Development of an *in situ* Remediation Strategy for a Metals-Contaminated, Alkaline
Groundwater

BY

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Abstract

Groundwater beneath a former industrial site in Tukwila, WA contains dissolved metals and organic material at high levels, as well as elevated pH (10-12). Contaminated groundwater discharge to site-adjacent waterways must be controlled to minimize impact to potential receptors. In a preliminary study, the efficacy of five amendments (chitosan, apatite, granular activated carbon (GAC), Thiol-SAMMS®, and limestone) was examined for the removal of copper, lead, vanadium, and arsenic for both unaltered and pH-adjusted (pH = 8) site groundwater in laboratory batch studies. Dissolved metals and dissolved organic carbon (DOC) concentrations in site groundwater were measured both before and after pH adjustment, and after application of amendments. pH adjustment generally improved amendment performance. The greatest reductions in dissolved copper (70%), lead (62%), and vanadium (62%) concentrations were observed under pH-adjusted conditions in the presence of apatite. Thiol-SAMMS® also performed well under pH-adjusted conditions (Cu: 69% reduction; Pb: 46% reduction; V: 24% reduction), and also removed both copper (55% reduction) and lead (31% reduction) at the original pH. GAC was somewhat effective at removing lead under all conditions (15-30% reduction) and copper (31% reduction) when the pH was adjusted, and also reduced DOC concentrations under all conditions (24-27% reduction). These results suggest that a strategy using pH adjustment and some combination of apatite, Thiol-SAMMS®, and/or GAC may be best suited for remediation at this site.

Further studies testing combinations of bone char (in place of apatite), GAC, and Thiol-SAMMS® were performed. In addition, the impacts of air sparging and pH adjustment through addition of hydrochloric acid or ferrous sulfate heptahydrate ($FeSO_4{:}7H_2O$), a coagulant commonly used in conventional water treatment, were evaluated. The introduction of

FeSO$_4$:7H$_2$O resulted in the formation of coagulation solids, further decreases in pH after the coagulation solids were removed, and the largest significant reductions of dissolved copper (at most 81%), arsenic (72%), vanadium (80%), and DOC (88%) of any treatment evaluated. Sparging with air increased reductions of lead concentrations for all pH adjustment strategies and slightly increased reduction of vanadium concentrations only when the pH was adjusted with FeSO$_4$:7H$_2$O. Combinations of bone char, GAC, and Thiol-SAMMS® generally did not confer a substantial advantage over single amendment treatments. Bone char, though, acted as a buffer to curb further decreases in pH after coagulation solids were removed. The drops in pH after the coagulation solids were removed, either with or without air sparging may be related to the oxidation of residual ferrous iron, but it is unclear if this single mechanism can explain the magnitude of the observed pH declines.

Using the ferrous sulfate treatment strategy potentially combined with passive barrier or cap of bone char, flow-through column experiments will be designed to show how implementation of the strategy would impact the subsurface hydrology and to determine whether this strategy can achieve applicable or relevant and appropriate requirements (ARARs).

Acknowledgements

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1.0 Introduction

1.1 Site Background

The former Rhone-Poulenc facility is located in Tukwila, Washington at 9299 East Marginal Way South. The site is bounded on two sides by water: the Lower Duwamish Waterway to the west and Slip 6 to the south (Figure 1). Industrial use of the site began in the 1930's when I.F. Laucks Co. constructed a pilot plant to formulate glue for use in plywood manufacturing. During the latter part of World War II, the eastern portion of the site was used as an internment camp for Italian prisoners. In 1949, Monsanto Chemical Company purchased the facility and continued the manufacture of glue and began producing paints, resins, and wood preservatives. Monsanto began vanillin production in 1952, which continued until the sale of the property to Rhone-Poulenc, Inc. in 1985. Rhone-Poulenc closed the facility permanently in April 1991 and transferred the title of the property to Rhodia, Inc. in January 1998. Rhodia sold the property in July 1998 to Container Properties L.L.C., the current owner.
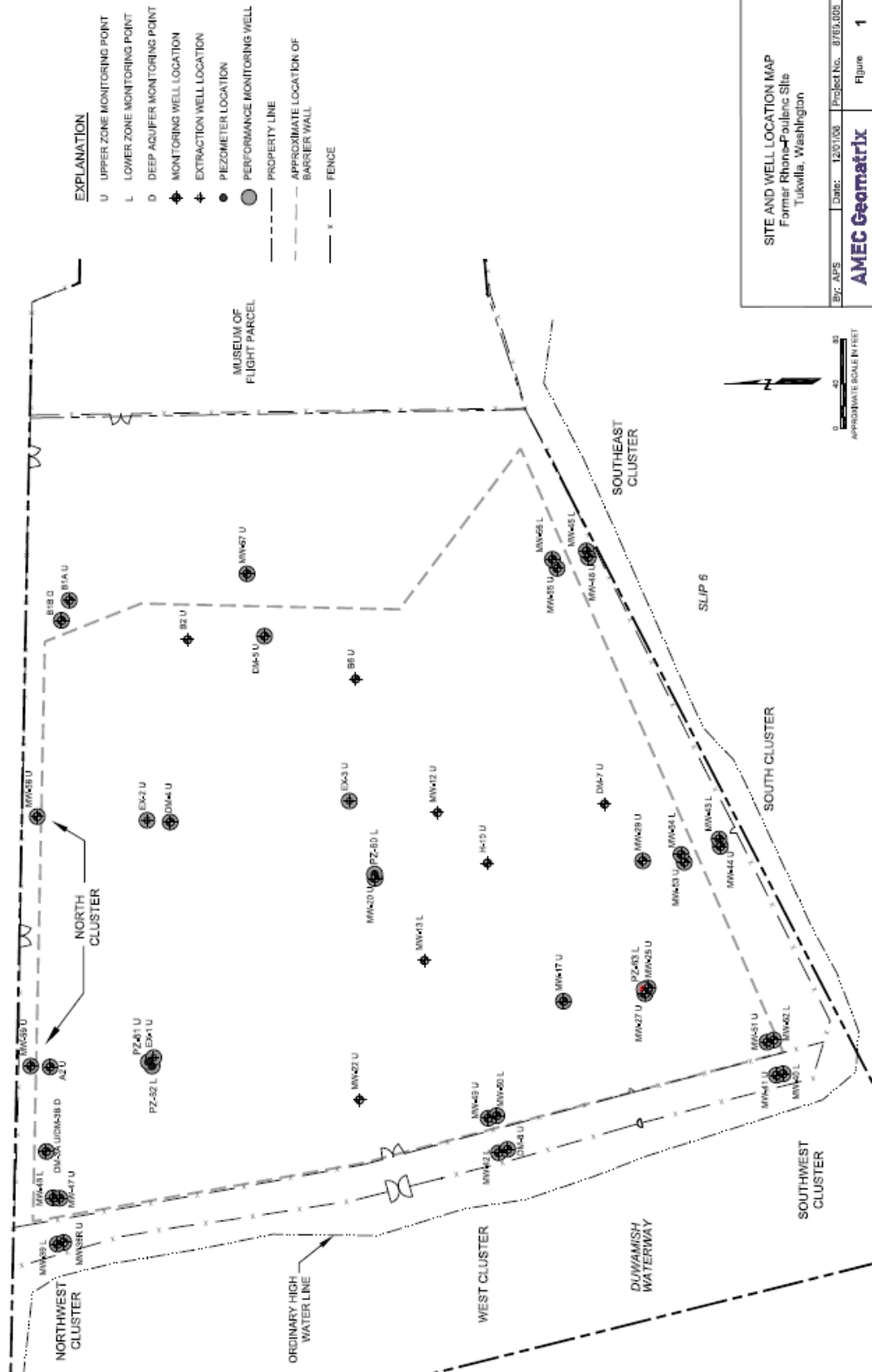
Figure 1. Site map of former Rhone-Poulenc facility (Geomatrix, 2008)

Because the facility stored hazardous wastes, it was subject to the requirements of the Resource Conservation and Recovery Act (RCRA). Monsanto submitted notice of application for permitting under RCRA in the form of a RCRA Part A Interim Status Permit Application. The site is under RCRA interim status and site environmental issues are regulated under RCRA.

In 1986, Dames and Moore, Inc. (1986) performed a site screening investigation for Rhone-Poulenc. After acquiring the property from Monsanto, Rhone-Poulenc wanted a thorough understanding of any potential soil or groundwater contamination at the site. The investigation included the installation of eleven groundwater monitoring wells that were sampled for a range of hazardous constituents. The report documented that wastes and waste materials had been spilled and disposed on site, and concluded that the potential for contamination of groundwater existed. Hazardous constituents, including toluene, were detected in groundwater.

In 1990, the United States Environmental Protection Agency (EPA) performed a RCRA Facility Assessment (RFA) of the entire facility (PRC Environmental Management, Inc., 1990). The RFA determined that hazardous wastes and/or hazardous constituents had been released to the soil and groundwater as a result of past activities at the facility. These activities included pipeline and tank leaks of toluene and caustic materials, disposal of autoclave scale and other waste materials, and use of waste vanillin black liquor solids for weed control.

In 1991, an independent site assessment was conducted by Landau Associates for Boeing Environmental Affairs (Landau Associates, Inc., 1991). This assessment evaluated soil and groundwater quality on the terrestrial portion of the property; sediment and seep quality were evaluated on the marine portion of the property. Consistent levels of contaminants of concern were detected at numerous areas onsite. The assessment concluded that at least two areas of the site would require remediation at an estimated cost between 5.6 and 12.3 million dollars.

In May, 1993, Rhone-Poulenc and EPA entered into an Administrative Order on Consent using EPA's corrective action authority in Section 3008(h) of RCRA to address releases of contaminants at the facility. The Order on Consent sets forth the process by which an investigation and cleanup of the facility is to be conducted, and requires Rhone-Poulenc and any subsequent owners of the property to perform a RCRA Facility Investigation (RFI), Interim Measures (IM) if necessary, and a Corrective Measures Study (CMS), as well as the option to conduct the final corrective measure selected by the EPA. Bayer CropScience (the current corporate successor of Rhone-Poulenc), Rhodia, and Container Properties are all responsible for carrying out the actions required by the Order on Consent.

The RFI was completed in 1995 (CH2M Hill). It documented the presence of hazardous constituents in the soils and groundwater. Most of the contamination was shown to be located on the western portion of the site, where the former processing plant and storage areas were located. Subsequent studies conducted in support of an interim measure design included Geoprobe and geotechnical investigations (URS, 2002) and a Geoprobe investigation (AGI Technologies, 2001). The Geoprobe sample results showed that shoreline areas along the Duwamish Waterway and Slip 6 contained elevated pH readings and elevated concentrations of metals, including copper, arsenic, and mercury.

Based on these previous investigations, the EPA required a hydraulic control interim measure (HCIM) to stop discharges of hazardous constituents into the Duwamish Waterway. The HCIM consists of two components: a subsurface barrier wall and a groundwater extraction and treatment system (Figure 1). From January to July 2003, a low permeability, subsurface barrier wall was constructed in the western portion of the site to discourage contaminant migration into the Duwamish Waterway and Slip 6. The barrier wall consists of grout and is approximately 70

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feet deep; it is approximately 50 feet inland from the waterway and the slip. The groundwater extraction and treatment system was completed in 2004 to establish an inward-directed hydraulic gradient from the waterway. The extracted groundwater is treated using granular activated carbon (GAC) and discharged to a publicly owned treatment works. The HCIM is monitored with a network of monitoring wells with a monitoring program designed to evaluate groundwater levels and chemical constituents in groundwater both within and outside of the HCIM area.

In the spring of 2006, Container Properties informed the EPA of its desire to proceed with the redevelopment of the site. Several additional investigations of historical structures and buildings, potential waste disposal areas, and sumps uncovered during the redevelopment process were conducted:

- Prior to redevelopment, buried facility structures, sumps, and basements were investigated (Geomatrix, 2006a). Elevated concentrations of metals, semivolatile organic compounds (SVOCs), polychlorinated biphenyls (PCBs), and toluene were detected in the former Scale Pit of the main warehouse, the Copper Sump, and the 1-120 Sump. All liquids and solids were removed from these structures, stabilized, and disposed properly.

- During redevelopment, soil near the former Hazardous Waste Storage Area catch basin was found to contain total petroleum hydrocarbons (TPH), SVOCs, and metals (Geomatrix, 2006b). The affected soil was removed, and the catch basin was pumped and abandoned in place. Also, a former electrical transformer had leaked and contaminated the underlying soil with TPH-diesel (TPH-D). The transformer was removed and thirty-six tons of TPH-D-affected soil was excavated and disposed of offsite.

- During regrading of the site, a former oil/water separator was discovered and investigated (Geomatrix, 2006c). The oil/water separator was drained of all liquids and solids, steam-cleaned, and abandoned in place. Materials removed were stabilized and treated offsite.

- Areas of the eastern portion of the site were investigated for possible soil contamination (Geomatrix, 2006d). Contaminated soils were excavated and removed.

- Soil in the northwest corner of the property outside of the barrier wall was characterized for copper, TPH-gasoline (TPH-G), and TPH-D (Geomatrix, 2007). Half of the copper-affected soil placed in the contained area within the barrier wall. The remaining soil was disposed offsite.

As part of the redevelopment activities, the property was split into two Parcels: the East Parcel and the West Parcel. In the extreme southwestern corner of the East Parcel, soil and groundwater exceed project-specific cleanup goals with respect to toluene. Corrective actions, including air sparge, biovent, and soil vapor extraction systems, were employed and were operated from December 2008 to June 2010. The East Parcel is now owned by the Museum of Flight. The West Parcel was regraded and repaved and is now leased by Container Properties to International Auto Auctions, Inc.

1.2 Historical Groundwater Data and Trends

Before the installation of the barrier wall, high concentrations of copper were documented in the shallow groundwater along Slip 6 between the South Well Cluster and the Southwest Well Cluster (Figure 1). Installation of the barrier wall to control contaminants that are discharging into the Lower Duwamish Waterway and Slip 6 appears to have cut through the source of groundwater contamination, leaving some of it outside the barrier wall and without the

original hydraulic gradient that was forcing contaminants into the adjacent water bodies. The

stranded mass of contamination is now subject to other gradients, such as those of the tides,

which have strong vertical components.

Physical parameters, conventional analytes, filtered metals, and non-filtered metals data

were collected from MW-44 in the shallow zone of the South Well Cluster as part of the required

monitoring program after the installation of the subsurface barrier wall. A summary of physical

parameter and conventional analyte data is provided in table 1(date-specific data available in

Appendices 1 and 2). Applicable or relevant and appropriate requirements (ARARs) for surface

water (freshwater and marine) were obtained from the Cleanup Levels and Risk Calculator

(CLARC) Database (maintained by the Washington State Department of Ecology at

https://fortress.wa.gov/ecy/clarc/CLARCHome.aspx) and are shown in Appendix 5.

Table 1. Maximum, minimum, median, and average measured historical values for physical
parameters and conventional analytes in groundwater from MW-44.

| Parameter	Maximum	Minimum	Median	Average
	Physical Parameters			
Temperature (°C)	16.71	11.74	14.58	14.79
pH	12.45	9.80	10.97	10.93
Specific Conductance (mS/cm)	8.06	0.680	4.84	4.91
Dissolved Oxygen (mg/L)	13.4	0	1.46	0.24
Redox Potential (mV)	2	-837.88	-375.32	-409.15
Turbidity (NTU)	999	0	79.9	13.6
	Conventional Analytes			
Nitrate (mg-N/L)	1.4	<0.05	0.492	0.403
Nitrite (mg-N/L)	1.0	<0.1	0.361	0.225
Nitrate + Nitrite (mg-N/L)	1.4	<0.1	0.497	0.403
Ammonia (mg-N/L)	5.42	2.20	3.61	3.35
Total Phosphorous (mg-P/L)	21.40	1.84	7.23	6.28
Sulfate (mg/L)	326	53	167	160
Sulfide (mg/L)	29.90	0.21	10.32	9.15
Chloride (mg/L)	92.2	62.8	78.8	76.9
Alkalinity (mg/L as $CaCO_3$)	2980	1000	2256	2490

Table 2. Maximum, minimum, median, and average measured historical values for filtered metals and non-filtered metals in groundwater from MW-44.

Parameter	Maximum	Minimum	Median	Average
	Filtered Metals			
Aluminum (mg/L)	1.50	0.78	1.02	1.02
Cadmium (mg/L)	<0.002	<0.002	<0.002	<0.002
Calcium (mg/L)	24.10	8.44	14.06	12.40
Chromium (mg/L)	0.057	0.026	0.035	0.033
Copper (mg/L)	0.165	0.048	0.108	0.109
Iron (mg/L)	13.9	6.76	9.77	9.80
Magnesium (mg/L)	9.35	0.88	3.94	3.04
Manganese (mg/L)	0.755	0.169	0.390	0.352
Nickel (mg/L)	0.02	<0.01	0.01	0.01
Potassium (mg/L)	12.60	8.30	9.49	9.25
Selenium (mg/L)	<0.05	<0.05	<0.05	<0.05
Silicon (mg/L)	668	83.5	471	495
Sodium (mg/L)	1320	634	918	891
Vanadium (mg/L)	0.555	0.259	0.330	0.295
Zinc (mg/L)	0.013	<0.006	0.009	0.008
Arsenic (mg/L)	0.014	0.001	0.005	0.004
Lead (mg/L)	0.015	0.002	0.009	0.009
Mercury (mg/L)	<0.0001	<0.0001	<0.0001	<0.0001
Thallium (mg/L)	0.003	<0.001	0.001	0.001
	Non-Filtered Metals			
Aluminum (mg/L)	1.88	0.90	1.28	1.20
Cadmium (mg/L)	<0.002	<0.002	<0.002	<0.002
Chromium (mg/L)	0.068	0.023	0.044	0.043
Copper (mg/L)	0.207	0.027	0.137	0.147
Nickel (mg/L)	0.02	0.01	0.02	0.02
Selenium (mg/L)	<0.05	<0.05	<0.05	<0.05
Silicon (mg/L)	121	121	121	121
Vanadium (mg/L)	0.587	0.222	0.405	0.406
Zinc (mg/L)	0.025	0.006	0.013	0.011
Arsenic (mg/L)	0.029	<0.001	0.010	0.008
Lead (mg/L)	0.02	0.00	0.01	0.01
Mercury (mg/L)	<0.002	<0.0001	0.0002	<0.0001
Thallium (mg/L)	<0.002	<0.001	<0.001	<0.001

Plots showing the trends in aluminum, arsenic, copper, lead, vanadium, and zinc concentrations from MW-44 are given in Figure 2. The gray stripe represents the period of time

when the subsurface barrier wall was being constructed. Where filtered metal results were not available, filtered metal concentrations were estimated using the median ratio of dissolved to total metals observed before filtered metal data became unavailable. Values reported at the detection level are not represented in the plots, but can be found in Appendices 3 and 4. Aluminum concentrations increased substantially beginning in June 2004, but fell back to pre-June 2004 levels in June 2007. For brief periods post-June 2007, dissolved aluminum concentrations are estimated to have fallen below the acute ARAR. Arsenic concentrations generally seemed to increase after the installation of the barrier wall, though there is considerable variability. Never has arsenic exceeded the most stringent chronic or marine ARARs. Copper concentrations increased substantially after the completion of the barrier wall, and have always been greater than acute or chronic ARARs. Like copper, lead concentrations have substantially increased after the installation of the barrier wall. Lead concentrations have always been greater than the most conservative chronic ARAR, and have occasionally been greater than the most conservative acute ARAR. Vanadium concentrations have steadily risen since the installation of the barrier. No ARARs for vanadium are available. Zinc concentrations fluctuated considerably after the completion of the barrier wall, but have more recently been below detection limits. Never have zinc concentrations been greater than the most conservative ARARs. Figure 3 indicates that pH quickly rose after the installation of the subsurface barrier wall and has remained near or above 10.5 since June 2004.
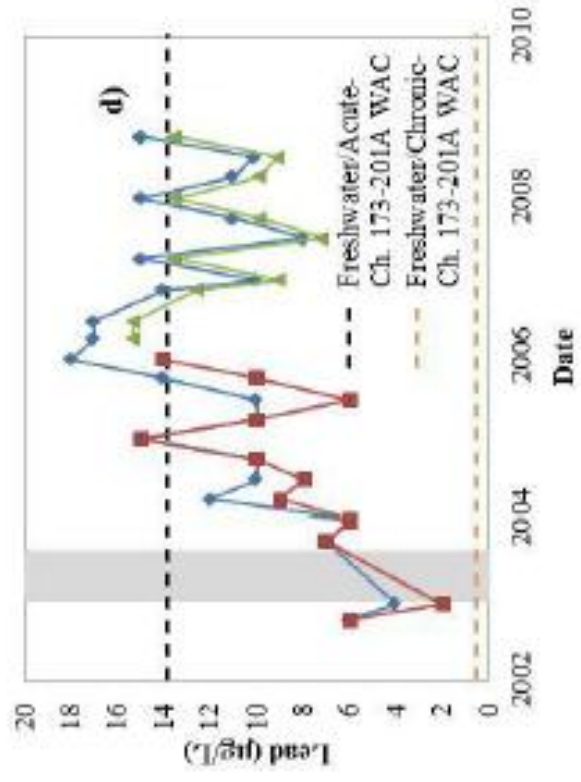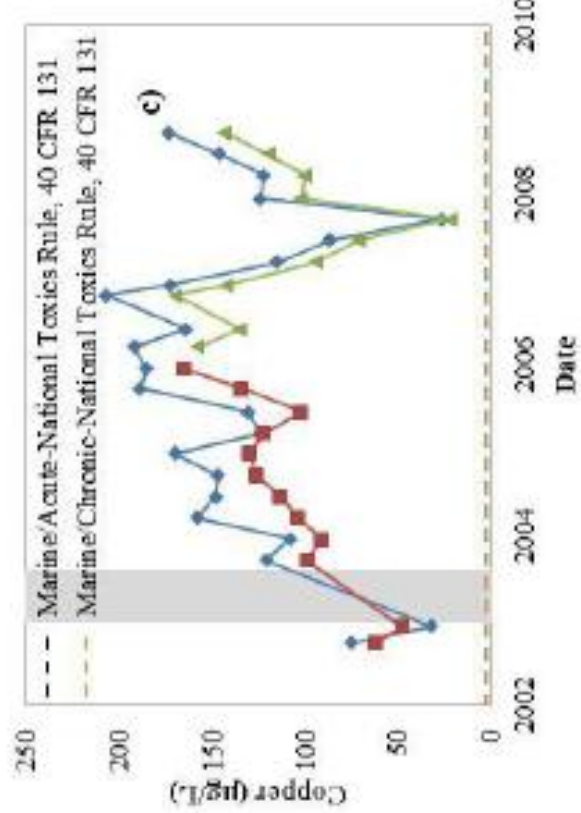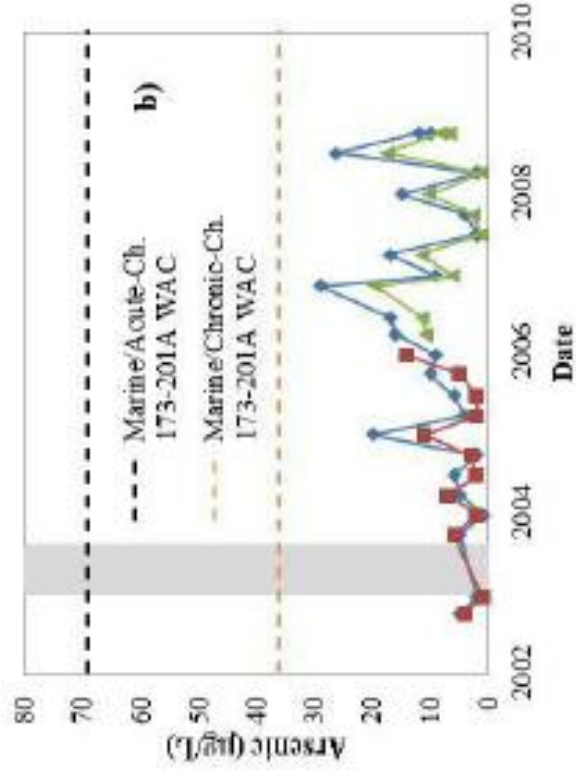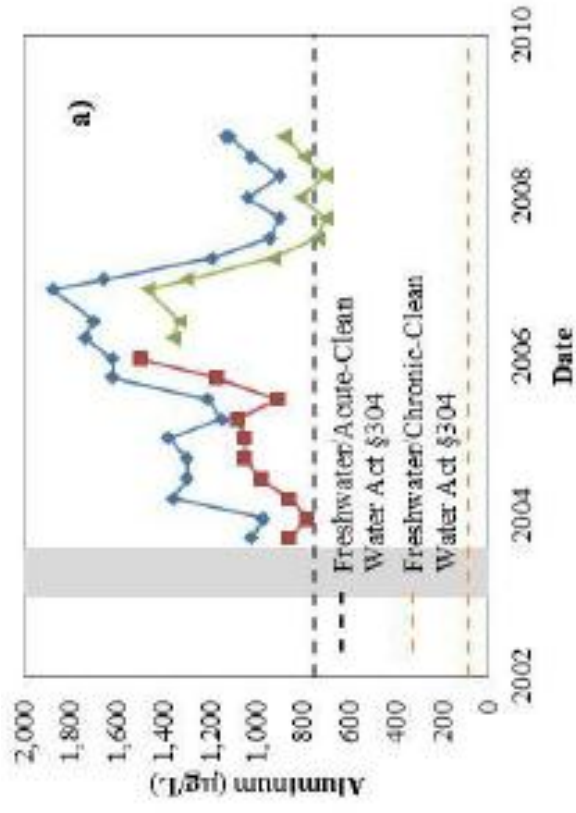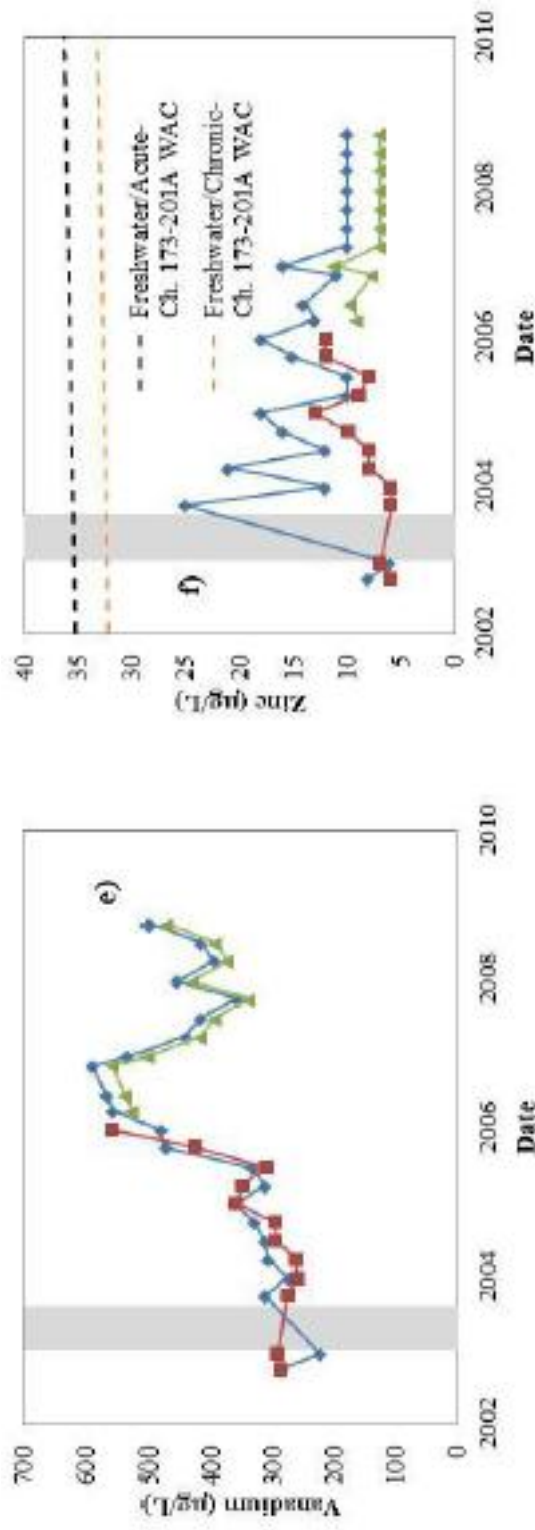
Figure 2. Data trends from MW-44 for metals: a) Aluminum, b) Arsenic, c) Copper, d) Lead, e) Vanadium, and f) Zinc. The vertical gray stripe represents the period of time when the subsurface barrier wall was being constructed. Dashed horizontal lines represent the most conservative acute and chronic ARAR, as indicated on the plot. Blue lines with diamonds (——◆——) represent the non-filtered metal. Red lines with squares (——■——) represent the observed filtered metal. Green lines with triangles (——▲——) represent estimated dissolved metal values (determined using the median dissolved/total ratio when dissolved metal data were available).
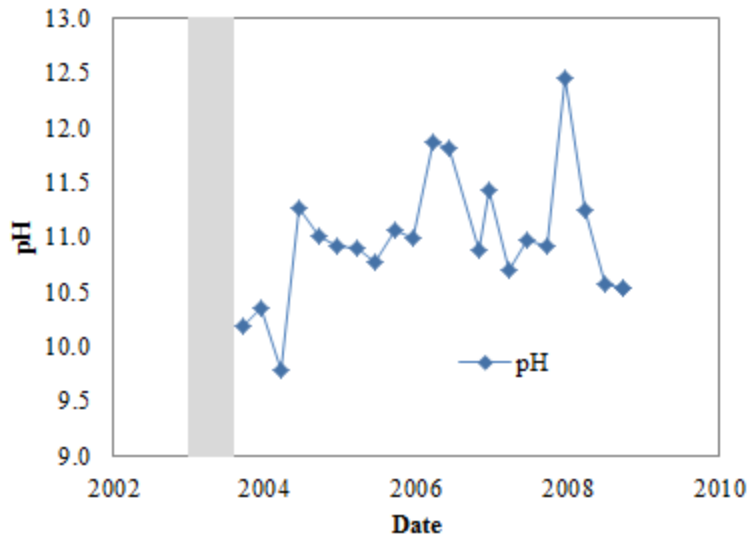
Figure 3. pH over time at MW-44 (shallow zone of the South Well Cluster).

1.3 Purpose and Scope

Since the installation of the barrier wall, arsenic, copper, lead, and vanadium concentrations have increased in the upper zone of the South Well Cluster and the pH has steadily grown more caustic. The ultimate goal is to develop and implement a groundwater remediation plan to control and/or remediate dissolved metals and pH in the area outside the barrier wall near the South and Southwest Well Clusters. The objective of this study is to identify and evaluate potential metal remediation and pH control strategies that will ultimately protect surface and porewater quality.

2.0 Development of Treatment Strategy

The selection of an appropriate groundwater remediation technique for dissolved metals depends on the site characteristics, types and concentrations of metals to be removed, and the end use of the contaminated water (Mulligan et al., 2001). For groundwater, metals remediation techniques include containment and isolation, extraction and treatment, chemical treatment, biochemical treatment, phytoremediation, and permeable reactive barriers (PRBs). The most widely used method to remediate groundwater, though, is the extraction and treatment approach (Morrison et al., 2002). This method requires pumping water above ground surface and treating it *ex situ*. Often, many pore volumes of water must be extracted over long periods of time to meet site-specific cleanup levels, leading to high treatment costs. Few sites have been remediated to regulated levels using the extraction and treatment approach, leading to uncertainty regarding the cost-effectiveness of such systems (Mackay and Cherry, 1989). An extraction and treatment system outside of the barrier wall may be appropriate, but could risk drawing large volumes of water from Slip 6 or the Duwamish Waterway. The costly nature of an extraction and treatment system provides the impetus for *in situ* remediation methods. *In situ* immobilization of metals can be accomplished by precipitation and/or adsorption (Morrison et al., 2002).

2.1 Review of Relevant Metal Chemistries

Groundwater in the area outside the barrier wall near the South and Southwest Well Clusters has high levels of dissolved metals (Figure 2), high pH (Figure 3), high levels of dissolved organic carbon, as suggested by the color of the water (Figure 4), and high alkalinity (Appendix 2). Although the focus of this treatment strategy is pH control and the remediation of dissolved copper, lead, vanadium, and arsenic, these parameters are depend on the groundwater's other properties. To develop a successful treatment strategy, it is first important to understand the

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unique metal chemistries with regard to both current and altered conditions. This helps identify

potential dissolved metal removal mechanisms and shows how changing the groundwater

conditions (e.g., lowering pH or increasing Eh) may result in dissolved metal species that are

more or less amenable to a particular removal mechanism. This section summarizes the relevant

environmental chemistries of copper, lead, arsenic, and vanadium from literature. However, the

water chemistry at the former Rhone Poulenc site is not common, and thus, geochemical

modeling also was completed to assess the relevant metal chemistries under both current and

altered conditions.

Figure 4. MW-44 Site Water

Geochemical modeling was completed using PHREEQC Version 2 (Parkhurst and

Appelo, 1999) to show the changes in metal speciation as pH and/or oxidation-reduction

potential varies. Site-specific groundwater concentrations of metals and other inorganic species

(Appendices 1-4) were used as PHREEQC input; see Appendix 6 for an example input file,

(which includes the database used). Where filtered metal results were not available, filtered

metal concentrations were estimated using the median ratio of dissolved to total metals observed

before filtered metal data became unavailable; these estimates were then used in the calculation of average filtered metal values for PHREEQC input. Median values were used in the cases of the physical parameters of redox potential (converted to pe for PHREEQC input) and dissolved oxygen in an effort to avoid measurements subject to potential sensor error (noted in Appendix 1).

Organic matter was not accounted for in the geochemical modeling, although dissolved organic matter (DOM) plays a significant role in the biogeochemical cycling of trace metals in aquatic environments (Aiken et al., 2011). In soil water, the dissolved organic carbon (DOC) ranges from 0.1 to 3 mM; in groundwater, from 0.01 to 1 mM; and in rivers draining swamps as high as 5 mM (Appelo and Postma, 2005). DOM is a broad classification of dissolved organic molecules of varied origin. It consists of a mixture of complex compounds of different molecular weights (Stumm and Morgan, 1996; Aiken et al., 2011). Under environmental conditions, metal-DOM binding is driven by functional group chemistry and structural constraints. The large chemical variety of neighboring functional groups provide for a range of affinities for metal ions. Also, electrostatic interactions can result in conformational changes among the various functional groups (Stumm and Morgan, 1996; Appelo and Postma, 2005). In natural waters, DOM often controls metal speciation (Tipping, 2002), alters the surface charge of particles (Tiller and O'Melia, 1993), interferes with mineral dissolution and precipitation reactions by sorbing to mineral surfaces (Slowey, 2010; Lau and Hsu-Kim, 2008), alters the kinetics of environmental reactions, and changes the bioavailability of metals (van Leeuwen and Buffle, 2009). Ignoring this important parameter may limit the relevance of the results of geochemical modeling, but the modeling was completed nonetheless.

2.1.1 Copper

Copper may occur in solution in either Cu^+ or Cu^{2+} oxidation states (Hem, 1985). The redox conditions in oxygenated water and the tendency of the cuprous ion to disproportionate ($2Cu^+ \rightarrow Cu^0 + Cu^{2+}$) favor the cupric form. Cupric ions form complexes with many different ligands, including sulfides, sulfates, and carbonates (Bradl et al., 2005). In solutions above neutral pH, $Cu(OH)_3^-$ may be the dominant form. $CuCO_3$ (aq) appears likely to be the major form in oxygenated water containing dissolved inorganic carbon species (Hem, 1977). Copper hydroxycarbonates are slightly soluble, but adsorption or coprecipitation with ferric oxyhydroxides can bring about even lower solubility.

Geochemical modeling with MW-44 representative parameters show that the predominant copper oxidation state is +1 under site conditions over the given pH range, with Cu^+ and $CuCl_2^-$ being the dominant species (Figure 5). Under more oxidizing conditions, the predominant copper oxidation state is +2 over the given pH range (Figure 5); $CuCO_3(OH)_2^{-2}$, $Cu(CO_3)_2^{-2}$, and $CuCO_3$ are the dominant species. Under oxidized conditions, lowering the pH to near 8 results in $CuCO_3$ being the dominant copper species (Figure 6). However, saturation indices indicate little potential for the precipitation of copper carbonates/hydroxides regardless of Eh or pH (Appendices 7 and 8), though some iron-copper complexes are oversaturated.

Figure 5. Copper speciation as a function of pH at Eh = -409 mV
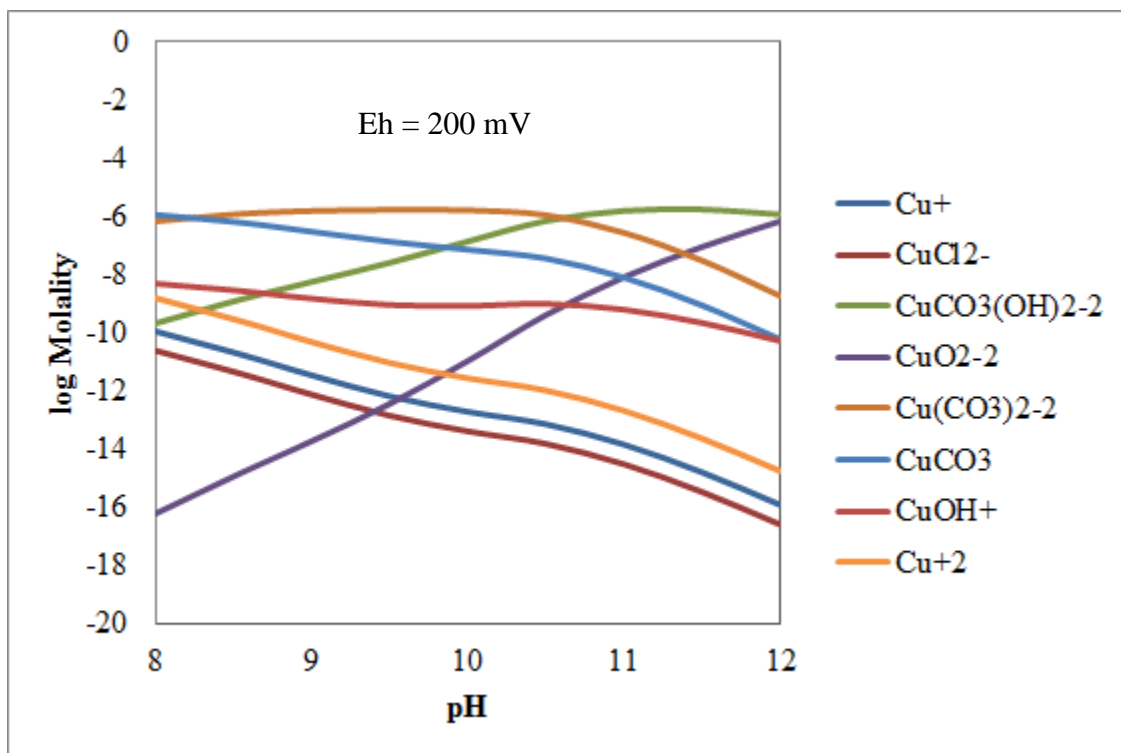
Figure 6. Copper speciation as a function of pH at Eh = 200 mV

Distribution of copper in soils is mostly influenced by the presence of soil organic matter and Mn and Fe oxides (Bradl et al., 2005). The most important copper sinks are Fe and Mn oxides, soil organic matter, sulfides, and carbonates while clay minerals and phosphate are of lesser importance. Manganese oxides and soil organic matter are most likely to bind copper in a nonexchangeable form. It has been shown that copper is extensively complexed by humic materials (Bradl et al., 2005).

2.1.2 Lead

Lead occurs in two oxidation states: +2 and +4 (Bradl et al., 2005), but is most commonly found in the +2 state. The principal dissolved forms of inorganic lead are Pb^{2+}, hydroxide complexes, and carbonate and sulfate ion pairs (Hem, 1985).The dominant inorganic species in seawater are lead carbonates which account for 40-80% of dissolved lead species, followed by chloro-species at 10-25% (Ferguson, 1990). Of lesser importance are the lead hydroxyl-species and perhaps some free Pb^{2+}. In fresh water, the dominant species are the lead carbonates at around 90%. In either case, as pH rises, the hydoxy species begin to dominate.

Geochemical modeling of site water indicates that the lead hydroxide and carbonate species dominate over the pH range 8-12 regardless of the Eh (Figures 7 and 8). As a result of lowering the pH to near 8, $PbCO_3$ becomes the dominant lead species, though saturation indices indicate that cerussite ($PbCO_3(s)$) is unlikely to precipitate under oxygenated or reduced conditions (Appendices 7 and 8).
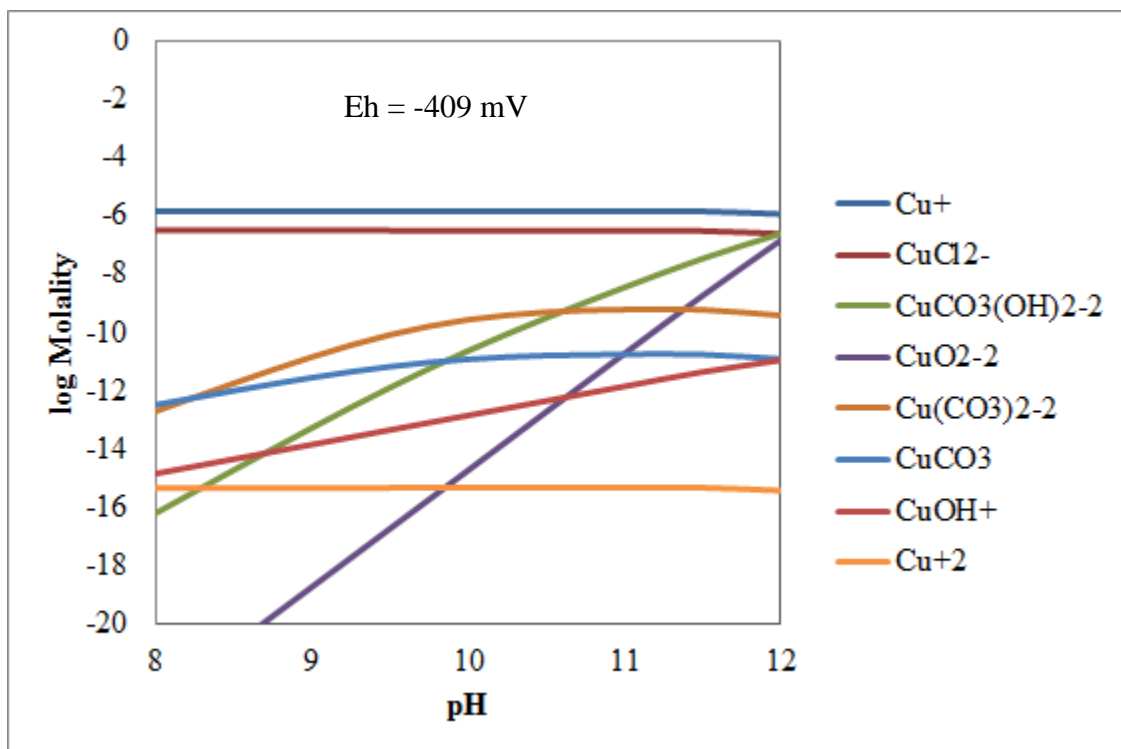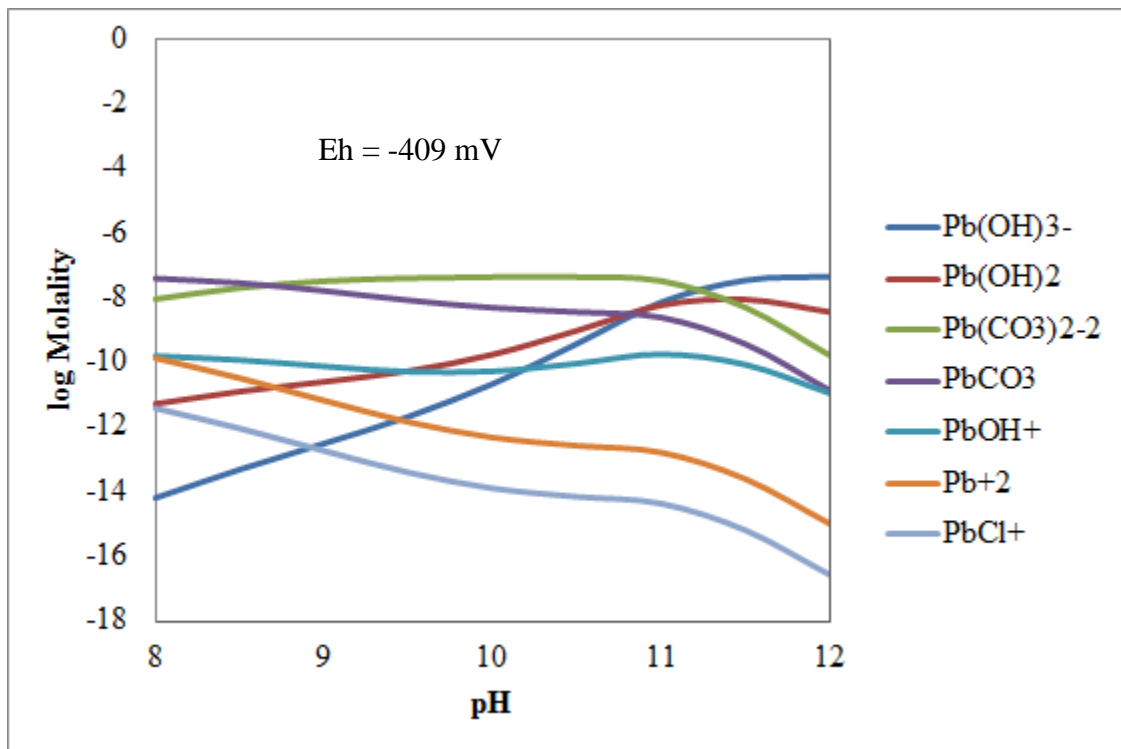
Figure 7. Lead speciation as a function of pH at Eh = -409 mV
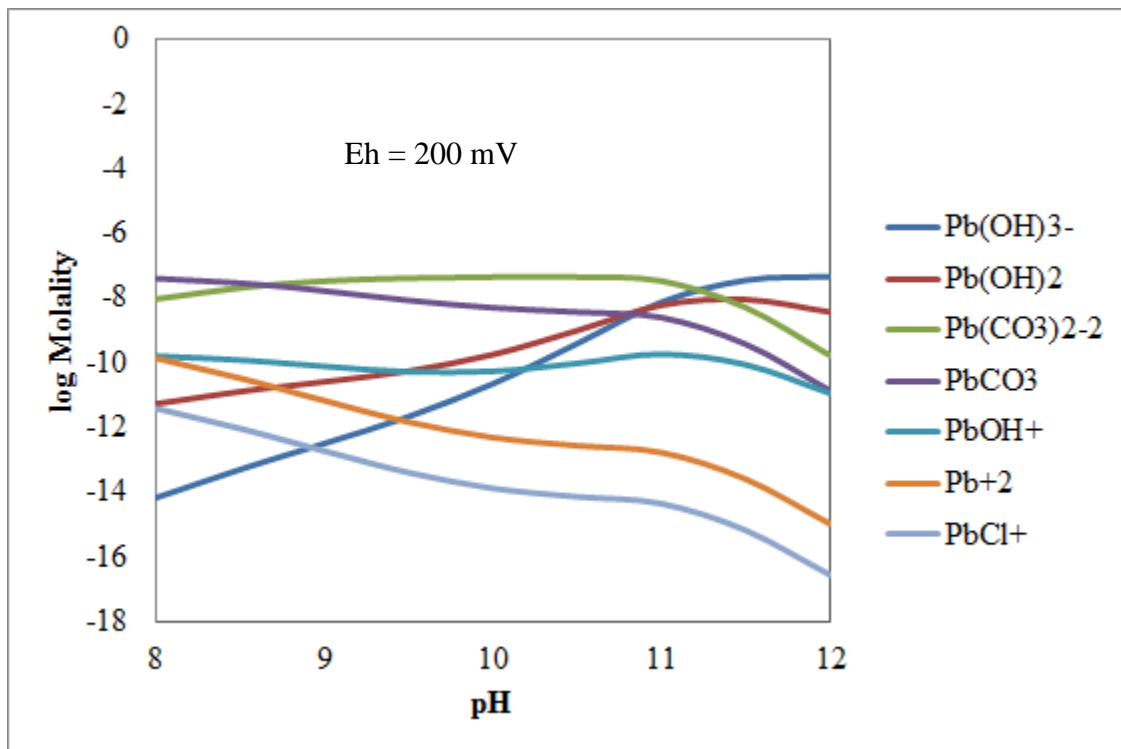
Figure 8. Lead speciation as a function of pH at Eh = 200 mV

The chemistry of lead in soils is affected by three main factors: specific adsorption to various solid phases, precipitation of sparingly soluble or highly stable compounds (e.g. lead carbonates, hydroxides, and phosphates), and the formation of relatively stable complexes or chelates that result from interaction with organic matter (Bradl et al., 2005). The presence of iron and manganese oxides may exert a predominant role on Pb adsorption in soils, though lead has been shown to exhibit strong affinities for clays, peats and usual soils as well. Carbonate content in soils can plays an important role in controlling Pb behavior; in systems where carbonate is low, Pb solubility is controlled by Pb hydroxides and phosphates. Lead phosphates are a very stable environmental form of Pb with low solubilities. Soil organic matter may immobilize lead via specific adsorption reactions, while mobilization of lead can also be facilitated by its complexation with organic ligands. As much as 100% of soluble lead may be contained in organic complexes (Ferguson, 1990).

2.1.3 Arsenic

Mobility of arsenic is primarily influenced by the species of As present, groundwater pH, presence of manganese or iron and clay minerals, redox potential, and competing ions (Bradl et al., 2005). In solution, the stable forms of arsenic are As^{5+} (arsenate) and As^{3+} (arsenite) oxyanions (Hem, 1985) with arsenate being important in oxygenated waters and arsenite being important in oxygen depleted waters; oxidation states of 0 and -3 occur under strongly reducing conditions, and are rare in the natural water environment (Ferguson, 1990). Arsenite is the more mobile than arsenate in sediments and groundwater (Bradl et al., 2005). An Eh-pH diagram (Figure 9) indicates that the divalent, monoprotic arsenate species $HAsO_4^{2-}$ would predominate from pH 7 to 11 (Hem, 1977). Reducing conditions would favor either the uncharged $HAsO_2(aq)$

or the AsO_2^- species. Arsenic solubility is likely controlled by the formation of $Mn_3(AsO_4)_2$ (s), $FeAsO_4$ (s), and $CaAsO_4$ (s) (Bradl et al., 2005).
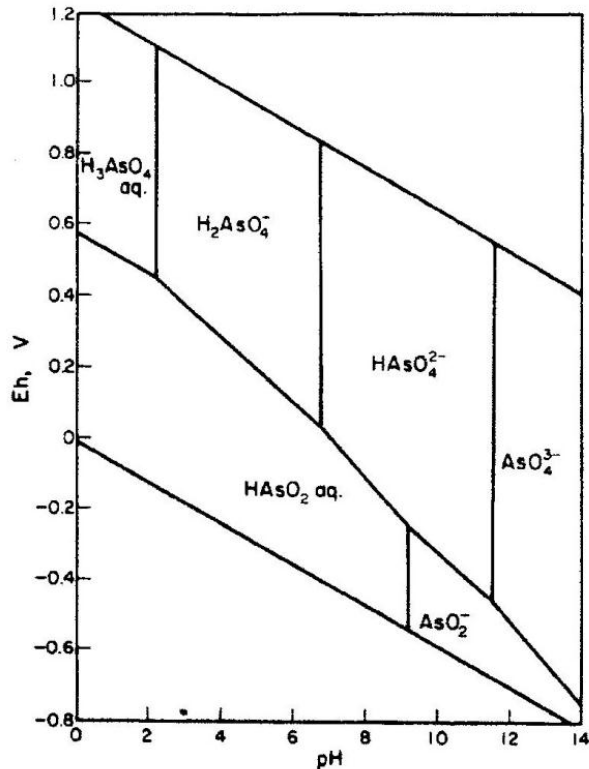
Figure 9. Arsenic Eh-pH diagram with fixed total activities of arsenic = 10^{-7}, sulfate = 10^{-4}, and bicarbonate = 10^{-3} M at 25 °C and 1 atm (Hem, 1977).

Under reduced conditions, the +5 oxidation state dominates roughly above pH 11, but the more reduced and mobile arsenic species dominate at lower pH (Figure 10). However, under more oxidized conditions, the +5 oxidation state dominates throughout the applicable pH range (Figure 11). Saturation indices for all phases that contain arsenic are undersaturated under all conditions (Appendices 7 and 8), suggesting that arsenic is not likely to precipitate as a solely arsenic compound.

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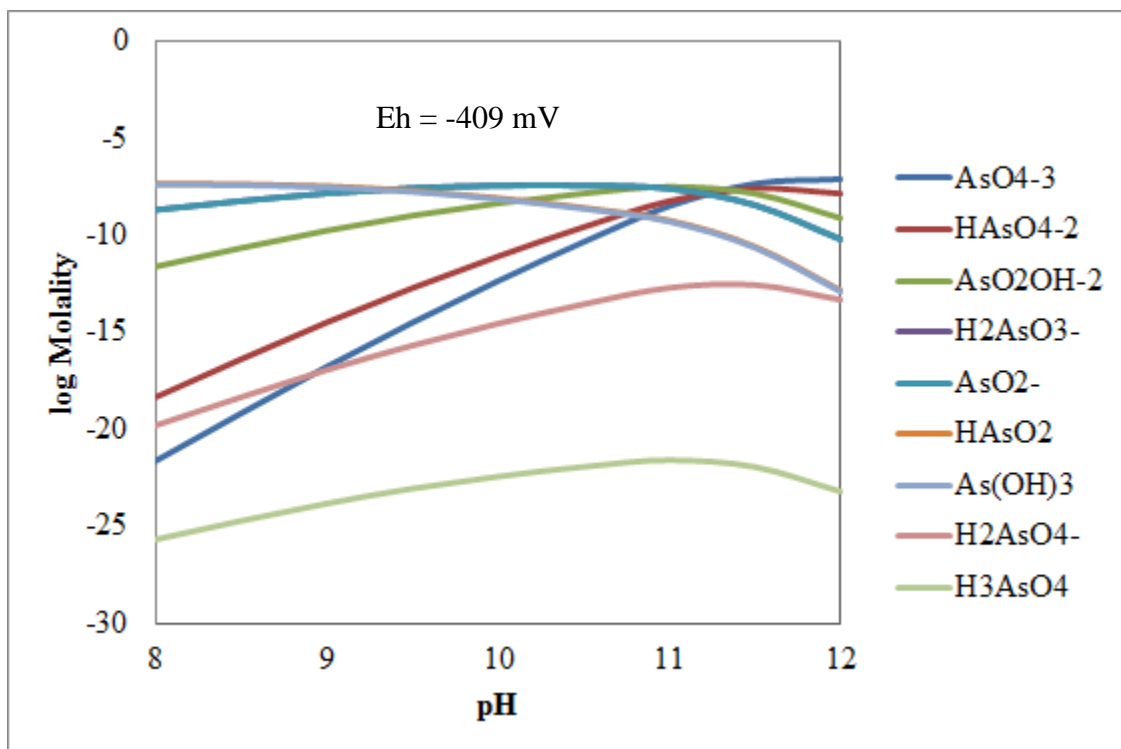
Figure 10. Arsenic speciation as a function of pH at Eh = -409 mV
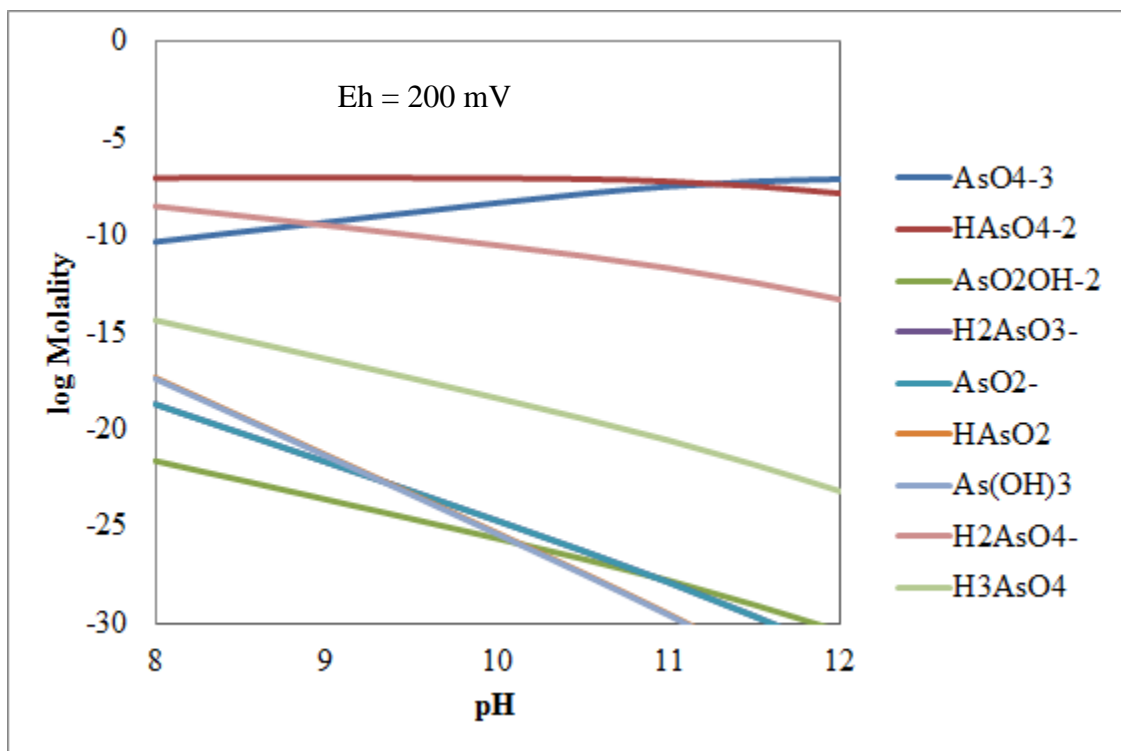
Figure 11. Arsenic speciation as a function of pH at Eh = 200 mV

The mobility of arsenic is generally greater in coarse soils than in soils having higher content of fines such as clay minerals (Bradl et al., 2005). Under low Eh conditions, the reductive dissolution of iron or manganese oxides and oxyhydroxides would enhance the leaching of arsenic (Bowell, 1994; Smedley and Kinniburgh, 2002). High pH (>8.5) may lead to the desorption of adsorbed arsenic (particularly arsenate species) and the desorption of a range of other anion forming elements (including vanadium) (Smedley and Kinniburgh, 2002). Large concentrations of phosphate (Singh, 2006), bicarbonate (Stachowicz et al., 2007), and organic matter (Sharma and Sohn, 2009; Bowell, 1994; Bauer and Blodau, 2006) can enhance the desorption of arsenic because of competition for adsorption sites. Organic matter can also form aqueous complexes of As (Sharma and Sohn, 2009; Liu et al., 2011).

2.1.4 Vanadium

Three oxidation states can be stable in aqueous systems: V^{3+}, V^{4+}, and V^{5+} (Hem, 1985). In oxic systems, the dominant forms are the V^{5+} anionic complexes with oxygen and hydroxide. Because of vanadium's tendency to form anionic species, a high solubility is possible in alkaline environments. The more reduced forms have solubilities lower than 10^{-7} mol/L in the $V(OH)_3^+$ and $V(OH)_2^+$ domains (Figure 12). In the presence of other metal cations (such as ferrous iron), the solubility of vanadium can be low over a wider range of conditions (Hem, 1977).
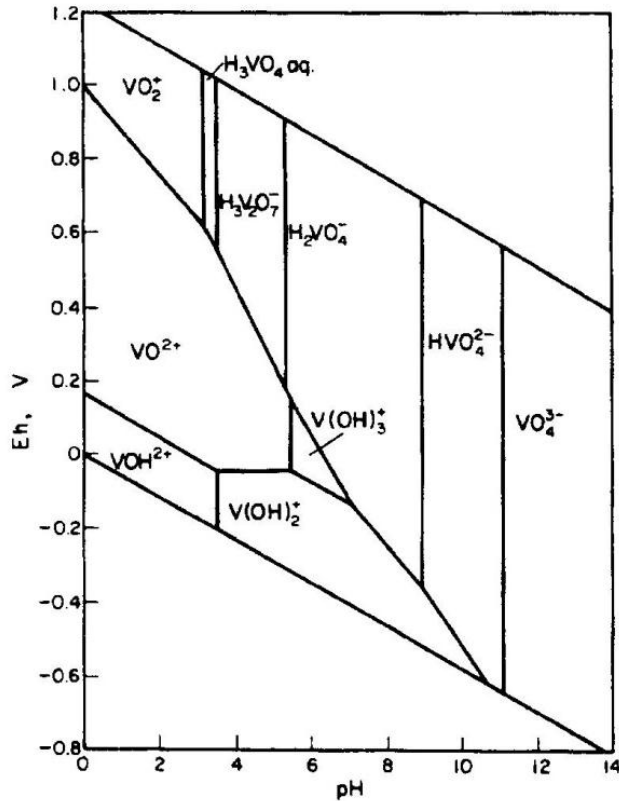
Figure 12. Vanadium Eh-pH diagram, with fixed total activities of vanadium = 10^{-7}, sulfate = 10^{-4}, and bicarbonate = 10^{-3} M at 25 °C and 1 atm (Hem, 1977).

Under reduced conditions, the +5 oxidation state dominates above pH 9.5, with VO_3OH^{-2} being the dominant species (Figure 13). Below pH 9.5, the reduced, positively charged species $V(OH)_2^+$ is predominant. This suggests that decreasing the pH may result in vanadium species more amenable to sorption. However, under more oxidized conditions, the +5 oxidation state dominates throughout the applicable pH range (Figure 14).
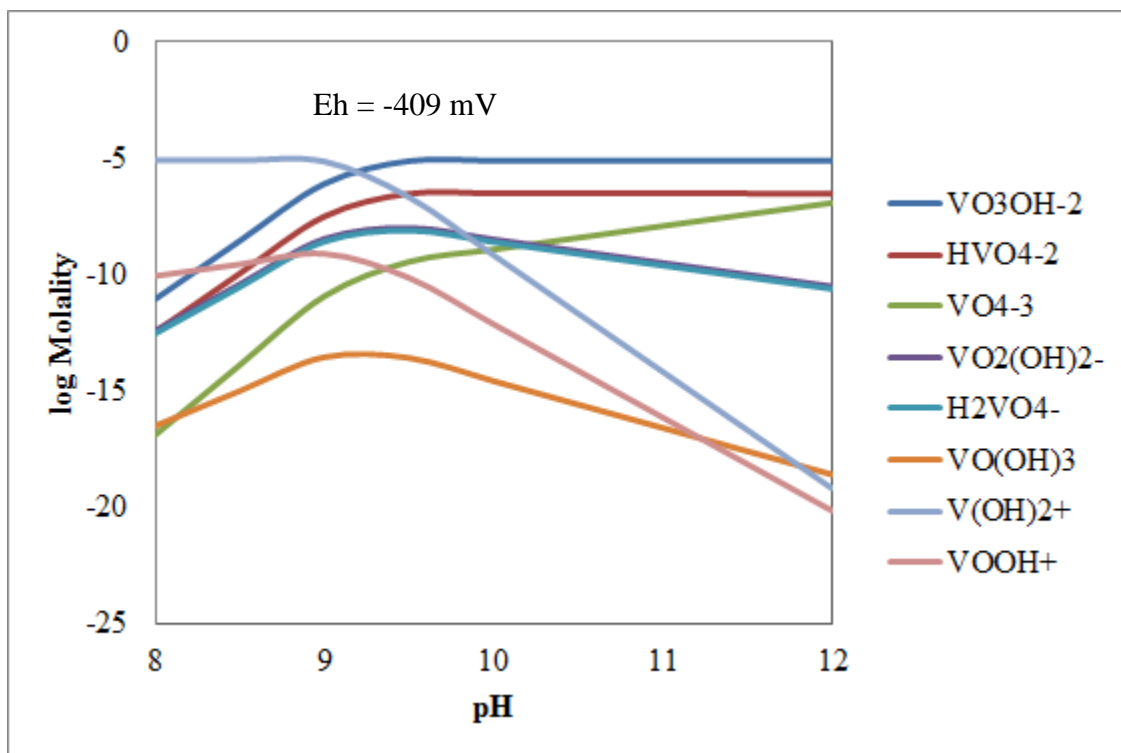
Figure 13. Vanadium speciation as a function of pH at Eh = -409 mV.
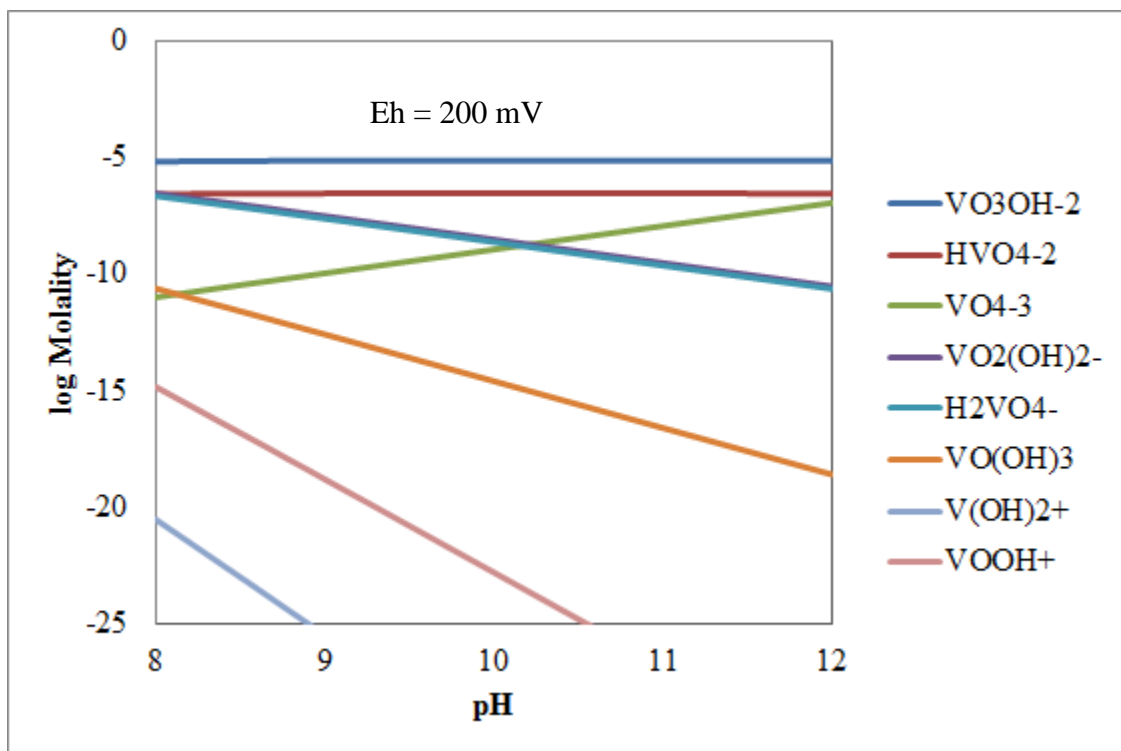
Figure 14. Vanadium speciation as a function of pH at Eh = 200 mV

2.2 Methods of Controlling pH

Extremely alkaline groundwater is observed only rarely in nature and, thus, has not been extensively studied (Roadcap et al., 2005). Human activities, though, can produce very alkaline waters. The weathering of steel slag, for example, can give rise to high pH leachates (Mayes et al., 2008; Roadcap et al., 2005). Remediation options at these alkaline, slag-leachate sites typically involve aeration and/or acid dosing. Roadcap et al. (2005) investigated four remediation techniques to decrease the pH of a water/sediment system contaminated by steel slag leachate: HCl addition, CO_2 sparging, air sparging, and dolomite addition. As separate treatments, both HCl addition and CO_2 sparging rapidly decreased the pH to near-neutral, though authors report the final toxicities of samples from these experiments were three to four times greater than that of the air sparging sample. This was likely due to the release of metals as calcite sediment dissolved. Air sparging decreased the pH of the water to 8.1 after roughly 36 hours of sparging. CO_2 cannot accumulate in air-sparged water beyond equilibrium with the atmosphere, so the pH did not drop sufficiently to dissolve calcite. Dolomite addition resulted in the pH slowly falling to 9.1 after nearly seven days. The authors attribute the pH decrease to the dissolution of silica (SiO_2) grains within the crushed aggregate that are more soluble at high pH than neutral pH.

Conestoga-Rovers and Associates (2008) completed a pilot study for Occidental Chemical Corporation with the goal of assessing the feasibility and effectiveness of field scale implementation of ferrous sulfate ($FeSO_4$) injection for pH source control. Iron acidifies water through the formation of iron hydroxides:

- $Fe^{2+} + 2H_2O = Fe(OH)_2 + 2H^+$

- $Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+$

Groundwater pH ranged from 8.5 to 14. The pH impacted groundwater extended as far as 160

feet below ground surface. Nine and eighteen percent by weight ferrous sulfate heptahydrate

(FeSO$_4$:7H$_2$O) solutions were made with water, and then injected at different locations on site.

Both solutions were effective in lowering the initial groundwater pH (10-14) approximately 4 pH

units near the injection point, though the 18% solution treated three times the volume that the 9%

solution treated. The spatial distribution of FeSO$_4$ varied significantly, potentially due to the

heterogeneous nature of the aquifer and preferential flow paths created by injection pressures.

Furthermore, alkalinity released from the soil as a result of FeSO$_4$ application caused the pH to

rebound, limiting the effectiveness of the FeSO$_4$ treatment.

2.3 Coagulation

Coagulation is the process by which metal salts (e.g. ferrous sulfate, alum) are added to

solution in order to destabilize colloidal material (Stephenson and Duff, 1996). Small particles

then aggregate into larger particles in a process termed flocculation. In aqueous solution, the

metal ion hydrates and is hydrolyzed to form monomeric and polymeric metal hydroxide species

(Dentel and Gossett, 1988). The metal hydroxide polymers which result have a larger surface

area, an amorphous structure, and a positive charge (Randtke, 1988). These polymers are

hydrophobic, causing them to adsorb to organic particle surfaces and become insoluble (Dentel

and Gossett, 1988). Iron has a strong tendency to form insoluble complexes with a number of

ligands, especially with polar molecules and oxygen containing functional groups (Stumm and

Morgan, 1996). These polar functional groups create a local negative charge which leads to

interaction with the iron cations. Charge neutralization results in colloid destabilization;

precipitation of the metal cations and organic anions occurs (Stephenson and Duff, 1996).

Particulate organic and inorganic compounds form large, amorphous particles due to adsorption

and bridging enmeshment (Jekel, 1986). Dissolved organic compounds are removed primarily by sorption on the iron hydroxide surface.

Hydrolyzing metal salts of iron and aluminum are widely used as coagulants in conventional water and wastewater treatment facilities to reduce the concentrations of particulates and dissolved organic compounds (Stephenson and Duff, 1996; Delphos and Wesner, 2005). Iron- and aluminum-based coagulants have also been effective in the removal of chemical oxygen demand and color from diluted black liquor (Garg et al., 2010). Furthermore, coagulants have been used to significantly reduce dissolved metal concentrations in the presence of DOM (Baskan and Pala, 2009; Martin and Kempton, 2000; Tubić et al., 2010; Henneberry et al., 2011). Pore plugging and the associated reduction in hydraulic conductivity that may arise with the addition of coagulants to the subsurface are likely to be a concern with regards to field implementation (Martin and Kempton, 2000; Sperry et al., 1996).

2.4 Sorbents/Amendments

In this study, five readily available, low-cost amendments/sorbents were selected for evaluation: apatite/bone char, chitosan, granular activated carbon (GAC), Thiol-SAMMS ®, and limestone.

2.4.1 Hydroxyapatite/Bone Char

Hydroxyapatite ($Ca_5(OH)(PO_4)_3$) and materials containing hydroxyapatite (e.g. bone char) have been widely used to immobilize metals (e.g. lead, zinc, cadmium, copper, and arsenate) (Ma et al., 1994; Mavropoulos et al., 2002; Lee et al., 2005; Ko et al., 2001; Cheung, et al., 2001; Chen et al., 2008; Sneddon et al., 2005) and radionuclides (e.g. uranium) (Fuller et al.; 2002). Immobilization may occur due to dissolution and formation of insoluble metal phosphates

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and/or sorption (Mavropoulos et al., 2002; Lee et al.; 2005; Chen et al., 1997), though geochemical modeling indicates that hydroxyapatite is unlikely to dissolve from pH 8 to 12, regardless of Eh (Appendices 7 and 8). This indicates that any metal removal would likely be due to sorption. Bone char has also been found to be a useful sorbent for humic substances and metal-humic complexes (Katsumata et al., 2004).

2.4.2 Chitosan

Chitosan is a biopolymer with a molecular structure similar to cellulose; it is widely found in the exoskeleton of fish and crustaceans (Babel and Kurniawan, 2003). The adsorption behavior of chitosan is attributed to its high hydrophilicity (due to a large number of hydroxyl groups), large number of primary amino groups with high activity, and the flexible structure of the polymer chain. Chitosan has been shown to be effective at removing copper, cadmium, mercury, nickel, and lead (Jha et al., 1988; Huang et al., 1996; Ngah et al., 2002; Wan et al., 2004). Soluble complexing agents like EDTA can decrease the sorption of metals on chitosan (Jha et al., 1988).

2.4.3 Granular Activated Carbon

GAC is a granular adsorbent generally used in water treatment facilities in the United States primarily to remove taste- and odor-causing compounds, pesticides, and other organic contaminants (Brady, 2005). However, GAC has been shown to remove cadmium, copper, lead, and zinc (Chen et al. 1996; Chen and Wang, 2000; Galbadón et al., 2000) with higher removals generally occurring at higher pH (Chen et al., 2003; Seco et al., 1999). The presence of humic acid and other organic metal chelators (e.g. citric acid, EDTA) may either increase or decrease

removal efficiencies depending on the type of metal and chelator, pH, ionic strength, and chelator concentration (Chen and Wu, 2004; Chen and Wang, 2000; Chu and Hashim, 2000).

2.4.4 Thiol-SAMMS®

SAMMS ® (stands for "Self-Assembled Monolayers on Mesoporous Supports) is a family of engineered adsorbents. These adsorbents contain functionalized organic monolayers within mesoporous silica (Feng et al., 1997; Figure 15). One end group of the functionalized monolayers is covalently bonded to the silica surface and the other end group can be used to bind heavy metals or other molecules. The terminal functional group confers specific adsorption behavior for heavy metal ions. This family of adsorbents has been effective at removing mercury, lead, copper, cesium, cadmium, cobalt, chromium, nickel, zinc, and manganese (Feng et al., 1997; Yantasee et al., 2003; Chouyyok et al., 2010; Lin et al., 2001; Mattigod et al., 1999). Thiol-SAMMS® is highly selective for mercury, silver, gold, platinum, palladium, lead, copper, cadmium, arsenite, antimony, and iodine (Steward Advanced Materials, Inc., 2012). It is also capable of operating over a wide pH range (roughly 3-12) and is not susceptible to most organics, meaning the presence of organics does not affect sorption capacity.
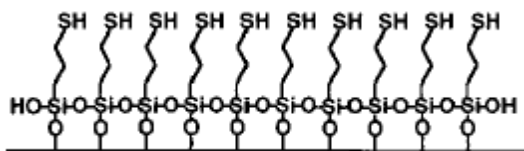
Figure 15. Schematic of closely-packed functionalized monolayers with a thiol end group (Feng et al., 1997)

2.4.5 Limestone

Limestone is a low cost reactive media that has been used extensively in the cleanup of acid-mine drainage-impacted groundwater (Bailey et al., 1999). The addition of limestone to an

aqueous media can provide alkalinity, assist in acid neutralization, and immobilize metals

through precipitation and/or adsorption (Komnitsas et al., 2004). Laboratory studies have shown

that cadmium, zinc, manganese, cadmium, copper, cobalt, and zinc can be effectively removed

from metals-contaminated water by limestone addition (Komnitsas et al., 2004; Aziz et al.,

2001). Saturation indices for calcite, aragonite, and dolomite indicate oversaturation under all

conditions modeled, suggesting that limestone is not likely to dissolve (Appendices 7 and 8) and

any metal removal would likely be due to sorption.

2.5 Potential Treatment Strategies- Summary

Based on the available literature and geochemical modeling, several treatment strategies

are available to address the goals of controlling pH and remediating metal contamination. The

addition of hydrochloric acid can decrease pH of the site groundwater. Sparging with air may

decrease the pH and/or increase the oxidation-reduction potential and potentially lead to the

precipitation of iron species (which, in turn, may remove metals of concern by coprecipitation or

sorption) or conversion of arsenic to its less mobile, oxidized forms. The addition of ferrous

sulfate heptahydrate may decrease the pH of the site groundwater, lower the solubilities of the

metals of concern, and/or induce coagulation. Finally, a wide variety of materials have been

shown to be effective metal sorbents. This study aims to test each of these techniques on site

water from MW-44 to determine which technique or combination of techniques can most

effectively achieve *in situ* pH control and metal remediation.

3.0 Materials and Methods

A compartmental approach consisting of pH adjustments, air sparging, and sorbent batch tests was used to evaluate different combinations of treatments for their effectiveness in lowering pH and decreasing metal concentrations in site water. Figures 14-20 illustrate *in situ* treatment combinations simulated in this experiment. Figure 20, for example, shows a simulation where the pH of site water was first adjusted with ferrous sulfate heptahydrate, then sparged with air, then treated with a sorbent or sorbent mixture. Vertical dashed lines separate the compartments and indicate that pH (and oxidation-reduction potential in the second round of batch tests) was measured and samples for organic carbon and metals analysis were taken. The Not Adjusted set (Figures 16 and 17) represents a situation where no measure was taken to adjust the pH. The HCl set (Figures 18 and 19) represents a situation where the pH was adjusted with HCl. The $FeSO_4$-A set (Figure 20) represents a situation where air was sparged in the same region where $FeSO_4:7H_2O$ was applied; the solids that formed were present in solution when air sparging occurred. The $FeSO_4$-B set (Figures 21 and 22) represents a situation where air was sparged in a region separate from the region where $FeSO_4:7H_2O$ was applied; the adjusted water was decanted, and then sparged with air. The $FeSO_4$-A and $FeSO_4$-B treatments are intended to simulate a range of conditions that could arise in situ during $FeSO_4$ treatment and air sparging. Samples and pH measurements were taken after every step to evaluate the effect of each step on the pH and metals concentrations.

Not Adjusted
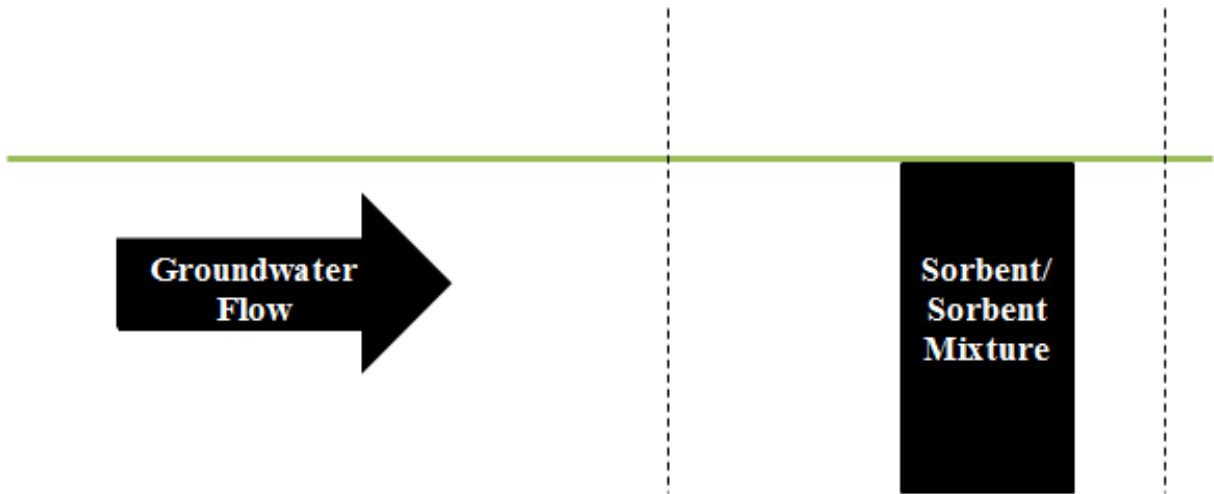
Figure 16. Site groundwater not adjusted

Not Adjusted + Air
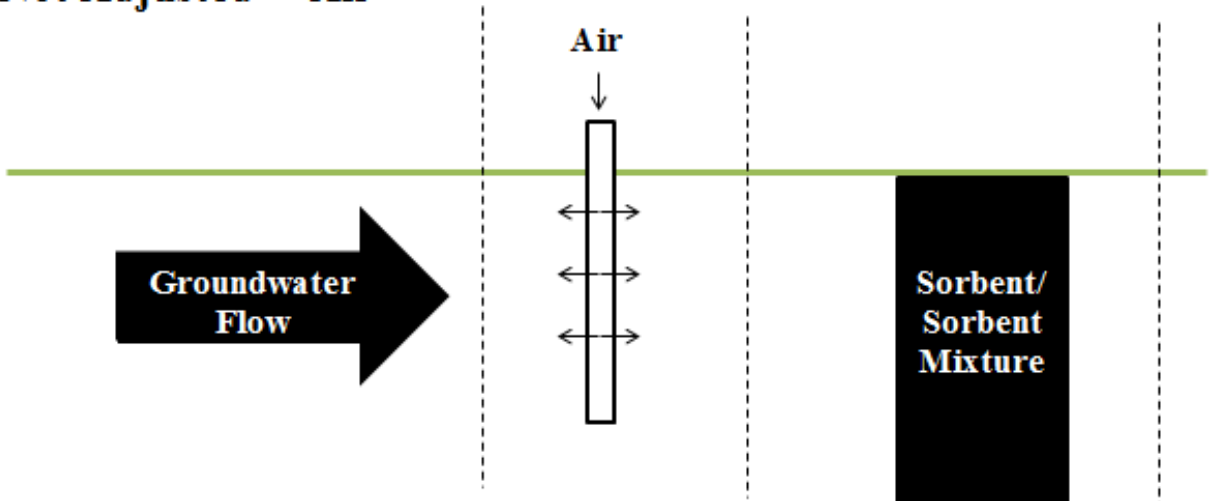
Figure 17. Site groundwater not adjusted, but sparged with air

HCl
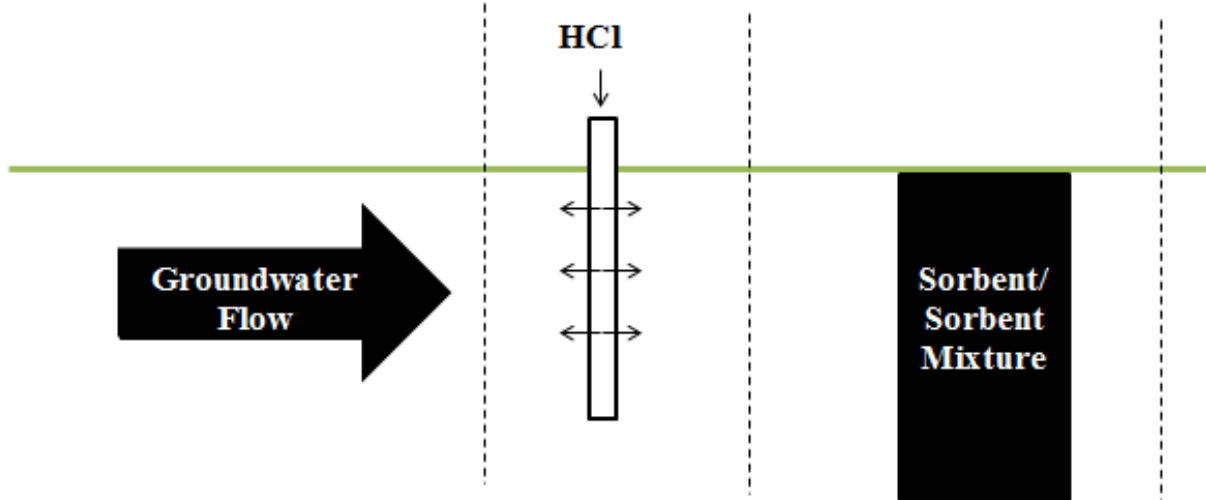
Figure 18. Site groundwater adjusted to pH 8 with HCl

HCl + Air
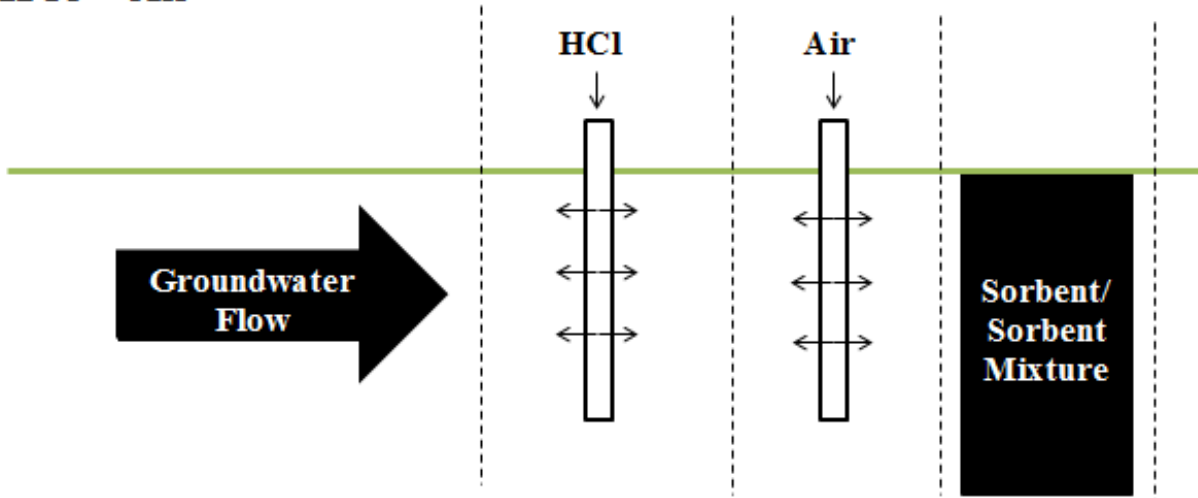
Figure 19. Site groundwater adjusted to pH 8 with HCl and sparged with air

FeSO₄-A + Air
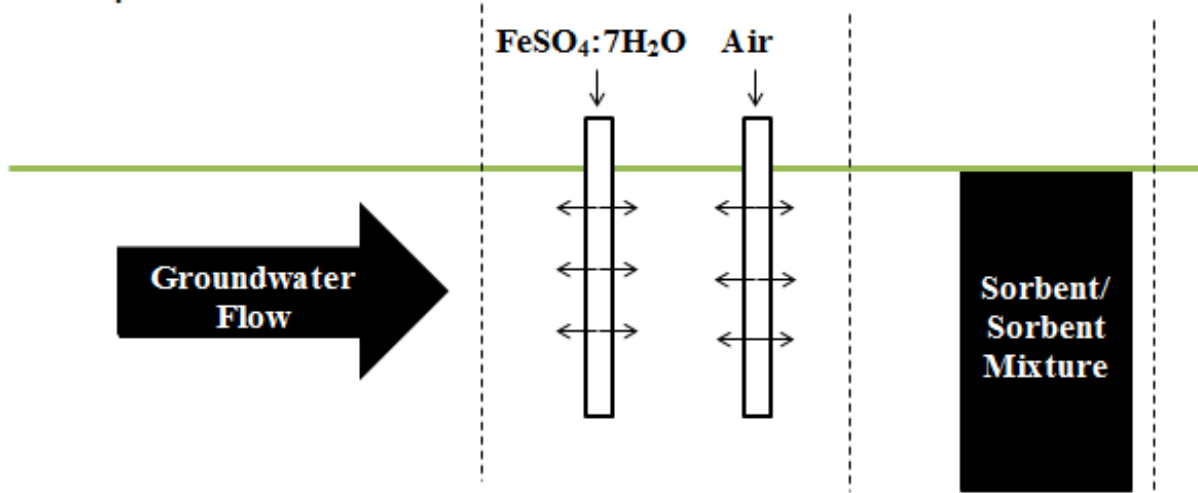
Figure 20. Site groundwater adjusted to pH 8 with FeSO$_4$:7H$_2$O and sparged with air in the same compartment. Solids were not removed prior to air sparging.

FeSO₄-B
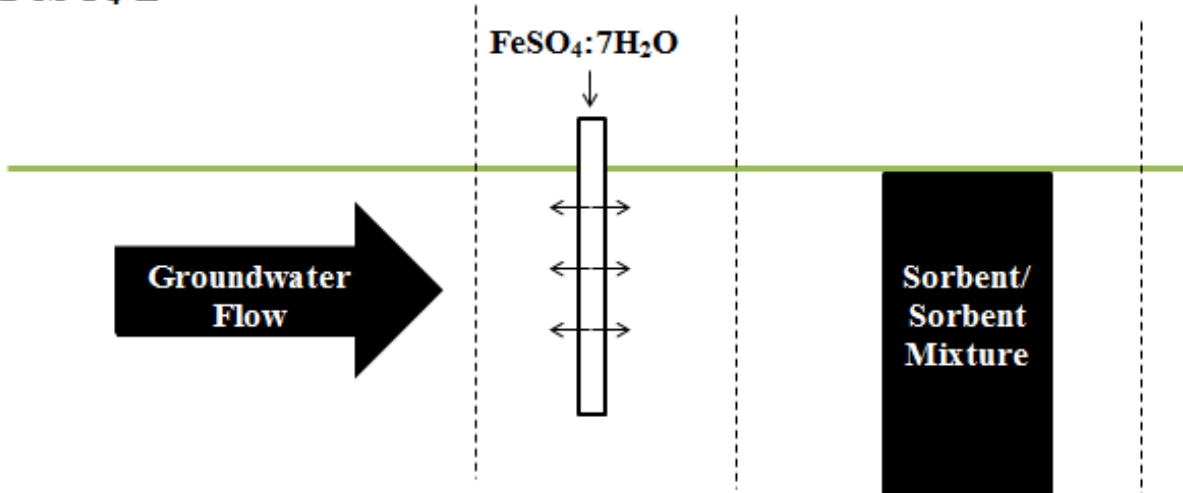
Figure 21. Site groundwater adjusted to pH 8 with FeSO$_4$:7H$_2$O. Solids were removed prior to sorbent application.

FeSO$_4$-B + Air
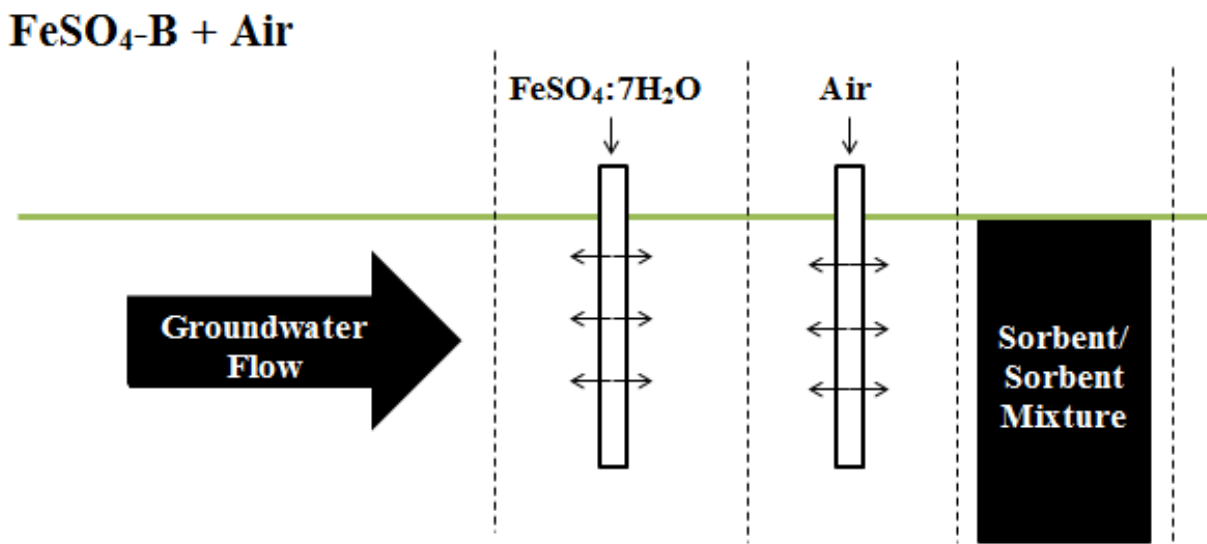
Figure 22. Site groundwater adjusted to pH 8 with FeSO$_4$:7H$_2$O and sparged with air in separate compartments. Solids were removed prior to air sparging.

Site water was obtained from MW-44 in December 2010 by submersible pump. Water was transferred either to 27 40-mL zero-head space, borosilicate EPA vials or 5-gallon plastic carboys and shipped in a cooler. Water was then kept in a cold room (4°C) until it was needed for experimentation. The total alkalinity of the site water was initially characterized by potentiometric titration to pH 4 using 0.1N HCl; the total alkalinity was calculated as 2,760 mg/L as CaCO$_3$ (titration curve shown in Appendix 9), which is similar to alkalinity values obtained previously (Appendix 2).

3.1 Initial Sorbent Screening and Effect of pH

An initial set of batch tests were completed to determine the coarse effects of pH adjustment and to narrow the list of potential sorbents (represented by Figures 16 and 18). These batch tests were performed in a nitrogen atmosphere in an anoxic glove box with the water that arrived in the borosilicate bottles. The adjustment to near pH 8 was achieved with 2 N HCl (titration curve provided in Figure 23 showing initial pH of 11.52), with dissolved samples being

taken before and after pH adjustment. pH was measured using an Accumet Accuflow Double Junction pH Combination Electrode and an Accumet AB15 pH/mV/^{o}C meter. Dissolved samples were prepared using 20-mL Luer lock syringes (Thermo Fisher, Inc.) and 25-mm, 0.45-µm PTFE Luer lock syringe filters (Thermo Fisher, Inc.). Five sorbents were initially tested: hydroxyapatite (powdered; Acros Organics), chitosan chips (8 x 30 mesh; produced from shrimp, lobster or crab shells; Federal Labs Chemical Corporation), GAC (12 x 40 mesh Filtrasorb 200; reagglomerated coal base virgin activated carbon generally used for potable water and wastewater treatment; Calgon Carbon Corporation), Thiol-SAMMS ® (average particle size of 560-620 microns; Steward Advanced Materials, Inc.), and limestone (crushed to roughly a quarter-inch; obtained from quarry near Pittsburg, KS operated by Midwest Minerals, Inc.). Sorbents were loaded into 60-mL HDPE Nalgene wide mouth bottles (Thermo Fisher, Inc.) at a 5 g/L loading rate (e.g., 250 mg sorbent per 50 mL site water). Water was introduced into the bottles and allowed to contact the sorbents for three days on a shaker table rotating at 120 rpm. pH measurements from each bottle were taken after the three day contact period. One dissolved sample was taken from each bottle. Each sample was split for separate DOC and metals (Cu, Pb, As, V) analyses.
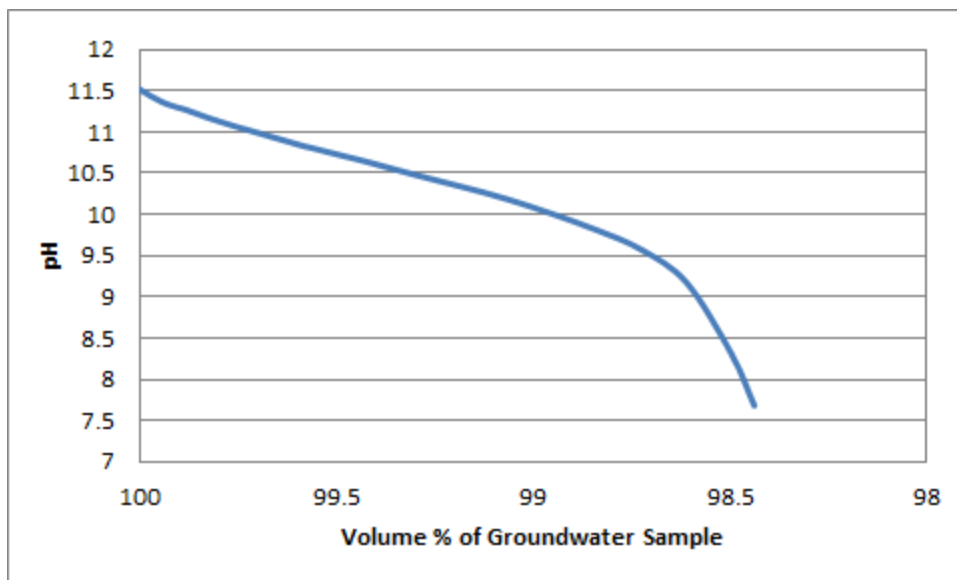
Figure 23. pH Adjustment of site water with 2 N HCl for Initial Amendment Screening

3.2 Evaluation of pH Adjustment Strategies, Air Sparging, and Sorbent Mixtures

Water from the plastic carboys was used. pH adjustment to near pH 8 was performed in a nitrogen atmosphere in an anoxic glove box with either 2 N HCl (Figure 24), 5.0% by weight $FeSO_4:7H_2O$ solution (Figure 25), or a 19.5% by weight $FeSO_4:7H_2O$ solution (Figure 26). $FeSO_4:7H_2O$ solutions were prepared by mixing solid $FeSO_4:7H_2O$ (Acros Organics) with Milli-Q water. Adjusted site water was allowed to sit for three days after pH adjustment to allow any particles that may have formed to settle. Oxidation-reduction potential was measured using an Accumet Platinum Combination Electrode (containing 4 M KCl saturated with AgCl) and an Accumet AB15 pH/mV/^{o}C meter before and after pH adjustment. The Platinum Combination Electrode probe was standardized using ZoBell's solution (Standard Method 2580; APHA et al., 2005), the components of which were obtained from Acros Organics. Total and dissolved samples were taken before and after pH adjustment. Air was sparged through diffusers outside of the anoxic glove box for 3 days; total and dissolved samples were taken after air sparging.
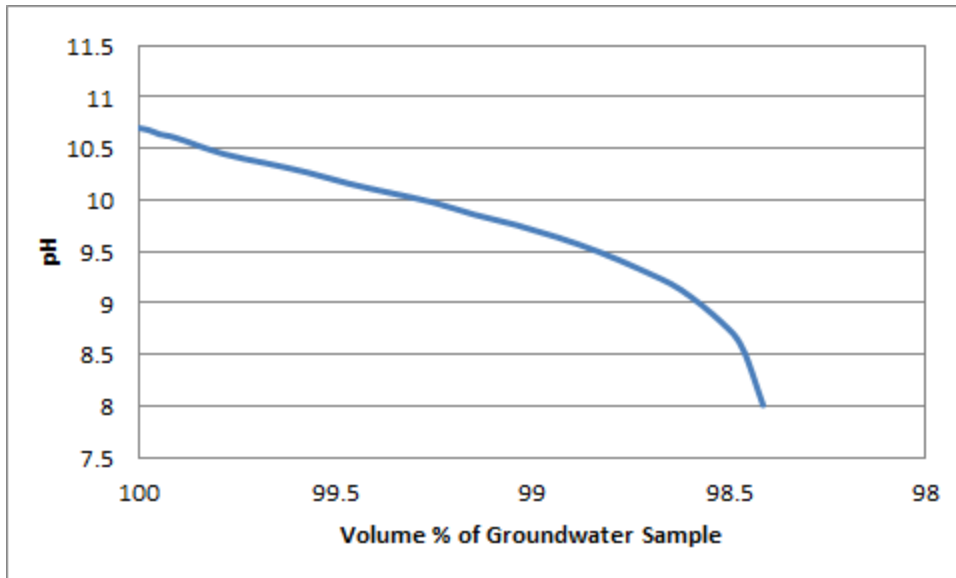
Figure 24. pH adjustment of site water with 2 N HCl
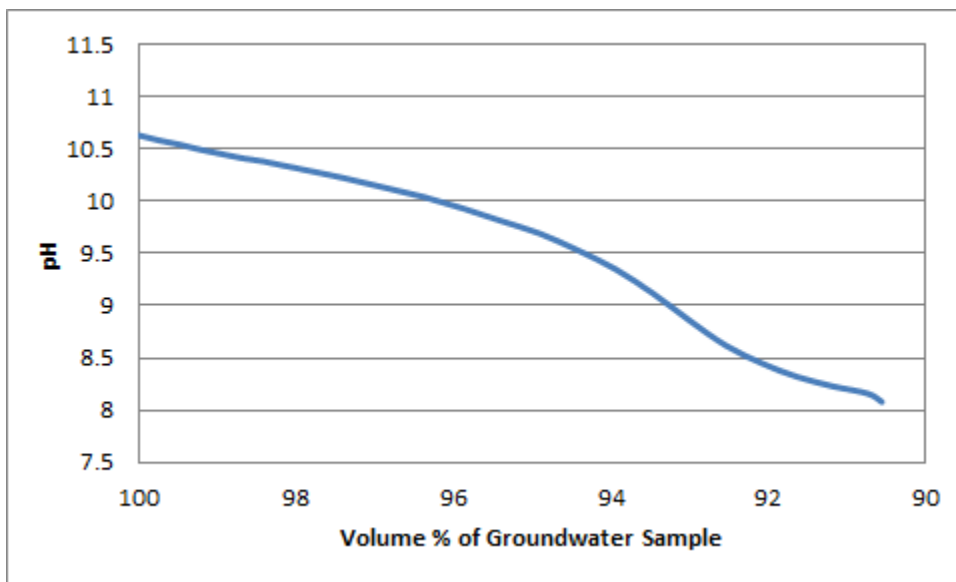
Figure 25. pH adjustment of site water with 5.0% by weight $FeSO_4:7H_2O$ solution
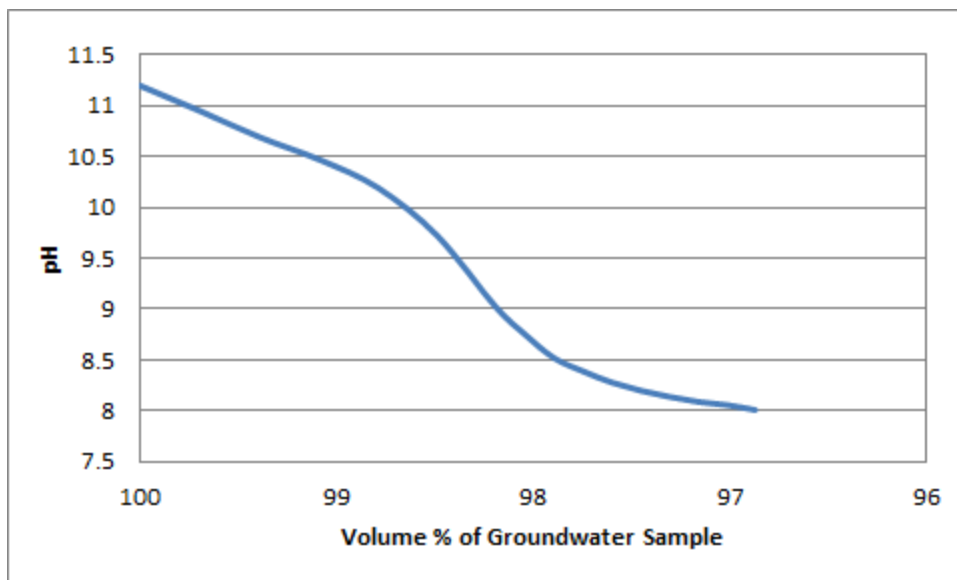
Figure 26. pH adjustment of site water with 19.5% by weight $FeSO_4:7H_2O$ solution

Batch tests included a no-amendment control (referred to as the control from here forward) and four sorbent mixtures: bone char (20 x 60 mesh; produced from aged bones and contains other carbon surface area and hydroxyapatite lattice surface area; Charcoal House LLC); GAC; bone char (BC)/GAC; and BC/GAC/SAMMS. Sorbents were loaded into 60-mL HDPE Nalgene wide mouth bottles at a 5 g/L loading rate. In the BC/GAC mixture, half of the sorbent mass was BC and half was GAC. In the BC/GAC/SAMMS mixture, each sorbent represented one-third of the total sorbent mass. Three bottles (replicates) for each sorbent mixture were prepared. Water was introduced into the bottles and allowed to contact the sorbents for seven days on a shaker table rotating at 120 rpm. pH and oxidation-reduction potential measurements were taken for each bottle after the seven day contact time. Total and dissolved samples were taken from each bottle. Each sample was split for separate organic carbon and metals (Cu, Pb, As, V, and Fe) analyses.

3.3 Sample Preparation and Analysis

Samples for total and dissolved metals analysis were digested using the *Digi*PREP MS (SCP Science) with concentrated nitric acid and hydrochloric acid for 60 minutes at 95 °C (similar to Standard Method 3030-F; APHA et al., 2005). Blanks were included in each digestion (1 for initial amendment screening, 8 for more comprehensive experiment) for quality assurance/quality control purposes. Each blank consisted of Milli-Q water, to which the acids were then applied. Digested samples were then vacuum filtered through 47-mm diameter, 0.45-µm pore size, Millipore mixed cellulose easter membranes (plain surface, white; Thermo Fisher, Inc.).

Copper, lead, arsenic, and vanadium analysis were performed using graphite tube atomic absorption and iron analysis was performed using flame atomic absorption with a Varian AA240FS Fast Sequential Atomic Absorption Spectrometer. Organic carbon analysis was performed using a Teledyne Tekmar TOC Torch analyzer. Milli-Q water was routinely analyzed for metals and organic carbon as an additional means of quality assurance/quality control.

3.4 Evaluation of Treatment Methods

Total percent reductions are used to evaluate the effectiveness of each treatment combination, where the raw groundwater sample is used for the baseline in the total percent reduction calculations. For example, the percent reduction for the case where the pH was adjusted and exposed to amendments would depend on the concentration after contacting an amendment and the concentration before any treatment was applied (site water from MW-44 that was not adjusted). Standard deviations are not shown for the first batch study because only one sample was taken for each treatment (only one replicate). Standard deviations are shown for the second batch studies; multiple replicates were analyzed. In addition, the mass of dissolved metal

and organic carbon removed per gram of amendment was determined. In the first batch study, the unadjusted and pH-adjusted waters were used as the baseline for this computation; in the second batch study, the control samples were used as the baseline.

4.0 Results and Discussion

4.1 Initial Amendment Screening and Effect of pH

Only slight pH changes were observed in both pH and non-pH adjusted site groundwater during the three day exposure period (Table 3). In unadjusted water, the magnitude of the decrease was greatest for chitosan at 0.45 pH units, followed by a decrease of 0.30 pH units for SAMMS. The pH of the pH-adjusted site water decreased slightly in the presence of chitosan, limestone, and SAMMS by 0.54, 0.16, and 0.03 pH units, respectively. Contact of pH-adjusted water with GAC and SAMMS resulted in a slight increase in pH by 0.58 and 0.10 pH units, respectively. With the exception of chitosan and potentially GAC after the pH was adjusted with HCl, none of the amendments appeared to have much effect of the pH of the water. Even so, the effects of those amendments were generally considered to be minimal because the largest deviation in pH was less than 0.6 pH units.

Table 3. pH of site water after three days contact time with amendments. In pH adjusted site water, 2N HCl was used to adjust the pH to 8.01 before contact with the amendments.

	pH	
Amendment	Not Adjusted	Adjusted with HCl
None	11.52	8.01
Chitosan	11.07	7.47
Apatite	11.33	8.11
GAC	11.37	8.59
SAMMS	11.22	7.98
Limestone	11.38	7.85

Table 4 shows the average concentrations of dissolved metals in the digestion blank and in Milli-Q water. Copper, arsenic, and vanadium concentrations in both the digestion blank and Milli-Q water samples were low compared to the experimental sample concentrations. The

average lead concentration in Milli-Q water was small compared to values measured in this study.

Table 4. Average concentration of metals in digestion blanks and Milli-Q water

Metal	Digestion Blank (µg/L)	Milli-Q Water (µg/L)
Copper	0.23	-0.22
Lead	6.80	0.01
Arsenic	-1.57	1.41
Vanadium	7.50	8.40

Dissolved copper, lead, arsenic, vanadium, and organic carbon concentrations before and after pH adjustment and contact with amendments/sorbents are shown in Figures 27 - 31. The most stringent chronic and acute ARARs are indicated in the Figures for copper, lead, and arsenic (Appendix 5), though only for reference. It is uncertain whether an amendment loading rate of 5 g/L is realistic in a full scale scenario. Therefore, amendments are not being evaluated on their ability to achieve the indicated ARAR, but rather the performance of each amendment is compared to the performance of the others. Standard deviations are not shown because only one sample was taken for each treatment (only one replicate).

Copper concentrations in MW-44 groundwater used in this study were comparable to those recently reported for site groundwater (Appendices 3 and 4). Simply decreasing the pH did little for the reduction of copper concentrations compared to the unadjusted groundwater from well MW-44 (4 % reduction), but did improve the performance of apatite, GAC, and SAMMS (Figure 27). Apatite reduced dissolved copper concentrations more than all other amendments in pH-adjusted samples (70% reduction), but did not reduce concentrations in unadjusted samples. Likewise, GAC showed a copper reduction (31%) when the pH was adjusted, but did not show a decrease compared to the raw groundwater sample when the pH was not adjusted. SAMMS, on

the other hand, performed comparatively well when the pH was adjusted (70% reduction), but also when the pH was not adjusted (55% reduction). Chitosan and limestone did not reduce copper concentrations in both pH adjusted and unadjusted samples. Copper concentrations increased following addition of apatite, chitosan, and limestone in pH adjusted samples, likely due to impurities in amendments. None of the amendments was able to achieve ARARs in either pH-adjusted or unadjusted samples.
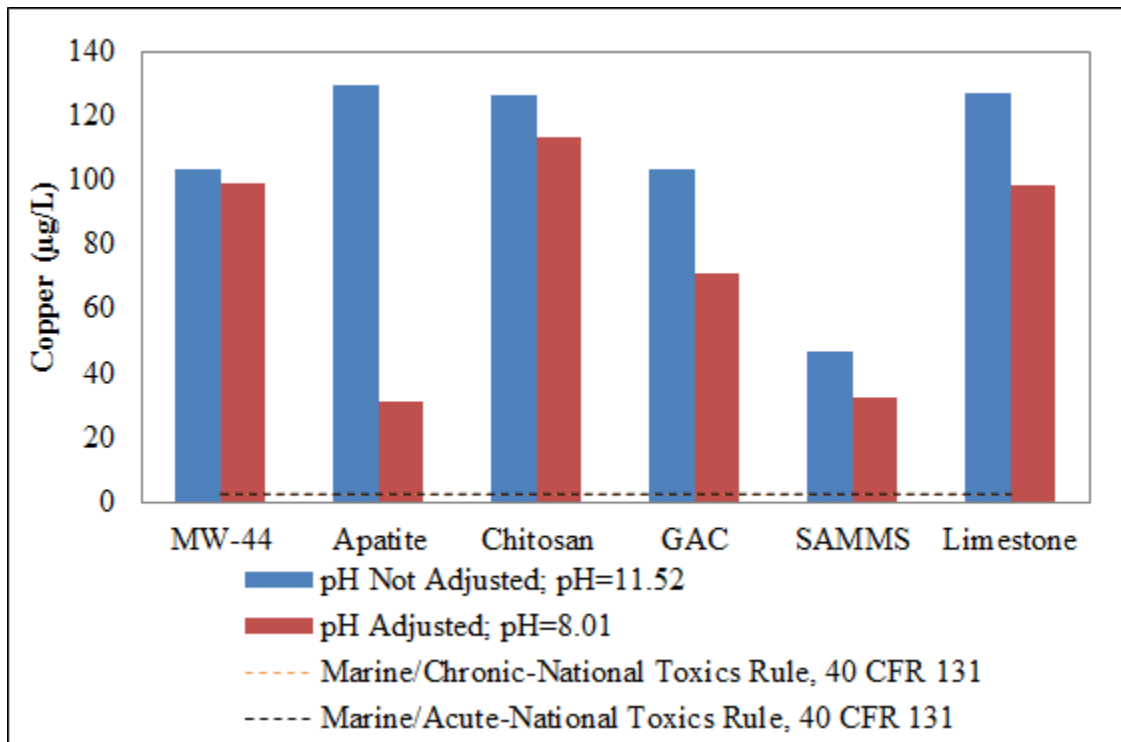
Figure 27. Dissolved copper concentrations resulting from pH adjustment and/or contact with amendments

Lead concentrations in MW-44 goundwater used in this study were roughly 2 - 3 times greater than those recently reported for site groundwater (Appendices 3 and 4), though historical data are only available through September 2008. The results of the second batch study showed similar lead concentrations. The lead concentration measured in the digestion blank (Table 4) was between 11 and 41% of lead concentrations measured in samples during this batch study.

Lead contamination may have occurred during the digestion phase of sample preparation. For this reason, lead concentrations may be lower than reported, but no adjustment was made to the results presented.

Decreasing the pH alone did not reduce lead concentrations much compared to the unadjusted groundwater from MW-44 (7% reduction), but did improve the performance of apatite, GAC, and SAMMS (Figure 28). Apatite showed the most substantial reduction in dissolved lead concentrations when the pH was adjusted (62% reduction); apatite also showed a 14% decrease when the pH was not adjusted. GAC was somewhat effective for reducing lead concentrations, providing a 15% decrease when the pH was not adjusted and a 31% reduction when the pH was adjusted. SAMMS performed fairly well regardless of pH adjustment: 47% reduction when pH was adjusted and 31% reduction when pH was not adjusted. As with copper, chitosan and limestone were the least effective at reducing dissolved lead concentrations for either pH condition. None of the amendments was able to achieve ARARs in either pH-adjusted or unadjusted samples.
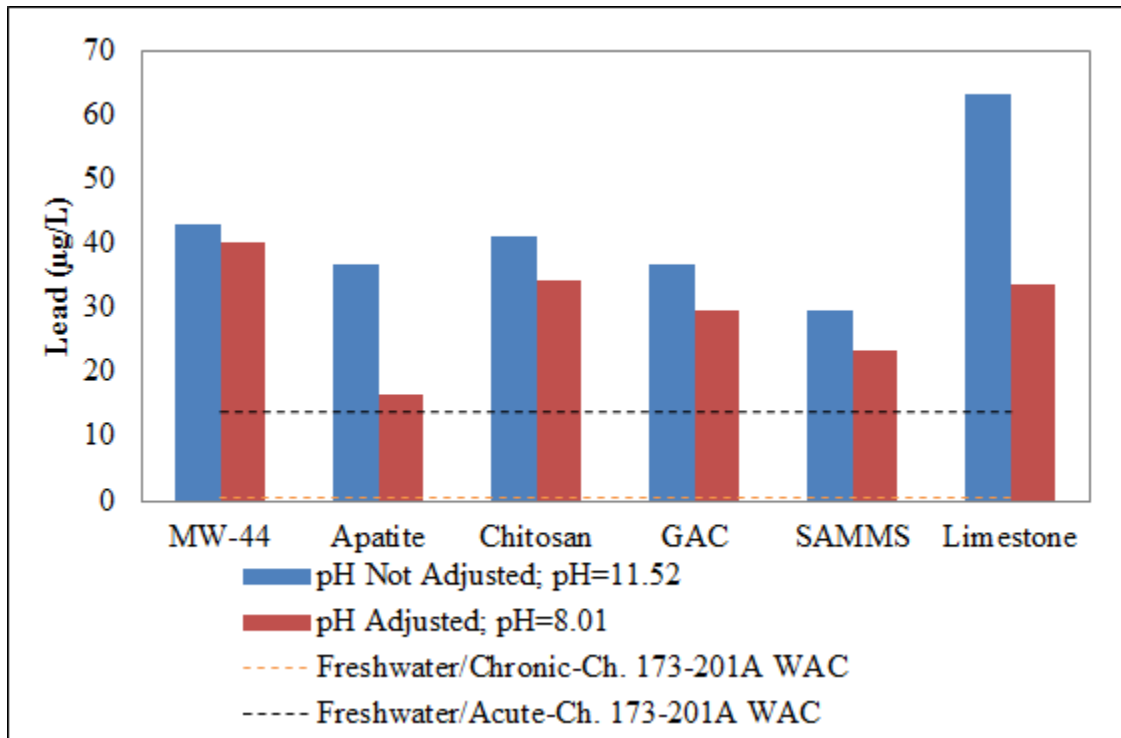
Figure 28. Dissolved lead concentrations resulting from pH adjustment and/or contact with amendments

Arsenic concentrations in MW-44 goundwater used in this study were much greater than those recently reported for site groundwater (Appendices 3 and 4), though historical data are only available through September 2008. The results of the second batch study also showed much larger arsenic concentrations. Decreasing the pH accounted a 28% reduction in dissolved arsenic compared to unadjusted water from well MW-44 (Figure 29). In unadjusted samples, chitosan produced a 15% reduction and SAMMS produced a 17% reduction. After pH adjustment, total reductions in arsenic concentrations were 43% for apatite, 30% for chitosan, 29% for SAMMS, and 39% for limestone. GAC did not reduce dissolved arsenic concentrations under either pH condition. None of the amendments was able to achieve ARARs in either pH-adjusted or unadjusted samples.
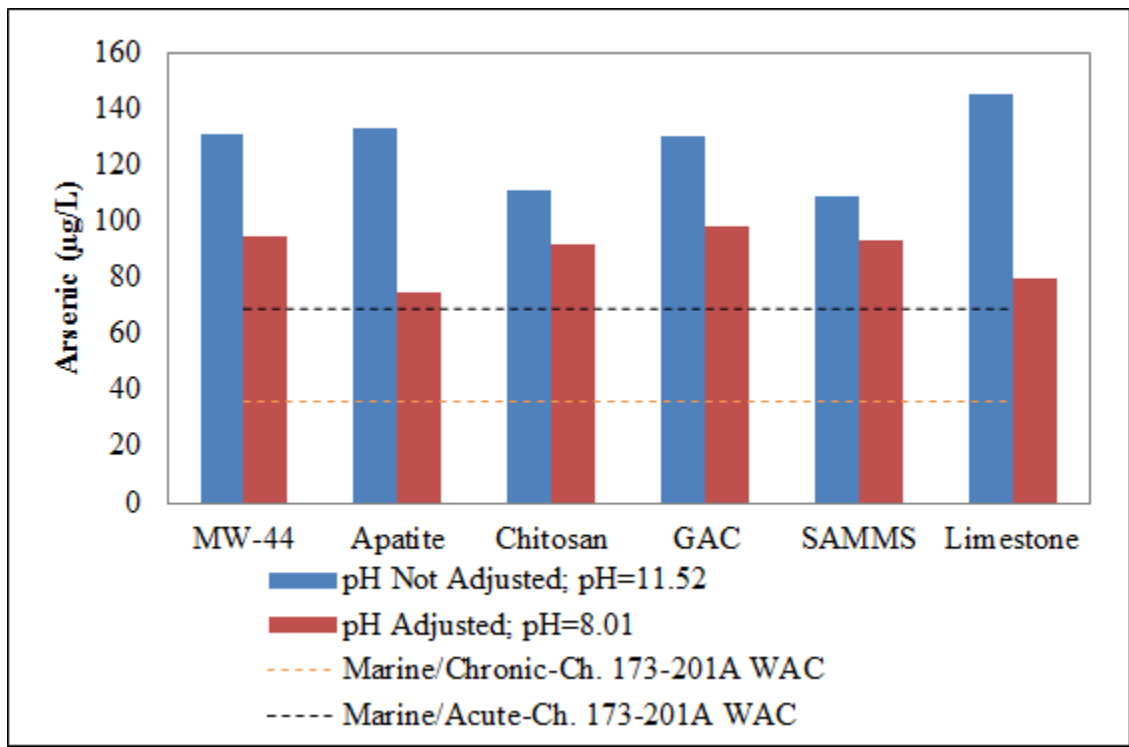
Figure 29. Dissolved arsenic concentrations resulting from pH adjustment and/or contact with amendments

Vanadium concentrations in MW-44 goundwater used in this study were comparable to those recently reported for site groundwater (Appendices 3 and 4). Simply decreasing the pH did not result in the reduction of vanadium concentrations, but did improve the performance of each amendment (Figure 30). Apatite reduced dissolved vanadium concentrations more than all amendments in pH-adjusted samples (62% reduction). Chitosan, GAC, and limestone produced reductions in vanadium concentrations of 39%, 12%, and 18%, respectively. SAMMS reduced the vanadium concentration by 24% and 7% in pH-adjusted and unadjusted samples, respectively.
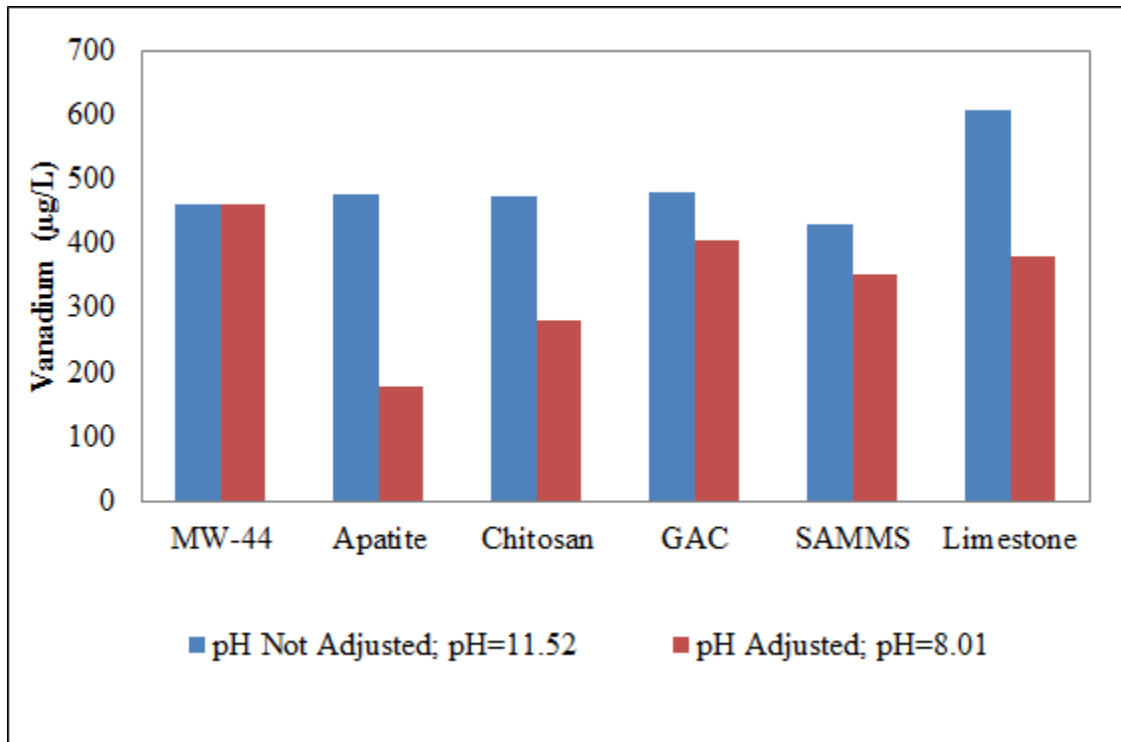
Figure 30. Dissolved vanadium concentrations resulting from pH adjustment and/or contact with amendments

Though DOC removal is not a primary objective, its removal may be related to the removal of metals (Katsumata et al., 2004; Chen and Wu, 2004). The decrease of pH itself did not do much to reduce dissolved organic carbon concentrations (6% reduction), but appears to have improved dissolved organic carbon removal in the presence of apatite (Figure 31). In pH-adjusted samples, the dissolved organic carbon concentration was reduced by 33 % in the presence of apatite. Contact with GAC resulted in a reduction of 27% and 24% in unadjusted and pH-adjusted samples, respectively. Contact with chitosan increased the dissolved organic carbon concentration by 96% and 24% in the unadjusted and pH-adjusted samples, respectively. Neither SAMMS nor limestone substantially affected dissolved concentrations of organic carbon.
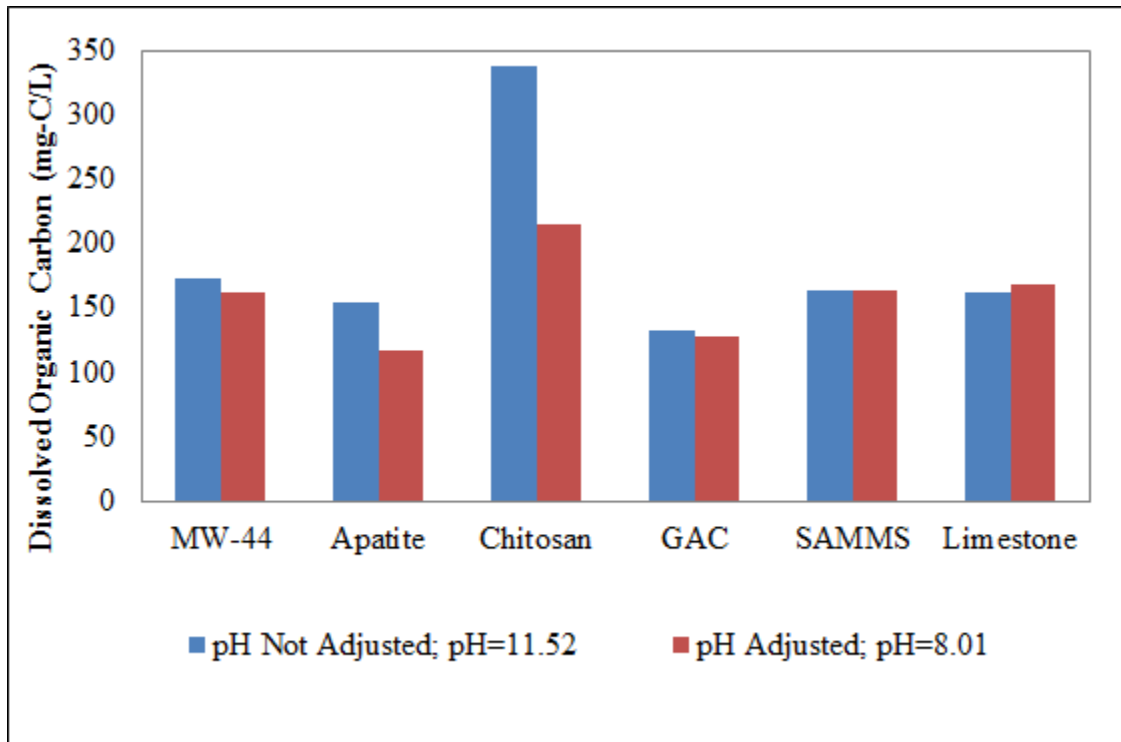
Figure 31. Dissolved organic carbon concentrations resulting from pH adjustment and/or contact with amendments

In unadjusted samples (Table 5), SAMMS removed the largest masses of copper, lead, arsenic, and vanadium from site water per gram of amendment than any of the other amendments. GAC removed the most dissolved organic carbon per gram of amendment. Limestone appeared to contribute copper, lead, arsenic, and vanadium in substantial amounts to the site water. Kansas Geological Survey Bulletin 119, Part 3 (Runnels and Schlelcher, 1965) indicates that traces of copper, lead, and vanadium can be found in limestone from Crawford County, Kansas (where the limestone was obtained). Mass balances using data in the bulletin indicate that measured contributions of copper, lead, and vanadium from the collected limestone were at least possible. An analysis on Mill-Q water that had contacted the limestone could determine if trace metal leaching actually occurred, but was not performed during this study. In pH-adjusted samples (Table 6), apatite removed the largest masses of copper, lead, arsenic

vanadium, and dissolved organic carbon. SAMMS removed the second largest masses of copper

and lead, and the third largest mass of copper per mass of amendment.

Table 5. Mass of indicated dissolved metal removed per mass of amendment applied; pH of site
water was not adjusted

Amendment	Cu (µg/g)	Pb (µg/g)	As (µg/g)	V (µg/g)	DOC (mg-C/g)
Apatite	-4.0	1.9	-0.2	0.1	2.8
Chitosan	-3.8	1.2	4.4	0.6	-36.0
GAC	1.0	1.9	0.2	-0.6	7.1
SAMMS	11.9	3.2	4.5	9.4	0.9
Limestone	-3.5	-3.1	-2.5	-24.7	1.4

Table 6. Mass of indicated dissolved metal removed per mass of amendment applied; pH of site
water was adjusted to 8.01 with 2N HCl

Amendment	Cu (µg/g)	Pb (µg/g)	As (µg/g)	V (µg/g)	DOC (mg-C/g)
Apatite	13.5	4.7	4.1	56.8	9.2
Chitosan	-3.0	1.2	0.7	37.6	-10.9
GAC	5.4	2.1	-0.6	10.5	6.8
SAMMS	12.6	3.2	0.3	20.7	-0.3
Limestone	0.1	1.2	2.9	15.4	-1.2

In summary, none of the amendments substantially affected the pH of site water either

with or without prior pH adjustment. The largest reductions in copper, lead, vanadium, and

dissolved organic carbon concentrations were observed under pH adjusted conditions in the

presence of apatite. Lead was the only metal removed by apatite when pH was not adjusted.

SAMMS performed comparatively well in pH-adjusted samples for copper, lead, and vanadium,

but also performed with comparative success in unadjusted samples for copper and lead. GAC

was somewhat effective for reducing lead concentration regardless of pH condition and

removing copper when the pH was adjusted. Chitosan was only effective at removing vanadium

when the pH was adjusted. Limestone was not particularly effective at removing dissolved

copper, lead, arsenic, and vanadium. Reductions in dissolved metal concentrations may be related to the removal of dissolved organic carbon when water contacted apatite (Katsumata et al., 2004) and GAC (Chen and Wu, 2004), but this appears unlikely for SAMMS because SAMMS did not appreciably reduce DOC concentrations.

4.2 Evaluation of pH Adjustment Strategies, Air Sparging, and Sorbent Mixtures

From the previous batch study, pH adjustment generally improved amendment performance. Apatite was the most successful at reducing dissolved metals concentrations under pH adjusted conditions. SAMMS also performed decently, and GAC was somewhat effective. One goal of this batch study was to evaluate mixtures of these amendments. Bone char replaced apatite in these experiments, because granular bulk bone char is less expensive and easier to obtain. Also, SAMMS was not tested as a primary mixture component, because, as a highly engineered sorbent, it may cost substantially more than bone char or GAC. Additionally, combinations of pH control techniques were evaluated.

Table 7 shows the average pH of site water after seven days of contact time with the amendments for all treatment combinations evaluated in this experiment. The MW-44 entry describes the pH of water before entering the batch tests and after any pH or air treatments. For example, the pH of MW-44 water after being dosed with HCl and sparged with air but before being transferred to bottles with amendments was 9.47. Like in the previous experiment, the pH in unadjusted site water generally decreased when amendments were applied, though none of the decreases are considered substantial compared to the control. Sparging site water with air resulted in a pH decrease of 0.93 pH units. Contact with amendments again had little effect on pH. Site water was adjusted with HCl to pH 8.01. The pH increased in the control to 8.36, and generally rebounded after contact with the amendments, with the largest increase being 0.31 pH

units for bone char. Sparging HCl-adjusted water with air increased the pH to 9.47; contact with

amendments slightly increased the pH of the water. When site water was adjusted to pH 8.08

with a 5% by weight $FeSO_4$:$7H_2O$ solution (Figure 25) and then sparged with air (Figure 32), the

resulting pH was 8.98; the pH of the control slightly decreased to 8.7. pH increased after contact

with bone char and the BC/GAC combination, while the other amendments caused slight

decreases in pH. Site water was also adjusted with a 19.5% by weight $FeSO_4$:$7H_2O$ solution to

pH 8.01. Coagulation solids were allowed to settle (Figure 33), and the water was decanted

(Figure 34). The pH of decanted water decreased to 5.52 in the control. Contact with amendment

combinations containing bone char resulted in pH increases, while GAC alone resulted in a

further pH decrease. Finally, decanted water that was sparged with air (Figure 35) had a pH of

3.30.The control pH did not change much (decreased 0.1 pH units), but the amendment

composition had a significant impact on the final pH. Contact with bone char alone raised the pH

to 7.10, contact with the BC/GAC combination raised the pH to 6.28, and contact with the

BC/GAC/SAMMS combination raised the pH to 5.28. Contact with GAC alone caused the pH to

decrease to 2.25.

Table 7. Average pH of site water after indicated treatments were applied

Treatment	pH						
	Not Adjusted	Not Adjusted + Air	HCl	HCl + Air	$FeSO_4$-A + Air	$FeSO_4$-B	$FeSO_4$-B + Air
MW-44	10.81	9.88	8.01	9.47	8.98	8.01	3.30
Control	10.64	9.86	8.36	9.64	8.70	5.52	3.20
Bone Char	10.59	9.94	8.67	9.67	9.00	6.25	7.10
GAC	10.60	9.99	8.42	9.67	8.68	5.38	2.25
BC/GAC	10.59	10.01	8.56	9.68	8.86	5.87	6.28
BC/GAC/SAMMS	10.57	9.99	8.27	9.62	8.34	5.87	5.28
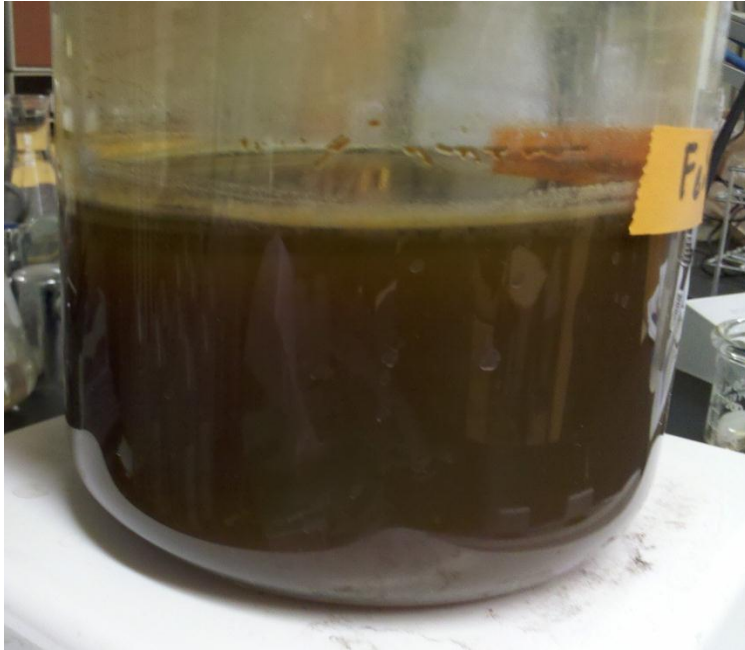
Figure 32. Site water adjusted with $FeSO_4:7H_2O$ and sparged with air without first removing the coagulation solids (representing $FeSO_4$-A + Air, Figure 20).
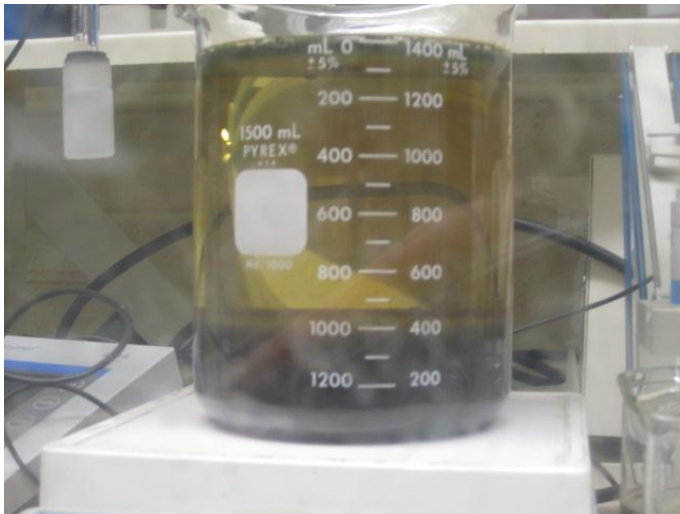
Figure 33. Site water adjusted with $FeSO_4:7H_2O$. The coagulation solids were allowed to settle before water was decanted.
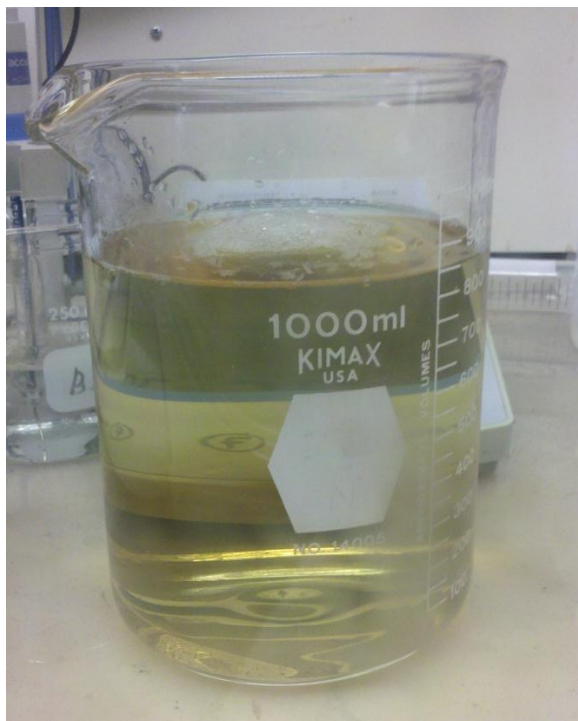
Figure 34. Water that had been adjusted with $FeSO_4{:}7H_2O$ decanted, removing the coagulation solids, before being applied to amendments or being sparged with air (representing $FeSO_4$-B, Figure 21).
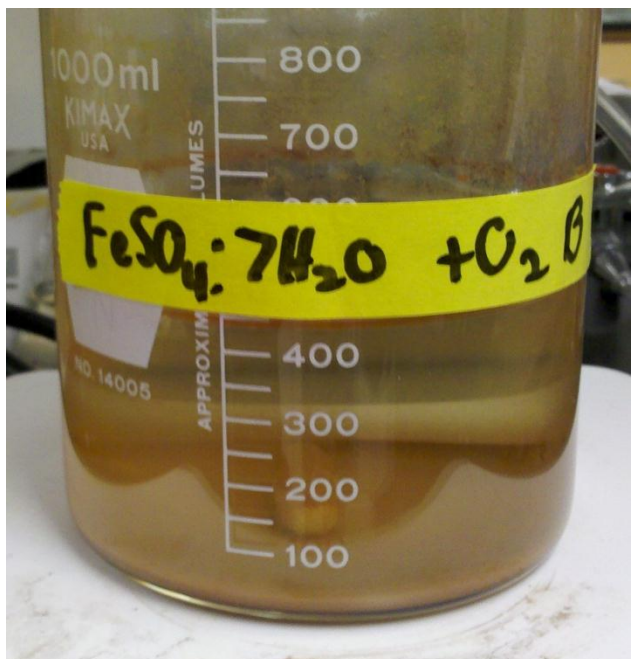
Figure 35. Decanted water after having been adjusted with $FeSO_4{:}7H_2O$ (representing $FeSO_4$-B + Air, Figure 22).

Table 8 shows the average oxidation-reduction potential (ORP) in mV of site water after seven days of contact time with the amendments for all treatment combinations evaluated in this experiment. The ORP in the case where site water was not adjusted generally decreased when amendments were applied. Sparging site water with air resulted in an ORP increase of 154 mV units. ORP in the control decreased to 149 mV, and contact with amendments resulted in a further ORP decrease. Adjusting the site water with HCl resulted in the ORP increasing to 200 mV. The ORP in the control, however, decreased to 39 mV, and contact with amendments had little effect of the ORP. Sparging HCl-adjusted water with air resulted in an ORP of 124 mV, which was lower than that of water adjusted with HCl alone; contact with amendments had little effect on the ORP of the water. When site water was adjusted to pH 8.08 with a 5% by weight $FeSO_4$:$7H_2O$ solution and then sparged with air, the resulting ORP was 188 mV. The ORP of the control decreased to 157 mV, and contact with the amendments had little effect on the ORP. Site water adjusted with a 19.5% by weight Fe $FeSO_4$:$7H_2O$ solution had an ORP of -447 mV. The ORP of decanted water increased to 67 mV in the control. Contact with amendment combinations containing bone char resulted in ORP decreases, while GAC alone resulted in a further ORP increase. Finally, decanted water that was sparged with air had an ORP of 254 mV. The ORP of the control slightly increased. As with pH, the amendment composition had a significant impact on the final ORP for this treatment. Contact with bone char alone decreased the ORP to 94 mV and contact with the BC/GAC/SAMMA combination decreased the ORP to 111 mV. Contact with GAC increased the ORP to 444 mV and contact with the BC/GAC/SAMMS combination raised the ORP to 304 mV.

Table 8. Average oxidation-reduction potential of site water after indicated treatments were applied

Treatment	Oxidation-Reduction Potential (mV)						
	Not Adjusted	Not Adjusted + Air	HCl	HCl + Air	$FeSO_4$-A + Air	$FeSO_4$-B	$FeSO_4$-B + Air
MW-44	32	186	200	124	188	-447	254
Control	-35	149	39	135	157	67	266
Bone Char	-29	108	25	122	149	-51	94
GAC	-28	105	22	138	152	75	444
BC/GAC	-16	108	20	156	142	11	304
BC/GAC/SAMMS	-30	83	26	121	141	-3	111

Table 9 shows the average concentration of dissolved metals in the digestion blank and in Milli-Q water. Detected values of copper, lead, arsenic, and organic carbon in either the digestion blank (not applicable for organic carbon because those samples were not digested) or in Milli-Q water are generally small compared to values measured throughout the experiment.

Table 9. Average concentration of metals and organic carbon in digestion blanks and Milli-Q water

Constituent	Digestion Blank	Milli-Q Water
Copper (µg/L)	2.80	-0.23
Lead (µg/L)	2.90	0.52
Arsenic (µg/L)	0.71	0.57
Vanadium (µg/L)	18.00	1.96
Iron (mg/L)	0.13	0.08
Dissolved Organic Carbon (mg-C/L)	--	5.26

Dissolved copper, lead, arsenic, vanadium, iron, and organic carbon concentrations before and after pH adjustment, air sparging, and contact with amendments/sorbents are shown in Figures 36 - 41. Plotted values are the average of three replicates, except for organic carbon

where only one replicate was analyzed. Total percent reductions are based on the unadjusted water from well MW-44.

Copper concentrations in MW-44 goundwater used in this study were comparable to those recently reported for site groundwater (Appendices 3 and 4). When no pH adjustment or air sparging was performed (and in contrast to the first batch study), contact with amendments resulted in significant decreases in dissolved copper concentrations (Figure 36). Average percent reductions ranged from 34-43% based on unadjusted water from well MW-44, though no significant difference is discernible between the amendments. Simply sparging with air showed no reduction, and reduced total removal percentages for amendments to 24-31%, though these total reductions were not significantly different from those obtained without air sparging. Adjusting site water with HCl did not affect dissolved copper concentrations, but generally improved amendment performance (comparable to the first batch study). Total reductions for amendment combinations of bone char, GAC, and BC/GAC ranged from 37-48%, though none were significantly different. The combination of BC/GAC/SAMMS resulted in a total reduction of 62% and an average dissolved copper removal of 16.43 µg per gram of amendment mixture (Table 10), which is the highest of any treatment combination. Sparging HCl-adjusted water with air did not appear to reduce copper concentrations, but the control shows a total reduction of 18%, potentially indicating that reactions were not completed at the time of water transfer to amendment bottles. Total reductions after contact with amendments ranged between 36 and 47%, though there was not a significant difference between the amendment combinations. In the $FeSO_4$-A + Air case, total percent reduction before amendment application was 66%. Contact with amendments increased the total reductions to between 70 and 77%. After the 19.5% by weight $FeSO_4$:$7H_2O$ solution was applied and the coagulation solids were allowed to settle, the

total reduction in copper concentration was 81%. None of the amendment combinations further

increased copper removal. Sparging the $FeSO_4:7H_2O$-adjusted water (the $FeSO_4$-B + Air case)

resulted in a total percent reduction of 80%. Additionally, contact with amendments also did

little to increase the overall percent reductions of copper (77-88%).

Figure 36. Dissolved copper concentrations resulting from pH adjustment, air sparging, and/or contact with amendments

Table 10. Average mass of dissolved copper removed per mass of amendment applied for treatments evaluated

Treatment	Mass of Copper removed per gram of amendment (µg/g)						
	Not Adjusted	Not Adjusted + Air	HCl	HCl + Air	$FeSO_4$-A + Air	$FeSO_4$-B	$FeSO_4$-B + Air
Bone Char	7.06	7.93	11.04	7.22	3.13	-0.50	0.22
GAC	6.76	6.35	10.32	4.52	3.48	-1.34	-0.92
BC/GAC	7.33	7.62	12.97	5.04	4.84	-0.80	0.43
BC/GAC/SAMMS	9.11	6.68	16.43	7.32	4.80	0.06	0.51

Similar to the first batch study, lead concentrations in MW-44 goundwater used in this study were roughly 2 - 3 times greater than those recently reported for site groundwater (Appendices 3 and 4). When no pH adjustment or air sparging was performed, contact with amendments resulted in slight decreases in dissolved lead concentrations (Figure 37). Average total percent reductions ranged from 9-19% based on unadjusted water from well MW-44, though no significant difference between the amendments is apparent. Simply sparging with air showed a reduction of 41%, though contact with amendments did not appear to significantly increase reduction percentages. Adjusting site water with HCl decreased the lead concentration by 25%, though the control only showed a 4% reduction. Contact with amendments resulted in removal percentages of 6-12%. Sparging HCl-adjusted water with air reduced the lead concentration by 56%. Total reductions slightly increased after contact with amendments, ranged between 61 and 69%, though there was not a significant difference between the amendment combinations. In the $FeSO_4$-A + Air case, total percent reduction before amendment application was 42%; contact with amendments increased had little effect on dissolved lead concentrations. After the 19.5% by weight $FeSO_4$:$7H_2O$ solution was applied and the coagulation solids were allowed to settle, the total reduction in lead concentration was only 2%, though the control

showed a reduction of 20%. None of the amendment combinations further increased lead

removal over that measured in the control. Sparging the $FeSO_4$:$7H_2O$-adjusted water (the $FeSO_4$-

B + Air case) resulted in a total percent reduction of 28%. Again, contact with amendments did

little to increase the overall percent reductions of lead (21-29%). None of the amendment

combinations appeared to be effective at reducing lead concentrations regardless of pH

adjustment or air sparging (Table 11).

Figure 37. Dissolved lead concentrations resulting from pH adjustment, air sparging, and/or contact with amendments

Table 11. Average mass of dissolved lead removed per mass of amendment applied for treatments evaluated

Treatment	Mass of Lead removed per gram of amendment ($\mu g/g$)						
	Not Adjusted	Not Adjusted + Air	HCl	HCl + Air	$FeSO_4$-A + Air	$FeSO_4$-B	$FeSO_4$-B + Air
Bone Char	-0.52	0.36	0.22	-0.16	-0.06	0.30	-0.11
GAC	0.19	-1.02	0.68	0.14	0.17	0.40	-0.36
BC/GAC	-0.34	-1.65	0.35	-0.18	0.57	0.08	-0.16
BC/GAC/SAMMS	0.55	0.13	0.78	0.65	0.54	0.30	0.54

Arsenic concentrations in MW-44 goundwater used in this study were again much greater than those recently reported for site groundwater (Appendices 3 and 4). When no pH adjustment or air sparging was performed, contact with amendments did not result in significant reductions of dissolved arsenic (Figure 38). Simply sparging with air showed a 19% reduction based on unadjusted water from well MW-44, though the control showed an 11% reduction. Amendments again did little to further reduce arsenic concentrations. Adjusting site water with HCl did not affect dissolved arsenic concentrations, though the control showed a 12% reduction. Total reductions for amendment combinations were not significantly higher than the reduction measured in the control. Sparging HCl-adjusted water with air reduced the arsenic concentration by 60%, but the control shows a total reduction of 54%. Total reductions after contact with bone char and GAC were 53 and 58%, though there was not a significant difference between the two. The BC/GAC and BC/GAC/SAMMS combinations showed reductions of 70 and 77%, respectively. In the $FeSO_4$-A + Air case, total percent reduction before amendment application was 70%. Contact with the BC/GAC and BC/GAC/SAMMS combinations increased the total reductions to 81 and 87%. After the 19.5% by weight $FeSO_4$:$7H_2O$ solution was applied and the coagulation solids were allowed to settle, the total reduction in arsenic concentration was 38%,

but the control showed a 72% reduction. Contact with bone char, BC/GAC, and

BC/GAC/SAMMS combinations resulted in total percent reductions of 99, 85, and 79 %,

respectively. The mixture with the largest percent of bone char resulted in the greatest arsenic

removal (Table 12). Sparging the $FeSO_4$:$7H_2O$-adjusted water (the $FeSO_4$-B + Air case) resulted

in a total percent reduction of 58%, though the control showed a 70% reduction. Contact with

bone char alone resulted in a 95% reduction in arsenic, and the other amendment combinations

resulted in reductions ranging from 90-91%.
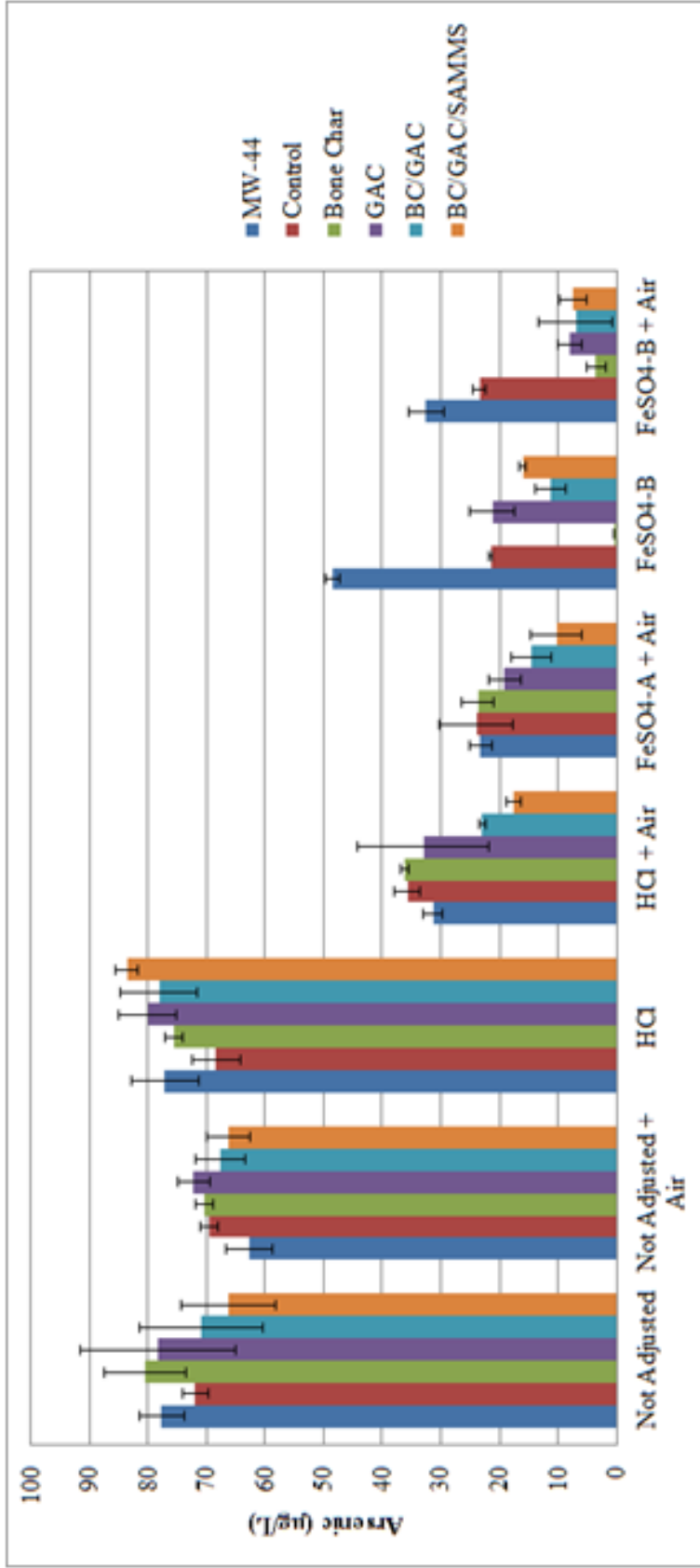
Figure 38. Dissolved arsenic concentrations resulting from pH adjustment, air sparging, and/or contact with amendments

Table 12. Average mass of dissolved arsenic removed per mass of amendment applied for treatments evaluated

Treatment	Mass of Arsenic removed per gram of amendment (µg/g)						
	Not Adjusted	Not Adjusted + Air	HCl	HCl + Air	FeSO$_4$-A + Air	FeSO$_4$-B	FeSO$_4$-B + Air
Bone Char	-1.70	-0.17	-1.44	-0.09	0.05	4.19	3.92
GAC	-1.26	-0.54	-2.30	0.54	0.96	0.05	3.06
BC/GAC	0.21	0.37	-1.93	2.53	1.88	2.01	3.24
BC/GAC/SAMMS	1.12	0.65	-3.02	3.59	2.70	1.10	3.20

The average vanadium concentration in Milli-Q water (Table 9) was small compared to values measured in this study. However, the average vanadium concentration in the digestion blanks is between 3 and 73% of vanadium concentrations measured in samples during this batch study, though only samples with low measured vanadium concentrations (e.g. any samples the underwent ferrous sulfate treatment) were likely to have been impacted substantially. Vanadium contamination may have occurred during the digestion phase of sample preparation. For this reason, vanadium concentrations may be lower than reported, but no adjustment has been made to the results presented.

Vanadium concentrations in MW-44 goundwater used in this study were comparable to those recently reported for site groundwater (Appendices 3 and 4). When no pH adjustment or air sparging was performed, contact with amendments did not result in significant reductions of dissolved vanadium (Figure 39). Simply sparging with air showed a 2% reduction based on unadjusted water from well MW-44, though the control showed a 19% reduction. Amendments did little to further reduce vanadium concentrations. Adjusting site water with HCl resulted in a 15% reduction, but the control showed no reduction. Total reductions for amendment combinations ranged from 9-13%, though no amendment combination performed significantly better than the others. Sparging HCl-adjusted water with air reduced the vanadium concentration

by 13%, but the control shows a total reduction of 37%. Percent reductions after contact with amendments ranged from 26-38%, though again, no combination performed significantly better than the others. In the $FeSO_4$-A + Air case, total percent reduction in vanadium concentration before amendment application was 90%. Contact with the GAC and BC/GAC combinations increased the total reductions to 96 and 94%. After the 19.5% by weight $FeSO_4{:}7H_2O$ solution was applied and the coagulation solids were allowed to settle, the total reduction in vanadium concentration was 77%, but the control showed an 80% reduction. Contact with amendments did not result in any further reduction in vanadium concentrations. Sparging the $FeSO_4{:}7H_2O$-adjusted water (the $FeSO_4$-B + Air case) resulted in a total percent reduction of 93%, though the control showed an 87% reduction. Again, amendment application did not reduce vanadium concentrations further. None of the amendment combinations produced vanadium removals comparable to those observed in the first batch study (Table 13).
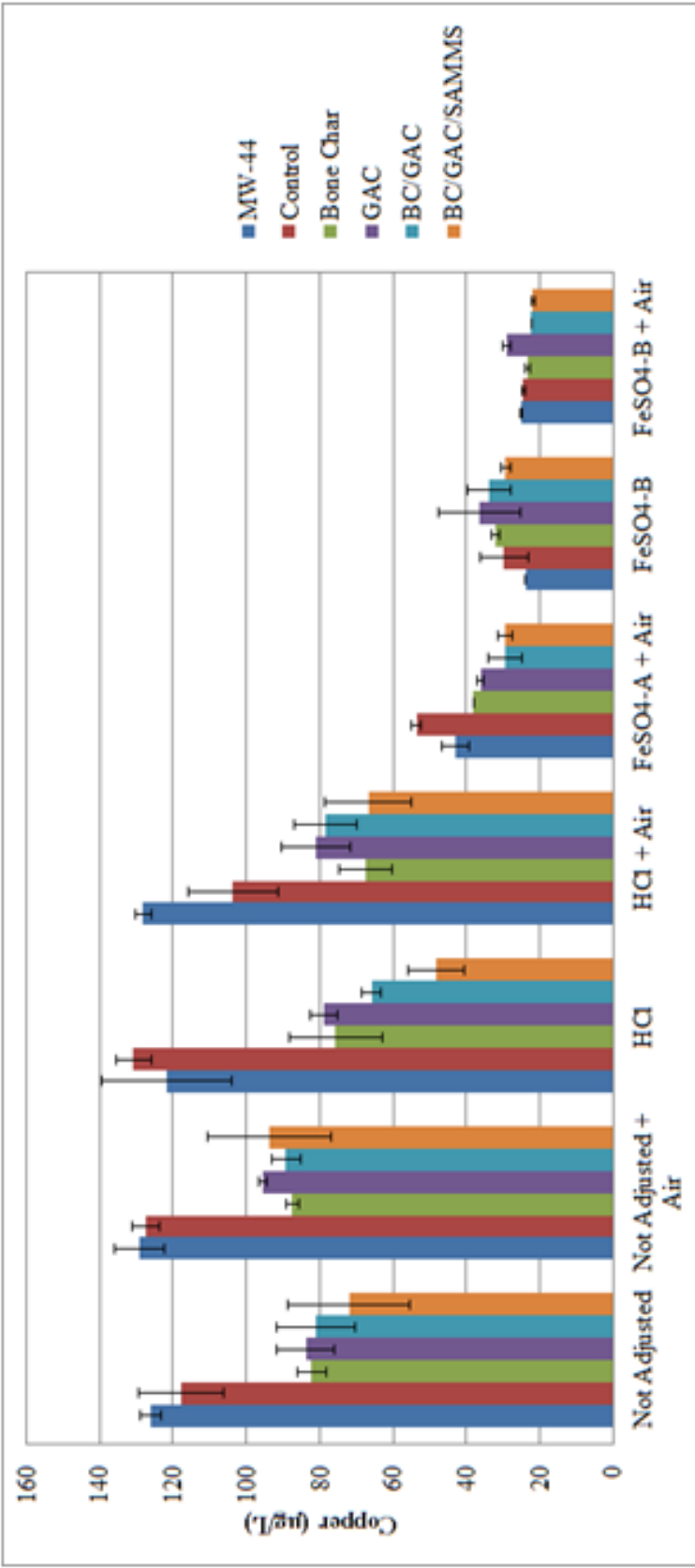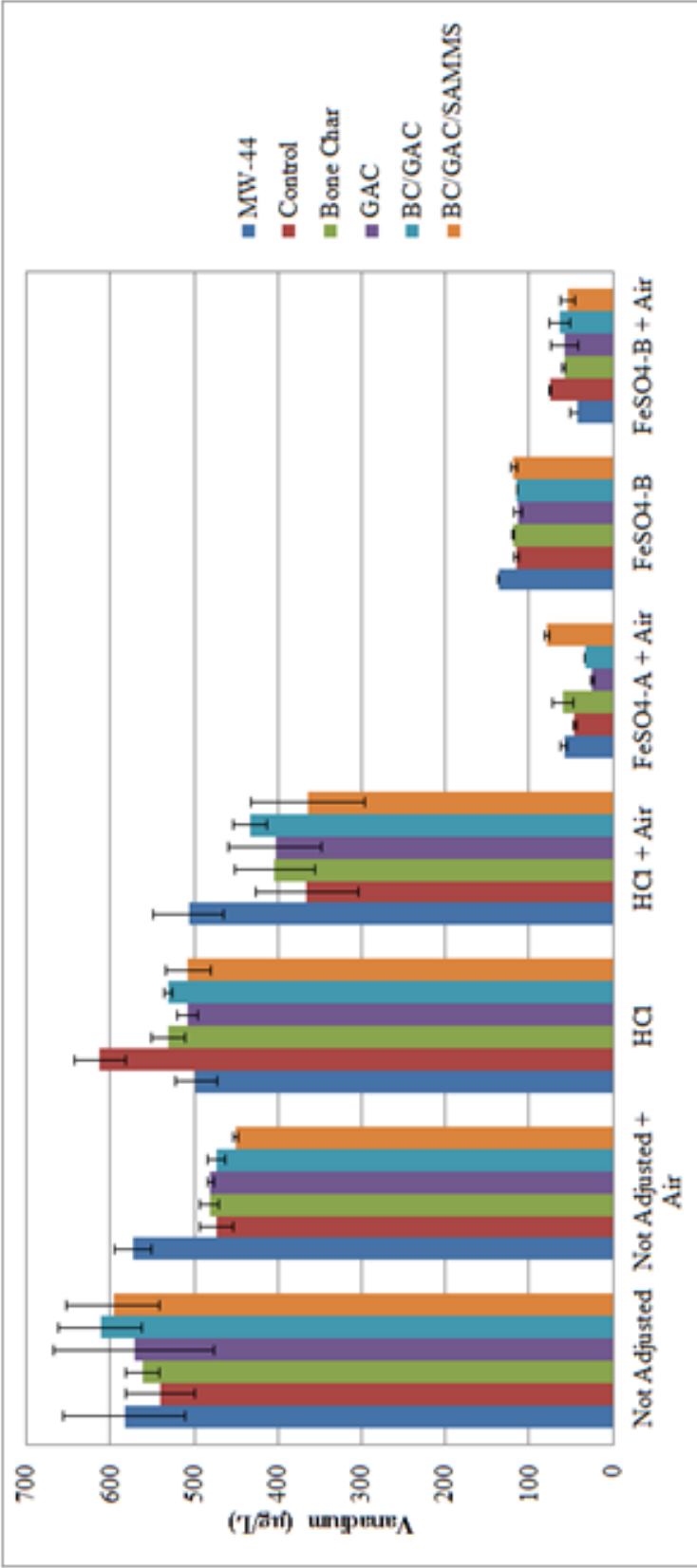
Figure 39. Dissolved vanadium concentrations resulting from pH adjustment, air sparging, and/or contact with amendments

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Table 13. Average mass of dissolved vanadium removed per mass of amendment applied for treatments evaluated

Treatment	Mass of Vanadium removed per gram of amendment (µg/g)						
	Not Adjusted	Not Adjusted + Air	HCl	HCl + Air	$FeSO_4$-A + Air	$FeSO_4$-B	$FeSO_4$-B + Air
Bone Char	-4.15	-1.62	16.30	-7.69	-2.76	-0.73	3.11
GAC	-6.14	-1.39	20.63	-7.46	4.16	0.54	3.25
BC/GAC	-14.22	0.02	16.24	-13.61	2.37	0.20	2.28
BC/GAC/SAMMS	-11.07	4.51	20.77	0.16	-6.55	-0.60	4.11

Iron concentrations in MW-44 goundwater used in this study were roughly one-quarter to one-half the values (before ferrous sulfate was added) measured previously (Appendices 3 and 4), that data was only available through September 2008. When no pH adjustment or air sparging was performed, contact with amendments resulted in percent reductions ranging from 9-14% (Figure 40). Simply sparging with air showed a 9% reduction, though the control showed a 14% reduction. Amendments did little to further reduce dissolved iron concentrations. Adjusting site water with HCl resulted in a 21% reduction, but the control showed only a 6% reduction. Total reductions for amendment combinations ranged from 16-19%, though no amendment combination performed significantly better than the others. Sparging HCl-adjusted water with air reduced the iron concentration by 16%, but the control shows a total reduction of 10%. Percent reductions after contact with amendments ranged from 4-13%, though again, no combination performed significantly better than the others. In the $FeSO_4$-A + Air case, the dissolved iron concentration increased by 276%, though the control only shows an 111% increase. Contact with the GAC, BC/GAC, and BC/GAC/SAMMS combinations resulted in iron reductions of 19, 20, and 24%, respectively. After the 19.5% by weight $FeSO_4$:$7H_2O$ solution was applied and the coagulation solids were allowed to settle, the iron concentration increased by 1,532%, but the

control showed a 449% increase. Contact bone char, GAC, BC/GAC, and BC/GAC/SAMMS

resulted in concentrations -69% (a reduction), 252% (an increase), 14%, and 136%, respectively.

As with arsenic, iron removal was greatest for the combinations with the highest percentage of

bone char (Table 14). Sparging the $FeSO_4:7H_2O$-adjusted water (the $FeSO_4$-B + Air case)

resulted in a 715% increase in iron concentration (compared to the original value), though the

control showed 227% increase. Amendment application resulted in percent reductions ranging

from 83-95%, with the greater removals occurring for the bone char and BC/GAC combinations.
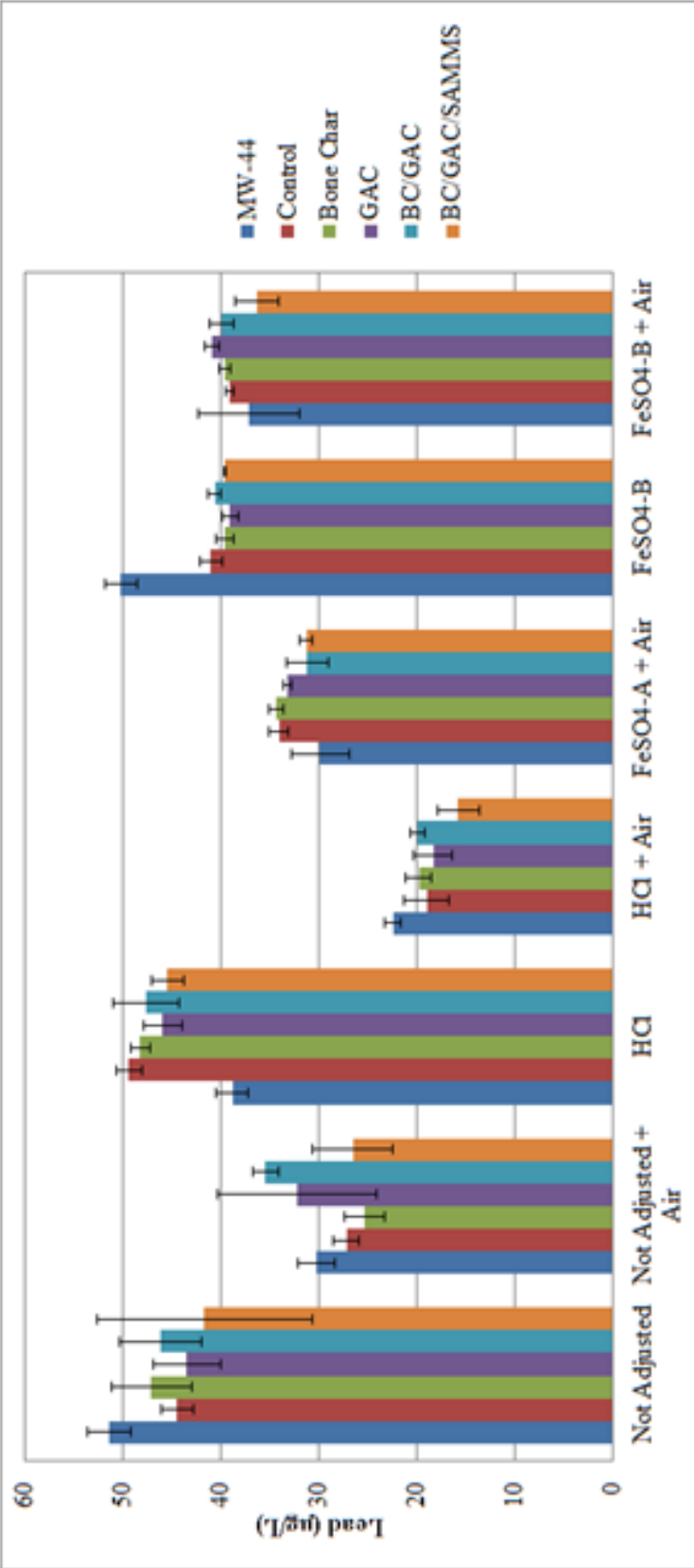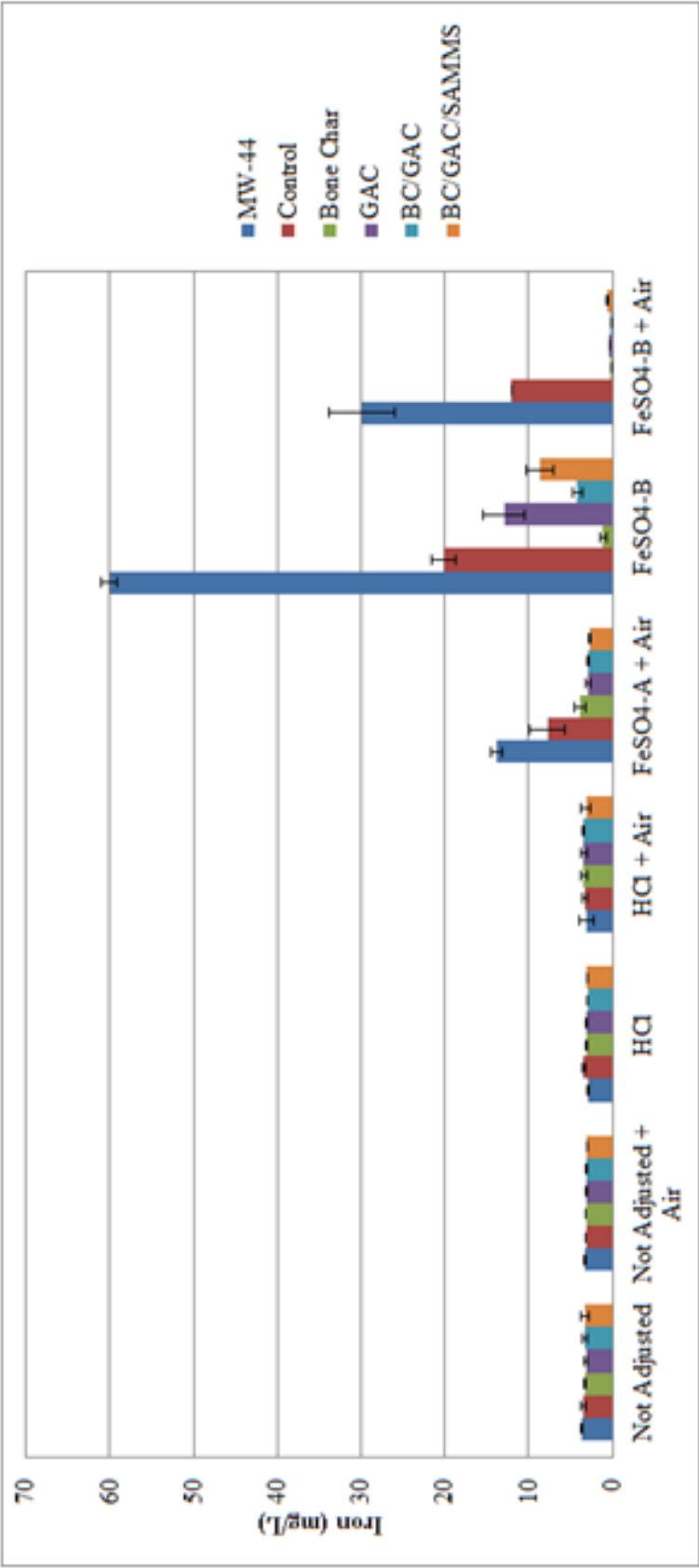
Figure 40. Dissolved iron concentrations resulting from pH adjustment, air sparging, and/or contact with amendments

Table 14. Average mass of dissolved iron removed per mass of amendment applied for treatments evaluated

Treatment	Mass of Iron removed per gram of amendment (mg/g)						
	Not Adjusted	Not Adjusted + Air	HCl	HCl + Air	$FeSO_4$-A + Air	$FeSO_4$-B	$FeSO_4$-B + Air
Bone Char	0.04	0.00	0.08	-0.02	0.76	3.80	2.33
GAC	0.08	0.01	0.07	-0.03	0.95	1.43	2.30
BC/GAC	0.05	0.03	0.09	-0.05	0.96	3.16	2.33
BC/GAC/SAMMS	0.05	0.02	0.08	0.02	0.98	2.28	2.28

When no pH adjustment or air sparging was performed, contact with the bone char, GAC, and BC/GAC combinations resulted in 19, 21, and 26% reductions, respectively (Figure 41). Simply sparging with air did not reduce DOC concentrations, but the combinations of bone char, GAC, and BC/GAC produced total percent reductions of 6, 14, and 11%, respectively. Adjusting site water with HCl resulted in no reduction. Total reductions for amendment combinations ranged from 24-34%, with the GAC containing combinations performing the best. Sparging HCl-adjusted water with air also did not reduce the dissolved organic carbon concentration. Percent reductions after contact with amendments ranged from 13-21%, again with the GAC containing combinations performing the best. In the $FeSO_4$-A + Air case, total percent reduction in DOC concentration before amendment application was 41%; the water still had significant color (Figure 32). Contact with the amendments increased DOC removal to between 58 and 63%. After the 19.5% by weight $FeSO_4$:$7H_2O$ solution was applied and the coagulation solids were allowed to settle, the total reduction in DOC concentration was 82%, but the control showed an 88% reduction. Contact with the bone char and BC/GAC combination resulted in further reductions to 90 and 93%, respectively. Sparging the $FeSO_4$:$7H_2O$-adjusted water (the $FeSO_4$-B + Air case) resulted in a total percent reduction of 86. Contact with bone char and GAC resulted

in further reductions of DOC concentration to 89 and 92% respectively. Bone char and GAC

(and the BC/GAC combination) removed organic carbon more efficiently than the combination

that includes SAMMS, especially when ferrous sulfate was not applied (Table 15).
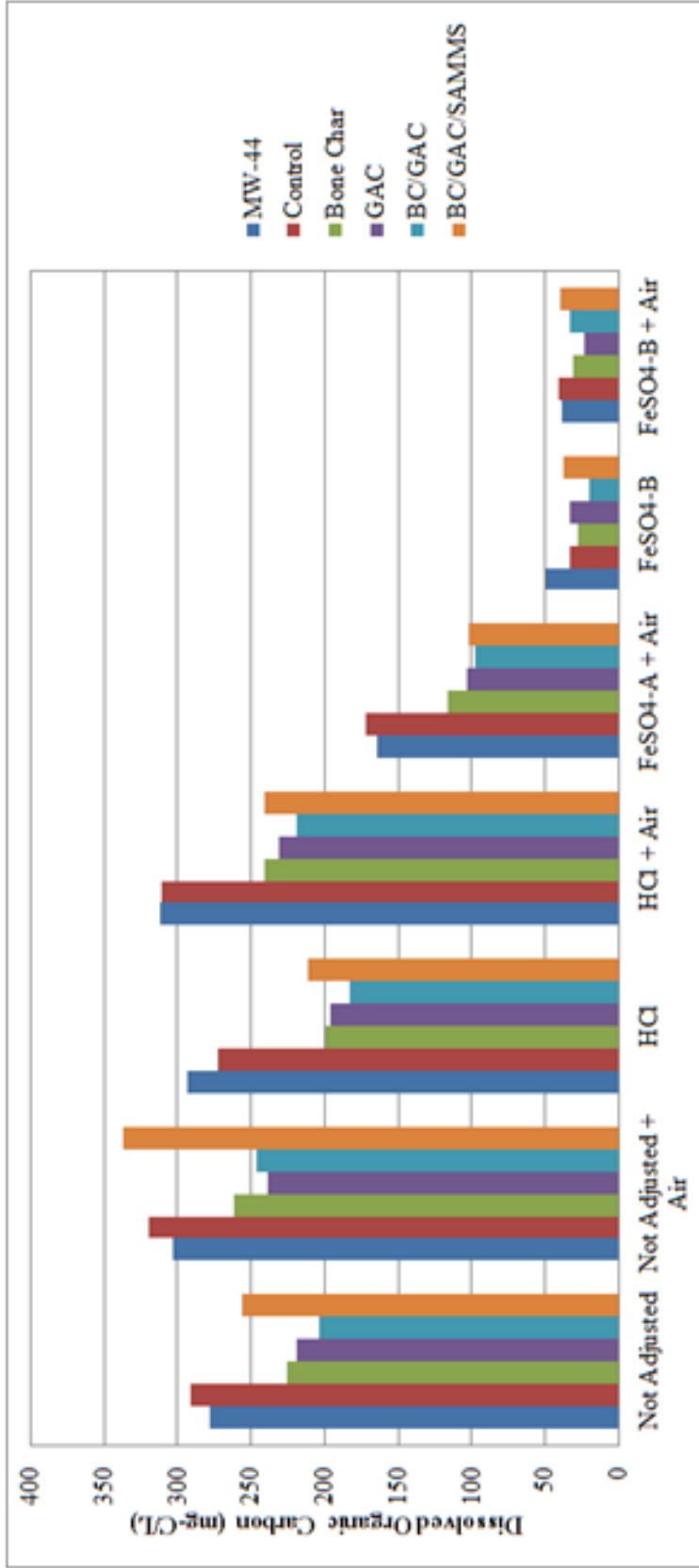
Figure 41. Dissolved organic carbon concentrations resulting from pH adjustment, air sparging, and/or contact with amendments

Table 15. Average mass of dissolved organic carbon removed per mass of amendment applied for treatments evaluated

Treatment	Mass of DOC removed per gram of amendment (mg-C/g)						
	Not Adjusted	Not Adjusted + Air	HCl	HCl + Air	FeSO$_4$-A + Air	FeSO$_4$-B	FeSO$_4$-B + Air
Bone Char	13.03	11.52	14.51	13.91	11.03	1.11	2.00
GAC	14.38	16.15	15.10	15.90	13.60	0.06	3.56
BC/GAC	17.34	14.72	17.92	18.39	14.89	2.61	1.63
BC/GAC/SAMMS	6.87	-3.41	12.18	14.03	13.77	-0.95	0.33

In summary, the amendments seemed to slightly affect pH for each case, excluding the FeSO$_4$-B cases. When the coagulation solids were removed (FeSO$_4$-B), the pH fell below 8. Sparging with air (FeSO$_4$-B + Air) further decreased the pH. In both cases, bone char appeared to have a buffering affect, with the highest pH values occurring in the bottles with the largest percentages of bone char. The addition of HCl and sparging of air increased the oxidation-reduction potential while the addition of ferrous sulfate initially decreased the ORP. Generally, contact with amendments seemed to decrease the ORP, again excluding the FeSO$_4$-B cases. After the coagulation solids were removed and amendments applied (FeSO$_4$-B), the ORP greatly increased for all amendment combinations. After being sparged with air, contact with GAC increased the ORP and contact with bone char decreased the ORP (with combinations containing the two settling to some intermediate value).

The single treatment that resulted in the largest reductions in copper, arsenic, vanadium and organic carbon was the addition of solutions FeSO$_4$:7H$_2$O. The removal of the coagulation solids seemed to result in greater removals of copper, arsenic, iron, and, in particular, DOC (FeSO$_4$-A + Air versus FeSO$_4$-B + Air). Sparging FeSO$_4$-adjusted water after removal of solids (FeSO$_4$-B versus FeSO$_4$-B + Air) resulted in the formation of rust-colored solids (Figure 35) and

generally seemed to increase the removals of copper, arsenic, and vanadium. Sparging with air when the pH was either not adjusted or adjusted with HCl was the most effective treatments for removing dissolved lead; the addition of ferrous sulfate did significantly less to affect dissolved lead concentrations.

The performance of amendments was highly dependent on the other treatments applied and the particular metal being removed; no one amendment combination performed significantly better than the others for the removal of all metals under all conditions. All amendment combinations were somewhat effective at removing dissolved copper for the Not Adjusted, Not Adjusted + Air, HCl, and HCl + Air cases, with the BC/GAC/SAMMS combination having a slight advantage in the HCl case. None of the combinations seemed effective for removing copper after ferrous sulfate application. For lead, the BC/GAC/SAMMS combination appears to perform better than the other amendments for the HCl + Air case. Otherwise, the combinations performed nearly equally. The BC/GAC and BC/GAC/SAMMS combinations performed well for arsenic in the HCl + Air and $FeSO_4$-A + Air simulations. Combinations containing bone char performed best for arsenic removal for the $FeSO_4$-B and $FeSO_4$-B + Air cases, with the combinations containing the larger percentages of bone char performing better. The GAC and BC/GAC combinations appear to perform better than other combinations for vanadium removal for the $FeSO_4$-A + Air case. Otherwise, no combination performed significantly better than the others for dissolved vanadium removal. Iron removal was unmemorable except for the $FeSO_4$-A + Air, $FeSO_4$-B, and $FeSO_4$-B + Air cases, which resembled removal patterns for arsenic. The bone char, GAC, and BC/GAC combinations were most effective at removing dissolved organic carbon; SAMMS appeared to reduce the effectiveness of bone char and GAC.

4.3 Further Discussion

The objective of this study was to identify and evaluate potential metal remediation and pH control strategies. The experiments described here present an initial step toward this objective, but these were not necessarily adequate to pinpoint mechanisms of removal, identify constituents or reactions that dominate the geochemistry of the water, etc. That said, the results may hint at some information about the behavior of site water constituents that may be useful going forward.

The first set of batch studies showed that pH adjustment generally improved metal removal for apatite and GAC; metal removal for SAMMS was generally improved, although this material also performed decently when the pH was not adjusted. This difference in behavior is likely related to the chemical structures of the amendments and the role of dissolved organic matter in the behavior of trace metals in an aquatic environment. Dissolved organic matter has previously been shown to affect the speciation, mobility, bioavailability, and reaction rates of copper, lead, arsenic, and other metals, largely through complexation or other interactions involving polar functional groups. The decrease of pH in water containing metal-DOM complexes may result in the liberation of metals from the complex due to increased competition for DOM binding sites from hydrogen ions. Data from drip waters in a hyperalkaline cave (Hartland et al.; 2011) support this idea; consistent with enhanced complexation by DOM, the ratio of trace elements (e.g., copper) to organic carbon was shown to increase with drip water pH (from 8 to 12). Metal binding strength may increase with increasing pH for the following reasons: i) stronger binding sites become available, including phenolic and poly-carboxylic acids, ii) the deprotonation of acid functional groups on humic substances results in a higher overall negative charge on humic molecules, and iii) multidentate binding may become

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increasingly important (Stern et al., 2007). Also, the decrease of pH may result in a shift in metal speciation to more positively charged species that are more amenable to sorption (e.g. Figure 13). The liberation of metals from metal-DOM complexes and/or the shift toward more positively charged metal species may explain the improvement in performance observed for the amendments/sorbents when the pH was decreased.

The removals of copper and lead by SAMMS without the pH adjustment coupled with the fact that SAMMS did not substantially reduce dissolved organic carbon concentrations suggests that copper and lead have a greater affinity for the terminal thiol groups in the Thiol-SAMMS structure (Figure 15) than some of the functional groups contained in the structure of the DOM or other sorbents. The fact that apatite performed better than SAMMS under pH-adjusted conditions for copper and lead may indicate that copper and lead species that dominate at lower pH have higher affinities for the phosphate and hydroxyl groups of the apatite than for the thiol groups of the SAMMS. However, the powdered apatite has a much larger surface area than the granular SAMMS, so it is difficult to make a definitive statement regarding the relative affinities of copper and lead for a particular sorbent given the results of these experiments. The poor performances of chitosan and limestone may be a result of low affinities of the metals of concern for the hydroxyl and amino groups of chitosan and the carbonate groups of the limestone, but is also likely an effect of surface area. Amendment performance as reported is likely subject to a bias based on surface area; further data manipulations should normalize metal removal to amendment surface area to give a true indication of the relative affinities of the metals for each amendment.

The second batch study showed that the addition of ferrous sulfate was the single most effective treatment to reduce copper, arsenic, and vanadium concentrations. These results

were expected based on literature (Section 2.1) showing that iron played a large role in the chemistry and mobility of each of these metals. Lead, on the other hand, was only significantly removed under very specific conditions (pH adjusted with HCl and sparged with air). These results were unexpected; according to the cited literature, iron exerts a predominant role in the adsorption of lead in soils (Bradl et al., 2005). However, lead was not greatly removed in the presence of excess iron. Also, lead behaved similarly to copper in the first batch study, but not in the second. The reasons for these discrepancies are unknown and these results should be confirmed. Excluding lead, metal reduction with ferrous sulfate application coincided with the formation of coagulation solids, indicating that the coagulation solids also contained significant amounts of copper, arsenic, and vanadium. There are multiple ways by which the metals could be removed with these solids, including precipitation of metal hydroxides or sulfides (e.g.) in the presence of increased iron and sulfate concentrations, coprecipitation with iron solids, or adsorption to iron solids or sorbed dissolved organic compounds, was not determined by these experiments and is likely a combination of processes. Characterization of the solids is likely important in determining the mechanisms of removal for each metal of concern.

The notion that hydrogen ions compete for metal binding sites within the DOM structure also means that DOM would confer some alkalinity (buffering capacity) to the water, though this generally depends on the DOM composition (Garnier et al., 2004). This is supported by the difference observed in pH measurements from cases where coagulation solids were removed. The coagulation solids contained much of the color (Figure 33) of the untreated site water (Figure 4), and it was shown that a substantial amount of the organic carbon was removed (Figure 41) with the removal of these solids. However, pH decreased drastically in control samples after the organics-rich solids were removed ($FeSO_4$-B and $FeSO_4$-B + Air), whereas the

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pH rebounded in almost all other cases, where the organic matter was not removed. This indicates that the organic matter may have had a buffering effect, but does not explain the initial source of the drop in pH (production of acidity). The drops in pH after the coagulation solids were removed, either with or without air sparging over the seven day "contact" period, may be related to the oxidation of residual ferrous iron to ferric iron (ferric iron produces more acidity than ferrous iron as shown in Section 2.2), but it is unclear if this single mechanism can explain the magnitude of the observed pH declines. Iron oxidation may have occurred slowly or not at all in the $FeSO_4$-A + Air case, potentially due to the interference of DOM.

The use of ferrous sulfate may present some operational challenges. First, the pH fell significantly after the organics-rich solids were removed. It is uncertain, though, how much of a pH excursion would occur on site because soil alkalinity was not taken into account in this study. Second, the formation of solids could cause pore clogging (Sperry et al., 1996). In a situation where a ferrous sulfate solution is injected, solids could form in the pore spaces near the well or on the well screen itself, which could reduce the overall effectiveness of the injection procedure. Clogging in certain areas may alter groundwater flow paths. Altering the flow path is generally a somewhat dangerous proposition, since this changes the groundwater hydrology from a state that is known to one that is unknown. This may require additional studies to determine how the groundwater hydrology was affected by pore clogging and would complicate the positioning of an amendment barrier or cap (if it is deemed necessary). However, contaminated groundwater is already discharging into the waterway; altering the flow path to the waterway may do little additional harm (though this would need to be assessed). Clogging the pore spaces may limit or reduce the discharge of contaminated site water into Slip 6 and the Duwamish Waterway; at the very least, ferrous sulfate application results in the immobilization of some contaminant mass,

reducing the amount of contaminant that could enter the biologically active zone. As alternative to the injection technique, ferrous sulfate might be applied as a solid phase as part of a reactive iron barrier, though the potential for this method of application must be assessed. The design of a system suitable for applying ferrous sulfate without adversely affecting contaminant transport would be critical for a $FeSO_4$-based treatment strategy.

5.0 Conclusions and Recommendations

Groundwater beneath a former industrial site contains dissolved metals and organic material at high levels, as well as elevated pH (10-12). Contaminated groundwater discharge to site-adjacent waterways must be controlled to minimize impact to potential receptors.

In a preliminary study, the efficacy of five amendments (chitosan, apatite, GAC, Thiol-SAMMS®, and limestone) was examined for the removal of copper, lead, vanadium, and arsenic for both unaltered and pH-adjusted (pH = 8) site groundwater in laboratory batch studies. Dissolved metals and dissolved organic carbon (DOC) concentrations were measured in site groundwater both before and after pH adjustment, and after application of amendments. pH adjustment generally improved amendment performance. The greatest reductions in dissolved copper (70%), lead (62%), and vanadium (62%) concentrations were observed under pH-adjusted conditions in the presence of apatite. Thiol-SAMMS® removed both copper (55% reduction) and lead (31% reduction) at the original pH and also performed well under pH-adjusted conditions (Cu: 69% reduction; Pb: 46% reduction; V: 24% reduction). GAC was somewhat effective at removing lead under all conditions (15-30% reduction) and copper (31% reduction) when the pH was adjusted, and also reduced DOC concentrations under all conditions (24-27% reduction). These results suggest that a strategy using pH adjustment and some combination of apatite, Thiol-SAMMS®, and/or GAC may be best suited for remediation at this site.

Further studies testing combinations of bone char (in place of apatite), GAC, and Thiol-SAMMS® were performed. In addition, the impacts of air sparging and pH adjustment through addition of hydrochloric acid or ferrous sulfate heptahydrate ($FeSO_4:7H_2O$), a coagulant commonly used in conventional water treatment, were evaluated. The introduction of

$FeSO_4:7H_2O$ resulted in the formation of coagulation solids, further decreases in pH after the coagulation solids were removed, and the largest significant reductions of dissolved copper (at most 81%), arsenic (72%), vanadium (80%), and DOC (88%) of any treatment evaluated. Sparging with air increased reduction of lead concentrations for all pH adjustment strategies and increased reduction of vanadium concentrations only when the pH was adjusted with $FeSO_4:7H_2O$. Combinations of bone char, GAC, and Thiol-SAMMS® generally did not confer a substantial advantage over single amendment treatments. Bone char removed arsenic significantly better than other amendments/combinations when pH was adjusted with $FeSO_4:7H_2O$; bone char also acted as a buffer to curb further decreases in pH after coagulation solids were removed. The drops in pH after the coagulation solids were removed, either with or without air sparging may be related to the oxidation of residual ferrous iron, but it is unclear if this single mechanism can explain the magnitude of the observed pH declines.

Using the ferrous sulfate treatment strategy, potentially combined with passive barrier or cap of bone char, flow-through column experiments should be designed to show how implementation of the strategy would impact the subsurface hydrology and to determine whether this strategy can achieve ARARs for copper, lead, arsenic, and vanadium. The goals of these future studies should be as follows:

- Confirm the pH declines after the coagulation solids are removed and determine the mechanisms for metal removal and pH change

- Discern how large a role soil alkalinity will play in pH control with $FeSO_4:7H_2O$

- Determine how $FeSO_4:7H_2O$ injection rates and groundwater hydrology might be affected by the formation of coagulation solids

- Evaluate different methods of $FeSO_4:7H_2O$ application (injection versus passive flow-through barrier or cap)

- Assess the long-term effect of this treatment strategy for *in situ* reduction of copper, lead, arsenic, and vanadium concentrations to levels below ARARs.

6.0 References

AGI Technologies, 1999, Risk Assessment/Media Cleanup Standards Report, Former Rhone-Poulenc East Marginal Way Facility, Tukwila, Washington, October 8.

APHA, AWWA, and WEF. 2005. *Standard Methods for the Examination of Water and Wastewater*, 21st Edition. APHA, Washington, D.C.

Aiken, G.R.; Hsu-Kim, H.; Ryan, J.N. Influence of Dissolved Organic Matter on the Environmental Fate of Metals, Nanoparticles, and Colloids. *Environ. Sci. Technol.* **2011**, 45, 3196-3201.

Appelo, C.A.J.; Postma, D. *Geochemistry, groundwater, and pollution*, 2nd ed.; CRC Press: Amsterdam, 2005.

Aziz, H.A.; Othman, N.; Yusff, M.S.; Basri, D.R.H.; Ashaari, F.A.H.; Adlan, M.N.; Othman, F.; Johari, M.; Perwira, M. Removal of copper from water using limestone filtration technique Determination of mechanism of removal. *Environment International* **2001**, *26*, 395-399.

Babel, S.; Kurniawan, T.A. Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *Journal of Hazardous Materials* **2003**, *B97*, 219-243.

Bailey, S.E.; Olin, T.J.; Bricka, R.M., Adrian, D.D. A review of potentially low-cost sorbents for heavy metals. *Water Res.* **1999**, 33, 2469-2479.

Baskan, M.B.; Pala, A. Determination of arsenic removal efficiency by ferric ions using response surface methodology. *Journal of Hazardous Materials* **2009**, *166*, 796-801.

Bauer, M.; Blodau, C. Mobilization of arsenic by dissolved organic matter from iron oxides, soils and sediments. *Science of the Total Environment* **2006**, *354*, 179-190.

Bradl, H.; Kim, C.; Kramar, U.; Stüben, D. Interactions of Heavy Metals. In *Heavy Metals in the Environment: Origin, Interaction, and Remediation*, 1st ed.; Elsevier Academic Press: Amsterdam, 2005, pp. 29-164.

Brady, R.D. Activated Carbon Processes. In *Water Treatment Plant Design*, 4th ed.; McGraw-Hill: New York, 2005, pp 14.1 – 14.38.

Bowel, R.J. Sorption of arsenic by iron oxides and oxyhydroxides in soils. *Applied Geochemistry* **1994**, *9*, 279-286.

CH2M Hill, 1995, Final RCRA Facility Investigation Report for the Marginal Way Facility, prepared for Rhone-Poulenc, Inc., June 19.

Chen, J.; Yiacoumi, S.; Blaydes, T.G. Equilibrium and kinetic studies of copper adsorption by activated carbon. *Separations Technology* **1996**, *6*, 133-146.

Chen, J.P.; Wang, X. Removing copper, zinc, and lead ion by granular activated carbon in pretreated fixed-bed columns. *Separation and Purification Technology* **2000**, *19*, 157-167.

Chen, J.P.; Yoon, J.T.; Yiacoumi, S. Effects of chemical and physical properties of influent on copper sorption onto activated carbon fixed-bed columns. *Carbon* **2003**, *41*, 1635-1644.

Chen, J.P.; Wu, S. Simultaneous adsorption of copper ions and humic acid onto an activated carbon. *Journal of Colloid and Interface Science* **2004**, *280*, 334-342.

Chen, X.; Wright, J.V.; Conca, J.L.; Peurrung, L.M. Effects of pH on heavy metal sorption on mineral apatite. *Environ. Sci. Technol.* **1997**, *31*, 624-631.

Chen, Y.N.; Chai, L.Y.; Shu, Y.D. Study of arsenic(V) adsorption on bone char from aqueous solution. *Journal of Hazardous Materials* **2008**, *160*, 168-172.

Cheung, C.W.; Porter, J.F.; McKay, G. Sorption kinetic analysis for the removal of cadmium ions from effluents using bone char. *Wat. Res.* **2001**, *35*, 605-612.

Chouyyok, W.; Shin, Y.; Davidson, J.; Samuels, W.D.; Lafemina, N.H.; Rutledge, R.D.; Fryxell, G.E. Selective removal of Cu(II) from natural waters by nanoporous sorbents functionalized with chelating diamines. *Environ. Sci. Technol.* **2010**, *44*, 6390-6395.

Chu, K.H.; Hashim, M.A. Adsorption of copper(II) and EDTA-chelated copper(II) onto granular activated carbons. *Journal of Chemical Technology and Biotechnology* **2000**, *75*, 1054-1060.

Conestoga-Rovers and Associates, 2008, Draft pH pilot study report, Groundwater and Sediment Remediation, Occidental Chemical Corporation, Tacoma, Washington, June.

Dames and Moore, Inc., 1986, Phase II Site Screening Investigation, Final Report, October.

Delphos, P.J.; Wesner, G.M. Mixing, Coagulation, and Flocculation. In *Water Treatment Plant Design*, 4th ed.; McGraw-Hill: New York, 2005, pp 6.1 – 6.25.

Dentel, S.K.; Gossett, J.M. Mechanisms of coagulation with aluminum salts. *J. Am. Wat. Wks. Assoc.* **1988**, *80*, 187-198.

Feng, X.; Fryxell, G.E.; Wang, L.Q.; Kim, A.Y.; Liu, J.; Kemner, K.M. Functionalized monolayers or ordered mesoporous supports. *Science* **1997**, *276*, 923-926.

Ferguson, J.E. The Heavy Elements in Water and Sediments. In *The Heavy Elements: Chemistry, Environmental Impact, and Health Effects*, 1st ed.; Pergamon Press: Oxford, 1990, pp. 243-347.

Fuller C.C.; Piana, M.J.; Bargar, J.R.; Davis, J.A.; Kohler, M. Evaluation of Apatite Materials for Use in Permeable Reactive Barriers for the Remediation of Uranium-Contaminated Groundwater. In *Handbook of Groundwater Remediation Using Permeable Reactive Barriers: Applications to Radionuclides, Trace Metals, and Nutrients*, 1st ed.; Academic Press: San Diego, 2002, pp 24.

Gabaldón, C.; Marzal, P.; Seco, A.; Gonzalez, J.A. Cadmium and copper removal by a granular activated carbon in laboratory column systems. *Separation Science and Technology* **2000**, *35*, 1039-1053.

Garg, A.; Mishra, I.M.; Chand, S. Effectiveness of coagulation and acid precipitation processes for the pre-treatment of diluted black liquor. *Journal of Hazardous Materials* **2010**, *180*, 158-164.

Garnier, C.; Mounier, S.; Benaïm, J.Y. Influence of dissolved organic carbon content on modeling natural organic matter acid-base properties. *Wat. Res.* **2004**, *38*, 3685-3692.

Geomatrix Consultants, Inc., 2006a, Revised Pre-Demolition Investigation Report, Former Rhone-Poulenc Site, Tukwila, Washington: Prepared for Davis Property and Investment, May.

Geomatrix Consultants, Inc., 2006b, Voluntary Interim Measure Report Hazardous Waste Storage Area and Transformer A Area Cleanup, Former Rhone-Poulenc Site, Tukwila, Washington: Prepared for Davis Property and Investment, August.

Geomatrix Consultants, Inc., 2006c, Letter to Christy Brown, EPA, Interim Remedial Action: Sump 1-190 Waste Removal, Administrative Order on Consent for Corrective Action (Order) Under the Resource Conservation and Recovery Act (RCRA), Docket Number 1091-11-20-3008(h) Former Rhone-Poulenc East Marginal Way Facility WAD 00928 2302, May 25.

Geomatrix Consultants, Inc., 2006d, East Parcel Soil Characterization and Voluntary Interim Measure Report, Former Rhone-Poulenc Site, Tukwila, Washington: Prepared for Container Properties, L.L.C., September 29.

Geomatrix Consultants, Inc., 2007, Northwest Corner Affected Soil Removal Report, Former Rhone-Poulenc Site, Tukwila, Washington: Prepared for Container Properties, L.L.C., January.

Geomatrix Consultants, Inc., 2008, Performance Monitoring Report Round 41, September 2008, Former Rhone-Poulenc Site, Tukwila, Washington: Prepared for Container Properties, L.L.C., December.

Hartland, A.; Fairchild, I.J.; Lead, J.R.; Zhang, H.; Baalousha, M. Size, speciation and lability of NOM-metal complexes in hyperalkaline cave dripwater. *Geochimica et Cosmochimica Acta.* **2011**, *75*, 7533-7551.

Hem, J.D. Reactions of metal ions at surfaces of hydrous iron oxide. *Geochimica et Cosmochimica Acta.* **1977**, 41, 527-538.

Hem, J.D., 1985, Study and interpretation of chemical characteristics of natural water (3rd ed.): U.S. Geological Survey Water-Supply Paper 2254, 263 p.

Henneberry, Y.K.; Kraus, T.E.C.; Fleck, J.A.; Krabbenhoft, D.P.; Bachand, P.M.; Horwath, W.R. Removal of inorganic mercury and methylmercury from surface waters following coagulation of dissolved organic matter with metal-based salts. *Science of the Total Environment* **2011**, *409*, 631-637.

Huang, C.; Chung, Y.C.; Liou, M.R. Adsorption of Cu(II) and Ni(II) by pelletized biopolymer. *Journal of Hazardous Materials* **1996**, *45*, 265-277.

Jekel, M.R. Interaction of humic acids and aluminum salts in the flocculation process. *Wat. Res.* **1986**, *20*, 1535-1542.

Jha, N.; Iyengar, L.; Rao, V.S.P. Removal of cadmium using chitosan. *Journal of Environmental Engineering* **1988**. *114*, 962-974.

Runnels, R.T.; Schlelcher, J.A., 1956, Chemical Composition of Eastern Kansas Limestones, Kansas Geological Survey Bulletin, Part 3, University of Kansas Publications, Lawrence, KS.

Katsumata, H.; Kaneco, S.; Kasai, H.; Itoh, K.; Masuyama, K.; Suzuki, T.; Funasaka, K.; Ohta, K. Removal of humic substances and their metal complexes by adsorption. *Environmental Engineering Science* **2004**, *21*, 341-348.

Ko, D.C.K,; Porter, J.F.; McKay, G. Determination of solid-phase loading for the removal of metal ion from effluents using fixed-bed adsorbers. *Environ. Sci. Technol*. **2001**, *35*, 2797-2803.

Komnitsas, K.; Bartzas, G.; Paspaliaris, I. Efficiency of limestone and red mud barriers: laboratory column studies. *Minerals Engineering* **2004**, *17*, 183-194.

Landau Associates, Inc., 1991, Site Assessment, Rhone-Poulenc Facility, Tukwila, Washington, prepared for Boeing Environmental Affairs, September.

Lau, B.L.T.; Hsu-Kim, H.H. Precipitation and growth of zinc sulfide nanoparticles in the presence of thiol-containing natural organic ligands. *Environ. Sci. Technol*. **2008**, *42*, 7236-7241.

Lee, Y.J.; Elzinga, E.J.; Reeder, R.J. Sorption mechanisms of zinc on hydroxyapatite: Systematic uptake studies and EXAFS spectroscopy analysis. *Environ. Sci. Technol*. **2005**, *39*, 4042-4048.

Lin, Y.; Fryxell, G.E.; Wu, H.; Engelhard, M. Selective sorption of cesium using self-assembled monolayers on mesoporous supports. *Environ. Sci. Technol*. **2001**, *35*, 3962-3966.

Liu, G.; Fernandez, A.; Cai, Y. Complexation of arsenite with humic acid in the presence of ferric iron. *Environ. Sci. Technol.* **2011**, *45*, 3210-3216.

Ma, Q.Y.; Tralna, S.J.; Logan, T.J.; Ryan, J.A. Effects of aqueous Al, Cd, Cu, Fe(II), Ni, and Zn on Pb immobilization by hydroxyapatite. *Environ. Sci. Technol.* **1994**, *28*, 1219-1228.

Mackay, D.M.; Cherry, J.A. Groundwater contamination: Pump-and-treat remediation. *Environ. Sci. Technol.* **1989**, *23*, 630-636. *Environ. Sci. Technol.* **1994**, *28*, 1219-1228.

Martin, T.A.; Kempton, J.H. In situ stabilization of metal-contaminated groundwater by hydrous ferric oxide: An experimental and modeling investigation. *Environ. Sci. Technol*. **2000**, *34*, 3229-3234.

Mattigod, S.V.; Feng, X.; Fryxell, G.E.; Liu, J.; Gong, M. Separation of complexed mercury from aqueous wastes using self-assembled mercaptan on mesoporous silica. *Separation Science and Technology* **1999**, *34*, 2329-2345.

Mavropoulos, E.; Rossi, A.M.; Costa, A.M. Studies on the mechanisms of lead immobilization on hydroxyapatite. *Environ. Sci. Technol.* **2002**, *36*, 1625-1629.

Mayes, W.M.; Younger, P.L.; Aumônier, J. Hydrogeochemistry of alkaline steel leachates in the UK. *Water Air Soil Pollut*. **2008**, *195*, 35-50.

Morrison, S.J.; Naftz, D.L.; Davis, J.A.; Fuller, C.C. Introduction to Groundwater Remediation of Metals, Radionuclides, and Nutrients with Permeable Reactive Barriers. In *Handbook of Groundwater Remediation Using Permeable Reactive Barriers: Applications to Radionuclides, Trace Metals, and Nutrients*, 1st ed.; Academic Press: San Diego, 2002, pp 15.

Mulligan, C.N.; Yong, R.N.; Gibbs, B.F. Remediation technologies for metal-contaminated soils and groundwater: an evaluation. *Engineering Geology* **2001**, 60, 193-207.

Ngah, W.S.W.; Endud, C.S.; Mayanar, R. Removal of copper(II) ions from aqueous solution onto chitosan and cross-linked chitosan beads. *Reactive and Functional Polymers* **2002**, *50*, 181-190.

Parkhurst, D.L; Appelo, C.A.J. (1999) User's guide to PHREEQC (Version 2)- A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S Geological Survey Water-Resources Investigations Report 99-4259.

PRC Environmental Management, Inc., 1990, RCRA Facility Assessment, Rhone-Poulenc, Inc. Marginal Way Facility, March 19.

Randtke, S. Organic contaminant removal by coagulation and related process combinations. *J. Am. Wat. Wks. Assoc.* **1988**, *80*, 40-56.

Roadcap, G.S.; Kelly, W.R.; Berthke, C.M. Geochemistry of extremely alkaline (pH>12) ground water in slag-filled aquifers. *Groundwater* **2005**, *43*, 806-816.

Seco, A.; Gabaldón, C.; Marzal, P.; Aucejo, A. Effect of pH, cation concentration and sorbent concentration on cadmium and copper removal by a granular activated carbon. *Journal of Chemical Technology and Biotechnology* **1999**, *74*, 911-918.

Sharma, V.K.; Sohn, M. Aquatic arsenic: Toxicity, speciation, transformations, and remediation. *Environment International* **2009**, *35*, 743-759.

Singh, A.K. Chemistry of arsenic in groundwater of Ganges-Brahmaputra river basin. *Current Science* **2006**, *91*, 599-606.

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

Sneddon, R.; Garelick, H.; Valsami-Jones, E. An investigation into arsenic(V) removal from aqueous solutions by hydroxylapatite and bone-char. *Mineralogical Magazine* **2005**, *69*, 769-780.

Sperry, J.M.; Peirce, J.J.; Yu, S. Evaluating coagulating systems for use as invasive barriers in the subsurface. *Hazardous Waste and Hazardous Materials* **1996**, *13*, 499-513.

Slowey, A.J. Rate of formation and dissolution of mercury sulfide nanoparticles: The dual role of natural organic matter. *Geochim. Cosmochim. Acta* **2010**, *74*, 4693-4708.

Stachowicz, M.; Hiemstra, T.; van Riemsdijk; W.H. Arsenic-bicarbonate interaction on goethite particles. *Environ. Sci. Technol.* **2007**, *41*, 5620-5625.

Stephenson, R.J.; Duff, S.J.B. Coagulation and precipitation of a mechanical pulping effluent- I. Removal of carbon, colour, and turbidity. *Wat. Res.* **1996**, *30*, 781-792.

Stern, J.C.; Sonke, J.E.; Salters, V.J.M. A capillary electrophoresis-ICP-MS study of rare earth element complexation by humic acids. *Chemical Geology* **2007**, *246*, 170-180.

Steward Advanced Materials, Inc. SAMMS Adsorbents by Steward. http://sammsadsorbents.com/page/products/ (accessed Feb 10, 2012).

Stumm, W.; Morgan, J.J. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 3rd ed.; John Wily & Sons, Inc.: New York, 1996.

Tipping, E. Cation Binding by Humic Substances; Cambridge University Press: Cambridge, UK, 2002; p 434.

Tubić, A.; Agbaba, J.; Dalmacija, B.; Ivančev-Tumbas, I.; Dalmacija, M. Removal of arsenic and natural organic matter from groundwater using ferric and alum salts: A case study of central Banat region (Serbia). *Journal of Environmental Science and Health Part A* **2010**, *45*, 363-369.

URS, 2002, Interim Measures Performance Monitoring Plan, Quality Assurance Project Plan, prepared for Container Properties, L.L.C., September.

van Leeuwen, H.P.; Buffle, J. Chemodynamics of aquatic metal complexes: From small ligands to colloids. *Environ. Sci. Technol.* **2009**, *43*, 7175-7183.

Wan, M.W.; Petrisor, I.G.; Lai, H.T.; Kim, D.; Yen, T.F. Copper adsorption through chitosan immobilized on sand to demonstrate the feasibility for in situ soil decontamination. *Carbohydrate Polymers* **2004**, *55*, 249-254.

Yantasee, W.; Lin, Y.; Fryxell, G.E.; Busche, B.J.; Birnbaum, J.C. Removal of heavy metals from aqueous solution using novel nanoengineered sorbents: Self-assembled carbamoylphosphonic acids on mesoporous silica. *Separation Science and Technology* **2003**, *38*, 3809-3825.

7.0 Appendices

Appendix 1. Historical Physical Parameters for well MW-44

Appendix 2. Historical Conventional Analyte Concentrations for well MW-44

Appendix 3. Historical Metals Concentrations (filtered) for well MW-44

Appendix 4. Historical Metals Concentrations (non-filtered) for well MW-44

Appendix 5. Surface Water Applicable or Relevant and Appropriate Requirements (ARARs) for Aquatic Life

Appendix 6. Example PHREEQC Input for Determining Speciation

Appendix 7. Saturation Indices for Relevant Phases from pH 8 to 12 for Eh = -409

Appendix 8. Saturation Indices for Relevant Phases from pH 8 to 12 for Eh = 200

Appendix 9. Total Alkalinity Potentiometric Titration Curve

Appendix 1. Historical Physical Parameters for well MW-44

[°C, degrees Celsius; mS/cm, millisiemens per centimeter; mg/L, milligrams per liter; mV, millivolts; NTU, nephleometric turbidity units; --, not determined]

Date	Temperature (°C)	pH	Specific Conductance (mS/cm)	Dissolved Oxygen (mg/L)	Redox Potential (mV)	Turbidity (NTU)
9/28/2002	--	--	--	--	--	--
12/8/2002	--	--	--	--	--	--
9/19/2003	15.06	10.20	3.70	1.68	-437	18.20
12/16/2003	13.89	10.35	3.59	0.27	-472	108
3/18/2004	13.95	9.80	4.05	1.70	-445	11
6/17/2004	15.30	11.27	4.10	1.75	-270	58
9/16/2004	14.78	11.02	4.82	0.44	-169	0
12/17/2004	14.31	10.93[a]	4.65	1.80	-227	7
3/16/2005	14.20	10.91[a]	5.14	1.04	2[b]	13
6/14/2005	14.90	10.78	5.00	0.20	-493	58
9/22/2005	15.26	11.07	8.06	0.02	-99	6.85
12/16/2005	11.74	11.00	4.33	7.01	-291.80	14.10
3/22/2006	14.00	11.88	5.41	1.00	-428	11
6/5/2006	15.00	11.82	4.29	0.20	-489	999[b]
10/27/2006	14.90	10.88	5.30	13.4[b]	-342	48.00
12/12/2006	14.27	11.43	4.68	0.21	-378	24.10
3/18/2007	13.80	10.71	4.76	0[b]	-463	0
6/20/2007	15.40	10.97	5.43	0.08	-431	252
9/19/2007	15.70	10.92	5.65	1.25	-413	31.90
12/17/2007	14.10	12.45	5.92	0.00	-363	3.20
3/25/2008	13.90	11.26	0.680[b]	0.00	-392	82.90
6/24/2008	16.71	10.58	5.61	0.00	-837.88	4.31
9/24/2008	14.80	10.54	5.67	0.00	-409.15	3.19
9/24/2008[c]	14.80	10.54	5.67	0.00	-409.15	3.19
Max	16.71	12.45	8.06	13.4	2	999
Min	11.74	9.80	0.680	0	-837.88	0
Average	14.58	10.97	4.84	1.46	-375.32	79.9
Median	14.79	10.93	4.91	0.24	-409.15	13.6

[a] Lab pH

[b] Potential instrument malfunction

[c] Duplicate

Appendix 2. Historical Conventional Analyte Concentrations for well MW-44

[mg-N/L, milligrams as nitrogen per liter; mg-P/L, milligrams as phosphorus per liter; mg/L, milligrams per liter; mg/L as CaCO₃, milligrams per liter as calcium carbonate; <, less than; --, not determined; J-, value is estimated and result is biased low]

Date	Nitrate (mg-N/L)	Nitrite (mg-N/L)	Nitrate + Nitrite (mg-N/L)	Ammonia (mg-N/L)	Total Phosphorous (mg-P/L)	Sulfate (mg/L)	Sulfide (mg/L)	Chloride (mg/L)	Alkalinity (mg/L as CaCO₃)
9/28/2002	<0.1	<0.1	<0.1	--	--	84	0.21	81.0	1400
12/8/2002	<0.1	<0.1	<0.1	--	--	53	3.30	90.0	1000
9/19/2003	<0.05	0.1	0.11	2.30	3.90	160	0.94	88.0	1900
12/16/2003	1.400	<0.2	1.4	2.20	5.50	210	5.00	73.0	1900
3/18/2004	<0.2	<0.2	<0.2	2.20	6.10	130	9.50	86.0	2200
6/17/2004	<0.5	0.127	<0.5	2.46	21.40	143	8.80	62.8	2440
9/16/2004	<0.5	<0.5	<0.5	3.20	6.34	231	29.9	69.5	2600
12/17/2004	<1	<1	<1	4.86	6.22	143	0.9J-	76.9	2760
3/16/2005	0.306	<0.25	0.306	3.49	6.62	159	13.2	76.9	2640
6/14/2005	<0.25	<0.25	<0.25	5.15	1.84	161	14.5	74.3	2980
9/22/2005	<1	<1	<1	4.80	7.60	326	17.4	74.4	2540
12/16/2005	<0.5	<0.5	<0.5	5.42	6.78	205	20.2	92.2	2710
3/22/2006	--	--	--	--	--	--	--	--	--
6/5/2006	--	--	--	--	--	--	--	--	--
10/27/2006	--	--	--	--	--	--	--	--	--
12/12/2006	--	--	--	--	--	--	--	--	--
3/18/2007	--	--	--	--	--	--	--	--	--
6/20/2007	--	--	--	--	--	--	--	--	--
9/19/2007	--	--	--	--	--	--	--	--	--
12/17/2007	--	--	--	--	--	--	--	--	--
3/25/2008	--	--	--	--	--	--	--	--	--
6/24/2008	--	--	--	--	--	--	--	--	--
9/24/2008	--	--	--	--	--	--	--	--	--
9/24/2008[a]	--	--	--	--	--	--	--	--	--
Max	1.4	1.0	1.4	5.42	21.40	326	29.90	92.2	2980
Min	<0.05	<0.1	<0.1	2.20	1.84	53	0.21	62.8	1000
Average	0.492	0.361	0.497	3.61	7.23	167	10.32	78.8	2256
Median	0.403	0.225	0.403	3.35	6.28	160	9.15	76.9	2490

[a] Duplicate

Appendix 3. Historical Metals Concentrations (filtered) for well MW-44

[mg/L, milligrams per liter; --, not determined; <, less than; J, value is estimated ; J+, value is estimated and result is biased high]

Date	Aluminum (mg/L)	Cadmium (mg/L)	Calcium (mg/L)	Chromium (mg/L)	Copper (mg/L)	Iron (mg/L)	Magnesium (mg/L)	Manganese (mg/L)	Nickel (mg/L)	Potassium (mg/L)	Selenium (mg/L)	Silicon (mg/L)	Sodium (mg/L)
9/28/2002	--	<0.002	21.40	0.040	0.062	10.3	7.55	0.625	<0.01	9.30	<0.05	--	646
12/8/2002	--	<0.002	24.10	0.041	0.048	13.9	9.35	0.755	<0.01	8.50	<0.05	83.5	634
9/19/2003	0.86	<0.002	16.50	0.033	0.099	12.4	6.05	0.574	<0.01	9.10	<0.05	280	728
12/16/2003	0.78	<0.002	16.10	0.028	0.091	11.3	6.26	0.536	<0.01	10.00	<0.05	310	748
3/18/2004	0.86	<0.002	12.40	0.026	0.104	9.84	4.10	0.368	0.01	9.20	<0.05	406	858
6/17/2004	0.98	<0.002	12.40	0.030	0.113	9.93	3.43	0.368	0.01	10.30	<0.05	481	928
9/16/2004	1.05	<0.002	11.20	0.028	0.126	9.76	2.65	0.335	0.01	9.70	<0.05J	495	922
12/17/2004	1.05	<0.002	11.10	0.034	0.130	9.06	1.99	0.263	0.01	12.60	<0.05	552	1120
3/16/2005	1.08	<0.002	10.20	0.032	0.122	8.18	2.18	0.275	0.01	10.00	<0.05	635	1050
6/14/2005	0.91	<0.002	8.44	0.031	0.102	6.76	1.36	0.196	0.01	8.30	<0.05	668	859
9/22/2005	1.17	<0.002	10.40	0.042	0.134	7.31	0.88	0.169	0.02	8.30	<0.05	640	1200
12/16/2005	1.50	<0.002	14.50	0.057	0.165	8.53	1.53	0.215	0.02	8.60	<0.05	628	1320
3/22/2006	--	--	--	--	--	--	--	--	--	--	--	--	--
6/5/2006	--	--	--	--	--	--	--	--	--	--	--	--	--
10/27/2006	--	--	--	--	--	--	--	--	--	--	--	--	--
12/12/2006	--	--	--	--	--	--	--	--	--	--	--	--	--
3/18/2007	--	--	--	--	--	--	--	--	--	--	--	--	--
6/20/2007	--	--	--	--	--	--	--	--	--	--	--	--	--
9/19/2007	--	--	--	--	--	--	--	--	--	--	--	--	--
12/17/2007	--	--	--	--	--	--	--	--	--	--	--	--	--
3/25/2008	--	--	--	--	--	--	--	--	--	--	--	--	--
6/24/2008	--	--	--	--	--	--	--	--	--	--	--	--	--
9/24/2008	--	--	--	--	--	--	--	--	--	--	--	--	--
9/24/2008[a]	--	--	--	--	--	--	--	--	--	--	--	--	--
Max	1.50	<0.002	24.10	0.057	0.165	13.9	9.35	0.755	0.02	12.60	<0.05	668	1320
Min	0.78	<0.002	8.44	0.026	0.048	6.76	0.88	0.169	<0.01	8.30	<0.05	83.5	634
Average	1.02	<0.002	14.06	0.035	0.108	9.77	3.94	0.390	0.01	9.49	<0.05	471	918
Median	1.02	<0.002	12.40	0.033	0.109	9.80	3.04	0.352	0.01	9.25	<0.05	495	891

[a] Duplicate

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[mg/L, milligrams per liter; --, not determined; <, less than; J, value is estimated ; J+, value is estimated and result is biased high]

Date	Vanadium (mg/L)	Zinc (mg/L)	Arsenic (mg/L)	Lead (mg/L)	Mercury (mg/L)	Thallium (mg/L)
9/28/2002	0.286	<0.006	0.004	0.006	<0.0001	<0.001
12/8/2002	0.291	0.007	0.001	0.002	<0.0001	<0.001
9/19/2003	0.275	<0.006	0.006	0.007	<0.0001	<0.001
12/16/2003	0.259	<0.006	0.002	0.006	<0.0001	<0.001
3/18/2004	0.261	0.008	0.007	0.009	<0.0001	<0.001
6/17/2004	0.294	0.008	0.002	0.008	<0.0001	<0.001
9/16/2004	0.295	0.010	0.003	0.010	<0.0001	0.002
12/17/2004	0.358	0.013	0.011	0.015	<0.0001	<0.001
3/16/2005	0.348	0.009	0.002	0.010	<0.0001	0.003J+
6/14/2005	0.310	0.008	0.002	0.006	<0.0001	<0.001
9/22/2005	0.424	0.012J+	0.005	0.010	<0.0001	<0.001
12/16/2005	0.555	0.012	0.014	0.014	<0.0001	<0.001
3/22/2006	--	--	--	--	--	--
6/5/2006	--	--	--	--	--	--
10/27/2006	--	--	--	--	--	--
12/12/2006	--	--	--	--	--	--
3/18/2007	--	--	--	--	--	--
6/20/2007	--	--	--	--	--	--
9/19/2007	--	--	--	--	--	--
12/17/2007	--	--	--	--	--	--
3/25/2008	--	--	--	--	--	--
6/24/2008	--	--	--	--	--	--
9/24/2008	--	--	--	--	--	--
9/24/2008[a]	--	--	--	--	--	--
Max	0.555	0.013	0.014	0.015	<0.0001	0.003
Min	0.259	<0.006	0.001	0.002	<0.0001	<0.001
Average	0.330	0.009	0.005	0.009	<0.0001	0.001
Median	0.295	0.008	0.004	0.009	<0.0001	0.001

[a] Duplicate

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Appendix 4. Historical Metals Concentrations (non-filtered) for well MW-44

[mg/L, milligrams per liter; --, not determined; <, less than; J-, value is estimated and result is biased low; J, value is estimated]

Date	Aluminum (mg/L)	Cadmium (mg/L)	Chromium (mg/L)	Copper (mg/L)	Nickel (mg/L)	Selenium (mg/L)	Silicon (mg/L)	Vanadium (mg/L)	Zinc (mg/L)	Arsenic (mg/L)	Lead (mg/L)	Mercury (mg/L)	Thallium (mg/L)
9/28/2002	--	<0.002	0.040	0.075	<0.01	<0.05	121	0.284	0.008	0.005	0.01	<0.0001	<0.001
12/8/2002	--	<0.002	0.033	0.032	<0.01	<0.05	--	0.222	0.006	0.002	0.00	<0.0001	<0.001
9/19/2003	1.02	<0.002	0.037	0.121	<0.01	<0.05	--	0.311	0.025	0.005	0.01	0.00	<0.002
12/16/2003	0.97	<0.002	0.029	0.108	<0.01	<0.05	--	0.274	0.012	<0.001	0.01	<0.0001	<0.001
3/18/2004	1.36	<0.002	0.033	0.158	0.01	<0.05	--	0.308	0.021	0.005	0.01	<0.0001	<0.001
6/17/2004	1.30	<0.002	0.033	0.148	0.01	<0.05	--	0.311	0.012	0.006	0.01	<0.0001	<0.001
9/16/2004	1.30	<0.002	0.033	0.147	0.01	<0.05	--	0.330	0.016	<0.002	0.01	<0.0001	<0.002
12/17/2004	1.38	<0.002	0.036	0.170	0.01	<0.05	--	0.360	0.018	0.020	0.02	<0.0001	<0.001
3/16/2005	1.15	<0.002	0.029	0.124	0.01	<0.05	--	0.311	0.010	0.004	0.01	<0.0001	<0.001
6/14/2005	1.21	<0.002	0.033	0.131	0.01	<0.05	--	0.333	0.010	0.006	0.01	<0.0001	<0.001
9/22/2005	1.62	<0.002	0.049	0.189	0.02	<0.05	--	0.474	0.015	0.010	0.01	<0.0001	<0.001
12/16/2005	1.62	<0.002	0.053	0.185	0.02	<0.05	--	0.481	0.018	0.009	0.02	<0.0001	<0.001
3/22/2006	1.74	<0.002	0.060	0.192J	0.02	<0.05J	--	0.554	0.013	0.016	0.02	<0.0001	<0.001
6/5/2006	1.70	<0.002	0.057	0.164	0.02	<0.05	--	0.566	0.014	0.017	0.02	0.00	<0.001
10/27/2006	1.88	<0.002	0.068	0.207	0.02	<0.05	--	0.587	0.011	0.029	0.01	<0.0001	<0.001
12/12/2006	1.66J-	<0.002	0.058J-	0.173J-	0.02J-	<0.05	--	0.531J-	0.016J-	0.009J-	0.01J-	<0.0001	<0.001
3/18/2007	1.19	<0.002	0.047	0.115	0.02	<0.05	--	0.441	0.010	0.017	0.015J	0.00	<0.002
6/20/2007	0.94	<0.002	0.033	0.087	0.02	<0.05	--	0.416	0.010	0.002	0.01	<0.0001	<0.001
9/19/2007	0.90	<0.002	0.023	0.027	0.01	<0.05	--	0.356	<0.010	0.004	0.01	<0.0001	<0.001
12/17/2007	1.04	<0.002	0.045	0.124	0.02	<0.05	--	0.455	<0.010	0.015	0.02	<0.0004	<0.001
3/25/2008	0.90	<0.002	0.045	0.122	0.02	<0.05	--	0.395	<0.010	0.002	0.01	0.00011	<0.001
6/24/2008	1.02	<0.002	0.048	0.146	0.02	<0.05	--	0.416	<0.010	0.026	0.01	<0.002	<0.001
9/24/2008	1.12	<0.002	0.061	0.174	0.02	<0.05	--	0.501	<0.010	0.012	0.02	<0.0001	<0.001
9/24/2008[a]	1.13	<0.002	0.064	0.174	0.02	<0.05	--	0.498	<0.010	0.010	0.02	0.0001	<0.001
Max	1.88	<0.002	0.068	0.207	0.02	<0.05	121	0.587	0.025	0.029	0.02	<0.002	<0.002
Min	0.90	<0.002	0.023	0.027	0.01	<0.05	121	0.222	0.006	<0.001	0.00	<0.0001	<0.001
Average	1.28	<0.002	0.044	0.137	0.02	<0.05	121	0.405	0.013	0.010	0.01	0.0002	<0.001
Median	1.20	<0.002	0.043	0.147	0.02	<0.05	121	0.406	0.011	0.008	0.01	<0.0001	<0.001

[a] Duplicate

Appendix 5. Surface Water Applicable or Relevant and Appropriate Requirements (ARARs) for Aquatic Life

[WAC, Washington Administrative Code; CFR, Code of Federal Regulations; μg/L, micrograms per liter; --, not researched or no data]

ARAR	Freshwater						Marine					
	Acute			Chronic			Acute			Chronic		
Metal	Ch. 173-201A WAC (μg/L)	Clean Water Act §304 (μg/L)	National Toxics Rule - 40 CFR 131 (μg/L)	Ch. 173-201A WAC (μg/L)	Clean Water Act §304 (μg/L)	National Toxics Rule, 40 CFR 131 (μg/L)	Ch. 173-201A WAC (μg/L)	Clean Water Act §304 (μg/L)	National Toxics Rule, 40 CFR 131 (μg/L)	Ch. 173-201A WAC (μg/L)	Clean Water Act §304 (μg/L)	National Toxics Rule, 40 CFR 131 (μg/L)
Aluminum	--	750	--	--	87	--	--	--	--	--	--	--
Arsenic	360	340	360	190	150	190	69	69	69	36	36	36
Cadmium	0.82	2	3.9	0.37	0.25	1	42.00	40.00	42.00	9.3	8.8	9.3
Copper	4.61	13	17	3.47	9	11	4.8	4.8	2.4	3.1	3.1	2.4
Lead	13.88	65	65	0.54	2.5	2.5	210	210	210	8.1	8.1	8.1
Mercury	2.10	1.40	2.10	0.01	0.77	0.01	1.8	1.8	2.1	0.025	0.94	0.025
Nickel	--	--	--	--	--	--	--	--	--	--	--	--
Selenium	20	--	20	5	5	5	290	290	290	71	71	71
Thallium	--	--	--	--	--	--	--	--	--	--	--	--
Vanadium	--	--	--	--	--	--	--	--	--	--	--	--
Zinc	35.36	120	110	32.29	120	100	90	90	90	81	81	81

Appendix 6. Example PHREEQC Input for Determining Speciation

DATABASE llnl.dat
Title Rhone-Poulenc Speciation
Solution 1 Average Groundwater Parameters

```
        units           mg/L
        pH        12
        density         1.000
        temp            14.57
        pe        -7.16
        O(0)      0.24

        Al        1.0068
        Cd        0.002
        Ca        14.06167
        Cr        0.04146
        Cu        0.11243
        Fe        9.7725
        Mg        3.9442
        Mn        0.38992
        Ni        0.01528
        K         9.49167
        Se        0.05
        Si        470.77
        Na        917.75
        V         0.38997
        Zn        0.00825
        As        0.00694
        Pb        0.01022
        Hg        0.00019
        Tl        0.00117

        N(5)      0.492
        N(-3)     3.608
        N(3)      0.3606
        Cl        78.75
        P         7.23
        S(6)      167
        S(-2)     10.32
        Alkalinity  2256
```

End

Appendix 7. Saturation Indices for Relevant Phases from pH 8 to 12 for Eh = -409

Chemical Formula	Phase	8	8.5	9	9.5	10	10.5	11	11.5	12
As	As	-57.37	-57.41	-57.51	-57.74	-58.12	-58.62	-59.28	-60.63	-62.89
As2O3	Arsenolite	-13.15	-13.23	-13.44	-13.9	-14.66	-15.65	-16.97	-19.67	-24.19
As2O3	Claudetite	-13.22	-13.3	-13.51	-13.97	-14.73	-15.72	-17.04	-19.74	-24.26
As2O5	As2O5	-58.14	-56.22	-54.43	-52.9	-51.65	-50.64	-49.96	-50.66	-53.18
As2S3	Orpiment	-64.12	-64.8	-65.62	-66.68	-68.04	-69.64	-71.56	-74.86	-79.98
As4O6	As4O6(cubi)	-26.18	-26.33	-26.76	-27.68	-29.19	-31.18	-33.81	-39.21	-48.25
As4O6	As4O6(mono)	-25.96	-26.12	-26.55	-27.47	-28.97	-30.97	-33.59	-39	-48.04
Ca5(OH)(PO4)3	Hydroxylapatite	2.16	3.87	5.13	5.97	6.76	7.65	8.54	9.37	10.05
CaCO3	Aragonite	0.49	0.91	1.22	1.39	1.45	1.45	1.42	1.37	1.33
CaCO3	Calcite	0.64	1.05	1.36	1.53	1.6	1.6	1.57	1.51	1.48
CaMg(CO3)2	Dolomite	2.08	2.94	3.61	4.01	4.15	4.14	4.05	3.91	3.81
CaMg(CO3)2	Dolomite-dis	0.47	1.33	2	2.39	2.54	2.52	2.43	2.29	2.2
CaMg(CO3)2	Dolomite-ord	2.09	2.95	3.62	4.02	4.16	4.15	4.06	3.92	3.82
Cu	Cu	-29.96	-28.96	-27.96	-26.96	-25.96	-24.96	-23.96	-22.97	-22.06
Cu2CO3(OH)2	Malachite	-15.17	-13.69	-12.24	-10.86	-9.61	-8.48	-7.44	-6.45	-5.69
Cu2O	Cuprite	6.24	7.24	8.24	9.24	10.23	11.23	12.23	13.21	14.02
Cu2S	Chalcocite	2.66	3.46	4.26	5.06	5.85	6.65	7.45	8.23	8.84
Cu3(AsO4)2	Lammerite	-56.31	-51.39	-46.6	-42.06	-37.82	-33.82	-30.14	-27.86	-27.67
Cu3(CO3)2(OH)2	Azurite	-27.8	-25.84	-23.94	-22.18	-20.67	-19.42	-18.34	-17.36	-16.74
Cu3(PO4)2	Cu3(PO4)2	-26.93	-25.91	-24.94	-24.02	-23.18	-22.5	-22	-21.62	-21.83
Cu3(PO4)2:3H2O	Cu3(PO4)2:3H2O	-28.68	-27.66	-26.69	-25.77	-24.93	-24.25	-23.75	-23.37	-23.58
Cu3(SO4)(OH)4	Antlerite	-26.85	-24.85	-22.85	-20.86	-18.87	-16.88	-14.88	-12.91	-11.19
Cu3Se2	Umangite	42.09	43.09	44.09	45.08	46.07	47.07	48.06	49.04	49.75
Cu4(SO4)(OH)6	Brochantite	-34.24	-31.24	-28.24	-25.25	-22.26	-19.27	-16.28	-13.31	-10.69
Cu4Cl2(OH)6	Atacamite	-35.22	-32.22	-29.23	-26.23	-23.24	-20.25	-17.26	-14.29	-11.67
Cu5FeS4	Bornite	-24.94	-21.93	-19.02	-16.15	-13.21	-10.18	-7.24	-5.4	-4.58
CuCl	Nantokite	-1.63	-1.63	-1.63	-1.63	-1.63	-1.64	-1.64	-1.65	-1.74
CuCl2	CuCl2	-25.16	-25.16	-25.16	-25.17	-25.17	-25.18	-25.18	-25.19	-25.28
CuCr2O4	CuCr2O4	4.43	5.95	7.04	7.68	7.97	8.08	8.11	8.12	8.03

Formula	Name									
CuFe2O4	Ferrite-Cu	-14.5	-10.87	-7.45	-4.09	-0.59	3.1	6.6	7.95	8.04
CuFeO2	Delafossite	6.79	8.6	10.31	11.99	13.74	15.59	17.33	18.01	18
CuFeS2	Chalcopyrite	-30.63	-29.22	-27.91	-26.63	-25.28	-23.84	-22.5	-22.22	-22.62
CuO	Tenorite	-7.72	-6.72	-5.72	-4.72	-3.72	-2.72	-1.72	-0.73	0.17
CuS	Covellite	-13.7	-12.9	-12.11	-11.31	-10.51	-9.71	-8.92	-8.12	-7.42
CuSe	Klockmannite	13.52	14.02	14.52	15.02	15.52	16.01	16.51	17	17.41
CuSe2	Krutaite	49.73	49.73	49.73	49.72	49.72	49.71	49.71	49.7	49.61
CuSeO3	CuSeO3	-54.78	-51.28	-47.78	-44.28	-40.79	-37.29	-33.79	-30.3	-26.89
CuSeO3:2H2O	Clinochalcomenite	-55.86	-52.36	-48.86	-45.36	-41.86	-38.36	-34.87	-31.37	-27.97
CuSiH4O5	Chrysocolla	-7.99	-7.01	-6.09	-5.25	-4.53	-3.91	-3.37	-2.88	-2.5
CuSiO2(OH)2	Dioptase	-7.98	-7	-6.08	-5.25	-4.52	-3.9	-3.36	-2.87	-2.49
CuSO4	Chalcocyanite	-22.17	-22.17	-22.17	-22.17	-22.18	-22.18	-22.19	-22.2	-22.29
CuSO4:5H2O	Chalcanthite	-16.14	-16.14	-16.14	-16.14	-16.15	-16.16	-16.16	-16.17	-16.26
Fe	Fe	-48.1	-47.28	-46.58	-45.89	-45.14	-44.3	-43.55	-43.87	-44.77
Fe(OH)2	Fe(OH)2	-3.78	-2.97	-2.26	-1.58	-0.82	0.02	0.77	0.45	-0.46
Fe(OH)3	Fe(OH)3	-7.78	-6.47	-5.26	-4.08	-2.83	-1.48	-0.23	-0.05	-0.46
Fe.9470	Wustite	-4.21	-3.38	-2.66	-1.96	-1.19	-0.34	0.42	0.17	-0.64
Fe2(SO4)3	Fe2(SO4)3	-65.29	-65.66	-66.24	-66.88	-67.4	-67.72	-68.24	-70.88	-74.68
Fe2Al2SiO5(OH)4	Chamosite-7A	6.59	7.9	8.25	8.45	8.68	8.98	9.02	6.88	3.54
Fe2Fe2SiO5(OH)4	Cronstedtite-7A	-1.61	2.62	6.38	9.95	13.68	17.68	21.21	20.44	17.29
Fe2O3	Hematite	-4.11	-1.48	0.94	3.3	5.81	8.5	10.99	11.35	10.54
Fe2SiO4	Fayalite	-0.69	0.91	2.26	3.46	4.69	6	7.03	5.9	3.56
Fe3(PO4)2:8H2O	Vivianite	-3.3	-2.83	-2.73	-2.76	-2.67	-2.45	-2.7	-6.26	-11.89
Fe3O4	Magnetite	-4.29	-0.84	2.28	5.33	8.59	12.12	15.37	15.41	13.69
Fe3Si2O5(OH)4	Greenalite	4.31	6.71	8.69	10.41	12.11	13.89	15.22	13.26	9.49
Fe3Si4O10(OH)2	Minnesotaite	9.24	11.59	13.42	14.8	15.96	16.98	17.38	14.44	9.61
Fe5AlAlSi3O10(OH)8	Daphnite-14A	14.22	17.92	20.26	22.16	24.1	26.19	27.54	23.46	16.34
Fe5AlAlSi3O10(OH)8	Daphnite-7A	10.75	14.45	16.78	18.69	20.63	22.71	24.07	19.99	12.87
FeAl2O4	Hercynite	2.05	2.57	2.29	1.97	1.72	1.56	1.3	-0.01	-1.92
FeAsS	Arsenopyrite	-29.4	-30.32	-31.42	-32.67	-34	-35.35	-36.96	-40.33	-45.2
FeCa2Al2(OH)(SiO4)3	Epidote-ord	3.36	6.18	7.89	9.16	10.19	11.14	11.86	11.45	10.48
FeCl2	Lawrencite	-20.36	-20.54	-20.83	-21.15	-21.41	-21.56	-21.82	-23.14	-25.04
FeCl3	Molysite	-48.26	-48.45	-48.74	-49.06	-49.32	-49.48	-49.73	-51.05	-52.96

Formula	Name									
FeCO3	Siderite	1.27	1.56	1.73	1.79	1.8	1.77	1.56	0.24	-1.71
FeCr2O4	Chromite	15.88	17.21	18.01	18.34	18.38	18.34	18.12	16.81	14.91
FeO	FeO	-3.48	-2.66	-1.95	-1.27	-0.52	0.33	1.07	0.76	-0.15
FeOOH	Goethite	-2.53	-1.22	-0.01	1.18	2.43	3.77	5.02	5.2	4.8
FePO4:2H2O	Strengite	-10.55	-10.22	-10.02	-9.88	-9.71	-9.52	-9.52	-10.64	-12.5
FeS	Pyrrhotite	-23.14	-22.53	-22.02	-21.54	-20.99	-20.34	-19.8	-20.31	-21.42
FeS	Troilite	-23.03	-22.42	-21.91	-21.43	-20.88	-20.23	-19.69	-20.21	-21.31
FeS2	Pyrite	-34.39	-34.17	-34.06	-33.98	-33.84	-33.59	-33.45	-34.37	-35.87
FeSe2	Ferroselite	20.93	21.24	21.45	21.63	21.88	22.22	22.46	21.64	20.24
FeSiO3	Ferrosilite	0.84	1.63	2.27	2.78	3.26	3.73	4.02	3.2	1.77
FeSO4	FeSO4	-11.5	-11.68	-11.97	-12.29	-12.55	-12.71	-12.96	-14.28	-16.19
FeSO4:7H2O	Melanterite	-5.97	-6.15	-6.44	-6.76	-7.02	-7.18	-7.43	-8.75	-10.66
FeV2O4	FeV2O4	-263.41	-261.59	-259.98	-261.36	-264.6	-267.77	-271.03	-275.35	-280.27
Pb	Pb	-40.57	-40.19	-39.89	-39.56	-39.05	-38.31	-37.52	-37.34	-37.73
Pb(H2PO4)2	Pb(H2PO4)2	-24.53	-26.13	-27.85	-29.6	-31.25	-32.82	-34.53	-36.96	-40.26
Pb2(CO3)Cl2	Phosgenite	-9.34	-10.1	-11.04	-12	-12.73	-13.13	-13.51	-15.16	-17.97
Pb2(SO4)O	Lanarkite	-7.16	-7.4	-7.8	-8.14	-8.12	-7.65	-7.08	-7.72	-9.49
Pb2Cl2CO3	Pb2Cl2CO3	-9.7	-10.46	-11.4	-12.36	-13.09	-13.49	-13.87	-15.52	-18.33
Pb2Cl5NH4	Pb2Cl5NH4	-26.92	-28.18	-29.63	-31.12	-32.39	-33.31	-34.2	-36.34	-39.6
Pb2Cu(PO4)(OH)3:3H2O	Tsumebite	-10.66	-9.89	-9.29	-8.67	-7.73	-6.41	-5.08	-5.04	-6.36
Pb2SiO4	Pb2SiO4	-9.01	-8.28	-7.74	-7.25	-6.5	-5.4	-4.29	-4.43	-5.73
Pb3(CO3)2(OH)2	Hydrocerussite	-3.33	-3.23	-3.42	-3.67	-3.62	-3.15	-2.7	-4.17	-7.42
Pb3(PO4)2	Pb3(PO4)2	-2.77	-3.61	-4.72	-5.81	-6.44	-6.53	-6.67	-8.74	-12.81
Pb3O4	Minium	-55.84	-53.71	-51.79	-49.8	-47.27	-44.05	-40.69	-39.16	-39.31
Pb3SO6	Pb3SO6	-12.78	-12.64	-12.73	-12.74	-12.21	-11	-9.64	-10.11	-12.26
Pb4Cl2(OH)6	Pb4Cl2(OH)6	-15.51	-14.99	-14.78	-14.46	-13.42	-11.46	-9.32	-9.61	-12.15
Pb4O(PO4)2	Pb4O(PO4)2	-4.36	-4.82	-5.63	-6.38	-6.5	-5.85	-5.2	-7.1	-11.55
Pb4SO7	Pb4SO7	-18.46	-17.94	-17.73	-17.41	-16.37	-14.42	-12.27	-12.57	-15.1
Pb5(OH)(PO4)3	Pyromorphite-OH	-4.94	-6.01	-7.53	-9	-9.68	-9.45	-9.26	-12.28	-18.58
Pb5(PO4)3Cl	Pyromorphite	5.95	4.38	2.36	0.39	-0.8	-1.07	-1.38	-4.9	-11.7
PbAl3(PO4)2(OH)5:H2O	Plumbogummite	7.28	5.23	2.02	-1.23	-4.38	-7.46	-10.67	-14.6	-19.39
PbCl2	Cotunnite	-10.64	-11.26	-11.96	-12.63	-13.12	-13.39	-13.6	-14.43	-15.81
PbClOH	Paralaurionite	-5.07	-5.19	-5.38	-5.56	-5.55	-5.31	-5.02	-5.35	-6.23

PbCO3	Cerussite	-0.33	-0.46	-0.71	-1	-1.23	-1.36	-1.53	-2.36	-3.79
PbCO3.PbO	PbCO3.PbO	-7.85	-7.61	-7.55	-7.51	-7.23	-6.62	-6	-6.65	-8.47
PbCrO4	Crocoite	-43.34	-41.21	-39.35	-37.7	-36.05	-34.25	-32.45	-31.27	-30.65
PbFe3(PO4)(SO4)(OH)6	Corkite	-28.45	-26.11	-24.2	-22.36	-20.18	-17.57	-15.29	-16.87	-20.93
PbHPO4	PbHPO4	1.45	0.84	0.13	-0.58	-1.15	-1.56	-2.03	-3.15	-4.99
PbO	Litharge	-7.24	-6.86	-6.56	-6.23	-5.72	-4.98	-4.19	-4.01	-4.4
PbO	Massicot	-7.43	-7.05	-6.75	-6.42	-5.91	-5.17	-4.38	-4.21	-4.59
PbO2	Plattnerite	-43.25	-41.87	-40.56	-39.23	-37.72	-35.98	-34.2	-33.02	-32.4
PbS	Galena	-16.33	-16.15	-16.05	-15.92	-15.61	-15.07	-14.49	-14.51	-15.09
PbSe	Clausthalite	13.61	13.49	13.3	13.13	13.13	13.37	13.66	13.34	12.45
PbSeO4	PbSeO4	-78.29	-74.41	-70.61	-66.78	-62.77	-58.53	-54.25	-50.57	-47.45
PbSiO3	Alamosite	-2.04	-1.69	-1.46	-1.29	-1.06	-0.7	-0.37	-0.69	-1.6
PbSO4	Anglesite	-5.35	-5.97	-6.67	-7.34	-7.84	-8.1	-8.32	-9.14	-10.53
PbSO4(NH3)2	PbSO4(NH3)2	-21.63	-21.29	-21.1	-21.06	-21.1	-21.16	-21.29	-22.09	-23.47
PbSO4(NH3)4	PbSO4(NH3)4	-35.65	-34.35	-33.28	-32.52	-32.12	-31.96	-32.02	-32.79	-34.16
V	V	-98.7	-98.2	-97.75	-98.78	-100.78	-102.79	-104.79	-106.79	-108.79
V2O3	Karelianite	6.47	7.47	8.38	6.31	2.32	-1.69	-5.7	-9.7	-13.71
V2O4	V2O4	-2.29	-0.3	1.61	0.55	-2.45	-5.46	-8.47	-11.47	-14.48
V2O5	Shcherbinaite	-25.22	-22.22	-19.32	-19.38	-21.37	-23.39	-25.39	-27.4	-29.4
V3O5	V3O5	6.12	8.12	9.98	7.39	1.9	-3.62	-9.14	-14.64	-20.15
V4O7	V4O7	3.84	6.84	9.65	6.53	-0.46	-7.49	-14.5	-21.51	-28.52
(VO)3(PO4)2	(VO)3(PO4)2	-78.45	-77.43	-76.6	-80.27	-86.92	-93.76	-100.76	-107.87	-115.29

Appendix 8. Saturation Indices for Relevant Phases from pH 8 to 12 for Eh = 200

Chemical Formula	Phase	pH 8	8.5	9	9.5	10	10.5	11	11.5	12
As	As	-67.39	-69.58	-71.38	-73.39	-75.41	-77.47	-79.59	-81.84	-84.21
As2O3	Arsenolite	-33.19	-37.57	-41.17	-45.19	-49.24	-53.35	-57.6	-62.09	-66.84
As2O3	Claudetite	-33.26	-37.64	-41.24	-45.26	-49.31	-53.41	-57.66	-62.16	-66.9
As2O5	As2O5	-35.53	-37.71	-39.51	-41.53	-43.58	-45.69	-47.93	-50.43	-53.17
As2S3	Orpiment	-84.16	-89.2	-93.35	-97.97	-102.62	-107.33	-112.19	-117.28	-122.62
As4O6	As4O6(mono)	-66.04	-75.01	-82.21	-90.25	-98.35	-106.57	-115.06	-124.06	-133.54
As4O6	As4O6(cubi)	-66.25	-74.8	-82	-90.04	-98.14	-106.35	-114.85	-123.84	-133.33
Ca5(OH)(PO4)3	Hydroxylapatite	2.18	4.05	5.17	6.02	6.83	7.76	8.64	9.38	10.05
CaCO3	Aragonite	0.49	1.09	1.36	1.53	1.59	1.59	1.55	1.51	1.48
CaCO3	Calcite	0.64	0.94	1.22	1.39	1.45	1.44	1.41	1.37	1.33
CaMg(CO3)2	Dolomite-ord	2.09	3.02	3.61	4	4.14	4.12	4.01	3.9	3.81
CaMg(CO3)2	Dolomite	2.08	1.4	2	2.39	2.53	2.5	2.39	2.29	2.2
CaMg(CO3)2	Dolomite-dis	0.47	3.03	3.62	4.01	4.15	4.13	4.02	3.91	3.82
Cu	Cu	-23.42	-23.12	-22.93	-22.66	-22.19	-21.62	-21.32	-21.28	-21.4
Cu2CO3(OH)2	Malachite	-2.1	-2.07	-2.19	-2.26	-2.07	-1.8	-2.16	-3.07	-4.36
Cu2O	Cuprite	-2.02	-2.52	-3.04	-3.49	-3.56	-3.42	-3.81	-4.73	-5.97
Cu2S	Chalcocite	-5.59	-6.32	-7.02	-7.67	-7.94	-8	-8.6	-9.71	-11.15
Cu3(AsO4)2	Lammerite	-14.09	-15.37	-16.61	-17.8	-18.45	-18.84	-20.19	-22.56	-25.65
Cu3(CO3)2(OH)2	Azurite	-8.2	-8.44	-8.87	-9.28	-9.37	-9.4	-10.41	-12.28	-14.73
Cu3(PO4)2	Cu3(PO4)2	-7.32	-8.59	-9.84	-11.08	-11.83	-12.39	-13.96	-16.54	-19.82
Cu3(PO4)2:3H2O	Cu3(PO4)2:3H2O	-9.07	-10.34	-11.59	-12.83	-13.58	-14.14	-15.71	-18.29	-21.57
Cu3(SO4)(OH)4	Antlerite	-7.25	-7.45	-7.78	-7.96	-7.57	-6.86	-6.96	-7.83	-9.19
Cu3Se2	Umangite	-7.16	-16.09	-23.61	-31.79	-39.41	-46.71	-54.89	-64.28	-75.1
Cu4(SO4)(OH)6	Brochantite	-8.1	-8.01	-8.15	-8.05	-7.2	-5.91	-5.71	-6.54	-8.01
Cu4Cl2(OH)6	Atacamite	-9.08	-8.99	-9.13	-9.03	-8.18	-6.89	-6.69	-7.52	-8.99
Cu5FeS4	Bornite	-35.81	-37.92	-40.01	-42.12	-43.41	-44.28	-46.55	-50.13	-54.52
CuCl	Nantokite	-5.76	-6.56	-7.27	-7.99	-8.53	-8.96	-9.66	-10.62	-11.74
CuCl2	CuCl2	-18.62	-19.43	-20.14	-20.87	-21.41	-21.84	-22.54	-23.5	-24.61
CuCr2O4	CuCr2O4	10.96	11.81	12.06	11.03	6.82	2.38	-2.33	-7.29	-12.4

Formula	Name									
CuFe2O4	Ferrite-Cu	11.57	11.94	11.99	11.91	11.75	11.48	10.83	9.89	8.78
CuFeO2	Delafossite	12.43	12.21	11.88	11.48	11.13	10.78	10.11	9.16	8.05
CuFeS2	Chalcopyrite	-24.99	-25.65	-26.34	-27.14	-27.89	-28.65	-29.72	-31.07	-32.58
CuO	Tenorite	-1.18	-0.88	-0.7	-0.42	0.05	0.62	0.92	0.96	0.84
CuS	Covellite	-7.17	-7.09	-7.08	-7.01	-6.74	-6.37	-6.27	-6.43	-6.75
CuSe	Klockmannite	-3.7	-7.77	-11.17	-14.9	-18.44	-21.88	-25.62	-29.84	-34.69
CuSe2	Krutaite	8.74	0.31	-6.69	-14.42	-21.97	-29.42	-37.2	-45.67	-55.26
CuSeO3	CuSeO3	-8.03	-8.8	-9.5	-10.23	-10.77	-11.21	-11.95	-13.16	-15.01
CuSeO3:2H2O	Clinochalcomenite	-9.1	-9.87	-10.57	-11.3	-11.84	-12.28	-13.02	-14.23	-16.09
CuSiH4O5	Chrysocolla	-1.45	-1.18	-1.06	-0.96	-0.76	-0.57	-0.73	-1.18	-1.83
CuSiO2(OH)2	Dioptase	-1.44	-1.17	-1.05	-0.95	-0.75	-0.56	-0.72	-1.17	-1.82
CuSO4	Chalcocyanite	-15.63	-16.43	-17.14	-17.87	-18.41	-18.84	-19.55	-20.5	-21.62
CuSO4:5H2O	Chalcanthite	-9.61	-10.41	-11.12	-11.84	-12.39	-12.82	-13.52	-14.48	-15.59
Fe	Fe	-48.99	-49.51	-50.03	-50.7	-51.52	-52.44	-53.41	-54.41	-55.4
Fe(OH)2	Fe(OH)2	-4.68	-5.19	-5.71	-6.39	-7.2	-8.12	-9.1	-10.09	-11.08
Fe(OH)3	Fe(OH)3	1.98	2.02	1.95	1.77	1.46	1.04	0.57	0.07	-0.42
Fe.947O	Wustite	-3.93	-4.36	-4.8	-5.39	-6.11	-6.93	-7.79	-8.68	-9.57
Fe2(SO4)3	Fe2(SO4)3	-45.75	-48.98	-51.82	-55.18	-58.83	-62.69	-66.64	-70.62	-74.61
Fe2Al2SiO5(OH)4	Chamosite-7A	4.81	3.35	1.35	-1.17	-4.08	-7.31	-10.71	-14.19	-17.71
Fe2Fe2SiO5(OH)4	Cronstedtite-7A	16.13	15.14	13.9	12.03	9.49	6.43	3.08	-0.38	-3.89
Fe2O3	Hematite	15.43	15.49	15.36	15.01	14.37	13.53	12.59	11.6	10.61
Fe2SiO4	Fayalite	-2.48	-3.54	-4.65	-6.17	-8.07	-10.3	-12.7	-15.18	-17.7
Fe3(PO4)2:8H2O	Vivianite	-5.97	-9.69	-13.06	-17.16	-21.75	-26.79	-32.18	-37.86	-43.77
Fe3O4	Magnetite	14.35	13.91	13.25	12.22	10.78	9.01	7.09	5.12	3.13
Fe3Si2O5(OH)4	Greenalite	1.63	0.03	-1.66	-4.03	-7.02	-10.55	-14.38	-18.35	-22.39
Fe3Si4O10(OH)2	Minnesotaite	6.56	4.89	3.07	0.37	-3.18	-7.46	-12.21	-17.17	-22.27
Fe5AlAlSi3O10(OH)8	Daphnite-14A	9.75	6.68	3	-1.89	-7.8	-14.55	-21.78	-29.23	-36.79
Fe5AlAlSi3O10(OH)8	Daphnite-7A	6.28	3.21	-0.47	-5.36	-11.27	-18.02	-25.26	-32.7	-40.26
FeAl2O4	Hercynite	1.16	0.25	-1.17	-2.84	-4.66	-6.59	-8.56	-10.55	-12.55
FeAsS	Arsenopyrite	-72.3	-76.88	-80.72	-85.11	-89.66	-94.33	-99.13	-104.07	-109.14
FeCa2Al2(OH)(SiO4)3	Epidote-ord	13.13	14.73	15.1	15	14.47	13.65	12.63	11.57	10.52
FeCl2	Lawrencite	-21.25	-22.87	-24.28	-25.96	-27.78	-29.71	-31.68	-33.67	-35.67
FeCl3	Molysite	-38.49	-40.11	-41.53	-43.21	-45.03	-46.96	-48.93	-50.93	-52.92

Formula	Mineral									
FeCO3	Siderite	0.37	-0.71	-1.73	-3.02	-4.58	-6.38	-8.31	-10.3	-12.34
FeCr2O4	Chromite	14.98	15.02	14.56	12.58	7.09	1.15	-4.83	-10.82	-16.81
FeO	FeO	-4.37	-4.89	-5.4	-6.08	-6.9	-7.82	-8.79	-9.78	-10.78
FeOOH	Goethite	7.24	7.27	7.21	7.03	6.71	6.29	5.82	5.33	4.83
FePO4:2H2O	Strengite	-0.77	-1.82	-2.8	-4.01	-5.39	-6.95	-8.67	-10.51	-12.47
FeS	Troilite	-23.93	-24.77	-25.47	-26.35	-27.37	-28.49	-29.66	-30.85	-32.05
FeS	Pyrrhotite	-24.04	-24.66	-25.36	-26.24	-27.26	-28.38	-29.55	-30.74	-31.94
FeS2	Pyrite	-35.28	-36.46	-37.51	-38.79	-40.22	-41.74	-43.31	-44.91	-46.5
FeSe2	Ferroselite	-16.83	-25.53	-32.78	-40.96	-49.29	-57.74	-66.29	-75.29	-85.26
FeSiO3	Ferrosilite	-0.05	-0.6	-1.18	-2.03	-3.12	-4.42	-5.85	-7.34	-8.86
FeSO4	FeSO4	-12.39	-14.01	-15.42	-17.11	-18.93	-20.85	-22.83	-24.82	-26.81
FeSO4:7H2O	Melanterite	-6.86	-8.48	-9.89	-11.57	-13.4	-15.32	-17.3	-19.29	-21.28
FeV2O4	FeV2O4	-295.13	-300.01	-304.12	-308.8	-313.63	-318.57	-323.55	-328.54	-333.54
Pb	Pb	-40.57	-40.16	-39.89	-39.56	-39.05	-38.31	-37.52	-37.34	-37.73
Pb(H2PO4)2	Pb(H2PO4)2	-24.52	-26.28	-27.83	-29.56	-31.19	-32.73	-34.42	-36.95	-40.26
Pb2(CO3)Cl2	Phosgenite	-9.34	-10.19	-11.04	-12.01	-12.73	-13.13	-13.51	-15.16	-17.97
Pb2(SO4)O	Lanarkite	-7.16	-7.44	-7.8	-8.14	-8.12	-7.65	-7.08	-7.72	-9.49
Pb2Cl2CO3	Pb2Cl2CO3	-9.7	-10.55	-11.4	-12.37	-13.09	-13.49	-13.87	-15.52	-18.33
Pb2Cl5NH4	Pb2Cl5NH4	-26.92	-28.32	-29.63	-31.12	-32.39	-33.31	-34.2	-36.34	-39.6
Pb2Cu(PO4)(OH)3:3H2O	Tsumebite	-4.12	-4.08	-4.26	-4.36	-3.94	-3.02	-2.39	-3.34	-5.69
Pb2SiO4	Pb2SiO4	-9.01	-8.22	-7.74	-7.25	-6.5	-5.4	-4.29	-4.43	-5.73
Pb3(CO3)2(OH)2	Hydrocerussite	-3.33	-3.24	-3.42	-3.67	-3.62	-3.15	-2.7	-4.17	-7.42
Pb3(PO4)2	Pb3(PO4)2	-2.76	-3.69	-4.7	-5.78	-6.38	-6.43	-6.55	-8.73	-12.81
Pb3O4	Minium	-34.52	-32.18	-30.47	-28.48	-25.95	-22.72	-19.37	-17.83	-17.99
Pb3SO6	Pb3SO6	-12.78	-12.64	-12.73	-12.74	-12.21	-11	-9.64	-10.11	-12.26
Pb4Cl2(OH)6	Pb4Cl2(OH)6	-15.51	-14.96	-14.78	-14.46	-13.42	-11.46	-9.32	-9.61	-12.15
Pb4O(PO4)2	Pb4O(PO4)2	-4.34	-4.87	-5.6	-6.35	-6.45	-5.76	-5.09	-7.09	-11.55
Pb4SO7	Pb4SO7	-18.46	-17.91	-17.73	-17.41	-16.37	-14.41	-12.27	-12.57	-15.1
Pb5(OH)(PO4)3	Pyromorphite-OH	-4.93	-6.12	-7.5	-8.95	-9.6	-9.31	-9.1	-12.27	-18.58
Pb5(PO4)3Cl	Pyromorphite	5.96	4.22	2.39	0.44	-0.71	-0.92	-1.21	-4.89	-11.7
PbAl3(PO4)2(OH)5:H2O	Plumbogummite	7.29	4.94	2.05	-1.19	-4.33	-7.36	-10.56	-14.59	-19.39
PbCl2	Cotunnite	-10.64	-11.33	-11.96	-12.63	-13.12	-13.39	-13.6	-14.43	-15.81
PbClOH	Paralaurionite	-5.07	-5.21	-5.39	-5.56	-5.55	-5.31	-5.02	-5.35	-6.23

PbCO3	Cerussite	-0.33	-0.48	-0.71	-1	-1.23	-1.36	-1.53	-2.36	-3.79
PbCO3.PbO	PbCO3.PbO	-7.85	-7.59	-7.55	-7.51	-7.23	-6.62	-6	-6.65	-8.47
PbCrO4	Crocoite	-11.35	-9.02	-7.37	-6.19	-6.52	-6.78	-7	-7.82	-9.21
PbFe3(PO4)(SO4)(OH)6	Corkite	0.86	-0.81	-2.55	-4.79	-7.3	-9.97	-12.84	-16.49	-20.82
PbHPO4	PbHPO4	1.45	0.78	0.14	-0.56	-1.12	-1.52	-1.97	-3.14	-4.99
PbO	Litharge	-7.24	-6.83	-6.56	-6.23	-5.72	-4.98	-4.19	-4.01	-4.4
PbO	Massicot	-7.43	-7.02	-6.75	-6.42	-5.91	-5.17	-4.38	-4.21	-4.59
PbO2	Plattnerite	-21.92	-20.41	-19.24	-17.91	-16.4	-14.66	-12.87	-11.69	-11.08
PbS	Galena	-16.33	-16.14	-16.05	-15.92	-15.61	-15.07	-14.49	-14.51	-15.09
PbSe	Clausthalite	-10.15	-14.1	-17.42	-21.1	-24.59	-27.86	-31.12	-35.2	-40.32
PbSeO4	PbSeO4	-16.75	-16.3	-16.02	-15.7	-15.19	-14.46	-13.72	-13.79	-14.91
PbSiO3	Alamosite	-2.04	-1.66	-1.46	-1.29	-1.06	-0.69	-0.37	-0.69	-1.6
PbSO4	Anglesite	-5.35	-6.04	-6.67	-7.34	-7.84	-8.1	-8.32	-9.14	-10.53
PbSO4(NH3)2	PbSO4(NH3)2	-21.63	-21.26	-21.1	-21.06	-21.1	-21.16	-21.29	-22.09	-23.47
PbSO4(NH3)4	PbSO4(NH3)4	-35.65	-34.23	-33.28	-32.52	-32.12	-31.96	-32.02	-32.79	-34.16
V	V	-114.12	-116.3	-118.09	-120.1	-122.11	-124.11	-126.12	-128.12	-130.12
V2O3	Karelianite	-24.36	-28.71	-32.31	-36.31	-40.33	-44.35	-48.35	-52.36	-56.36
V2O4	V2O4	-11.8	-15.06	-17.75	-20.76	-23.77	-26.79	-29.79	-32.8	-35.8
V2O5	Shcherbinaite	-13.4	-15.56	-17.35	-19.36	-21.37	-23.39	-25.4	-27.4	-29.4
V3O5	V3O5	-29.46	-35.44	-40.38	-45.89	-51.42	-56.94	-62.45	-67.96	-73.46
V4O7	V4O7	-36.49	-44.11	-50.39	-57.41	-64.44	-71.47	-78.48	-85.49	-92.5
(VO)3(PO4)2	(VO)3(PO4)2	-92.7	-99.75	-105.61	-112.19	-118.85	-125.65	-132.64	-139.85	-147.28

Appendix 9. Total Alkalinity Potentiometric Titration Curve