
<td>GW</td>
<td>Cl₂</td>
<td>No</td>
</tr>
<tr>
<td>PM Well</td>
<td>GW</td>
<td>Cl₂/UV</td>
<td>No</td>
</tr>
<tr>
<td>QJWTP</td>
<td>SW</td>
<td>Coagulation/Membrane Filters</td>
<td>No</td>
</tr>
<tr>
<td>SWTP</td>
<td>GW</td>
<td>Coagulation/Sand Filters</td>
<td>Yes</td>
</tr>
<tr>
<td>Thiriot</td>
<td>GW</td>
<td>Mixed w/SWTP</td>
<td>No</td>
</tr>
</tbody>
</table>
(As), thallium (Tl), and mercury (Hg). During this time, the water leaving the SWTP into the distribution system was in compliance with all MCLs (Appendix A). All of the complaints came from one zone supplied by SWTP in the distribution system, indicated by the yellow-shaded zone on the map in Figure 1. Park City Municipal Corporation (PCMC) responded by collecting samples from taps, and by taking samples from flushing the pipes. They started internal studies, worked closely with the Utah Division of Drinking Water, and began collaborating with the Water Research Foundation on researching the cause of these events. This thesis represents an in depth discussion of some of the results from those research studies.

Preliminary Monitoring

Water quality throughout the Park City water distribution system was monitored during 2012-2013 to assess the discolored water events. Monitoring consisted of sampling every month from November 2012 through October 2013 from 14 locations in the system, including 5 premise plumbing locations, 7 pump stations, and 2 pressure reducing valve vaults (PRVs) (Figure 1). The monitoring sites were chosen to sample a wide range of locations within the distribution system. These sites also overlap with some of the sites that PCMC regularly samples. Water temperature, pH, chlorine residual, dissolved oxygen, electrical conductivity, and turbidity were measured in the field using Hach probes and test kits provided by Park City. Samples were field processed and preserved,
Figure 1 - Map of Park City. Colors indicate different zones in the system. Includes sources, 14 monitoring sites (pump stations, premise, and PRVs), and two cleaning trial swab sample sites: AST and UPA.
and taken back to the Utah Water Research Laboratory (UWRL) for lab analysis of total and dissolved trace elements, organic carbon, and major anions and cations. Trace elements of particular concern are As, Sb, and Tl. By monitoring at the above locations, DWDS water quality was compared to that entering the distribution system from the sources, in an attempt to detect any non-conservative behavior. Samples from the entry points into the distribution system were taken twice, in July and in October 2013, and subjected to the same water quality measurements as in the DWDS. Through the study it was found that the majority of the contaminants in the solids from the distribution system were under the MCLs concentration. However, the area indicated by the red section in Figure 1 had a few occurrences of high As approaching the MCL of 10 µg/L and high Sb at or above the MCL of 6 µg/L. Compliance was met at the DWDS point of entry as required, but there were higher concentrations within the distribution system; this suggests non-conservative behavior within the system.

By monitoring the system for a year, the baseline water quality was established, including the variability of the system. This background information about Park City DWDS was used in this study to set limits for high and low factors, as well as compare experimental data to what was found within the DWDS. A full accounting of these results is given in Friedman et al. (2016).
CHAPTER 2

LITERATURE REVIEW

Trace Inorganic Contaminants (TICs)

The trace inorganic contaminants explored for this study were chosen based on findings from the release event and monitoring data from Park City. The TICs chosen for this study were Sb, As, Cr, Cu, Pb, and Tl. These TICs are toxic, are known to have non-conservative behavior (Cu, Pb) within DWDSs, and occur in concentrations nearing the MCLs for Sb, As, Pb, and Tl at the point of entrance and within the DWDS in Park City (Table 2). Iron and Mn are also included since these elements provide the matrix for TIC sorption in pipes. Information on Logan tap water (LTW) is included (Table 2) because it gives a comparison to Park City and because Logan tap water will be used in the study.

Table 2 - TIC maximum contaminant level (MCL), and total concentrations in Park City distribution system and all points of entry (POE), and LTW filtered through 0.2 µm in µg/L

<table>
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<tr>
<th>TIC</th>
<th>MCL</th>
<th>Park City DWDS</th>
<th>Park City POE</th>
<th>LTW</th>
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</thead>
<tbody>
<tr>
<td>Sb</td>
<td>6</td>
<td>&lt; 1.2 – 8**</td>
<td>&lt; 1.2 – 6.7**</td>
<td>0.6</td>
</tr>
<tr>
<td>As</td>
<td>10</td>
<td>&lt; 0.2 – 10**</td>
<td>0.5 – 10.5**</td>
<td>0.3</td>
</tr>
<tr>
<td>Cr</td>
<td>100</td>
<td>&lt; 0.3 – 3</td>
<td>&lt; 0.3 – 1.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Cu</td>
<td>1300*</td>
<td>&lt; 0.75 – 100</td>
<td>&lt; 0.75 – 41</td>
<td>1.6</td>
</tr>
<tr>
<td>Pb</td>
<td>15*</td>
<td>&lt; 0.4 – 8**</td>
<td>&lt; 0.4 – 7.9**</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Tl</td>
<td>2</td>
<td>&lt; 0.1 – 1**</td>
<td>&lt; 0.1 – 0.55</td>
<td>0.1</td>
</tr>
</tbody>
</table>

*Secondary Standard

Fe  | 300  | < 10 – 500     | < 10 – 918    | 1.3  |
Mn  | 50   | < 0.75 – 10    | < 0.75 – 27.5 | 0.4  |

*Cu and Pb are action level concentrations

** Contaminants within range or above the MCL
Antimony (Sb)

Antimony concentration at the point of entry and within the distribution system in Park City was found to exceed the MCL at least at one location (Table 2). Antimony occurs naturally in some rock formations, often jointly with silver, copper, and gold, and can be released via dissolution into the groundwater that enters the mine tunnels. There are several industrial uses of Sb including petroleum refineries, fire retardants, glassware, ceramics, metal coating, brake lining, and lead batteries.

Antimony can cause both long and short-term human health effects, including increase in blood cholesterol and decrease in blood sugar, as well as nausea and vomiting (Cooper and Harrison 2009). It exists primarily in two oxidation states in aqueous systems: Sb(III) and Sb(V). The pKa for Sb(III) is 11.8 so the dominant free form under typical pH values in DWDS is the neutral complex, H$_2$SbO$_2$. The pKa for Sb(V) is 2.8, so it forms the complex SbO$_3^-$ in oxidizing conditions (Friedman et al. 2010; Wilson et al. 2010; Xi et al. 2014). Antimony(III) has a strong attraction to red blood cells and is ten times more acutely toxic than Sb(V) at the same concentration (Krachler et al. 2001). Xi et al. (2014) showed that Fe (range used in study: 0.9-16 g/kg) and Al (0.3-3.4 g/kg) oxides in river sediments have a high sorption capacity for both Sb(III) and Sb(V), as well as complexation with total organic carbon (TOC) (0.2-1.9 %). However, these river sediments are lower in concentration than what was found associated with the Park City DWDS pipe solids, which ranged from Fe 22-26 g/kg, Al 4.3-18 g/kg, and TOC 7.8-38 %.
One way to remove Sb from drinking water is using ferric chloride coagulation at a pH of 4.5-5.5. However, this may still be a challenge due to the competitive sorption between Sb(V) (the form that most commonly occurs, although since the oxidation of Sb(III) to Sb(V) is slow at near neutral pH (Leuz and Johnson, 2005), the two forms can coexist in solution) and HCO$_3^-$, SO$_4^{2-}$, PO$_4^{3-}$, and humic acids onto Fe oxides, while the more toxic form of Sb(III) is not affected by competing anions (Guo et al. 2009; Xi et al. 2011). These competitive anions will occupy the sorption sites on the Fe oxides first, interfering with the removal of Sb. Antimony is in the same column (group 15, pnictogens) on the periodic table as phosphorus which makes phosphorus a sorption competitor (Wu et al. 2010). Both sorb onto Fe and Mn oxides, and Sb(V) and As(V) behavior are very pH dependent with increase in sorption as pH decreases. Another factor that can decrease the sorption of Sb(V) is increase in ionic strength; however, this is heavily dependent on the point of zero charge of the soil minerals, pH, and whether sorption is controlled by outer-sphere complexation (electrostatic interactions) or inner sphere complexation (Wilson et al. 2010). The presence of all these factors can influence the sorption capabilities of Sb on solids in drinking water pipes. In addition, the low pH required for Sb removal would likely interfere with the coagulation of fine sediment that typically requires more neutral pH.
Arsenic (As)

Arsenic is a commonly encountered contaminant in drinking water and is a known carcinogen. Long term effects of consuming As above the MCL are skin, lung, bladder, kidney, prostate, and liver damage (USEPA 2006). Arsenic is a naturally occurring contaminant which is found in over 200 minerals (Smedley and Kinniburgh 2002), and is commonly associated with hard rock mining. In water As exists mainly in two oxidation states: arsenite (III) and arsenate (V). Arsenite, the reduced form, exists mainly as H$_3$AsO$_3$; is the more soluble form with a pK$_a$ of 9.2, and is neutrally charged from a pH of 6 to 9. In contrast, arsenate, the oxidized form, exists as H$_2$AsO$_4^-$ at pH 2 to 7 or HAsO$_4^{2-}$ at a pH range of 7 to 9. Arsenic is known to sorb to positively charged Fe and Mn oxides, and sorption increases with a decrease in pH. Competing ions such as phosphates, sulfates, and carbonates can cause As to desorb from Fe and Mn oxides (Smedley and Kinniburgh 2002). The presence of Ca$^{2+}$ can increase sorption of As(V) to soil. Ca$^{2+}$ increases the overall positive charge which increases anion sorption sites (Smith et al. 2002). Because many DWDS have high concentrations of Fe, the sorption and desorption of As is a constant concern (Copeland et al. 2007). Arsenic releases within a DWDS have been studied by Lytle et al. (2010) who showed that arsenate existed within the scale matrix of a water distribution pipe that has Fe oxide build-up, and be released at higher concentrations than those entering the system. Arsenic can be treated at the point of entry to a DWDS by a variety of ways including sorptive media, ion exchange, coagulation,
oxidation, and filtration. Park City Municipal Corporation’s (PCMC) SWTP currently targets the removal of As from the Spiro tunnel water source using coagulation and sand filters.

**Chromium (Cr)**

Chromium is a contaminant found in groundwater from both natural and anthropogenic sources. It is used in water-cooling as a corrosion inhibitor, leather tanning, and dyes. There is evidence of leaching of Cr from cement lined drinking water pipe walls (Guo et al. 1998).

Chromium has two major oxidation states: Cr(III) a cation and Cr(VI) an oxyanion, which leads to diverse behavior in the environment. Total Cr (Cr(III) and Cr(VI)) has an MCL of 100 µg/L. Of the two forms, Cr(VI) is toxic and has health effects that include liver, kidney, nerve tissue, and respiratory damage, and is a known carcinogen by inhalation (Costa and Klein 2006; USEPA 2012). Chromium(III) however is an essential nutrient for humans that improves insulin function and the recommended human intake is at least 50 µg per day (Anderson 1997).

Chromium(III) is a cation and forms an insoluble precipitate (Cr(OH)₃) at pH >6, and at acidic pH, Cr(III) co-precipitates with Fe. Cr(III) sorbs to Fe hydroxides at pH values found in DWDS (pH 6-9), although sorption decreases when competing ions are in solution. Due to its low solubility and high retention onto soils Cr(III) has limited bioavailability (Fendorf 1995). Chromium(III) can be oxidized by Mn oxides in natural
systems, and by chemicals like chlorine and chloramines in DWDS (Rai et al. 1989). The oxidation by Mn oxides can be limited by the presence of competing ions.

Chromium(VI) is an oxyanion that exists as CrO$_4^{2-}$, which resembles sulfate and phosphate under oxidizing conditions. It is highly soluble and mobile at a neutral pH in soil and water. Chromium(VI) can be reduced by a variety of materials such as ferrous ions, reduced sulfur compounds, and organic matter, which are common conditions in natural systems. Sorption of Cr(VI) is mainly on Fe and Al hydroxide at a pH below 8 and decreases with increasing pH (Rai et al. 1989). Sorption and mobility behavior of hexavalent Cr is significantly affected by competing ions (Richard and Bourg 1991). It complexes and precipitates with Fe, which can be a way to treat Cr(VI) from drinking water (Fendorf 1995).

**Copper and Lead (Cu & Pb)**

Copper and lead are required to be monitored in the DWDS by USEPA’s Lead and Copper Rule (USEPA 2012). These metals are monitored at the consumer’s tap and no more than 10% of the samples can exceed the Action Level (AL) which is 1300 µg/L for Cu and 15 µg/L for Pb. They are both materials commonly present in household plumbing, especially in older homes where lead was used as a piping material, and in new homes with copper pipes assembled using lead-based solder. Although Pb is no longer used in DWDS pipes as of 1986, there is a concern for corrosion to occur in older pipes. As metal
cations, both Cu and Pb are known to be less soluble in the presence of orthophosphate and at a higher pH (Schock et al. 1995).

Copper is known to have stomach and intestinal effects, and can also cause liver and kidney damage (USEPA 1995). Copper is a naturally occurring metal which exists in minerals as well as in the elemental state. In the aqueous environment Cu exists in two oxidation states: Cu(I) and more commonly Cu(II). Cu can be present at the tap either through corrosion of the pipes or leaching of pipe material. Many factors affect the release of Cu from pipes, including chloride, sulfate, phosphate, dissolved oxygen, organic matter, temperature, alkalinity, and pH, with pH being a main factor. An increase in pH above 6 will cause precipitation and can decrease Cu releases into distribution systems (Friedman et al. 2010; Sylva 1976; Xiao et al. 2007).

Lead is a regulated metal with an MCL goal of zero because it can interfere with red blood cells and delays development in the young. It has also been shown to cause kidney disease and strokes (USEPA 2012). Lead has two oxidation states in aqueous environments, Pb(II) and Pb(IV), and it is most commonly found as Pb(II). Lead is a naturally occurring heavy metal and is also a product of industrial sources like mining, refining, smelting and others. It can be found in drinking water pipes from leaching from Pb bearings, piping solder, and other plumbing components. As pH increases the solubility of Pb decreases and its sorption to Fe oxides increases (Friedman et al. 2010). In corrosion products from pipes Pb occurs mostly as Pb carbonates or Pb oxides. In highly oxidized
systems, such as those with chlorine levels of 0.5 – 1 mg/L, PbO₂ will be present which is insoluble (Kim and Herrera 2010).

**Thallium (Tl)**

Thallium is very toxic to humans, more toxic than Pb, Cd, and Hg. It has two oxidation states in aqueous environments: Tl(I) which is more stable and typically found in aqueous systems at a neutral pH, and Tl(III) which is found under highly oxidizing conditions. Monovalent Tl(I) resembles potassium (K⁺) and is highly soluble which makes it more toxic than Tl(III), which has a similar aqueous chemistry behavior as aluminum. The MCL for Tl is set at 2 µg/L to protect against short-term health effects such as gastrointestinal irritation and nerve damage, as well long term health effects such as hair loss and damage to the liver, kidneys, and testicular tissue (Peter and Viraraghavan 2005; USEPA 1995). Removal of Tl at drinking water treatment plants has traditionally been done using activated alumina or ion exchange techniques. However, there is strong competitive exchange with Na(I), K(I) and Ca(II), and the MCL may not be achieved by ion exchange methods in the presence of high concentrations of these elements (Wan et al. 2014). Through monitoring of the Park City DWDS it was found that there are high concentrations and variability for these competing elements with Ca ranging from 50-120 mg/L and Na ranging from 5-50 mg/L. The presence of Ca and Na may be a factor in the behavior of Tl throughout the distribution system. Mn dioxide is a good sorbent for Tl(I) with maximum sorption at neutral pH. Thallium(I) sorbed to laboratory prepared Mn
oxides was oxidized to Tl(III) at pH values less than 4 (Gadde and Laitinen 1974). Increasing concentration of Ca did not affect the retention of Tl(III) to the Mn oxide (Wan et al. 2014). Solids collected from Park City DWDS were analyzed for Mn oxides by the Amacher (1998) sequential extraction method, and there was a significant amount (20%) of Tl associated in the Mn oxide phase, confirming that these solids behave similar to what Wan et al. (2014) found.

**Matrix Elements**

**Iron and Manganese (Fe & Mn)**

Iron is a common product used in piping material and manganese is naturally occurring in many source waters. Both are important metals within the distribution system because they are highly associated with other trace contaminants, such as As and Pb by a sorption mechanism (Dong et al. 2003; Schock et al. 2008). Both metals have a secondary standard for drinking water, but it is optional for water systems to meet the standard. Iron is a commonly used material within DWDS pipes, and pipe corrosion products are mainly made up of Fe oxides which can contain high concentrations of TICs that could be released into the distribution system. Iron typically exists as two oxidation states in aqueous environments: Fe(II) and Fe (III) (Mutoti et al. 2007; Sarin et al. 2001). Iron(II) can also be used to reduce Cr(VI).

Manganese in drinking water is primarily present as a highly soluble form manganous (Mn^{+2}), or manganic (Mn^{+4}) which readily precipitates. Permanganate (Mn^{+7},
which occurs as MnO₄⁻ is a strong oxidizing agent and is used in drinking water treatment to provide preoxidation of some organic matter to help control disinfection by-products (Friedman et al. 2010). Mn oxides have been shown to adsorb heavy metals such as Pb and Tl(I) at a pH > 4.5 (Gadde and Laitinen 1974).

Non-Conservative Behavior of Distribution Systems

It has recently come to the attention of the drinking water industry that distribution system pipes may behave non-conservatively (Figure 2). Within the distribution system, water interacts with the pipe wall forming pipe scale and rust. Scale is the buildup of mineral deposits from the water such as calcium and magnesium carbonates, and biofilms, while rust (mainly Fe oxides) is formed by the oxidation of the Fe in the pipe materials. Contaminants entering the distribution system at low levels, below the MCL, may slowly accumulate onto the scale. The two main factors affecting accumulation are water chemistry and the mineralogical composition of the solids on the pipes (USEPA 2006). Building up the concentrations of TICs increases the potential for the release of those TICs back into the drinking water at higher concentrations. Water quality conditions can drive these accumulation and release mechanisms, and may include changes in pH, oxidation state, temperature, alkalinity, chlorine level, hardness, and other factors (Friedman et al. 2010). Some of these conditions have been studied on select contaminants such as effects of pH on As, Cu, Pb, and Cr, where a high pH increased the release of As but decreased the release of the cations (Copeland et al. 2007; Farquhar et
Physical processes such as hydraulic changes can also cause the TICs to be released from the loose scale into the distribution system. Hydrant flushing is done to clean the pipes of loose deposits and has shown high concentrations of contaminants such as As, Cr, and Pb in the flush water (Peng et al. 2012). This shows that there is accumulation of TICs occurring within the distribution system. However, the causes of the releases are not fully understood.

Figure 2 - Contaminant accumulation and release mechanisms that may occur in a distribution system piping (modified from Friedman et al. (2010))

**Accumulation**

Accumulation of TICs can occur within a DWDS by a variety of mechanisms including sorption, precipitation, and sedimentation. The main TICs that have been studied within a distribution system are As, Cu, and Pb.
Sorption is a chemical mechanism where TICs attach onto pipe solid or byproduct material, or biofilms. Sorption reactions of TICs in a distribution system are complex and are highly dependent on pH, oxidation reduction potential (ORP), and ionic strength (Schock 2005). Fe and Mn oxides are the most common materials within a DWDS and have sorption characteristics for TICs. For example, there have been many studies on the sorption reaction in soil of Fe oxides for As (Smedley and Kinniburgh 2002). There has also been research demonstrating the sorption of Tl onto Mn oxides (Wan et al. 2014). Water chemistry, pipe age, pipe type, and flow demand all have an influence on sorption properties (Hill et al. 2010).

Another way of accumulating TICs within a distribution system is precipitation, where dissolved TICs combine and form solid material. Forming precipitates is highly pH and temperature dependent (Friedman et al. 2010). Three major precipitates can form within a DWDS: Fe oxides, and in bicarbonate water systems with a high total hardness, calcium and magnesium carbonates. These precipitate readily at pH above 7.5, or with an increase in concentration. Iron oxides precipitate with a decrease in temperature and carbonates precipitate with an increase of temperature. The co-precipitation of As and Fe oxides has been widely studied and is shown to be most dominant from pH 6.5-7.6 (McNeill and Edwards 1997).

Sedimentation is a physical mechanism for accumulating contaminants in a distribution system, and is a major cause of discoloration at customer taps. Small particles
can enter the distribution system after the treatment process and accumulate, forming sediments throughout the distribution system. Sediments accumulate in areas within the pipe that have low flows/usage or curves within the pipe. These sediments can be composed of a variety of materials, including soil and organic matter, which also contain metals and other contaminants. Sediments mainly contain Fe, Mn, and Al oxides; Fe is a main material used for distribution system pipes, while Mn and Al are contributed from what is in the finished water either through treatment or as part of the source water (Friedman et al. 2003; Hill et al. 2010; USEPA 2006; Vreeburg et al. 2008).

**Release**

Release mechanisms are a large concern related to the non-conservative nature of the pipes. This includes both physical disturbances such as hydraulic changes and flushing, or water chemistry changes that can cause desorption, dissolution, and corrosion. Changes in source water, for example switching from surface to ground water, can change the stability of the current conditions causing a release (Lytle et al. 2004). The overall concentration of TICs can also affect the equilibrium sorption capacity.

Since desorption of TICs is not always accompanied by colored water or turbidity increases, this can be harmful to consumers because releases can go unnoticed at the tap. By changing pH and adding phosphates, As has been shown to desorb from distribution pipe solids (Copeland et al. 2007). TIC releases need to be explored further to fully identify the causes (Hill et al. 2010).
Corrosion of pipes is a large concern for water quality in DWDS. In old iron and steel pipes, Sarin et al. (2001) found that there were high concentrations of ferrous iron deposits composing the corrosion scales. Peng et al. (2010) characterized material from corrosion scale and found Fe oxides were the major compounds. Corroded pipes have also been found to contain inorganic contaminants. Corrosion can also affect the water quality by causing the decay of disinfectants when using chlorine (Zhang et al. 2008).

Hydrant flushing is a cleaning technique used to help remove particles and tubercles from inside the pipes of the distribution system (Friedman et al. 2012). However this generally only removes loosely attached particles and does not remove all of the contaminants.

Changes in release can be caused by factors such as temperature, pH, disinfectants, electrical conductivity, and presence of compounds that compete with the TICs for sorption sites.

**Temperature**

Temperature is an important factor because it influences other variables concerned with chemical stability such as solubility, viscosity, reaction rates, biological growth. Generally, a higher temperature increases solubility and reaction rates. Temperature also controls the rate at which sorption equilibrium is reached.
pH

pH affects the speciation, precipitation, and solubility of contaminants and other metals, especially Fe and Mn. In drinking water treatment, pH plays a major role in reaction rates as well as coagulation and flocculation treatment. pH is a large controller of the sorption process and changes in pH may destabilize sorbed TICs. Depending on the compound, a higher or lower pH can increase the sorption capabilities. For example, Copeland et al. (2007) investigated the effect of pH on As release and found that As was desorbed at higher concentrations with increase in pH. A higher pH decreases the solubility Pb, Cu, and Cr(III) at the tap (Veschetti et al. 2010). Another example of pH affecting solubility of TICs is when using copper piping, if the pH is lower than 7.5 there is an increase of Cu released into the water (Xiao et al. 2007).

Chlorine

Drinking water distribution systems in the United States are required to maintain a disinfectant residual in the system that does not exceed 4 mg/L as Cl₂ for chlorine and chloramines and 0.8 mg/L as ClO₂. These disinfectants are oxidants that can increase oxidation-reduction potential (ORP) in the pipes. By increasing the ORP using chlorine, Lytle and Schock (2005) found an increase in soluble Pb concentrations. The levels of disinfectant can affect the growth of biofilms which accumulate or release contaminants. Chlorine is a weak acid when added to water, and thus will drive the pH to drop. pH is a factor in the disinfection efficiency of free chlorine; at a pH above 7.5, chlorine is primarily
in the form of the hypochlorite ion (OCl\(^-\)), which is less available as a disinfectant than the hypochlorous (HOCl) form which is dominant at a lower pH. This is controlled by the pK\(_a\) around 7.5 for the reaction (Gordon et al. 1948).

**Ionic Strength – NaCl**

Ionic strength can be calculated from measurements of electric conductivity or total dissolved solids. It can be used as a surrogate measurement for total dissolved solids, as well as an indicator of solubility for other metals. By increasing the ionic strength, the overall charge of free ions decreases and there is a potential for desorption to occur. However the system is complicated and the effects of ionic strength are highly dependent on pH, the point of zero charge of the soil minerals, and whether the sorption mechanism is inner sphere or outer sphere complexes (Harter and Naidu 2001; Wilson et al. 2010).

**Competitive Sorption 1 – CaSO\(_4\)**

Calcium and sulfate are common ions in drinking water. Sulfate is a weak competitor with As and Sb(V), but noncompetitive with Sb(III) for sorption sites on Fe oxides (Frau et al. 2008; Xi et al. 2011). Sulfate is even potentially a competitor for Cr(VI) (Friedman et al. 2010). Ca\(^{2+}\) can compete with cations such as Tl for sorption sites (Wan et al. 2014).
Competitive Sorption 2 – KH₂PO₄

Phosphate inhibitors are used as corrosion control for Pb and Cu in water treatment plants and distribution systems (McNeill and Edwards 2002). In Copeland et al. (2007) orthophosphate was found to increase As desorption from a DWDS. Arsenic desorption depended on PO₄³⁻ concentration, with the highest As concentrations released at 5 mg/L phosphate. There is also a potential for higher concentrations of Sb to be released (Wilson et al. 2010). Potassium and TI⁺ have similar properties, by being similar size and monovalent, which makes KH₂PO₄ a potential competing ion for TI. Thallium poisoning is due to the replacement of K⁺ in the blood with TI⁺ (Peter and Viraraghavan 2005).
CHAPTER 3

PROBLEM STATEMENT AND OBJECTIVE

Problem Statement

Solid materials present in water distribution pipes can cause non-conservative behavior of TICs. TIC sorption and subsequent high level releases into the distribution system are outcomes of non-conservative behavior. It is necessary for the drinking water community to understand these releases, their causes, and control strategies, in order to protect the public from harmful levels of contaminants.

Objective

The objective of the proposed project is to test the effects of changes in the water quality factors temperature, pH, chlorine, ionic strength, and competitive sorption, on the release of trace inorganic contaminants (TICs) from pipe solids into drinking water.

Null Hypothesis

Changing drinking water quality conditions, such as temperature, pH, chlorine, ionic strength, and competitive sorption will not cause TICs to desorb from solids in DWDS.
CHAPTER 4

METHODS AND MATERIALS

Experimental Design

To fulfill the objective, solids collected from drinking water pipes during swab cleaning trials in Park City in September 2013 were used as the matrix for the desorption trials (Friedman et al. 2016). These solids were shaken in 0.2 μm filtered tap water from Logan, UT (LTW), adjusted with varying parameters, and the supernatant was analyzed for TICs of concern (As, Cu, Cr, Pb, Sb, and Tl) and metals that contribute to the matrix, Fe and Mn. LTW is a consistent drinking water source throughout the year and it has lower levels of TICs, anions, and cations compared to Park City (Table 2 and Table 3). Due to its initial low concentrations of anions and cations, LTW was adjusted to a wider range of ionic concentrations, to encompass the range observed in Park City. The low TIC levels in LTW were also necessary to test the solids for desorption.

The research was carried out in two stages. In Stage I, a fractional factorial experimental design was used to determine the most influential factors. In Stage I six factors were chosen: temperature, pH, chlorine dose, competitive sorption by cations Ca\(^{2+}\) and K\(^+\), and anions SO\(_4^{2-}\) and PO\(_4^{3-}\) as CaSO\(_4\) and KH\(_2\)PO\(_4\), and ionic strength using NaCl. These factors and their levels were chosen based on literature showing their potential effects on sorption, and their ranges and the variability found during 12 months of monitoring at 14 locations in the Park City DWDS (Table 3). In Stage II, a subset of the
most influential factors was selected for study in a full factorial experiment that allows independent assessment of all of the main effects and the 2 and 3-way interactions. In both phases, each set of experiment conditions were examined in triplicate.

Table 3 - Water quality in LTW filtered through 0.2 µm, compared to Park City. NA = not analyzed

<table>
<thead>
<tr>
<th>Parameter</th>
<th>LTW</th>
<th>Park City</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl (mg/L)</td>
<td>1.4</td>
<td>5.0 - 125</td>
</tr>
<tr>
<td>SO4 (mg/L)</td>
<td>7.8</td>
<td>15 - 260</td>
</tr>
<tr>
<td>NO3-N (mg/L)</td>
<td>0.2</td>
<td>&lt; 0.04 - 2.0</td>
</tr>
<tr>
<td>HCO3 (mg/L)</td>
<td>203</td>
<td>30 - 255</td>
</tr>
<tr>
<td>Na (mg/L)</td>
<td>1.1</td>
<td>5.0 - 50</td>
</tr>
<tr>
<td>K (mg/L)</td>
<td>&lt; 0.5</td>
<td>1.0 - 2.0</td>
</tr>
<tr>
<td>Mg (mg/L)</td>
<td>19.4</td>
<td>18 - 30</td>
</tr>
<tr>
<td>Ca (mg/L)</td>
<td>43.5</td>
<td>50 - 130</td>
</tr>
<tr>
<td>pH</td>
<td>7.6</td>
<td>7.1 - 8.3</td>
</tr>
<tr>
<td>EC (μS/cm)</td>
<td>285</td>
<td>300 - 1000</td>
</tr>
<tr>
<td>Cl2 (mg/L)</td>
<td>0.26</td>
<td>0.02 - 1.3</td>
</tr>
<tr>
<td>Alkalinity (mg CaCO3/L)</td>
<td>166</td>
<td>25 - 210</td>
</tr>
<tr>
<td>TSS (mg/L)</td>
<td>NA</td>
<td>0 - 2.5</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>NA</td>
<td>218 - 1350</td>
</tr>
</tbody>
</table>

Solids were collected during a pipe cleaning trial using swabbing methods from two locations in Park City, Upper Park Avenue (UPA) and Aspen Springs (AST) (Figure 1) as described in Friedman et al. (2016). Solids from each location were collected on-site by centrifugation and chemically characterized at the UWRL. Total and exchangeable concentrations of the TICs from both sites are found in Table 4. Total TIC concentrations were determined after hot block digestion following EPA Method 3050 on an Environmental Express 54-Well 50 mL HotBlock (model #SC154, Charleston, SC).
Exchangeable cations were extracted from the solids using 1M NH₄Cl (Amacher 1998), since NH₄⁺ is a selective exchangeable ion for Tl plus the other cations. Exchangeable anions (As, Sb) were extracted using 5 mM ammonium phosphate at pH 7 as recommended by Huang and Kretzschmar (2010) for the specific ligand exchange for As. This procedure was modified using a solids:solution ratio of 0.1:60 to match the ratio used in the desorption isotherm studies. The two different exchangeable TIC methods were used to achieve a maximum concentration of exchangeable properties for the worst case scenario. Additional steps of the selective dissolution of mineral phases followed the method of Amacher (1998). Both total and extractable TICs were analyzed using an Agilent Inductively Coupled Plasma Mass Spectrometer (ICP-MS, Model# 7700x, Santa Clara, CA) following EPA Method 6020.

AST solids were collected from a newer section of the distribution system and were found to have 38 % total organic carbon. In contrast, UPA was collected from an older section of the distribution system and only contained 7.8 % total organic carbon. The majority of the solids (95 %) ranged in size from 1.5 µm to 38 µm (Appendix B). They had high moisture content; for AST it was 190 % and UPA 240 % moisture on a dry weight basis at the time of the experiment. The pH for both solids was approximately 7.8, and the alkalinity of the solids was 202 and 250 mg CaCO₃/L for AST and UPA, respectively.
Table 4 - Characteristics of TICs on solids AST and UPA in µg/g, extraction for the exchange was done using the Amacher (1998) method, or * indicates samples were extracted using Huang and Kretzschmar (2010) (a ligand exchange As specific method).

<table>
<thead>
<tr>
<th>TIC</th>
<th>AST</th>
<th>Exchange</th>
<th>UPA</th>
<th>Exchange</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb</td>
<td>19.5</td>
<td>1.21*</td>
<td>36.3</td>
<td>3.56*</td>
</tr>
<tr>
<td>As</td>
<td>1.7x10³</td>
<td>58.1*</td>
<td>672</td>
<td>84.6*</td>
</tr>
<tr>
<td>Cr</td>
<td>36.5</td>
<td>&lt;MDL+</td>
<td>62.3</td>
<td>0.33</td>
</tr>
<tr>
<td>Cu</td>
<td>2.6x10³</td>
<td>27.7</td>
<td>1.6x10⁴</td>
<td>55.3</td>
</tr>
<tr>
<td>Pb</td>
<td>3.4x10³</td>
<td>&lt;MDL+</td>
<td>6.7x10³</td>
<td>&lt;MDL+</td>
</tr>
<tr>
<td>Tl</td>
<td>1.6x10³</td>
<td>81.7</td>
<td>785</td>
<td>85.7</td>
</tr>
<tr>
<td>Fe</td>
<td>1.5x10⁵</td>
<td>&lt;MDL+</td>
<td>1.4x10⁵</td>
<td>&lt;MDL+</td>
</tr>
<tr>
<td>Mn</td>
<td>1.8x10⁴</td>
<td>43.7</td>
<td>1.0x10⁵</td>
<td>0.42</td>
</tr>
<tr>
<td>TOC (%)</td>
<td>38.1</td>
<td>7.83</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*MDL – as defined in Table 6.

Experimental Methods

The first stage saturated fractional factorial design tested the main effects of all 6 treatments; details of the design and the raw results are in Appendix (C). The second stage used the most influential factors from the first stage in a full factorial design. In the Stage I experiments it was found that all factors except for ionic strength significantly impacted the release of TICs. From there, the Stage II experiments moved to a full factorial design using the remaining 5 factors in triplicate, for a total of 33 different treatments in 99 experiments. Treatments included high and low levels of the factors and one factor of a midrange level for all factors (2⁵ + 1 center point).

The desorption experiments were performed using 0.1 g of solids collected from UPA and AST in 60 mL of 0.2 µm filtered LTW. This ratio was determined from the amount
of solids scraped from piping in the two locations (AST and UPA). There were two sections of pipe cut from the distribution system at each location, 112 cm long by 20 cm diameter, equaling a volume of 39.5 L. Included in Table 5 is the mass of dry solids collected from each pipe by scraping the interior wall with a rubber spatula, converted to g/L, and a calculated ratio of 0.1 g in 60 mL water was determined. Treatments for the factorial experiment were prepared in triplicate using wet solids equivalent to 0.1 g dry mass and placed in 60 mL glass bottles. Solids from the two sites were treated separately using the same technique. Then, LTW was added and samples were placed on a horizontal shaker (Eberbach Corporation, Ann Arbor, MI) and shaken at a speed of 200 osc/min to eliminate mass transfer resistance. All treatments were the same with respect to the amount of solids (0.1 g), water (60 mL) (Table 5), reaction duration (24 hrs), and shaking speed (200 osc/min). These parameters were determined based on preliminary kinetic studies where concentrations reached equilibrium and based on maximum retention time in a distribution system (Appendix C, Figure C1).

After the reaction period, each sample was split in half and filtered through two different sizes of nylon membrane syringe filters: 1.5 µm and 0.45 µm pore sizes (Life Science Products, Denver, CO), which gives a representative sample of both sizes less than 1.5 µm and dissolved species. The 1.5 µm size cut-off is based on the monitoring data where there were little to no total suspended solids larger than 1.5 µm found, and this is representative of water at a consumers’ tap. Samples filtered through 1.5 µm were then
digested for total metals. If there was a statistically significant difference between the filtered sizes they were separated in the analysis; otherwise the two filtered sizes were combined. Both digested and dissolved samples were preserved with HNO3 and analyzed using ICP-MS.

Table 5 - Calculation for mass to volume ratio

<table>
<thead>
<tr>
<th>Pipe Sample</th>
<th>Total Solids per pipe (g)</th>
<th>Solids per pipe volume (g/L)</th>
<th>Solids (g) in 60 mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>AST – A</td>
<td>79.5</td>
<td>2.0</td>
<td>0.12</td>
</tr>
<tr>
<td>AST – B</td>
<td>67.6</td>
<td>1.7</td>
<td>0.10</td>
</tr>
<tr>
<td>AST – C</td>
<td>90.1</td>
<td>2.3</td>
<td>0.14</td>
</tr>
<tr>
<td>AST – D</td>
<td>74.1</td>
<td>1.9</td>
<td>0.11</td>
</tr>
<tr>
<td>UPA – A</td>
<td>53.3</td>
<td>1.4</td>
<td>0.08</td>
</tr>
<tr>
<td>UPA – B</td>
<td>73.7</td>
<td>1.9</td>
<td>0.11</td>
</tr>
<tr>
<td>UPA – C</td>
<td>61.6</td>
<td>1.6</td>
<td>0.09</td>
</tr>
<tr>
<td>UPA – D</td>
<td>66.7</td>
<td>1.7</td>
<td>0.10</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td></td>
<td><strong>0.11</strong></td>
</tr>
</tbody>
</table>

The Method Detection Limit (MDL) indicated in Table 6 for the TICs was used as the minimum value when reporting the results. MDLs were calculated by measuring a low concentration of the elements 7 times and multiplying the standard deviation by the t distribution; for 6 degrees of freedom and confidence level of 99 %, this value is 3.14.

Final results are reported as TICs released into solution, calculated as the measured concentration minus the blank background concentration. Statistical analysis, including analysis of variance (ANOVA), linear regression, and Student’s t-tests, using the
statistical software R (R Core Team 2016), was carried out using the TICs released concentration as the response variables, and this in turn determined which of the Stage II factors have the largest effect on TIC release from the solids.

Table 6 - ICP-MS Method Detection Limit (MDL) for TICs in µg/L

<table>
<thead>
<tr>
<th></th>
<th>As</th>
<th>Sb</th>
<th>Cr</th>
<th>Cu</th>
<th>Pb</th>
<th>Tl</th>
<th>Fe</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDL</td>
<td>0.05</td>
<td>0.06</td>
<td>0.02</td>
<td>0.08</td>
<td>0.1</td>
<td>0.01</td>
<td>0.14</td>
<td>0.05</td>
</tr>
</tbody>
</table>

For each factor tested, Table 7 shows the various ranges used. To adjust the levels of each of the experimental factors, these protocols were followed:

**Temperature:** The temperature was controlled by shaking each of the treatments in either a refrigerator (7 °C), in a constant temperature room (25 °C), or in a separate controlled temperature room (16 °C).

**pH:** 1 M HNO₃ was used to lower the pH to 6.5 and 1 M NaOH to raise the pH to 8.5; the middle level was controlled at 7.5. A subset of the samples was checked every half hour and adjusted accordingly until the pH was stable in the range of +/- 0.2 pH units around the target pH. Once the pH was stabilized (after approximately one hour) adjustments for the remaining treatments were made and the 24 hour shaking time began. During the experiment, random samples were tested to confirm the pH was within range. Initial calculations were made to estimate the total amount of acid or base to be used on all samples.
**Chlorine:** Chlorine levels were adjusted using a sodium hypochlorite (NaOCl) solution (Clorox bleach) of 1500 mg/L. Due to Cl\(_2\) consumption/loss processes in the solids/liquid matrix, the Cl\(_2\) concentrations decreased throughout the shaking period and were not adjusted, similar to its behavior in a DWDS. The degradation curves and calculations of Cl\(_2\) are presented in Appendix C (Figure C2) showing Cl\(_2\) decreased by half within the first hour. The chlorine residual was checked at the time of spiking and after the 24 hour shaking time using a Hach spectrophotometer (Model# DR-2800, Hach Method 8167, Loveland, CO). Consistent Cl\(_2\) concentrations were measured throughout the preliminary saturated factorial design set, and measurements were not repeated during the full factorial set. After 24 hours of shaking, the Cl\(_2\) was below the detection limit (0.02 mg/L) for all sets of experimental conditions.

**Ionic Strength:** NaCl was used to control the ionic strength by adding a 350 mg/L NaCl stock solution to raise the overall ionic strength to 18.5 mmol/L.

**Competitive Sorption 1:** CaSO\(_4\) was used as the first competitive sorption component as calcium for cations and sulfate for anions. Logan tap water’s calcium (43.5 mg/L) and sulfate (7.8 mg/L) concentrations were slightly below those of the lowest observed concentrations in the Park City monitoring (50 mg calcium/L and 15 mg sulfate/L). LTW was first adjusted to approximate the calcium and sulfate in the Park City water at its lowest concentration of by adding 10 mg/L CaSO\(_4\) producing the low (-) level
for this test parameter. The mid-point (0) and high (+) levels were produced by adding 175 mg/L CaSO₄ and 350 mg/L CaSO₄ to LTW.

**Competitive Sorption 2:** PO₄-P was tested as the second sorption parameter; a low of 0 and high of 1 mg-P/L and a midpoint were tested, using the salt KH₂PO₄. These doses resulted in K⁺ concentrations of 0 and 1.2 mg/L.

<table>
<thead>
<tr>
<th>Level</th>
<th>Temp (°C)</th>
<th>pH</th>
<th>Cl₂ (mg/L)</th>
<th>Ca (mg/L)</th>
<th>SO₄ (mg/L)</th>
<th>K (mg/L)</th>
<th>PO₄-P (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High (+)</td>
<td>25</td>
<td>8.5</td>
<td>2.0</td>
<td>103 (146)</td>
<td>247 (255)</td>
<td>1.2</td>
<td>1.0</td>
</tr>
<tr>
<td>Mid Point (0)</td>
<td>16</td>
<td>7.5</td>
<td>1.0</td>
<td>52 (96)</td>
<td>124 (132)</td>
<td>0.6</td>
<td>0.5</td>
</tr>
<tr>
<td>Low (–)</td>
<td>7</td>
<td>6.5</td>
<td>0.0</td>
<td>0.0 (46.5)</td>
<td>0.0 (15)</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

**Quality Control**

All sorption experiments were run in triplicate, and are compared to the same experimental treatments using a blank control (i.e., no solids), which consisted of 8 samples of Logan tap water filtered through a 0.2 µm filter. These blank controls were run through a subset of the 32 high/low treatments as described above to insure that no contamination was coming from the bottles or treatments. These blanks were then used as a baseline for TICs present in Logan tap water. For the results of this study the concentrations released from the solids are calculated by subtracting the Logan tap water baseline.
To test against effects of experimental equipment (e.g. bottles) and processes on TICs, a prepared TIC solution was filtered through both the 0.45 and 1.5 µm filters and processed through the same subset of treatments resulting in 8 samples for each filter group.

Saturated Fractional Factorial Design Results

Full ANOVA results (p values, etc.) for the saturated design are tabulated in Appendix C Table C-2. For most treatments, the equilibrium TIC concentrations were greater than the background, indicating that desorption had released the TICs to the aqueous phase in excess of the no-solids control. In some treatments, the TICs adsorbed onto the solids leaving a residual concentration less than that of the control, resulting in net adsorption.

Full Factorial Design Results

The results from the full factorial design are analyzed using linear regression methods and ANOVA using the statistical software R (R Core Team, 2016). The factorial experimental designs consist of independent variables (or factors), \( x \), of temperature, pH, \( \text{Cl}_2 \) dose, \( \text{KH}_2\text{PO}_4 \) addition, and \( \text{CaSO}_4 \) addition, coded as -1, 0, or +1 for the low, mid, and high levels. The dependent variables, \( y \), are the concentrations of TICs and matrix elements released from the solids into the desorption solution. Linear regression was used to determine the main effects each factor as well as two and three factor interactions had on the desorption of elements (Berthouex and Brown 2002). Because
there are five factors, it is possible to analyze up to five way interactions using a full factorial design (Box et al. 2002); however, to interpret the four- and five-way interactions in the data with confidence as meaningful chemical or physical processes is more difficult. To reduce the complexity and increase confidence of the analysis only the most important factors and up to 3-way interactions were examined.

In the results discussed below, the critical effects and interactions were selected first by statistical significance, then second by engineering importance. Statistical significance is related to the uncertainty in measurements, reproducibility of experiments and the numbers of observations that are used to test for differences. With enough observations, almost every factor is likely to be found statistically significant, and significance is calculated as part of the statistical hypothesis test. In contrast, importance represents whether or not the observed difference between treatments, which may be statistically significant, but is important from a scientific and engineering perspective. Below, we’ll adopt the word ‘significant’ to mean statistical significance from the hypothesis test and ‘important’ variables (in a strict sense) are calculated using the sums of squares from ANOVA, as the ratio of sum of squares due to a variable to the total sum of squares for all statistically significant variables. The importance, in effect, provides the measure of how effective a variable is in explaining the variance in the data. From here on, only the variables/factors that contribute more than 5 % to the total variance were kept for further analysis. Due to analyzing the data up to 3-way interactions it was
important to be able to assess the model with confidence. Therefore, all factors must have achieved importance more than 5% to the overall change to be further analyzed.

Desorption Isotherms

Based on results from the factorial desorption studies, desorption isotherm studies were carried out using the same solids as described in the previous section. The desorption behavior of As and Tl were evaluated using the factor levels found to have released the highest concentrations. In a desorption test, different masses of solids were added to water and the equilibrium TIC concentration was measured. In this study, the masses of solids used were 0.05, 0.1, 0.25, 0.5, and 1 g in triplicate added to 60 ml of Logan tap water. These mixtures were shaken for 24 hours, and filtered through 0.45 µm membrane nylon filters as in the desorption studies. The experimental conditions for Tl were temperature = 25 °C, pH = 6.5, Cl₂ = 0 mg/L, KH₂PO₄-P = 0 mg/L, and CaSO₄ = 350 mg/L. Conditions for As were temperature = 7 °C, pH = 8.5, Cl₂ = 0 mg/L, KH₂PO₄-P = 1 mg/L, and CaSO₄ = 0 mg/L.

A Freundlich isotherm was fit to the data, using equilibrium concentrations (Cₑ) vs sorption density (qₑ). This was determined by first converting the aqueous phase TIC concentrations (Cₐq) to a mass basis (Cₑ) as shown in Eq 1. The maximum concentration (C₀) was based on the exchangeable fraction using two modified methods scaled to use the same solids/liquid ratio as the desorption studies described earlier; Huang and Kretzschmar (2010) for As, and Amacher (1998) for Tl. To calculate the equilibrium mass
of contaminant remaining on the solids \( (q_e, \text{ see Eq 2}) \), \( C_0 \) was used as the maximum value, where \( C_0 \) for As: AST = 58.1 and UPA = 84.6 \( \mu g/g \), and Ti: AST = 81.7 and UPA = 85.7 \( \mu g/g \) (Table 4). Finally, the parameters for the Freundlich isotherm equation \( q_e = K_f C_e^{1/n} \), were estimated against the data by nonlinear regression analysis using the nls function in R (R Core Team 2016).

\[ C_{aq} = \text{Concentration in aqueous phase} \ (\mu g/L) \]
\[ V = \text{Volume of solution} \ (L) \]
\[ M = \text{Mass of solids added} \ (g) \]
\[ C_e = \text{Concentration in equilibrium} \ (\mu g/g) \]
\[ C_0 = \text{Maximum desorbable concentration on solids} \ (\mu g/g) \]
\[ q_e = \text{sorption density} \ (\mu g/g) \]

**Eq 1 - Equilibrium concentrations on a mass basis**

\[ C_e \left( \frac{\mu g}{g} \right) = \frac{C_{aq} \left( \frac{\mu g}{L} \right) \times V (L)}{M (g)} \]

**Eq 2 – Sorption density**

\[ q_e \left( \frac{\mu g}{g} \right) = C_0 \left( \frac{\mu g}{g} \right) - C_e \left( \frac{\mu g}{g} \right) \]
CHAPTER 5

RESULTS

Results from the factorial desorption experiments and isotherms are described in this chapter in the tables and figures. Figures for each statistically significant main effect and 2- and 3-way interaction are provided beginning with Figure 4 for each TIC analyzed. The numbers of factors and interactions included were then reduced based on importance, as defined in Chapter 4, and include only factors that contribute to at least 5% of the variance reduction for the total change in desorption. From the first figure of each TIC the factors determined as Important are shown above the dashed line. The Important factors are then summarized via boxplots showing those main effects and interactions considered important by the 5% criterion.

Assessment of Data Quality

The results from the LTW (Logan Tap Water) blanks and control samples are summarized (as described in chapter 4) in Table 8. The blank is LTW filtered through a 0.2 µm filter, and its mean was then subtracted out of the equilibrium concentrations in the results to determine the amount of each TIC released for a specific treatment.

The control samples consisted of a solution with a known dissolved concentration of TICs and filtered through both 1.5 and 0.45 µm nylon filters, shaken for 24 hours, and then filtered again to determine if sorption was occurring within the glass vials and lids.
used. The recovery of these known concentrations across the range of TICs and treatments are provided in Table 8. For most of the TICs, recovery ranged between 75 % and 115 %, with the exception of the low recovery for the 0.45 µm filtered Pb and Fe. The low recovery was due to precipitation of Pb and Fe, as PbO₂ and a variety of Fe minerals which would precipitate in the moderate hardness and alkaline pH of the test water (Brown et al. 2015), potentially causing precipitated Pb and Fe to be trapped on the filters.

**Table 8 – Quality assurance and quality control from filtered LTW blanks and controls using a solution with known concentration TICs to LTW filtered through 0.45 and 1.5 µm in µg/L, ± refers to the standard deviation of the triplicate samples.**

<table>
<thead>
<tr>
<th></th>
<th>Sb</th>
<th>As</th>
<th>Cr</th>
<th>Cu</th>
<th>Pb</th>
<th>Tl</th>
<th>Fe</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.57±</td>
<td>0.26±</td>
<td>0.17±</td>
<td>1.59±</td>
<td>&lt;MDL</td>
<td>0.12±</td>
<td>1.26±</td>
<td>0.38±</td>
</tr>
<tr>
<td></td>
<td>0.41</td>
<td>0.03</td>
<td>0.12</td>
<td>1.17</td>
<td></td>
<td>0.08</td>
<td>1.04</td>
<td>0.39</td>
</tr>
<tr>
<td>1.5 µm</td>
<td>3.36±</td>
<td>10.9±</td>
<td>9.54±</td>
<td>33.2±</td>
<td>14.8±</td>
<td>2.29±</td>
<td>444±</td>
<td>32.4±</td>
</tr>
<tr>
<td>Initial</td>
<td>0.60</td>
<td>0.5</td>
<td>0.86</td>
<td>1.6</td>
<td>0.6</td>
<td>0.13</td>
<td>32</td>
<td>4.5</td>
</tr>
<tr>
<td>1.5 µm</td>
<td>3.89±</td>
<td>10.3±</td>
<td>8.81±</td>
<td>25.1±</td>
<td>11.4±</td>
<td>2.02±</td>
<td>333±</td>
<td>31.0±</td>
</tr>
<tr>
<td>Final</td>
<td>0.14</td>
<td>0.7</td>
<td>0.26</td>
<td>5.5</td>
<td>3.2</td>
<td>0.14</td>
<td>108</td>
<td>1.3</td>
</tr>
<tr>
<td>Percent Recovery</td>
<td>116 %</td>
<td>95 %</td>
<td>92 %</td>
<td>76 %</td>
<td>77 %</td>
<td>88 %</td>
<td>75 %</td>
<td>96 %</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Sb</th>
<th>As</th>
<th>Cr</th>
<th>Cu</th>
<th>Pb</th>
<th>Tl</th>
<th>Fe</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.45 µm</td>
<td>2.91±</td>
<td>7.18±</td>
<td>8.84±</td>
<td>9.64±</td>
<td>0.53±</td>
<td>2.12±</td>
<td>3.47±</td>
<td>29.4±</td>
</tr>
<tr>
<td>Initial</td>
<td>0.56</td>
<td>0.47</td>
<td>0.28</td>
<td>2.23</td>
<td>0.21</td>
<td>0.11</td>
<td>2.4</td>
<td>1.4</td>
</tr>
<tr>
<td>0.45 µm</td>
<td>3.13±</td>
<td>7.82±</td>
<td>8.71±</td>
<td>8.79±</td>
<td>0.32±</td>
<td>2.01±</td>
<td>0.94±</td>
<td>28.0±</td>
</tr>
<tr>
<td>Final</td>
<td>0.40</td>
<td>0.11</td>
<td>0.06</td>
<td>0.41</td>
<td>0.02</td>
<td>0.03</td>
<td>0.18</td>
<td>0.3</td>
</tr>
<tr>
<td>Percent Recovery</td>
<td>108 %</td>
<td>109 %</td>
<td>98 %</td>
<td>91 %</td>
<td>60 %</td>
<td>95 %</td>
<td>27 %</td>
<td>95 %</td>
</tr>
</tbody>
</table>
Factorial Analysis Results

The factorial analysis results are presented for TICs and matrix elements. Both the dissolved (0.45 µm) and particulate (1.5 µm) portions were analyzed separately. The data are presented for all significant factors and interactions, and separated by importance. The important treatments were then plotted using notched box and whisker plots (these are defined as (Figure 3): a) the solid center line is the median, b) the box (hour glass shaped) is the interquartile range (IQR) representing the center 50% of the data, c) the whiskers are the observations just below the upper 75th quantile or just below the lower 25th quantile ± 1.5 * IQR, and finally d) the notches are the 95% confidence interval on the median (median ± 1.57 * IQR/√n). If the notches overlap for two treatments, this indicates that those treatments are similar in release, with 95% confidence. Each element includes a figure showing the regression coefficient estimates for all significant variables and interactions representing the magnitude of the increase or decrease from the overall mean, as well those that are found to be important.

TICs

Antimony (Sb)

At both sites Sb release was below the MCL, though at UPA the concentrations approached the MCL of 6 µg/L. At AST the mean release was 0.8 µg/L, and only temperature was a significant factor, which increased release by 0.3 µg/L. UPA had higher release with a mean of 2.73 µg/L, with temperature and CaSO₄ having the biggest effect
Figure 3 - Boxplot diagram

on release. The filtered size, labeled as “type” in Figure 4 did have a small effect with pH; however this was not considered important. The interaction of temperature:pH and temperature:CaSO₄ did have a significant effect on release. Finally, the interaction of temperature:PO₄:CaSO₄ had a small but still important effect on Sb release. The parameters above the dashed line in Figure 4 indicate importance, which describes the releases from UPA; there are no plots for AST because there was only one significant factor and the site had a very low mean release, well below the MCL for Sb.
Figure 4 - All significant factors in Sb release, and importance > 5 % of the variance indicated by those above dashed line. Values presented are the change from the mean. No plot for AST because there is only one factor that was significant.

Overall, the Sb releases were under the MCL; however, the maximum concentration released, at 5 µg/L at UPA at the higher temperature, approached the MCL (6 µg/L). Figure 5 shows the main effects and the important 2-way, and 3-way interactions for UPA; this plot shows that temperature has the greatest main effect on Sb release. The interquartile ranges for both temperatures 7 and 25 °C (Figure 5A) are very small, indicating that the single factor dominates the release of Sb, despite any other interactions. The midpoint concentration shown by the blue dashed line shows at a temperature of 16 °C the release concentration was 3.31 µg/L, which is near the median for temperature at 25 °C. This indicates that there is not a linear relationship to
temperature and potentially temperatures below 16 °C can cause high release and that temperatures higher than 25 °C may not cause more Sb to be released.

The treatments with the highest release were the combination of temperature = 25 °C + and CaSO₄ = 0 mg/L, or temperature = 25 °C + pH = 8.5 (Figure 5B). The effect of PO₄³⁻ was significant, but alone proved to be unimportant; only when PO₄⁻P = 1 mg/L did it have a slightly higher release when temperature = 25 °C and with CaSO₄ = 350 mg/L (Figure 5C). All three plots show that when the temperature = 7 °C there is no difference in interactions of pH, CaSO₄, or PO₄³⁻. The midpoint is the same as the interactions where pH = 6.5 and temperature = 25 °C and temperature = 25 °C with CaSO₄ = 350 mg/L.

**Arsenic (As)**

The filter size did not prove to be a significant factor at either site, leading to the combination of data from the two filter sizes in Figure 6. AST had a mean release of 11.1 µg/L and UPA had a mean release of 6.12 µg/L. For UPA, there are several 2 and 3-way interactions that were significant; however they are not all important. The most important factors that drive the change in release for As are pH, PO₄³⁻, CaSO₄, and their 2 and 3-way interactions. For both locations pH was the largest contributor, especially at UPA where pH controls 55 % of the change in release. Figure 7 shows important factor main effects, Figure 8 important 2-way effects, and Figure 9 important 3-way effects for both locations.
Both locations showed similar trends, but AST solids released twice the As concentration as at UPA. At both locations, when pH and PO$_4^{3-}$ were low and CaSO$_4$ is high, the interquartile range is very small and less than the MCL, indicating the changes of any additional factors do not increase the release to above the MCL. The midpoint also
falls below the MCL and at or near the median of pH = 6.5, PO₄-P = 0 mg/L, and CaSO₄ = 350 mg/L. Conversely, at high pH = 8.5 and PO₄-P = 1 mg/L the interquartile ranges are wider, indicating that other factors influence the decrease in the amount of As to below the MCL.

The 2-way interactions in Figure 8 show more detail about the influence of the factors. For both locations, when the pH and PO₄³⁻ are low, the concentration released was below the MCL, and when the pH and PO₄³⁻ are high the concentrations were above the MCL at both locations. However, these high concentrations were reduced to below the MCL with the addition of CaSO₄, as seen at both locations.

The 3-way interactions of pH:PO₄³⁻:CaSO₄ on As release (Figure 9) describe the 2-way interactions even more fully. Each box is small showing more precisely what is happening within each treatment. At both locations high pH = 8.5, PO₄-P = 1 mg/L, and CaSO₄ = 0 mg/L caused the highest As releases with means of 40 and 17.7 µg/L at AST and UPA. In both plots when the pH is low there are minimal effects from other parameters, mainly CaSO₄. However, when the pH is high at 8.5 both CaSO₄ and PO₄³⁻ have significant effects on the released concentrations. Also the biggest effect of CaSO₄ with PO₄³⁻ is shown at high pH, where the addition of CaSO₄ significantly reduces the As concentration. From the midpoint it is aligned with pH = 6.5, PO₄-P = 1 mg/L, with or without CaSO₄, and it also the same as pH = 8.5, PO₄-P = 0 mg/L, and CaSO₄ = 350 mg/L.
Figure 6 - All significant factors in As release, and importance indicated by those above dashed line. Values are the change from the mean.

**Chromium (Cr)**

For Cr, at AST none of the dissolved portions were above the MDL (<0.45 µm, all concentrations were < MDL), and therefore Figure 10 only includes the releases for total portions of <1.5 µm particulates. For both locations the released concentrations were
Figure 7 - Important single factor effect on release for As. The red line indicates the MCL; blue dashed line is the mean mid-point concentration.

very low (100 times lower) compared to the MCL of 100 µg/L. Figure 11 shows the data for AST and UPA, where the difference between releases at the two temperatures is statistically significant. An increase in temperature caused a decrease in Cr release at AST but an increase at UPA. At AST the only other significant factors were the three way interactions between temperature, pH, and PO₄³⁻. However from Figure 11 it is shown that the releases are all close to 0 µg/L, and the range is very small from > -0.25 µg/L to < 1.0 µg/L (- implies sorption as opposed to desorption). UPA behaves very similarly, with
Figure 8 - Important 2-way interactions release for As, red line indicating MCL; blue dashed line is the mid-point concentration. Each letter on top shows the difference in treatment, i.e. same letter means there is no difference between treatments.

the only other significant factor being a 3-way interaction with filter size, temperature and Cl₂. These also had very low releases ranging from $> 0.25 \mu g/L$ to $< 1.5 \mu g/L$. Again the MCL is $100 \mu g/L$ for Cr making these releases negligible from an engineering perspective at both locations. At both locations when temperature = 25 °C the release concentration is same as the midpoint.
Figure 9 - Important interactions affecting the release of As; red line indicates the MCL; blue dashed line is the midpoint concentration. The letters on top of the plots indicate which treatments are significantly different, i.e. same letter indicates there is no difference between treatments. For those with two letters, both letters are interpreted individually (e.g. ‘de’ means no different from those marked with either d or e or both).

Copper (Cu)

Both locations had a significant difference between filter sizes, and Figure 12 shows the significant factors affecting release. Overall, both locations had multiple factors influencing release concentrations and changes; however, the concentrations are all well below the Action Level (AL, Cu = 1300 µg/L). For a filter size < 0.45 µm, the factors pH,
Figure 10 - All significant and important factors in Cr release; no dashed line indicates they are all important. Values are the change from the mean.

Figure 11 - Important single and 3-way interactions release for Cr, blue dashed line is the mid-point concentration. Each letter on top shows the difference in treatment, i.e. the same letter means there is no difference between treatments. For those with three letters, the interpretation is the same as those with two letters.
CaSO₄, and the combinations of pH:CaSO₄, temperature:pH:CaSO₄, and temperature:CaSO₄ had statistically significant effects on the release of Cu at AST, with the overall mean of release of 0.16 µg/L. The change in pH from 6.5 to 8.5 had the largest decrease in release of -1.09 µg/L. The 3-factor interactions between CaSO₄:temperature:pH had a larger effect than CaSO₄ alone, which caused a small decrease in release. CaSO₄ did not have an effect on the release for the <1.5 µm filtered size.

At UPA the mean release was higher than at AST, 3.3 and 1.96 µg/L for the < 0.45 and 1.5 µm filter sizes, respectively, with the single factors of temperature and pH also being important. For the < 0.45 µm data set, only three of the two way interactions were important, temperature:CaSO₄, pH:Cl₂, and pH:CaSO₄, while no three way interactions were important. For the < 1.5 µm set the important interactions were the temperature:pH, temperature:CaSO₄, and Cl₂:PO₄³⁻. As observed at AST, pH was the most influential factor with low pH (6.5) having the highest release at UPA, the single factors of temperature and pH on both filtered sizes contribute to most of the release.

Overall both locations had a very low mean of release of 0.16 and -0.14 µg/L at AST, and 3.30 and 1.96 µg/L at UPA. These release concentrations are low compared to the AL of 1300 µg/L, so this was not considered a high enough release to be further analyzed.
Figure 12 - All significant factors in Cu release, and importance indicated by those above dashed line. Values presented are the change from the mean.
Lead (Pb)

The dissolved and particulate Pb concentrations for both AST and UPA were below the method detection limit under all conditions, which indicated the tested factors did not cause detectable Pb release. No interpretation of the effects of the treatments is possible.

Thallium (Tl)

Most factors had a statistically significant effect for both the dissolved and particulate Tl at both sites, but filter size did not have an important impact, so the data in Figure 13 are for the combined sizes (labeled as Type). For both sites, temperature, pH, Cl₂, and CaSO₄ were significant and important (Figure 13). There were also significant two-way and three-way interactions from many factors. Both locations had similar concentrations, with the mean Tl release at AST being 43.5 µg/L, and at UPA being 41.9 µg/L. Simultaneous increases in temperature and CaSO₄ caused an increase in release, whereas the decrease in pH and Cl₂ caused an increase in release. The largest two-way interactions for both sites were temperature:pH, and temperature:Cl₂. At AST the interactions of pH:Cl₂, pH:PO₄³⁻, and temperature:pH:CaSO₄ were also important factors. At UPA the interaction of pH:CaSO₄ was important.

Figure 14 shows both AST and UPA with the single important factors temperature, pH, Cl₂, and CaSO₄. Tl release was far exceeding the MCL of 2 µg/L for all treatments. Temperature and pH show the largest differences. The main effects have high variance,
meaning that they are heavily influenced by the interactions. For better interpretation and more precise detail on the interactions effects on the change in release are in Figure 15 and Figure 16. At both locations the midpoint release concentration is very high at 60.9 and 59.6 µg/L at AST and UPA respectively, which corresponds best with pH = 6.5. This indicates that overall there is very high release and a nonlinear effect from the change in factors.

Figure 15 shows the important 2-way interactions. Here, for clarity boxplots are broken up into sections of each 2-way interaction, with letters above each plot indicating a difference in treatment. These two plots show that each different treatment within the 2-way interaction is significantly different. For both sites the interaction of temperature:pH has the smallest interquartile range, indicating that those interactions best describe the releases. Both locations show that at a high temperature = 25 °C and low pH = 6.5 (Figure 15, second panel from the left labeled “a”) there is the highest release of Tl with both locations having a mean of 75 µg/L.

Finally there was one important three-way interaction for Tl; it was at AST and it includes the interactions of temperature, pH, and CaSO₄ (Figure 16). This graph shows most of the box ranges are smaller than the single factors indicating reduced variability. The highest release was with high temperature = 25 °C and low pH = 6.5, with the interaction of CaSO₄ showing no change. Though the change due to CaSO₄ is significant,
Figure 13 - All significant factors in Ti release, and importance indicated by those above dashed line. Values presented are the change from the mean.

There are only small differences with or without the addition of CaSO₄ as shown by the overlapping of notches between treatments (Figure 16).
Figure 14 - Important single factor effect on release for Tl. The red line indicates the MCL; blue dashed line is the mean mid-point concentration.

**Matrix Elements (Fe & Mn)**

**Iron (Fe)**

Unlike for the TICs, there were significant levels of Fe in LTW that needed to be filtered through a 0.2 µm filter before the experiment, lowering Fe concentrations to 1.3±1.0 µg/L. Results show at UPA there was high variability that resulted in no significant effects of the tested factors. At AST, all factors except Cl₂ affected dissolved Fe
Figure 15 - Important 2-way interactions release for Ti. The red line indicates the MCL; and blue line indicates the mid-point concentration. Each letter on top shows the difference in treatment, i.e. the same letter means there is no difference between treatments.

concentration (filter < 0.45 µm) in solution and were important, although no factors were significant for particulate release (filter < 1.2 µm).

Overall, despite the filtering any remaining Fe in LTW was sorbed onto the solids, resulting in a mean of -1.08 µg/L Fe released, meaning that Fe from the water was reassOCIated with the solids, resulting in a net decrease of Fe in the LTW. Figure 17 shows the important factors.
Figure 16 - Important 3-way interactions release for Tl at AST. The red line indicates the MCL; and blue line indicates the mid-point concentration. Each letter on top shows the difference in treatment, i.e. the same letter means there is no difference between treatments.

Figure 18 shows the significant and important main effects and 2-way interactions; however from the Tukey test and figures there is no real difference in treatments. This could be due to the high variability from the mean and outliers in Fe release combined with the low concentrations.

**Manganese (Mn)**

The solids from AST released 100 times more Mn than from UPA. All of the main effects were statistically significant, but only pH, Cl₂, and CaSO₄ were important effects on the release, with pH being the most important at AST (Figure 19), and the important interactions include pH:Cl₂ and pH:CaSO₄. The overall mean release at AST was 38.8 µg/L, and ranged from below the method detection limit (<0.05 µg/L) to 150 µg/L at pH 6.5.
This is above the secondary maximum contaminant level for Mn of 50 µg/L. Overall the change in pH had the largest effect on release, and when the pH was 8.5 the concentrations were below the detection limit.

The UPA solids showed very low concentrations of Mn released with averages of 0.05 and 0.2 µg/L for dissolved and particulate. Statistically temperature, pH, Cl₂, and CaSO₄ had an effect on the Mn release, following the same pattern as AST. Despite there being many significant and important 2-way and 3-way interactions (Figure 19) at UPA, the released concentrations was more than 50 times lower than the secondary limit; therefore no further analysis is reported and the significance of the treatments is ascribed to the unusually high reproducibility of the Mn measurements.
Figure 18 - Important single factor effect on release for Fe (upper), and 2-way interactions (lower). The blue dashed line is the mean mid-point concentration.

Figure 20 shows the extreme effect of pH and Cl₂ on release for AST. When pH = 6.5 the release concentration is above the secondary limit; however, with the addition of Cl₂ this reduces the release to the secondary limit. It also shows the effect of CaSO₄, where the addition of CaSO₄ causes an increase in release.
Figure 19 - All significant factors in Mn release, and importance indicated by those above dashed line. Values presented are the change from the mean. No dashed line indicates all factors are important.
Figure 20 - Important single factor effect on release for Mn (upper), and 2-way interactions (lower). The orange line indicates secondary limit; blue dashed line is the mean mid-point concentration.

Isotherm

TI and As were selected to generate desorption isotherms because these elements were both highly active in the desorption studies, and had concentrations in solution above the MCLs. The upper graphs in Figure 21 show the equilibrium concentration of TIC in solution ($\mu$g/L) versus the mass of solids added (g). The concentration in solution was expected to increase with an increase in solids; however, the concentration of As decreased with an increase in solids. The bottom graphs show traditional sorption isotherm plots where $q_e$, the concentration left on the solids ($\mu$g/g) is calculated by taking
the initial solid concentration from the sequential extraction exchange step, then subtracting out the concentration released into solution (µg/L) which was divided by each mass added.

![Figure 21](image)

Figure 21 – Tl and As desorption isotherm data Top) are equilibrium concentrations vs mass, Bottom) are concentrations remaining on solids vs equilibrium concentrations. Freundlich isotherm parameters in Eq 3, and curve in Figure 22
From the Tl isotherm data in Figure 22, a Freundlich model, as shown in Eq 3, was fitted to the data, after adjusting the intercept through 0 as explained below. Figure 21 shows that at UPA there were some small negative calculated values for the lowest net mass remaining on the solids, indicating there may be higher desorption than the maximum concentration assumed to be available based on the sequential extraction results. Since this is physically highly unlikely there are a few plausible explanations, the first being that the Tl concentration found from the exchangeable step of the sequential extraction (Amacher 1998) was not the same as in the treatment of Logan tap water which produced the high Tl release. The treatment that provided the highest release of Tl was also that of Mn, which could be introducing dissolution of Tl from Mn as well as exchangeable Tl. If the total exchangeable was underestimated and the amount released exceeded this value, negative solid phase TIC concentrations would be calculated. The second explanation is that the low mass used (0.05 g) introduced a higher amount of uncertainty and the negative estimated release is interpreted as random noise.

If the exchangeable capacity is underestimated this will have the effect of shifting the isotherm to the right on the $q_e$ vs $C_e$ plot. These inconsistencies make it difficult for interpretation because, by definition, the isotherm equation goes through the origin as $C_e$ tends to zero. For purposes of estimating the isotherm behavior the $C_e$ data in Figure 22 was shifted to the left by subtracting the lowest measured concentration from each $C_e$ observation to force the model through the origin. The Freundlich parameters (intercepts
and slopes) were determined using non-linear parameter estimation (nls(... procedure in R) and the estimated parameters are shown in Eq 3. Due to the shift in the Ce values along the x axis, the Kf value is not well defined. However, Kf represents the sorption capacity under the conditions of 25°C, 6.5 pH, no Cl2, or PO4, 350 mg/L CaSO4. The exponent (1/n) should be relatively unaffected by the shift in the sense that it determines the sensitivity of the sorbed phase concentration to changes in the aqueous phase concentration. A larger value of n indicates less sensitivity and that sorption of Tl onto AST solids is more sensitive to Ce than are the solids at UPA. The magnitude of the Ce axis shift can be interpreted as a measure of the error in the estimate of C0 (values are located in Chapter 4, Desorption Isotherm).

The As isotherm had unusual behavior in which the solid phase shows a decrease as the aqueous phase concentration increased (Figure 21, lower right panel). This behavior does not follow that of the Freundlich isotherm and would have resulted in a negative exponent (1/n) in the isotherm equation. It was speculated that this non-standard behavior could have been a result of changes in the solution chemistry during equilibration, particularly in the pH. However, the pH was measured at the beginning, about halfway through, and at the end of the equilibration period and showed only a small decrease (pH 8.5 to 8.2-8.3), a change unlikely to have dramatically modified desorption isotherm behavior. Another possibility is that, to some extent, desorption of As from the AST solids is irreversible.
Figure 22 - TI isotherm data with the Freundlich model

Eq 3 - Freundlich isotherm for TI

\[
AST \ q_e = (2.97 \pm 0.64)C_e^{1/(1.44\pm0.1)} \\
UPA \ q_e = (9.82 \pm 4.62) \ C_e^{1/(1.76\pm0.43)}
\]
CHAPTER 6

DISCUSSION

The main TICs discussed below are those that showed high release approaching or above the MCL: As, Tl, and Mn at AST and Sb, As, and Tl at UPA. The most influential factors are discussed below.

Main Effects of Factors

The most influential factors from this set of experiments are summarized in Figure 23 by showing the five most important for the TICs and matrix elements. The three strongest main effects were pH, temperature, and Cl₂, where pH was the most important factor for all elements, except for Sb, for which pH had no effect. An increase in release was caused at pH 8.5 for As, and pH 6.5 for Tl and Mn, contributing to 42-80% of the change in release. Temperature had the largest effect on the change in release for Sb, accounting for over 85% of the change, and accounted for 32-40% of the release for Tl. Both Sb and Tl had increased release at 25 °C versus 7 °C. The addition of Cl₂ from 0 to 2 mg/L was an important factor for Tl and Mn, accounting for 10% of the variance for Tl, and 30% for Mn. Releases of both Tl and Mn were reduced with the addition of Cl₂. Two key parameters that consistently decreased release were temperature = 7 °C and the addition of Cl₂ to 2 mg/L, on those TICs that were affected by these factors.
The addition of PO$_4^{3-}$ and CaSO$_4$ were the smaller main effects. The addition of PO$_4^{3-}$ caused As to increase release, and accounted for 20-40 % of the total change. CaSO$_4$ was the single factor that affected release of all stated significant elements, but the importance only ranged from 2.5-15 %. Increasing CaSO$_4$ to 350 mg/L caused As and Sb to decrease and the Tl and Mn to increase in release concentrations.

**pH 6.5 to 8.5**

pH was the factor that had the largest effect on release of As, Tl, and Mn. pH is a critical factor for sorption, considering matrix elements' point of zero charge, and the pK$_a$ for each element as discussed below.
pH Effects on Arsenic

For As, setting the single factor of pH to 6.5 kept the As concentration below the MCL (10 µg/L), regardless of any other factors. However when the pH was raised to 8.5 it was clear that interactions with the other factors were contributing to the release (Figure 9). Considering the large concentration of Fe present in the solids and the strong sorption relationship of As onto Fe (Friedman et al. 2016), the point of zero charge (pzc) relative to the solution pH is an important determinant of sorption behavior. For the form FeOOH the pzc is pH 7.8 (Stumm and Morgan 1981), and the forms Fe₂O₃ and Fe(OH)₃ the pzc is pH 8.5. When the pH is below the pzc, Fe oxide becomes increasingly positive, attracting anions such as As, decreasing the amount of As released. At pH 8.5 Fe oxides are neutral or negatively charged, and As would tend to be released into solution. Considering the pzc of Fe oxides, desorption of arsenite increases at pH > 9, whereas desorption of arsenate increases at pH values of 7-9 (Lenoble et al. 2002).

pH Effects on Thallium

For Tl all concentrations during the release experiments were above the MCL (2 µg/L), but pH 6.5 caused a large increase in release relative to pH 8.5, and was the most important factor at both locations. Low pH of 6.5 caused an increase in release of 33.6 µg/L at both sites, compared to release at pH 8.5 (Figure 14), accounting for 45-50 % of the change in release due to all factors. In these experiments, the Tl was primarily present
as Tl(I), (Tl\(^+\)). In this form, much like most alkali metals such as potassium ions, K\(^+\), pH in the range of 6.5 to 8.5 does not influence its chemistry. The most likely influence of pH is on the solids surfaces where those surfaces would be more positively charged than at a higher pH due to the association of hydrogen ions with negatively charge surface functional groups. This reduction in (-) charges on the surface would tend to repel Tl\(^+\), and increase the concentration in the aqueous phase.

Though the single factor of pH is significant, the interquartile range is still large at both levels, indicating interactions of other factors with pH are also important. The most significant interaction with pH is temperature, where an increase in temperature caused a large increase in release at both pH levels (Figure 15). Only the two-way interaction of pH = 6.5 and temperature = 25 °C caused all released concentrations to be above the midpoint concentration for both sites. In addition, the difference in concentration from pH 6.5 to pH 7.5 is much smaller than that from pH 7.5 to pH 8.5. This suggests that the change in released concentrations to pH is non-linear, where concentration released decreases to a larger extent for higher pH values. As the effect of pH on Mn is very similar to that for Tl, and the pH effect of Tl(I) follows the same trend as Mn oxides; that and the high affinity of Tl for Mn oxides means that the pH effect on Tl may be due mainly to Mn oxides being released. Further research would be required to confirm this.
**pH Effects on Manganese**

For Mn at AST in all cases when the pH was 8.5 the release concentrations were near the detection limit (0.05 µg/L), but pH 6.5 caused the concentrations to rise over the secondary MCL (50 µg/L). Figure 20 shows this large change in release from the change in pH from 6.5 to 8.5. The largest change was due to the interaction with pH and Cl₂ where the addition of Cl₂ significantly lowered the release concentrations at pH 6.5 to below the secondary limit. The midpoint concentration with pH 7.5 caused a decrease in release concentration from pH 8.5 to just below the secondary limit. The point of zero charge for crystalline MnO₂ range from 4.3 to 6.2 depending on the specific mineralogy (O’Reilly and Hochella 2003); above this point MnO₂ is negatively charged, attracting cations.

**Temperature 7 to 25 °C**

An increase in temperature is generally expected to increase release through increase in reaction rates and solubility. This proved to be true for the temperature effects on Sb and Tl, where higher temperature of 25 °C caused a significantly higher release. In contrast, temperature had little effect on release of Mn and As.

**Temperature Effects on Antimony**

Antimony had high concentrations released only at UPA where concentrations approached the MCL, and where temperature controlled almost 85 % of the change in release. Xi et al. (2011) studied the effect of temperature on adsorption of Sb(III) on
bentonite, a 2-1 expanding clay, and found that Sb(III) decreased in adsorption with an increase in temperature (from 5 to 50 °C) though the opposite was true for Sb(V). It was also shown that the solubility of Sb(III) was not affected by competing anions or changes in pH, which indicates that Sb(III) is bound by inner sphere complexes (Wilson et al. 2010). The lack of desorption of Sb in the presence of phosphate and sulfate observed in this study indicates that Sb(III) could be the dominant form, which could be problematic in drinking water applications due to the fact that Sb(III) is ten times more toxic than Sb(V) (Krachler et al. 2001).

At AST the Sb release concentrations were very low, with a mean release = 0.8 µg/L, and temperature was the only significant factor in release.

**Temperature Effects on Thallium**

Overall Tl was sensitive to all of the factors at both sites, and temperature was the second most influential factor controlling Tl release. By increasing the temperature from 7 to 25 °C the concentrations from both sites increased by an average of 29.3 µg/L with the median being 50-60 µg/L, which is over 30 times higher than the MCL of 2 µg/L. If the main mechanism is Tl sorption onto Mn-oxides, this suggests that that mechanism may be sensitive to temperature.
Chlorine 0 to 2 mg/L – Effects on Thallium and Magnesium

Thallium readily sorbs onto Mn oxides (Jacobson et al. 2005), and solution concentration of both Tl and Mn were affected by the addition of Cl₂. By adding 2 mg/L Cl₂ the concentrations released were reduced, for Tl by 14.6 µg/L, and Mn by 38 µg/L. An effective method for the removal of Mn is by oxidation to Mn(IV) and precipitation as MnO₂, which can be achieved with the addition of chlorine at pH > 8 (e.g. Hao et al. 1991). By oxidizing and precipitating Mn, the newly formed solids surfaces would readily sorb Tl, causing overall decrease in both elements. This looks to be a potentially effective treatment method for removal of Tl(I), by sorption to MnO₂(s) (Wan et al. 2014).

Calcium Sulfate 0 to 350 mg/L

All of the TICs were affected to some extent by CaSO₄, but it was the smallest single important factor. For Sb and As, the change from 0 to 350 mg/L CaSO₄ decreased the released concentrations. Initially it was hypothesized that CaSO₄ would increase release concentrations via ion exchange with the SO₄²⁻. However, it appears the Ca may have precipitated with portions of any released Sb and As, causing a net decrease in their concentrations in solution. The changes in release from CaSO₄ of 0 to 350 mg/L for both As and Sb were modest as shown by the notches in the box plots overlapping. However, when interactions with temperature for Sb, and pH and KH₂PO₄ for As are considered there is a significant difference in the released concentration remaining in solution, depending on the amount of CaSO₄ addition. It could also be that, since Ca precipitation
would only occur for Sb(V) or As(V), Ca only precipitates the oxidized forms of these TICs in solution and leaves the sorbed neutral reduced forms unaffected. For future studies, mass balances on Ca, Sb, and As before and after desorption would help clarify their behavior during CaSO₄ addition.

For Tl and Mn the addition of CaSO₄ increased release concentrations by 9 and 14 µg/L respectively, enough for the Tl concentration to exceed its MCL. In Figure 14 for Tl, though the CaSO₄ factor is significant, the 95% confidence intervals for the medians (notches) overlap for the 0 and 350 mg/L additions. This indicates that there are other interactions contributing to the release. Figure 20 shows similar results for Mn, where CaSO₄ is significant but the interactions with pH are far more significant. Only when pH is 6.5 versus at 8.5 is there an effect from the change in CaSO₄, from Mn being more mobile at pH 6.5.

**Phosphate-P 0-1 mg/L – Effects on Arsenic**

The addition 1 mg/L PO₄-P was only significant for As, causing an increase in release by 13.9 and 4.7 µg/L at AST and UPA respectively. As hypothesized for this study PO₄³⁻ is a sorption competitor with As in its arsenate form on many solids including Fe oxides (Wilson et al. 2010) and this was consistent with the findings in this experiment.
TICs (Sb, As, and Tl) and Manganese

A variety of results is shown in Table 9, including the monitoring samples, closest source to the sampled area, sequential extraction exchange step, and range in the results of the desorption experiment. This table is discussed for each key TIC. The source and monitoring data are a subset from the entire distribution system data set and sources that correspond to the AST and UPA regions. All concentrations were converted to µg/L except for the total concentration to be easily comparable.

Table 9 - TICs and matrix elements range in PC monitoring compared to the closest source and concentrations found in desorption studies. In (µg/L) unless otherwise stated

<table>
<thead>
<tr>
<th>Site</th>
<th>Sb</th>
<th>As</th>
<th>Cr</th>
<th>Cu</th>
<th>Pb</th>
<th>Tl</th>
<th>Fe</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCL/2nd Limit</td>
<td>6</td>
<td>10</td>
<td>100</td>
<td>1300</td>
<td>15</td>
<td>2</td>
<td>300</td>
<td>50</td>
</tr>
<tr>
<td>Source</td>
<td>0.5-5</td>
<td>2</td>
<td>0.2-0.5</td>
<td>1.5</td>
<td>0.2</td>
<td>&lt; MDL</td>
<td>2.5-55</td>
<td>0-0.2</td>
</tr>
<tr>
<td>Monitoring</td>
<td>2-5</td>
<td>3-6</td>
<td>0.5-2.5</td>
<td>10-40</td>
<td>1-4</td>
<td>&lt; MDL</td>
<td>10-350</td>
<td>0-10</td>
</tr>
<tr>
<td>Exchangeable</td>
<td>2.02</td>
<td>96.8</td>
<td>&lt;MDL</td>
<td>46.2</td>
<td>&lt; MDL</td>
<td>136</td>
<td>&lt; MDL</td>
<td>72.8</td>
</tr>
<tr>
<td>Desorption</td>
<td>0-2.4</td>
<td>0.9-42</td>
<td>0-0.8</td>
<td>&lt;MDL-2.8</td>
<td>&lt; MDL</td>
<td>4.5-87</td>
<td>&lt;MDL-10</td>
<td>&lt;MDL-150</td>
</tr>
<tr>
<td>Total (mg/kg)</td>
<td>19.5</td>
<td>1.7x10³</td>
<td>36.5</td>
<td>2.6x10³</td>
<td>3.4x10³</td>
<td>1.6x10³</td>
<td>1.5x10⁵</td>
<td>1.8x10⁴</td>
</tr>
<tr>
<td>Source</td>
<td>6.7</td>
<td>8.8</td>
<td>0.4</td>
<td>33.2</td>
<td>7.9</td>
<td>&lt; MDL</td>
<td>465</td>
<td>12</td>
</tr>
<tr>
<td>Monitoring</td>
<td>2-8</td>
<td>2-8</td>
<td>0.5-3.2</td>
<td>0-110</td>
<td>0-8</td>
<td>&lt; MDL</td>
<td>10-700</td>
<td>0-50</td>
</tr>
<tr>
<td>Exchangeable</td>
<td>5.93</td>
<td>141</td>
<td>0.55</td>
<td>92.2</td>
<td>&lt; MDL</td>
<td>143</td>
<td>&lt; MDL</td>
<td>0.70</td>
</tr>
<tr>
<td>Desorption</td>
<td>1.1-5.1</td>
<td>1.1-19</td>
<td>0.7-1</td>
<td>0.04-7</td>
<td>&lt; MDL</td>
<td>1.9-92</td>
<td>&lt;MDL</td>
<td>&lt;MDL-1.5</td>
</tr>
<tr>
<td>Total (mg/kg)</td>
<td>36.3</td>
<td>672</td>
<td>62.3</td>
<td>1.61x10⁴</td>
<td>6.7x10³</td>
<td>785</td>
<td>1.4x10⁵</td>
<td>1.0x10⁶</td>
</tr>
</tbody>
</table>

Antimony

As stated above temperature was the main factor contributing to the release of Sb at UPA (mean release = 2.74 µg/L). UPA was the only location where release
concentrations approached the MCL. Table 9 shows that of the two sites, UPA had higher Sb concentrations measured in Park City’s water distribution system monitoring throughout 2013, exchangeable from the pipe solids, and at the source. At the higher temperature of 25 °C, the Sb concentration sometimes exceeded the MCL. In fact, temperature determined almost 85% of the change in release in the desorption study.

Antimony may not have had high releases due to its being a neutral complex at the pH ranges tested (Sb(OH)$_3^{(aq)}$) (Wilson et al. 2010). As stated in the literature review, the removal of Sb(III) from solids using competitive ions is not expected. In this study no release due to competing ions was found indicating the Sb form may be Sb(III). From both locations less than 10% of the total Sb was released in the exchange step of the sequential extractions (Tables B2 and B3), which is still a low concentration below the MCL.

Exchangeable Sb was determined by sequential extraction step developed for As, using 0.005M PO$_4^{3-}$ as KH$_2$PO$_4$ and shaking for 2 hours (Huang and Kretzschmar 2010) (Table 9). The maximum concentrations released during desorption were 2.4 and 5.1 µg/L at AST and UPA respectively, and using 0.1 g of solids in 60 mL, AST had 1.4 µg/g, and UPA had 3 µg/g. The maximum release from the experiment was caused where temperature = 25 °C, CaSO$_4$ = 0 mg/L, and PO$_4$-P = 0 mg/L, Sb desorbed >100% of the defined exchangeable Sb at AST and 86% at UPA. This shows that Sb was released at similar concentrations to that expected from surface exchange. While at this time the maximum
Sb released is still below the MCL, this does cause concern that moderate changes to the water chemistry can cause all of the surface exchangeable Sb to be released in the Park City water distribution system, particularly in locations where the solids might have more Sb to exchange.

**Arsenic**

Arsenic was affected by the factors pH, PO$_4^{3-}$, and CaSO$_4$. Figure 9 shows that the treatment with pH = 6.5, PO$_4$-P = 0 mg/L, and CaSO$_4$ = 350 mg/L controlled As release below the MCL at both locations. Also, released concentrations from those single factor effects all had a small interquartile range compared to those at pH = 8.5, PO$_4$-P = 1 mg/L, and CaSO$_4$ = 0 mg/L, indicating the interactions of pH, PO$_4^{3-}$, and CaSO$_4$ describe As desorption more fully.

Focusing on conditions of high pH where the concentrations had wider interquartile ranges than at low pH and measurements that were near the MCL, the solids were more susceptible to PO$_4^{3-}$ and CaSO$_4$ changes (Figure 9). When the pH was high the addition of PO$_4^{3-}$ caused the As concentrations to rise well above the MCL, while the addition of CaSO$_4$ had the opposite effect of lowering most of the concentrations to below the MCL at UPA and lowered the concentration median to below the MCL at AST. Further, the 3-way interaction for these factors had the smallest interquartile range for describing As release. At AST, all pH = 8.5 scenarios caused the release concentrations to be above the MCL except for the addition of CaSO$_4$ without PO$_4^{3-}$ (Figure 9). UPA followed the same
pattern but at lower concentrations, where only those with the addition of PO$_4^{3-}$ were above the MCL. Overall pH caused the largest change in releases, followed by PO$_4^{3-}$ causing significant releases above the MCL. And finally the addition of CaSO$_4$ caused a decrease in release, even lowering by half the concentration at AST to below the MCL, which may be partially explained by precipitation of Ca$_3$(AsO$_4$)$_2$ as discussed previously.

The As at both sites had similar responses in direction to each of the test variables in the desorption studies, though they differed in magnitude, from 0.9 to 42 µg/L at AST and from 1.1 to 19 µg/L at UPA. The differences between the two sites were in the total concentration of As in the solids, the amount desorbed under test conditions, and mineral association as defined during the sequential extractions (Table 9, Table B2, and Table B3). The total concentration of As in the AST solids was greater than in the UPA (1,700 mg/kg vs. 672 mg/kg, Table 9). Interestingly between the two sites, the ratio of the maximum release concentrations (0.45) is very similar to the ratio of the total concentrations at each location (0.39), and can help explain the differences in behavior and underscore the similarity of the surface interactions with the dissolved species.

From the sequential extraction exchange step AST had a lower concentration (96.8 µg/L) compared to UPA (141 µg/L); however, from the desorption studies AST had higher concentrations released. This points to differences in the strength of association of the As to these exchange sites as shown by the difference in total Mn concentrations in the solids (1.8x$10^4$ mg/kg for AST, $10^5$ mg/kg for UPA), as well as the As associated with Fe and Mn
at each site. At AST 117 and 177 mg/kg of As were associated with the Mn and Fe oxides respectively, whereas at UPA only 50 and 108 mg/kg of As was associated with the Mn and Fe oxides (Table B2 and Table B3). This could help explain why there are differences in the magnitude of As behavior between sites, and their relation to the desorption studies compared to the exchangeable portion.

During the Park City release events in 2007 and 2010 there was release of As of up to 50 µg/L (Friedman et al. 2016). From the desorption studies the same high concentrations in the AST solids were seen, which are from a similar location in the distribution system as the release events, inferring that similar physical-chemical processes could have occurred at that time.

Overall, all of these factors illustrated in Figure 6 are important in controlling As release, with the pH being the most important factor followed by PO₄³⁻. Arsenic is a common toxin that can be found in source water, and it is has been well studied with many treatment options at the source. From this study the nonconservative behavior of As in pipes can be better understood to prevent future release events.

**Thallium**

Thallium was very reactive during the desorption studies; almost every factor and many 2- and 3-factor interactions affected the release of Tl (Figure 13), resulting in concentrations consistently exceeding the 2 µg/L MCL. Both sites behaved similarly during
the desorption studies, reaching around 90 µg/L, which accounts for 64% of the exchangeable amount. The addition of K₂HPO₄ was the only factor that wasn’t important in the change of release.

The most important single factors were pH and temperature, where conditions with pH = 6.5 and temperature = 25 °C resulted in higher release. However, for all main effects there is a large interquartile range indicating the interactions are important. The major two way interactions are with temperature:Cl₂ and temperature:pH at both sites, pH:K₂HPO₄ and pH:Cl₂ at AST, and pH:CaSO₄ at UPA. Figure 15 shows the 2-way interactions, with the largest difference in release corresponding to the pH:temperature interaction. Temperature = 7 °C, pH = 8.5, and Cl₂ = 2 mg/L caused a decrease in released concentrations. The 2-way interaction of temperature = 25 °C + pH = 6.5, had high release and was the only treatment that exceeded the midpoint treatment of 60 µg/L. Finally, the most important 3-way interaction was temperature:pH:CaSO₄. The addition of CaSO₄ caused an increase in release; however, the overall impact was very small. Most of the release concentrations for the treatments tested were below the midpoint concentration, showing a non-linear effect.

During the 2007 and 2010 Park City release events the Tl concentration reached 190 µg/L (Friedman et al. 2016). For this desorption study, concentrations only reached half of that concentration; however, both concentrations were well above the MCL. This is cause for concern because there was little to no Tl in the monitoring or source data
when no unusual conditions existed. There is a high level of Tl in the solids, creating conditions for potentially large releases of Tl into the bulk water.

Overall Tl is very toxic and 64 % of the exchangeable amount was released in these desorption studies. Even though a system may not detect Tl through monitoring in the distribution system or detection at the source, there still may be exchangeable Tl present that could be released through plausible chemical or temperature changes. Low frequency routine monitoring would not likely fully represent Tl behavior in a distribution system.

**Manganese**

Interestingly Mn only had a large release at AST, which had 10 times less total Mn, but 100 times more exchangeable Mn than UPA, suggesting that there is a difference in the mineralogy of Mn at the two sites (Table B2 and Table B3). Routine water quality monitoring during 2013 showed five times less Mn at sites near AST than at UPA and even less at the AST source. At UPA the sequential extraction exchange step showed only 0.7 µg/L and only 1.5 µg/L during the desorption studies; 99 % of the total Mn at UPA was associated with Mn oxide and amorphous Fe oxide minerals that were not solubilized by any of the desorption test parameters. In contrast, even though the total concentration of Mn was lower at AST, 90 % of the total Mn was associated with these insoluble mineral phases (Table B2 and Table B3).
pH, Cl₂, and CaSO₄ were the important individual factors in the change in Mn release, and the interactions between the pH:Cl₂, and pH:CaSO₄ were also important (Figure 19). When pH = 8.5 all the release concentrations were very low, near the detection limit, regardless of any other factors (Figure 20). When pH was 6.5 only the addition of Cl₂ = 2 mg/L could keep the concentrations below the secondary limit of 50 µg/L; without Cl₂ addition the Mn concentration reached 150 µg/L. The addition of CaSO₄ also caused an increase in release of Mn. The knowledge of Cl₂ addition decreasing the amount of Mn present is useful considering the strong relationship Mn has with Sb and Tl.

In the Park City release event the Mn concentration reached up to 370 µg/L (Friedman et al. 2016). Again this was primarily in the AST section of the city, which corresponds to the high concentrations found in these desorption studies.

Desorption Isotherm

Arsenic

The As isotherm did not produce results that were anticipated (Figure 21), indicating other mechanisms were occurring. The overall concentration of As decreased with the increase of solids added. Because the solids were filtered through 0.45 µm after shaking the As could have coprecipitated with Fe instead of dissolving. The additional amount of solids could have produced more Fe, causing As to precipitate. This particular experiment with As desorption using the DWDS solids should be further investigated.
**Thallium**

Figure 22 shows that UPA Tl concentrations in solution increase very rapidly with the mean qe concentration remaining on the solids, removing up to 80 µg/g of Tl to solids. Both locations have the same concentrations in the exchangeable phase, and the same percentage associated with the Mn oxides. The main differences are: AST had twice as much total Tl compared to UPA, and the associations with the Fe oxides were 23 % and 11 % of Tl at AST and UPA respectively. The retention of Tl onto the Fe oxides could explain why less Tl was desorbed from AST solids even though there is more Tl at AST (Table B2 and Table B3). This could provide a basis for Tl to remain sorbed to AST solids.

For Tl at AST the Freundlich isotherm agrees closely with the data, with an R² of 0.98; however, for UPA it is less so with an R² of 0.65. For the AST solids, the Freundlich model fits very well especially at the lower concentrations; however, at the higher concentrations the data appear to be approaching equilibrium, which is not consistent with the Freundlich model. Further investigations should be done to confirm and ultimately improve the model. For UPA the concentrations released into solution are almost constant from all amounts of solids added, with a range of 95 to 120 µg/L. This indicates a release of Tl at UPA into solution that is nearly insensitive to the aqueous phase concentration. Further studies should be done to reach the total exchangeable amount of Tl within the solids. This could also provide a more consistent set of data to improve the models.
CHAPTER 7

SUMMARY AND CONCLUSIONS

In this project, the interactions of trace inorganic contaminants (TICs) with solids from a water distribution system from two sites in Park City, UT, were examined to determine desorption characteristics and their sensitivities to general water quality conditions. Preliminary testing using factorial experiments showed that pH, temperature, Cl₂ concentration, the presence of the common corrosion inhibitor PO₄, and the addition of CaSO₄, potentially impacted the desorption of the TICs from the pipe solids. This information, coupled with data from sequential extraction of the TICs from the solids, and the data from monthly monitoring of the Park City water distribution systems and raw water sources, was used to design a full factorial experiment to quantify those interactions. The TICs examined in this study were Sb, As, Cr, Cu, Pb, and Tl, plus the matrix elements Fe and Mn. The pipe solids were exposed to different conditions of the factors above, equilibrated by shaking for 24 hr, and analyzed for the dissolved (0.45 µm) and particulate fractions (1.5 µm) of each TIC in triplicate. These data were subjected to linear regression analysis to determine the main effects of each factor, plus the two- and sometimes 3-factor interactions. Finally, desorption isotherm experiments were used to establish relationships between the aqueous phase concentrations and the amount of desorbable TIC quantities at equilibrium.
From these desorption studies it is observed that three elements responded significantly to the experimental factors at each site: As, Tl and Mn at AST and Sb, As, and Tl at UPA. pH was shown to be the most important factor contributing to release of these TICs. Primarily, a higher pH lowers the concentrations released for the cations Tl and Mn, while with As higher pH increased the amount released. Similar to pH, CaSO₄ was an important factor where high CaSO₄ caused less desorption to occur for the Sb and As, and the opposite for Tl and Mn. Temperature was also significant where a higher temperature increased release on all TICs that were affected by temperature, primarily contributing to the release of Sb. Chlorine was only important in the Tl and Mn release, decreasing desorption with the addition of Cl₂, results that are likely related since Tl/Mn interactions are well established. The addition of PO₄⁻⁻P was only an important factor for As desorption, causing an increase in desorption with increase in PO₄⁻⁻P. The two key parameters that affected all TICs in decreasing release were temperature = 7 °C and Cl₂ = 2 mg/L. Decreasing the temperature reduces the overall reaction rates, and Cl₂ addition contributes as an oxidizing agent.

The dissolved and particulate phases overall behaved similarly. There was a slight increase in desorbed concentrations for Cr, Cu, Fe, and Mn for the 0.45 μm filtrate vs. those for 1.2 μm, but overall there was no difference in factors that affected these elements.
In the desorption studies, although most of the released TIC concentrations were below their MCL or SMCL, as set by the EPA, results did show released concentrations approaching or above the MCL for Sb, As, Tl, and Mn under some conditions. Most notably, there were concentrations well above the MCL for two contaminants of concern, As and Tl, both of which are very toxic, even carcinogenic. This may prove to be a concern in the Park City distribution system, though from the monitoring data levels were much lower than the concentrations observed in this study.
CHAPTER 8

RECOMMENDATIONS

From the knowledge and experienced gained in this research, it is recommended that monitoring of complex water systems with low level contaminants be expanded. This could provide a better understanding of the transport of contaminants throughout other drinking water systems. It would be interesting to see how other drinking water systems with TICs react to the treatments tested. It would provide further information on how best to control the release of TICs.

The routine monitoring requirements of the Safe Drinking Water Act could not have detected the release events with high TIC concentrations that triggered this study. New ways of monitoring drinking water systems need to be developed to enable rapid detection and correction of those events.

The behavior of As and Sb in the presence of CaSO₄ were anomalous to some extent in that our initial hypothesis was that the SO₄²⁻ would displace AsO₄³⁻ and SbO₄³⁻ (Sb(V)) from the solid surfaces and increase in concentration in the dissolved phase. The opposite was observed leading to a potential explanation that these ions precipitated with Ca²⁺ from the CaSO₄. This was not proven; future studies could address this possibility by a thorough mass balance of the different species in dissolved and particulate forms. The potential implication for the drinking water industry is that As or Sb could be
mobilized in the presence of excess SO$_4^{2-}$ and bound by Ca-based precipitates in waters with naturally high Ca levels. If monitoring does not consider the solid phase, elevated levels of As or Sb could be present in treated water without alerting drinking water officials.

In future studies, a more in-depth experiment on only one specific TIC should be done testing more levels of the various treatments. This could give a detailed model as to how a specific TIC is moving throughout the water and solids.
CHAPTER 9

ENGINEERING SIGNIFICANCE

The non-conservative behavior of TICs throughout the DWDS is not fully understood. By studying the possible causes of these releases in the DWDS the drinking water community can better address the problems and prevent future releases. This may lead to changes in the treatment process as well as monitoring and controlling the water in the distribution system. By better understanding the chemistry of not only the water but solids within it, release events can be minimized through preventive maintenance. Being aware that there are high concentrations of TICs potentially readily available in the pipe solids also means that development of better cleaning techniques to remove all contaminants should be a priority, particularly as climate change produces the potential for water chemistry changes in previously stable distribution systems.

The primary recommendation from this work for Park City in particular is to first reduce the amount of TICs entering the distribution system by modifying water sources and treatment systems to target those compounds, particularly As, which is already targeted in Park City for some sources, and Tl. Controlling Tl could be done by removal of Mn by oxidation. Next, continued monitoring of the system will provide operators with awareness of what contaminants might be present and entering the distribution system. Even though Cl₂ proved to only be important for Tl and Mn it is an easy parameter to
control and maintaining a Cl₂ residual (2 mg/L) had a positive effect on all systems in preventing release of these TICs.

Generally, for all utilities, it is important to monitor the input of trace contaminants even at low levels. Monitoring of extreme changes in water chemistry or temperature can drastically affect the mobility and solubility of contaminants. Due to the dynamic nature of chemistry changes in complex water systems like Park City’s, the current practice of infrequent monitoring for various TICs may be inadequate to characterize the full extent of this important problem. In Park City, the release events that triggered this study occurred once each in 2007 and 2010 and then for short time periods and alert consumers were important factors in identifying these events. More frequent, even continuous, monitoring and/or the development of release-event surrogates (e.g. high frequency turbidity sensors in the distribution system) in water systems that are potentially exposed to TICs is worth considering.
REFERENCES


APPENDICES
APPENDIX A U.S. EPA Maximum Contaminant Level
Table A1 - Inorganic Maximum Contaminant Levels (MCL) and Maximum Contaminant Level Goals (MCLG)

<table>
<thead>
<tr>
<th>Contaminants</th>
<th>MCL (mg/L)</th>
<th>MCLG (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony</td>
<td>0.006</td>
<td>0.006</td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.01</td>
<td>0</td>
</tr>
<tr>
<td>Barium</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Beryllium</td>
<td>0.004</td>
<td>0.004</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Copper</td>
<td>1.3*</td>
<td>1.3</td>
</tr>
<tr>
<td>Cyanide</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Fluoride</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Lead</td>
<td>0.015*</td>
<td>0</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>Nitrate – N</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Nitrite – N</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Selenium</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Thallium</td>
<td>0.002</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

* Action level controlled at taps, if more than 10% of samples are above the action level water system must take additional steps
APPENDIX B Preliminary Findings
Characteristics

Solids collected from the swab cleaning UPA centrifuge solids were size fractionated using 1.5 µm glass fiber filters, followed by 0.45 µm membrane filters. Figure B1 shows the solids on the filters and the remaining dissolved solids in the beaker. It was found that 95% of the solids were greater than 1.5 µm, and because of this the solids were then fractioned out using a wet sieve. Wet solids were rinsed through 1000, 500, 250, 106, 53, and 38 µm sieves then finally into a beaker. From this experiment it was found that 96% of the solids were smaller than 38 µm.

![Figure B1 - Size fractioning between < 0.45, 0.45 - 1.5, and > 1.5 µm](image)

During preliminary investigations, the solids were filtered through 1.5 µm and 0.45 µm filters, and then centrifuged. The equivalent diameter was estimated as 0.075 µm using the Svedberg equation below (Svedberg and Nichols 1923). The samples were measured in triplicate (errors bars represent the standard deviation), and there is no observable difference in TIC concentrations between the 0.45 µm and the 0.075 µm size particles Figure B2. This indicates that filtering through 0.45 µm for this experiment effectively separates the dissolved species from these solids. Therefore, it is proposed that the desorption experiments will be filtered using only 1.5 µm and 0.45 µm filters.
Figure B2 - TICs desorbed versus different filter sizes of 1.5, 0.45, and 0.075 µm on a log scale showing 0.45 and 0.075 µm sizes capture the same contaminant released

Centrifuge Size Calculations

Centrifugal diameter size calculation equation from (Svedberg and Nichols 1923).

Where:

\[ r = \frac{9\eta \ln\left(\frac{x_2}{x_1}\right)}{\sqrt{2(\rho_p - \rho)\omega^2(t_2 - t_1)}} \]
\[ t = \text{centrifuge time} = 1200 \text{ sec} \]
\[ \eta = \text{water viscosity} = 0.00089 \]
\[ x_2 = \text{radius to bottom} = 0.165 \text{ m} \]
\[ x_1 = \text{radius to top} = 0.051 \text{ m} \]
\[ \rho_p = \text{particle density} = 3763 \text{ (from average of Sarin et al. (2001) Table B1)} \]
\[ \rho = \text{water density} = 1000 \]
\[ \omega = \text{angular velocity} = 1047 \]

Where:

\[ 9 \eta \ln \left( \frac{x_2}{x_1} \right) = 9 \times 0.00089 \ln \left( \frac{0.165}{0.051} \right) = 0.0094 \left( \frac{kg}{m \cdot s} \right) \]

\[ 2 (\rho_p - \rho) \omega^2 (t_2 - t_1) = 2 \left( 3550 \frac{kg}{m^3} - 1000 \frac{kg}{m^3} \right) \left( 1047 \frac{rad}{s} \right)^2 (1200 \text{ sec}) \]

\[ = 7.27 \times 10^{12} \frac{kg \cdot rad^2}{m^3 \cdot sec} \]

\[ r = \sqrt{\frac{0.0094 \left( \frac{kg}{m \cdot s} \right)}{7.27 \times 10^{12} \frac{kg \cdot rad^2}{m^3 \cdot s}}} = 3.60 \times 10^{-8} \text{ m} = 0.036 \mu m \]

\[ d = 0.036 \mu m \times 2 = 0.072 \mu m \]

Table B1 - Density and porosity determination of corrosion scales (Sarin et al. 2001)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>True density (g/cm³)</th>
<th>Bulk density (g/cm³)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIWC-A</td>
<td>3.89</td>
<td>2.20</td>
<td>43.30</td>
</tr>
<tr>
<td>NIWC-B</td>
<td>3.93</td>
<td>2.34</td>
<td>40.51</td>
</tr>
<tr>
<td>Boston#1</td>
<td>3.72</td>
<td>1.75</td>
<td>53.02</td>
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<tr>
<td>Boston#2</td>
<td>3.92</td>
<td>1.80</td>
<td>54.18</td>
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<tr>
<td>Boston#3</td>
<td>3.78</td>
<td>1.73</td>
<td>54.33</td>
</tr>
<tr>
<td>Boston#4</td>
<td>3.60</td>
<td>2.01</td>
<td>44.13</td>
</tr>
<tr>
<td>Boston#5</td>
<td>3.59</td>
<td>1.99</td>
<td>44.43</td>
</tr>
<tr>
<td>Boston#6</td>
<td>3.67</td>
<td>2.22</td>
<td>39.56</td>
</tr>
</tbody>
</table>
Preliminary data total concentration and sequential extraction

Table B2 - AST solids total concentration and sequential extraction steps, means and standard deviation for each TIC in mg/kg

<table>
<thead>
<tr>
<th>AST</th>
<th>Sb</th>
<th>As</th>
<th>Cr</th>
<th>Cu</th>
<th>Pb</th>
<th>Tl</th>
<th>Fe</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>19.5</td>
<td>1742</td>
<td>36.5</td>
<td>2600</td>
<td>3428</td>
<td>1595</td>
<td>1.54x10^5</td>
<td>1.8x10^4</td>
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<tr>
<td>Total SD</td>
<td>5.4</td>
<td>56</td>
<td>0.6</td>
<td>1000</td>
<td>150</td>
<td>553</td>
<td>0.5x10^5</td>
<td>0.09x10^4</td>
</tr>
<tr>
<td>Exchangeable</td>
<td>1.21</td>
<td>58.1</td>
<td>&lt;MDL</td>
<td>27.7</td>
<td>&lt; MDL</td>
<td>81.7</td>
<td>&lt; MDL</td>
<td>43.7</td>
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<tr>
<td>Exchangeable SD</td>
<td>0.45</td>
<td>6.6</td>
<td>1.6</td>
<td>40</td>
<td>22</td>
<td>4</td>
<td>0.08x10^4</td>
<td>5.1</td>
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<tr>
<td>Carbonate Complex</td>
<td>3.28</td>
<td>33.2</td>
<td>2.06</td>
<td>964</td>
<td>220</td>
<td>314</td>
<td>1.12x10^4</td>
<td>547</td>
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<tr>
<td>Carbonate Complex SD</td>
<td>0.18</td>
<td>1.3</td>
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<td>Organic Complex</td>
<td>7.41</td>
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<td>712</td>
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<td>Organic Complex SD</td>
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<td>6</td>
<td>0.07</td>
<td>26</td>
<td>10</td>
<td>1.5</td>
<td>0.14x10^4</td>
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<tr>
<td>Mn Oxides</td>
<td>8.05</td>
<td>117</td>
<td>0.20</td>
<td>34.0</td>
<td>19.4</td>
<td>253</td>
<td>2220</td>
<td>3170</td>
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<tr>
<td>Standard Deviation</td>
<td>0.35</td>
<td>2</td>
<td>0.06</td>
<td>21.1</td>
<td>12.0</td>
<td>4</td>
<td>1550</td>
<td>0.25</td>
</tr>
<tr>
<td>Non Crystalline Fe Oxides</td>
<td>8.07</td>
<td>162</td>
<td>7.10</td>
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<td>1880</td>
<td>321</td>
<td>2.65x10^4</td>
<td>8560</td>
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<tr>
<td>Non Crystalline Fe Oxides SD</td>
<td>1.23</td>
<td>15</td>
<td>0.25</td>
<td>29</td>
<td>130</td>
<td>30</td>
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<tr>
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<td>8.98</td>
<td>14.8</td>
<td>7.37</td>
<td>19.3</td>
<td>102</td>
<td>40.3</td>
<td>3.97x10^4</td>
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<td>&lt; MDL</td>
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<td>263</td>
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Table B3 - UPA solids total concentration and sequential extraction steps, means and standard deviation for each TIC in mg/kg

<table>
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<tr>
<th>UPA</th>
<th>Sb</th>
<th>As</th>
<th>Cr</th>
<th>Cu</th>
<th>Pb</th>
<th>Tl</th>
<th>Fe</th>
<th>Mn</th>
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<tr>
<td>Total</td>
<td>36.3</td>
<td>672</td>
<td>62.3</td>
<td>1.61x10^4</td>
<td>6733</td>
<td>785</td>
<td>1.35x10^5</td>
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<td>Total SD</td>
<td>0.3</td>
<td>6.7</td>
<td>8.1</td>
<td>0.22x10^4</td>
<td>212</td>
<td>28.6</td>
<td>0.03x10^5</td>
<td>0.02x10^5</td>
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<td>Exchangeable</td>
<td>3.56</td>
<td>84.6</td>
<td>0.33</td>
<td>55.3</td>
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<td>85.7</td>
<td>&lt; MDL</td>
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<td>1.8</td>
<td>0.02</td>
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<td>Carbonate Complex</td>
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<td>30.3</td>
<td>2.68</td>
<td>8610</td>
<td>575</td>
<td>485</td>
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<td>Carbonate Complex SD</td>
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<td>Organic Complex</td>
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<td>Non Crystalline Fe Oxides</td>
<td>17.7</td>
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<td>Crystalline Fe Oxides</td>
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APPENDIX C Preliminary Studies
Preliminary equilibrium tests were done on the wet solids to determine the optimum desorption time. Studies were done in duplicate, shaking three different mass to volume ratios of 0.05, 0.1, and 0.5 g dry weight in 60 mL Logan tap water. Samples were shaken for 1, 2, 16, and 24 hours and then filtered through 0.45 µm membrane syringe filters. Filtrate was analyzed using method 6020 on the ICP-MS. Graphical results for Cr, Sb, As, and Tl are in Figure C1. A Tukey HSD test found no significant differences between shaking times of 1 and 24 hours. However, for desorption of antimony there was some significant change for the 0.05 and 0.1 g samples with an increase in shaking time. For future experiments the samples will be shaken for 24 hours.

![Graphs showing equilibrium results for Cr, Sb, As, and Tl](image)

Figure C1 - Preliminary equilibrium tests on Cr, Sb, As, and Tl at 1, 2, 16, and 24 hours.
Saturated Design Results

From the saturated design testing 6 factors, temperature, pH, Cl$_2$, PO$_4$, CaSO$_4$, and NaCl (Table C1) it was found that all factors except NaCl were significant. Table C-2 shows the p values from the ANOVA test, proving NaCl is not an important factor and the rest are very important.

Table C1 - High and low levels of factors for saturated design and saturated treatment runs

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<th></th>
<th>Temp (°C)</th>
<th>pH</th>
<th>Cl$_2$ (mg/L)</th>
<th>EC (µS/cm)</th>
<th>SO$_4$ (mg/L)</th>
<th>PO$_4$ (mg/L)</th>
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<td>High(+)</td>
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</table>
Chlorine Degradation

Three different chlorine concentrations were shaken and measured to determine the rate of degradation over 5 hours.

Figure C2 - Chlorine degradation for 4, 8, and 11 mg/L over 5 hours
Table C2 - Significant p values from the ANOVA test on the saturated design

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<th></th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Cu</th>
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