Title: Manganese deposition in Drinking Water Distribution Systems

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Abstract

This study provides a physicochemical assessment of manganese deposits on brass and lead components from two fully operational drinking water distributions systems. One of the systems was maintained with chlorine; the other, with secondary chloramine disinfection. Synchrotron-based *in-situ* micro X-ray adsorption near edge structure was used to assess the mineralogy. *In-situ* micro X-ray fluorescence mapping was used to demonstrate the spatial relationships between manganese and potentially toxic adsorbed metal ions. The Mn deposits ranged in thickness from 0.01 to 400 micrometers (μm). They were composed primarily of Mn oxides/oxhydroxides, birnessite (Mn^{3+} and Mn^{4+}) and hollandite (Mn^{2+} and Mn^{4+}), and a Mn silicate, braunite (Mn^{2+} and Mn^{4+}), in varying proportions. Iron, chromium, and strontium, in addition to the alloying elements lead and copper, were co-located within manganese deposits. With the exception of iron, all are related to specific health issues and are of concern to the U.S. Environmental Protection Agency (U.S. EPA). The specific properties of Mn deposits, i.e., adsorption of metals ions, oxidation of metal ions and resuspension are discussed with respect to their influence on drinking water quality.

Key Words: manganese, drinking water, chlorine, chloramine, micro-XANES, micro-XRF

1. Introduction

Manganese (Mn), ubiquitous in the environment, comprises about 0.1 percent of the earth's crust (WHO, 1999). Divalent manganese (Mn^{2+}) can be solubilized from soils and bedrock (Ljung and Vahter, 2007) into surface and ground waters, sources of drinking water. Manganese concentrations from natural processes are typically low, but can range up to 1.5 mg L^{-1} or higher. Manganese can also be introduced into surface and ground waters from anthropogenic activities. Heal (2001) investigated the relationship between land use and Mn concentrations in surface waters in Scotland. She reported that conifer afforestation, liming, fertilization addition, drainage ditch construction and ploughing increased Mn concentrations in runoff (Heal, 2001). In addition flooding and waters associated with mining (surface and deep; NAWQA, 2000) can contribute to dramatic increases in Mn concentrations in ground water sources used for drinking water.

Soluble Mn^{2+} in drinking water can be oxidized to insoluble Mn^{3+} and Mn^{4+} (Cerrato et al., 2006; Kohl and Mediar, 2006; Manceau and Charlet, 1992; Negra et al., 2005) by oxidizing disinfectants and by metal oxidizing bacteria. The result is precipitation, and in the case of drinking water distribution systems (DWDS), Mn deposition on internal pipe surfaces or on established corrosion products. Mn oxides/oxhydroxides are highly effective at adsorbing metal ions such as chromium (Cr), copper (Cu), iron (Fe), lead (Pb), and strontium (Sr) ions (Courtin-Nomade, 2009; Manceau and Charlet, 1992; Manceau et al., 1992; Negra et al., 2005; Nelson et al., 1999; Takahashi et al., 2007; Tanaka et al., 2010; Villalobos et al., 2005;). In addition Mn oxides can oxidize adsorbed metal ions. For example Mn oxides can oxidize Cr^{3+} to Cr^{6+} resulting in the metal ion being converted from a non-toxic to toxic state (Courtin-Nomade, 2009; Manceau and Charlet, 1992; Manceau et al., 1992).

Mn deposits can be readily resuspended (Cerrato et al., 2006; Schlenker et al., 2008; Sly et al., 1990) in DWDS by numerous factors including changes in water disinfection chemistry, especially transitioning from chlorine to chloramine (Torrey, 2013). Manganese in tap water at concentrations greater than 0.05 milligrams per liter of water (mg/L) can be detected as changes in color, odor, or taste to the water. Because of this Mn is regulated by the U.S. Environmental Protection Agency (U.S. EPA; U.S. EPA, 2004) for aesthetic issues (e.g., black water).

Health effects from Mn ingestion are not a concern until concentrations are approximately 10 times 0.05 mg/L. Ingestion of elevated Mn concentrations from drinking water may cause neurological disorders (Alvarez-Bastida et al., 2013; Bourchard et al., 2010; Chai et al., 2010; Ljung and Vahter, 2007; Schlenker et al., 2008, U.S. EPAa, 2004, U.S. EPAa, 2012). An additional health concern, that has not been addressed by regulators, is the potential impact of adsorbed toxic metal ions released at elevated concentrations when Mn deposits disassociate. Therefore the action level (AL) established by several states for Mn concentrations is 0.5 mg L⁻¹ to ensure protection against manganese toxicity and aesthetic issues. This AL is consistent with the World Health Organization guidance level for manganese in drinking water (WHO, 2004). Individual states may abide by federal regulations or adopt more stringent standards (Torrey, 2013).

The purpose of this paper is to provide the first known physicochemical characterization of Mn deposits from two fully operational DWDS, one using chlorine; the other, secondary chloramine disinfection. A combination of traditional physiochemical characterization techniques and synchrotron-based *in-situ* micro X-ray adsorption near edge structure (μ -XANES) spectroscopy and X-ray fluorescence mapping (μ -XRF) were used to assess

potentially toxic metal ions associated with the deposits. In this study, Mn deposition was evaluated on lead and brass surfaces to avoid any contamination from a corroding iron substratum.

2. Materials and Methods

2.1. Sampling

2.1.1. Water Chemistry

Surface waters are used as source waters by both utilities. Utility A (UA) uses secondary chloramine and Utility B (UB), free chlorine. UA and UB are fully operational DWDS. Water quality parameters for treated water were provided by the utilities (Table 1).

2.1.2. Lead and Brass Pipe Sample Collection and Preparation

Lead and brass pipe sections examined in this study were exposed to daily periods of stagnation while in service. One section (30.48 cm long, 1.75 cm inner diameter) of lead service line with a brass (predominantly Cu) connector was collected from UA. A section (38 cm long, 2.00 cm inner diameter) of lead service line with a brass connector was provided by UB. Pipes, obtained as a result of pipe replacements, were transported to the laboratory, cut longitudinally with a saw, allowed to air dry for up to 72 h, and digitally imaged.

Surface layer samples (up to 1.0 g) were obtained (Figure 1), using brushes and metal spatulas. Materials were ground by hand with an agate mortar and pestle. Approximately 0.25 g

of each sample was thoroughly mixed with 2.25 g of cellulose and pressed into 31 mm pellets for X-ray fluorescence (XRF) analysis.

Representative lead and brass pipes with associated corrosion products from UA (samples UAPb and UACu) and UB (samples UBPb and UBCu) were used for synchrotron-based, *in-situ* micro-XRF (μ -XRF) and micro-XANES (μ -XANES) analyses. A 1-cm long section of each pipe composition was encased in Buehler Epo Thin[®] low viscosity epoxy and a sub-sample of each was cut to include the pipe and surface deposits. One side of each sub-sample was polished and digitally imaged. Images were used to determine locations for μ -XRF mapping and μ -XANES analyses.

2.2. Sample Analytical Methods

2.2.1 Bulk X-ray fluorescence

Pressed pellets were analyzed for major oxides and trace elements at the Department of Geology, University of Cincinnati, Cincinnati OH using a Rigaku 3070 X-ray fluorescence spectrometer. Intensity data were converted to percent (by weight) or mg kg⁻¹ (Gerke et al., 2010).

2.2.2. Synchrotron μ -XRF and μ -XANES Run Conditions and Analysis

X-ray μ -beam studies were performed at beamline XOR/PNC 20 BM-B (Heald, 1999) of the Advanced Photon Source (APS), Argonne National Laboratory (Argonne, IL) under standard operating conditions; 7 GeV operation and a ring current of 101 mA in top-up mode.

μ -XRF maps of the relative concentrations of Cr, Cu, Fe, Mn, Pb, and Sr were recorded using a 4-channel Si-drift detector. Relative elemental concentrations were depicted using a color scale where dark blue represents low concentrations and red represents comparatively higher concentrations. The monochromatic beam energy was set to 17 KeV using a Si (111) channel-cut monochromator and the beam focused to approximately 15 x 15 μ m using rhodium-coated Kirkpatrick-Baez focusing optics.

The monochromator beam energy position was calibrated to the first inflection of the absorption edge of Mn metal foil; 6539 eV. A 0.5 mm pre-monochromator slit width and a Si(111) double crystal monochromator, detuned by 10% to reject higher-order harmonics, was used. Five to six Mn *K*-edge μ -XANES scans were collected from each sample at ambient temperature in fluorescence mode with a solid-state 4-channel Si-drift detector.

Three to four bulk XANES scans were collected for each Mn standard; Mn^{4+}O_2 (pyrolusite), Mn^{4+}O_2 (ramsdellite), $(\text{BaMn}^{4+}\text{Mn}^{2+})_8\text{O}_{16}$ (hollandite), $\text{K}(\text{Mn}^{4+}\text{Mn}^{2+})_8\text{O}_{16}$ (cryptomelane), $(\text{NaCaK})_x(\text{Mn}^{4+}\text{Mn}^{3+})_2\text{O}_4 \bullet 1.5(\text{H}_2\text{O})$ (birnessite), Mn_2O_3 (bixbyite), and $(\text{Mn}^{2+}\text{Mn}^{4+})_6\text{SiO}_{12}$ (braunite). Standards were provided by Dr. Steve Held, Sector 20 of APS, ANL, Argonne IL and Dr. J.B. Maynard, Department of Geology, University of Cincinnati, Cincinnati, OH. All spectra were placed on the same energy grid, aligned to 6539 eV, averaged, normalized, and the background removed by spline fitting using IFEFFIT (Ravel and Newville, 2005).

Linear combination fitting (LCF) was conducted using the chi plots of the standards and the samples. Levenberg–Marquardt least squares algorithm was applied to a fit range of 1.6 to 10 k ($\text{\AA}^{-1}$). Best-fit scenarios were defined as having the smallest residual error and the sum of all fractions close to 1. To fully describe any particular sample within 1% reproducible error, a minimum fit to two standards was necessary. Results have a ± 10 percent accuracy.

3. Results

3.1. Physicochemical Characterization of Corrosion Products

Morphologically the upper surface of the Mn deposits was irregular and located at the surface-water interface and ranged in thickness from 0.01 to 400 micrometers (μm), regardless of the water chemistry. The colors of sample UAPb (lead pipe) and UACu (brass pipe) were reddish-brown and brown, respectively (Figure 1a). Sample UBPb (lead pipe) was light brown and UBCu (brass pipe) was black-brown (Figure 1b).

3.2 Concentration of Mn in the Surface deposits

The Mn concentration for UAPb ranged from 1.93 to 4.45 percent by weight (%), from 0.21 to 2.12 % for UACu, from 2.54 to 3.26 % for UBPb and from 0.23 to 0.65% for UBCu (Table 2). Average concentrations for Cu, Cr_{total}, Pb, and Sr for all four samples are listed in Table 2.

3.3 Speciation of Mn Deposits

Mn *K*-edge in-situ μ -XANES spectra from UAPb and UACu (four representative spectra each) and bulk XANES spectra for three Mn standards are shown in Figure 2a and b. Additional in-situ sample and bulk Mn standard spectra are present in Figure SI1. The Mn *K*-edge in-situ μ -XANES spectra for locations examined in UAPb and UACu had prominent peaks at 6575.65,

6617.13, and 6721.54 eV. The Mn *K*-edge in-situ μ -XANES spectra from UBPb and UBCu and bulk XANES spectra for three Mn standards are shown in Figure 3 a and b. UBPb and UBCu had prominent peaks at 6575.65, 6618.04, and 6724.02 eV. The energies of the predominant sample peaks typically corresponded to characteristic peaks of the standards (Table SI1).

Linear combination fit spectra, generated using all standards and the chi plot of a given sample, were superimposed on the chi space spectrum of UAPb, UACu, UBPb, and UBCu respectively (Figure 4). Hollandite, braunite and birnessite were the main Mn phases comprising the Mn deposits (Table 3). Trace amounts of bixbyite (less than 5 percent) and ramsdellite (up to 15 percent) were detected in both systems associated with both pipe materials, but not in all locations. Cryptomelane ($\text{K}(\text{Mn}^{4+}\text{Mn}^{2+})_8\text{O}_{16}$) (up to 5 percent) was detected in two locations on UBPb (Table 3).

3.4. Metal distribution in Mn deposits

Micro-XRF maps for key elements for all samples are presented in Figures 5 through 8. The μ -XRF map for UAPb and key elements corresponded to the region outlined by the red box in the digital image (Figure 5). In the subsequent figures (5 b-g) the white lines correspond to the Mn deposit, which was 0.01 μm thick (Figure 5e). Fe was co-located with Mn (Figure 5d). Cu was concentrated in a few places in the Mn deposit (Figure 5c). Cr, Pb, and Sr were present in the lower portion of the Mn deposit and in the underlying reddish-colored material (Figures 5a, b, f, and g).

In UACu map 1, the white lines correspond to the approximately 300 μm thick Mn deposit (Figure 6e). Cr and Fe were present throughout the Mn deposit but in relatively low

concentrations (Figures 6b and d). Cu was located in the Mn deposit in some locations (Figure 6c) and Pb and Sr were present primarily in the lower most portions of the Mn deposit and the underlying blue-green material (Figures 6a, f, and g). The white lines correspond to the Mn (Figure SI2a) deposit, which was approximately 400 μm thick in the UACu map 2 (Figure SI2e). Cr and Fe were present in the Mn deposit (Figures SI2c and e). Cu, Pb, and Sr were present in isolated locations in the central and lower region of the Mn deposit (Figures SI2 c, f, and g). Cr, Cu, and Sr were also present in the blue-green material underlying the Mn deposit (Figures SI2 a, b, c, and g).

The Mn deposit associated with UBPb (Figure 7e) was approximately 200 μm thick (Figure 7b). Cr, Cu, Fe, Pb, and Sr were present throughout the Mn deposit in varying concentrations (Figures 7b-d and 7f and g). In UBCu map, the white lines correspond to the 0.07 μm thick Mn deposit (Figure 8e). Cu, Pb, and Sr were present in varying relative concentrations within the Mn deposit (Figures 8c, f, and g). Cr, Cu, and Sr were also located in the material underlying the Mn deposit (Figures 8b,c, e, and g).

4. Discussion

Stiles (1978) estimated that 20 percent of US municipal water supplies contained more than 0.05 mg L^{-1} Mn. Therefore it is likely that many DWDS have Mn deposits associated with the piping. Brandhuber et al. (2015) estimated that approximately 122 lbs year^{-1} of Mn could be deposited on DWDS infrastructure when the water Mn concentration was 0.02 mg L^{-1} and the system had a water flow rate of approximately 2 million gallons per day.

Once deposited in DWDS infrastructure or premise plumbing, Mn can be resuspended by physical processes (internal and external to DWDS) and chemical processes (Brandhuber et al. 2015; Cerrato et al., 2006; Lakin and Bryan, 2007; Schlenker et al., 2008; Sly et al., 1990).

Physical disturbances include changes in flow rate, flow reversals, hydraulic pressure changes, and construction activities above drinking water lines (Friedman et al., 2010; Lakin and Bryan 2007; Sarin, et al., 2004a). Chemical processes include, but are not limited to, changes in the treated water pH, dissolved oxygen concentration, alkalinity, and oxidation-reduction potential (Al-Jasser, 2007; Friedman et al., 2010; Sarin et al., 2004). In-situ changes in these parameters can occur in service lines during periods of intermittent flow (stagnation) (Arnold and Edwards, 2012). Converting/transitioning from free chlorine to chloramine can also produce changes in water chemistry (Boyd et al., 2008).

Chloramine, more specifically monochloramine (NH_2Cl), is formed when ammonia is added to chlorine. Because chloramine has a lower oxidation reduction potential than free chlorine (Torrey, 2013) it is less reactive and is not effective as a primary disinfectant, i.e., chloramine cannot be used to control taste and odor in drinking water. However, chloramine is more persistent in drinking water, leading to longer contact times with pipe materials.

Because of the higher oxidation reduction potential, free chlorine produces more stable corrosion products on copper and iron pipes i.e., more tenacious, than those formed as a result of exposure to chloramine (Torrey, 2013). No differences were observed in the stability of the Mn deposits from the two fully operations DWDS examined in this study even though one uses one chloramine (UA) and one free chlorine (UB).

Differences in bulk water chemistry i.e. pH, dissolved oxygen, oxidation-reduction potential reportedly influence iron corrosion product mineralogy (Sarin et al., 2001 and 2004). However, Gerke et al. (2008) concluded that water chemistry was not a key influence in iron corrosion product mineralogy in a DWDS. Similarly, the Mn deposits in this study, were composed primarily of hollandite with varying amounts of birnessite and braunite. Hollandite is a Mn

oxide; birnessite, a Mn oxyhydroxide and braunite, a Mn silicate. Even though bulk water chemistries of the two DWDS were different, it is possible that during periods of stagnation, interfacial water chemistries were similar. The variation in Mn speciation (Mn^{2+} , Mn^{3+} and Mn^{4+}) and mineral structures indicate the complex nature of Mn deposits within a DWDS.

The MnO_6 octahedron is the basic structure of most Mn oxide/oxyhydroxides, arranged in either layers or chains/tunnels. In addition, Mn oxides have very large surface areas and low point of zero charges (approximately 1.0 to 5) (Dixon and White, 2002). Water and cations can be adsorbed and/or exchanged between the layers of Mn oxide/oxyhydroxides (e.g. birnessite), Hollandite, which has a tunnel-structure, can be partially filled with water molecules, and large uni- or divalent cations (Post, 1999). Mn phases, in natural environments, readily incorporate metal ions into their atomic structures or adsorb metal ions. In circumneutral to high pH waters, like drinking water, Mn oxides/oxyhydroxides adsorb transition metal ions, i.e., hollandite and birnessite could provide locations for potentially toxic metal ion incorporation into the mineral phase.

The Mn deposits on lead piping, regardless of disinfectant, had similar metal ion concentrations but had roughly an order of magnitude more Mn compared to deposits associated with the brass piping (Table 3). There was also greater variability in the associated metal ion concentrations in Mn deposits associated with brass piping, even for samples from the same DWDS (Table 3). This variability in the samples from the two DWDS may reflect the differences in the percentages of the three main Mn minerals in the deposits and the effectiveness of each Mn mineral for adsorbing/incorporating metal ions. However, that variability cannot explain the differences in the trace metal concentrations of the Mn deposits between the Pb and brass pipes.

Several of the metal ions associated with the Mn deposits characterized in this study are currently regulated or monitored by the US EPA UCMR3 (US EPA, 2009; US EPA, 2012). The data demonstrated that destabilization of the Mn deposits could increase the likelihood of Cr and Cu ions in consumer taps. Complete suspension of Mn deposits could result in Pb and Sr ions in drinking water. Furthermore, Cr bound in Mn phase structures is susceptible to oxidation to Cr⁶⁺. Hexavalent chromium bound to Mn oxides/oxyhydroxides and ingested by consumers is a potential risk for exposure to a highly toxic metal ion.

5. Conclusions

The risk of drinking water contamination by metal ions cannot be accurately assessed without considering the physicochemical characteristics of Mn deposits. Mn deposits, including an oxide, an oxyhydroxide and a silicate were identified on brass and lead components from two DWDS. Differences in alloying elements and water treatment chemicals did not influence the formation of the deposits. In all cases potentially toxic metal ions were associated with the deposits.

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Supplementary materials related to this article can be found online.

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Table 1. Selected water quality parameters of finished drinking waters for the two drinking water distribution systems that samples for this study were obtained.

Parameter	Utility	
	A	B
pH	7.26 to 7.69	8.6
Hardness (mg L ⁻¹ as CaCO ₃)	91 to 196	91 to 177
alkalinity (mg L ⁻¹ as CaCO ₃)	37 to 111	68
Ca (average)	NR	36
Chlorine - Free (mg L ⁻¹)	NA	0.97
Chlorine - Total (mg L ⁻¹)	0.0 to 4.3	NR
orthophosphate (mg-PO ₄ L ⁻¹)	2.1 to 3.0	NA
phosphate (mg-PO ₄ L ⁻¹)	NA	0.083

Parameter	Utility	
	A	B
Fe (mg L ⁻¹)	ND	0.05
Mn (mg L ⁻¹)	0.0005	<0.002

NA - not applicable; NR – not reported; ND – not detected

Table 2. X-ray fluorescence results for the lead and brass corrosion product and Mn deposits from Utility A (chloramine) and Utility B (free chlorine) treated drinking water.

Sample ID	Fe	Cr	Cu	Mn	Pb	Sr
%						
<i>Utility A (UA)</i>						
Lead pipe						
<i>01_PXP_03-MX</i>	0.97	0.05	14.5	1.93	20.86	0.01
<i>01_PXP_02A-MX</i>	1.12	0.08	0.89	4.45	24.21	0.01
Brass Pipe						
<i>01_PX_01B1-MX</i>	0.90	0.02	53.30	0.27	0.41	0.00
<i>01_PXB_03A1-MX</i>	BD	0.01	49.30	0.21	0.74	0.00
<i>01_PXB_03-MX</i>	1.39	0.01	39.00	2.12	4.03	0.00
<i>Utility B (UB)</i>						
Lead pipe						
<i>02_PXP_02A-MX</i>	0.64	0.02	3.69	3.26	23.7	0.01
<i>02_PXP_05B1-MX</i>	0.52	0.02	7.29	2.54	21.87	0.01
Brass Pipe						
<i>02_PXB_02A-MX</i>	0.61	0.01	44.40	0.65	1.60	0.00
<i>02_PXB_05B1-MX</i>	0.26	0.01	41.00	0.23	7.97	0.00
<i>02_PXB_05D1-MX</i>	0.25	0.01	42.80	0.43	4.70	0.00

BD – below detection

Table 3.Linear combination fitting results for MnK-edge μ -XANES spectra in Figure5 and Figure SI1. Data presented as weighted percents ($\pm 10\%$) over the fit range of 1.6 to 10 k ($\text{\AA}^{-1}$). The M number corresponds to the map number and the L number to the location with a given map.

Sample ID	bixbyite	birnessite	braunite	cryptomelane	hollandite	ramsdellite	R-factor
	%	%	%	%	%	%	%
<i>Utility A</i>							
UAPbM1L1	2.8	10.8	30.9		45.4	10.0	0.0809
UAPbM1L3		22.6	18.8		58.3	0.2	0.0728
UAPbM1L5		42.7	19.4		37.9		0.0798
UAPbM1L8		14.9	28.7		51.5	4.8	0.1001
UAPbM1L9		21.1	15.4		63.4		0.0780
<i>avgUAPb</i>	<i>2.8</i>	<i>22.4</i>	<i>22.6</i>		<i>51.3</i>	<i>5.1</i>	
UACuM1L1		27.1	13.2		59.6		0.0729
UACuM1L2		32.6	4.74		62.6		0.0627
UACuM1L3		23.0	10.1		52.3	14.6	0.0460
UACuM1L4		37.6	6.0		56.3		0.0711
UACuM1L5		40.5	13.8		32.1	13.6	0.0602
UACuM1L6	2.7	30.8	14.9		47.6	3.9	0.0484
UACuM2L1		40.7	3.9		55.4		0.0656

UACuM2L2		35.7	14.8		49.5		0.0519
UACuM2L3		27.1	10.0		62.9		0.0442
UACuM2L4		31.4	15.3		42.2	11.1	0.0456
UACuM2L5		32.5	10.1		57.5		0.0530
<i>avgUACu</i>	<i>2.7</i>	<i>32.6</i>	<i>10.6</i>		<i>52.5</i>	<i>10.8</i>	
<hr/>							
<i>Utility B</i>							
UBPbM1L1	1.9	30.3	16.6		48.8	2.3	0.0582
UBPbM1L2		25.6	23.9		50.5		0.0647
UBPbM1L4	3.9	18.3	19.8		57.9		0.0665
UBPbM1L6		5.6	22.2		72.1		0.0833
<i>avgUBPb</i>	<i>2.9</i>	<i>24.7</i>	<i>20.6</i>		<i>57.3</i>	<i>2.3</i>	
<hr/>							
UBCuM1L2		19.6	31.4	5.0	43.9		0.1443
UBCuM1L3		29.6	30.6		39.8		0.1547
UBCuM1L4		13.9	37.5		48.6		0.1331
UBCuM1L5		25.8	34.4	1.7	38.1		0.2136
<i>avgUBCu</i>	-	<i>22.2</i>	<i>33.5</i>	<i>3.4</i>	<i>42.6</i>		

Chemical formulas for the Mn phases Mn standard; $Mn^{3+}_2O_3$

(bixbyite), $(NaCaK)_x(Mn^{4+}Mn^{3+})_2O_4 \bullet 1.5(H_2O)$ (birnessite), $(Mn^{2+}Mn^{4+})_6SiO_{12}$ (braunite),

$K(Mn^{4+}Mn^{2+})_8O_{16}$ (cryptomelane), $(BaMn^{4+}Mn^{2+})_8O_{16}$ (hollandite), and $Mn^{4+}O_2$ (ramsdellite).

a)

b)

Figure 1. Images of lead service line with brass connector from a) Utility A and b) Utility B. The scale in both images is in cm.

Figure 2. Manganese K-edge for XANES of three standard spectra and in-situ μ -XANES for samples a) UAPb and b) UACu.

Figure 3. Manganese K-edge for three buk XANES Mn standards spectra and the in-situ μ -XANES for samples a) UBPb and b) UBCu.

Figure 4. Linear combination fitting (red) superimposed on the Mn chi space spectrum (blue) over the fit range of 1.6 to 10 k ($\text{\AA}^{-1}$) (black lines) of UAPb map 1 location 1(a), UACu map1 location 3 (b), UACu map 2 location 2 (c), UBPb map 1 location 2 (c), and UBCu map 1 location 3 (d) respectively.

Figure 5. μ -XRF maps and location positions UAPb. Relative elemental concentrations are depicted using a color scale where dark blue represents low concentrations and red represents comparatively higher concentrations. The red box indicated the region of the pipe wall and overlying material that was mapped. The white lines in images b-g correspond to the upper and lower boundaries of the Mn deposit.

Figure 6. μ -XRF maps for UACu map 1. Relative elemental concentrations are depicted using a color scale where dark blue represents low concentrations and red represents comparatively higher concentrations. The red box indicated the region of the pipe wall and overlying material that was mapped.

Figure 7. μ -XRF maps for UBPb. Relative elemental concentrations are depicted using a color scale where dark blue represents low concentrations and red represents comparatively higher concentrations. The red box indicated the region of the pipe wall and overlying material that was mapped.

Figure 8. μ -XRF maps for UBCu. Relative elemental concentrations are depicted using a color scale where dark blue represents low concentrations and red represents comparatively higher concentrations. The red box indicated the region of the pipe wall and overlying material that was mapped.