FINAL REPORT

Impacts on Groundwater Quality Following the Application of ISCO: Understanding the Cause of and Designing Mitigation for Metals Mobilization

SERDP Project ER-2132

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14. ABSTRACT

The objectives of this project were to: (1) develop a fundamental and predictive understanding of metals release as a result of three common ISCO treatments; (2) develop a mechanistic geochemical model to describe release and to design mitigation measures; (3) experimentally evaluate the fate of redox and pH perturbations and elevated metals released; (4) demonstrate efficacy of pre-, co-, or post-treatment metals mitigation measures; and (5) develop guidance for the design community to predict release, understand mechanisms, and design mitigation strategies, as well as maximize the utility of ISCO, reduce impacts to groundwater, and minimize life-cycle costs of the remedial technology.

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LIST OF ACRONYMS

AAP	Alkaline-Activated Persulfate
ANC	Acid Neutralization Capacity
CEC	Cation Exchange Capacity
CHP	Catalyzed Hydrogen Peroxide
CHP+CA	Catalyzed Hydrogen Peroxide + Citric Acid
COCs	Contaminants of Concern
DI	Deionized Water
DHA	Dissolved Humic Acid
DNAPL	Dense Non-Aqueous Phase Liquid
DOC	Dissolved Organic Carbon
DoD	Department of Defense
DOE	Department of Energy
DOM	Dissolved Organic Matter
FOM	Figure of Merit
HA	Humic Acid
HDPE	High Density Polyethylene
HFO	Hydrous Ferric Oxide
HP	Hydrogen Peroxide
HPC	Heterotrophic Plate Counts
IAP	Iron-Activated Persulfate
IAP+CA	Iron-Activated Persulfate + Citric Acid
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
ISCO	In Situ Chemical Oxidation
ITRC	Interstate Technology and Regulatory Council
LS	Liquid to Solid Ratio
MCL	Maximum Contaminant Level
MCE	Mixed Cellulose Ester (filter)
MR	Molar Ratio
NA	Not Applicable
ND	Non-Detectable
NPT	National Pipe Taper
NOD	Natural Oxidant Demand
NOM	Natural Organic Matter
ORP	Oxygen Reduction Potential
PM	Permanganate
POM	Particulate Organic Matter
RPMs	Remedial Project Managers
rpm	revolutions per minute
ROD	Residual Oxidant Demand
ROM	Residual Oxidant Measurement
SERDP	Strategic Environmental Research and Development Program
SI	Saturation Index
SOM	Soil Organic Matter
TOC	Total Organic Carbon
TOD	Total Oxidant Demand
TT	Treatment Technology
UNH	University of New Hampshire
USEPA	United States Environmental Protection Agency
USDA	United States Department of Agriculture

KEYWORDS

In situ chemical oxidation, metals mobilization, catalyzed hydrogen peroxide, alkaline-activated persulfate, iron-catalyzed persulfate, permanganate, mitigation of metals release, return to baseline conditions, column studies

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ABSTRACT

Objectives. In situ chemical oxidation (ISCO) has proven effective in reducing potential Department of Defense (DoD) liability and health risks by oxidation of organic contaminants in situ. ISCO has been applied widely at DoD and non-DoD sites, and while it is effective for organic contaminant removal, it has also resulted in significant release of metals and metalloids in groundwater. The release of metals and metalloids is not fully understood nor is it predictable; elevated levels of metals in groundwater have recently prohibited a number of site closures and represent significant uncertainty in the remedial selection process. For ISCO to be a cost-effective and predictable remediation method, the unintended reactions that release metals and metalloids need to be understood and mitigation methods need to be developed and demonstrated.

The objectives of this project were to develop a fundamental and predictive understanding of metals release as a result of three common ISCO treatments; develop a mechanistic geochemical model to describe release and to design mitigation measures; experimentally evaluate fate of redox and pH perturbations and elevated metals released; demonstrate efficacy of pre-, co-, or post-treatment metals mitigation measures; and develop guidance for the design community to predict release, understand mechanisms, and design mitigation strategies as well as maximize the utility of ISCO, reduce impacts to groundwater, and minimize life-cycle costs of the remedial technology.

Technical Approach. A database of historical ISCO actions was developed using 89 field implementation case studies. Metals were monitored in 21% of the case studies (19 out of the 89 case studies). The database includes a compilation of chemistry, soils, and site data relevant to metals release. Leaching studies were conducted on 10 DoD site soils using standard protocols, and geochemical speciation modeling was conducted using LeachXS to determine controlling solid phase speciation and enable prediction of metals release issues for a site. Laboratory batch experiments were also performed to evaluate potential mitigation measures to reduce metals release and to describe and predict propagation of redox and pH fronts and metals migration. Column experiments were also used with site soils to measure migration of geochemical perturbations. A guidance document was produced to aid site managers and design engineers to predict metals release at a site, understand how and why it may occur, and design strategies to minimize or eliminate the release.

Results. An increase in metals concentration was observed in 63% of the field implementation case studies (12 out of 19 case studies) that were included in the historical ISCO applications database. Chromium (total and hexavalent), iron, manganese and arsenic were the four most frequently observed mobilized metals in these 12 sites. Results of the metal mobilization screening experiments showed that the leaching of metals depended on soil type, ISCO treatment applied, and the metal in question. Several metals were released at elevated levels in each oxidant system compared to control batches, but more metals were mobilized in the catalyzed hydrogen peroxide and persulfate systems than in the presence of permanganate. Differences in metals mobilization were also observed within the various catalyzed hydrogen peroxide and persulfate chemistries; the citric acid chelating agent contributed to metals release. In general,

dissolved metal concentrations increased with the addition of higher oxidant dose. Subsequent pH-dependent leaching studies revealed that while the release of most metals was controlled by pH, the mobilization of select metals was determined by ISCO chemistry. In the latter case, metals mobilization either increased or decreased in the presence of the oxidant. Geochemical speciation modeling revealed that secondary effects such as the formation of organic complexes and the dissolution of iron oxides and other minerals also contributed to the release of select metals.

Column studies also verified that metals release was due to contact with an ISCO regent is site-specific (aquifer specific) and metal specific. This observation reinforces the recommendation that all sites should be initially screened for the presence of metals, especially if there is knowledge of historical uses and/or suspected prior metal releases that could have a legacy in the subsurface.

Mitigation studies determined that mobilized metal concentrations, from ISCO treatment applications, consistently occurred but returned to near baseline concentrations within 90 days without any additional treatment. This indicates that mobilized metals may be a temporary phenomenon and that measures may need to be taken to monitor and help mitigate the potential for metals mobilization in the transition period immediately following application.

Testing found that citrate and acetate were effective in mitigating the mobilization of metals during the application of IAP. The addition of acetate with IAP consistently helped maintain metal concentrations close to those observed in the control reactors. The addition of acetate and citrate were similarly beneficial during the application of CHP, with slower kinetics. The addition of lactate to PM treatments was also observed to reduce the mobilization of metals. No additive intended to stimulate biotic activity was deemed successful enough to warrant addition evaluation for AAP.

The apparent trade off to mitigating the mobilization of metals in ISCO systems with electron donors such as lactate, acetate and citrate is an observed general tendency toward a decrease in treatment efficacy of the target COC. In many instances the impact was minimal and in other instances the decrease in treatment efficacy may still be acceptable to the ISCO designer and associated stakeholders.

Benefits. This project improved the understanding and knowledge of the impacts to groundwater quality following the application of ISCO technologies. The research helped identify the factors contributing to the release and fate of mobilized metals that had been documented to occur during remedial activities. In addition, modifications to ISCO technology that minimize or eliminate the degree to which metals are mobilized were designed and evaluated. This understanding and knowledge will aid site owners, design engineers, and scientists during site characterization, remedial selection, and the design and implementation of ISCO.

1.0 OBJECTIVES

The objectives of this research are: to develop a fundamental and predictive understanding of metals release as a result of three common ISCO approaches; to develop a mechanistic geochemical model to describe release and to design mitigation measures; to experimentally evaluate fate of redox and pH perturbations and elevated metals released; to demonstrate efficacy of pre-, co-, or post-treatment metals mitigation measures; and to develop a useful guidance for the design community to predict release, understand mechanisms and design mitigation strategies.

1.1 SERDP RELEVANCE

This project responds directly to the Statement of Need ERSON-11-03: "Improve our understanding of impacts to groundwater quality due to implementation of common remediation approaches (in-situ chemical oxidation)". ISCO has proven very effective in reducing potential DoD liability and health risks by oxidation of organic contaminants in-situ. ISCO has been applied widely at DoD and non-DoD sites, and while it is effective for organic contaminant removal, it has also resulted in significant release of metals and metalloids in groundwater. Metals release has been shown to occur in 50% of DoD ISCO remedial actions, resulting in inability to close sites, additional regulatory scrutiny and more costly monitoring requirements.

As the release of metals and metalloids is not fully understood nor is it predictable, methods to mitigate release either during or after treatment have not been developed. In order for ISCO to be a cost-effective, predictable and ultimately useful remediation method, the unintended reactions that release metals and metalloids need to be understood and mitigation methods need to be developed and demonstrated.

This research improves our understanding of mechanisms responsible for metals release at ISCO sites, developed predictive models based on fundamental chemistry and developed and demonstrated mitigation approaches. Results of this work will enable site remedial project managers (RPMs) to predict potential metals mobilization in ISCO applications, design appropriate mitigation measures, and limit uncertainty in the possibilities of unintended consequences and site closure time frames. This research identifies when and why site owners and design engineers need to be concerned about metals mobilization and provides approaches to mitigate metals release.

1.2 TECHNICAL OBJECTIVES

This study evaluated the release and fate of metals mobilized during the application of ISCO in an effort to better understand the post-remediation impacts on groundwater quality and assess modifications to the remedial design strategy and ISCO process chemistry that may help alleviate issues related to mobilizing metals at DoD sites. The improved understanding of the ISCO chemistry will lead to better ISCO designs by appropriately accounting for and understanding the factors resulting in the release and fate of mobilized metals.

Task specific objectives of this work are as follows:

Task 1: Pre-Experimental Evaluation

- Solicit feedback from site owners/responsible parties who have implemented ISCO and monitored post-ISCO groundwater quality (Tasks 1.1 and 1.2)
- Collect soil samples to support Tasks 2 through 4 (Task 1.3)
- Develop a database to help assess the site-specific potential for post-ISCO metals mobilization (Tasks 1.3 and 1.4)

Task 2: Evaluation of ISCO Technologies and Mobilization of Metals

- To measure metals released from 10 site soils exposed to three common in-situ chemical oxidation approaches (persulfate, permanganate, and hydrogen peroxide oxidation)
- Develop an understanding of release processes and develop a quantitative model to describe and predict release chemistry

Task 3: Evaluation of Post-ISCO Recovery/ Return to Baseline Conditions

- Understand post-remediation impact on groundwater quality and the factors influencing recovery and return to baseline conditions for a site
- Evaluate the length of time required for a site to return to baseline conditions following ISCO application
- Identify the factors governing the time required; e.g. experimentally evaluate the fate of redox and pH perturbations and elevated metals released in column experiments conducted with site soils

Task 4: Mitigating Metals Mobilization as a Result of the Application of ISCO

- Demonstrate the efficacy of pre-, co- or post-treatment metals mitigation strategies in batch experiments conducted with site soils

Task 5: Develop ISCO Metals Byproduct Reference Guide

- Develop a guidance document for the design community to predict release, understand mechanisms and design mitigation strategies; the guidance will relate site conditions to anticipated formation and fate of metals following the application of ISCO.

2.0 BACKGROUND

2.1 ENVIRONMENTAL ISSUE

ISCO has been applied at numerous DoD facilities to treat subsurface organic contamination and has evolved as a standard remedy for cost-effective remediation of contaminated soil and groundwater (Siegrist et al., 2009). ISCO involves the delivery of a chemical oxidant into contaminated soil and groundwater to destroy the organic contaminants of concern (COCs). Typical chemical oxidants used include catalyzed hydrogen peroxide, persulfate, and permanganate. While ISCO has proven very effective in treating organic COCs, the application of ISCO alters the geochemical conditions (pH, Eh) of the treatment area in the subsurface and creates a variety of oxidation products that have the potential to interact with naturally occurring metals in both soil and groundwater. The rate and extent of geochemical changes is dependent upon a number of factors including the lifetimes of the chemical oxidants, total quantity and concentration of oxidant delivered, the buffering capacity of the subsurface, and local hydrodynamics. Primary goals of this study were to identify and address the key factors contributing to metals mobilization and design a modified ISCO approach to mitigate, *a priori,* the potential for mobilization of metals.

This project responds directly to the SERDP Statement of Need "ERSON-11-03: improve our understanding of impacts to groundwater quality due to implementation of common remediation approaches (in-situ chemical oxidation)." A survey of 23 ISCO applications found elevated metals concentrations at over half of the sites (Seigrist et al., 2009), emphasizing the potential importance of this problem. Metals release at ISCO sites has resulted in inability to close sites, additional regulatory scrutiny and more costly monitoring requirements.

2.2 SUMMARY OF PRIOR RESEARCH

Application of ISCO can alter metal mobility through the following processes: reaction with natural particulate or dissolved organic matter to produce metal chelants; reaction with aquifer material to produce colloids susceptible to hydrologic transport; increases in ORP resulting in the oxidative dissolution of minerals (e.g. Cr hydroxides and metal sulfides); changes in pH conditions resulting in changes in adsorption affinity, sorbent phase stability or metal-containing mineral phase solubility; and formation of organic contaminant byproducts that act as chelants. A significant increase in the concentration of metals in groundwater following the application of ISCO has been observed, presumably from one or a combination of several of these processes. Several of these metals are regulated by the Environmental Protection Agency (US EPA).

The Interstate Technology and Regulatory Council (ITRC) identified several metals of concern that should be monitored during the application of ISCO (ITRC, 2005). Table 2.2.1 shows the range of metals and metalloids that have been observed being released in bench scale testing of ISCO for a DoD site; different ISCO technologies resulted in release of elevated element concentrations, in many cases above regulatory threshold values. There was also the release of very different types of elements (e.g. catalyzed hydrogen peroxide resulted in significant release of divalent metals and Cr). Releases like this were the motivation for this research: to understand why release occurs, how to predict and model the release, and how to control the release when necessary. This project significantly advanced the fundamental understanding of mechanisms that govern release and that will therefore govern the design of mitigation measures.

Table 2.2.1 Background: ITRC Dissolved Metal Regulatory Limits During ISCO Application[1]

Metal	**MCL or TT [2] Action Level[1] (*mg/L*)**	**Bench Scale Results for DOD Site**			
		Baseline (*mg/L*)	**Control (mg/L)**	**Persulfate (*mg/L*)**	**Catalyzed Hydrogen Peroxide (*mg/L*)**
Antimony	0.006	ND	ND	ND	ND
Arsenic	0.01	0.041	ND	1.1	ND
Barium	2	0.07	ND	ND	ND
Cadmium	0.005	ND	0.05	ND	0.08
Chromium	0.1	ND	ND	3.6	3.7
Copper	TT = 1.3	ND	0.2	0.3	3.7
Iron	-	18	ND	ND	305
Lead	TT = 0.015	ND	ND	ND	0.3
Mercury	0.002	ND	NA	NA	NA
Nickel	-	0.05	1	ND	1.5
Selenium	0.05	ND	ND	0.25	ND

Note: Highlighted values indicate exceedance of MCL or TT

[1] XDD, 2007,(http://www.epa.gov/safewater/contaminants/index.html)

ND = Not Detected; NA = Not Applicable

After ISCO application, the rate to re-establish baseline conditions is dependent upon several factors involving the nature of the oxidant (the chemical composition, concentration, and volume of the oxidant), groundwater chemistry (pH, alkalinity, redox equilibria, and presence of organic chelants or colloidal phases), physical properties of the aquifer (hydraulic conductivity, groundwater flow rates, and mineralogy). Data available from the literature support that groundwater metals concentrations in some cases can return to baseline conditions within 6 months to 12 months. However, a re-establishment to native conditions has not always resulted in these time horizons; metal concentrations can remain elevated for long periods of time. For example, a survey of 23 ISCO applications found elevated metals concentrations at over half of the sites as well as metals migration beyond the ISCO application area in a number of these cases (Seigrist et al., 2009). Mobilization of metals (especially Cr) upon ISCO application has been observed at several ISCO sites (discussed below). Oxidants, such as permanganate, are known to persist in the subsurface for greater than a year. These oxidants can produce elevated or depressed pH and ORP conditions following an ISCO application (Siegrist et al., 2009). Furthermore, Mn, in particular, has the potential to form new mineral phases (e.g. MnO_2) causing long term changes to the aquifer mineralogy and potentially the aquifer permeability (Crimi and Siegrist, 2003). Thus, the potential exists for long-term changes to the aquifer and groundwater geochemistry, resulting in the potential of increased dissolved metals and metals migration for extended periods of time following the application of ISCO. Therefore, mobilization of potentially harmful metals can be problematic from a site-closure perspective for undefined periods of time after application of ISCO as well as present a human health risk if an exposure pathway is present.

In-situ chemical oxidation was applied at two sites located at a DoD facility in Northern California. Applications consisted of hydrogen peroxide followed by iron-activated sodium persulfate at Site 1 and iron-activated persulfate at Site 2. Table 2.2.2 summarizes the status of metals at both sites before and after ISCO treatment. This example shows two typical sites, where concentrations increased one to two orders of magnitude after 6 months (short term increases were significantly higher).

Table 2.2.2 Background: Average groundwater concentrations before and after 2 ISCO treatment applications.

Metals	HP followed by IAP		IAP Only	
	Average GW Concentration Prior to Treatment	Average GW Concentration 6 mo. Following Treatment	Average GW Concentration Prior to Treatment	Average GW Concentration 6 mo. Following Treatment
Chromium	0.7 µg/L	78.2 µg/L	ND	33.8 µg/L*
Arsenic	10.8 µg/L	8.4 µg/L	9.5 µg/L	10.5 µg/L
Manganese	1.4 mg/L	9.5 mg/L	0.77 mg/L	67 mg/L
Vanadium	2 µg/L	10 µg/L	1.5 µg/L	10.5 µg/L

Note: *Increased in only 3 out of 20 wells, conc. provided is the average of those 3 detectable readings.

3.0 MATERIALS AND METHODS

3.1 PRE-EXPERIMENTAL EVALUATION

The pre-experimental evaluation was conducted to collect data and material from ISCO remedial sites and the literature. This included the development and distribution of surveys to document metals mobilization from historic and existing ISCO sites; a scouring of state and federal databases to collect additional ISCO site data; the development of a new database to categorize and evaluate the collected information from the identified sites and literature; the collection of ISCO treated soils to conduct a series of metals mobilization laboratory experiments; and a preliminary characterization of the materials collected. The methods used to conduct these evaluations are described below.

3.1.1 ISCO Site Survey

Battelle developed two sets of surveys for the pre-experimental evaluations. These included a preliminary *background* survey and a follow up *detailed* survey (provided in Appendix A). The background survey was constructed as a preliminary screening tool to identify potential in situ chemical oxidation (ISCO) sites. No specific site data was requested as part of the preliminary screening to minimize the amount of time required to complete the survey and maximize response. Brevity and broader questioning was also expected to facilitate a more rapid response rate. The follow up, detailed survey, was designed specifically based upon the responses received from the background survey for sites where metal mobilization was observed.

Information requested in the background survey included: the number of current and past ISCO sites, types of oxidants used, media and contaminants treated, and whether metals mobilization occurred. The information requested in the detailed survey was more comprehensive. It included: information about the general project background, site background characteristics, contamination nature and extent, ISCO operation and performance, and monitoring results. The site baseline characteristics section requested geologic and hydrogeologic information (e.g., soil type, groundwater velocity, and groundwater quality) while the contamination section requested impacted media (e.g., soil, groundwater) and pre-remediation concentrations. For the ISCO operation section, general operation parameters (oxidant type, volume, and injection method) for implementing ISCO were requested, and performance goals and lessons learned (unintended consequences) were requested for the ISCO performance section. To conclude the survey, the post-ISCO monitoring results (residual oxidant, contaminant levels, metals concentrations and groundwater quality) were requested.

Drafts of both the background and detailed surveys were distributed within the project team for review prior to distribution. The background survey was made available online through SurveyMonkey® (www.surveymonkey.com), an independent survey platform, as well as distributed manually/electronically to targeted audiences at the events listed below.

- First Bioremediation and Sustainable Environmental Technologies Symposium (June 2011),
- ITRC Meeting to the Integrated DNAPL Site Strategy Team (October 2011),
- Partners in Environmental Technology Technical Symposium & Workshop (December 2011),
- Ninth International Conference on Remediation of Chlorinated and Recalcitrant Compounds (May 2012),
- Second Bioremediation and Sustainable Environmental Technologies Symposium (June (2013),
- Navy co-performers requested survey responses and potential field sites through the Alternative Restoration Technology Team (ARTT) and Optimization Work Groups, and
- Colleagues at the Navy, Air Force, Army, and ITRC were requested to participate in the survey and offer potential field sites.

The response rate for the background survey was low. The project team only 13 responses to the preliminary background survey out of the 100+ distributed. Due to this insufficient response, additional methods for collecting data were pursued. Methods included a literature search for published site information (including the USEPA's Superfund on-line information to collect information on ISCO sites), state databases such as Oculus (Florida's Department of Environmental Protection) and GeoTracker (California Department of Toxic Substances Control); assistance in collecting site data was also requested from the in-progress reviewers for each agency, and by contacting site managers of known ISCO sites directly. Furthermore, the project team gained access to the Navy's database (NIRIS) allowing direct download of data after discussing the project with individual Remedial Project Managers (RPM) that utilized ISCO at their sites. Compilation of ISCO data from available survey responses, literature data, and reports gathered from direct contact with RPMs was completed. A detailed listing of the final sites included in the study is provided in Section 4.1.1.

3.1.2 ISCO Site Database

A Microsoft® Access database was developed to identify trends in existing and historical ISCO remedial sites. The database was populated with a total of 89 sites collected from the results of surveying, literature review, direct contact and other methods described in section 3.1.1. Project data was normalized to prevent any redundant data in the tables. The database tables also were joined via Relationships Manager by unique key in a relational manner. Finally, cascading deletions enabled the easy removal of unnecessary Project Info entries. The user interface for the database uses the basic Access master/detail relationship (Figure 3.1.1). Observations and trends from the development of this database are provided in Section 4.1.2.

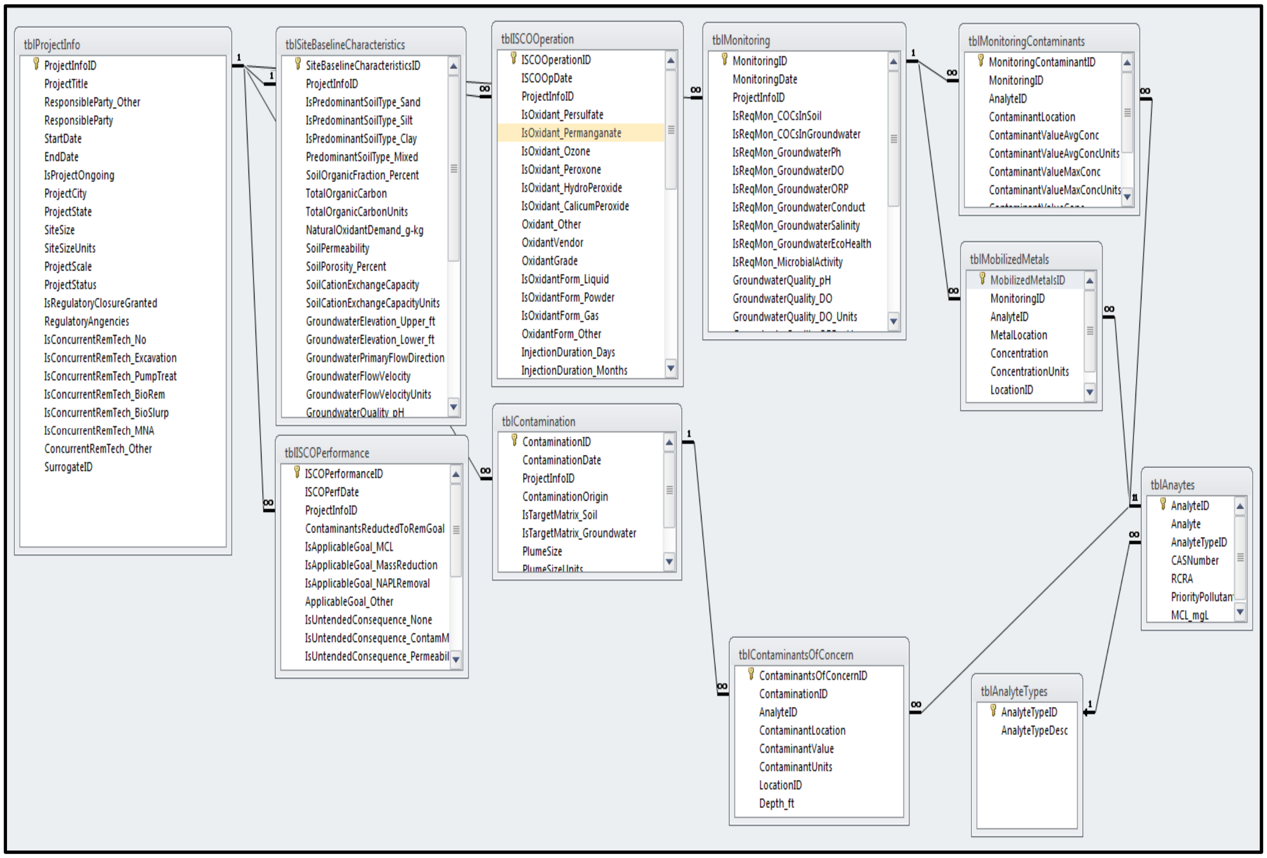


Figure 3.1.1 ISCO Site Database: Structure relationship

3.1.3 ISCO Site Material Collection

A request for ISCO site soils was extended to all parties receiving the background survey. Out of the 100+ requests, 10 sites offered to provide material to the project team for experimental evaluation. All 10 offers were accepted. In addition, an eleventh ISCO site was identified for soil collection through a connection made at the Battelle Chlorinated Conference in May 2012 (Soil #11). A summary of the received soils are listed below in Table 3.1.1. Given confidentiality concerns, all soil samples are described by general location and site owner.

Table 3.1.1 ISCO Site Material Summary

Soil #	Site Description	Site Owner	Soil Type	Total Organic Carbon (%)	Historic Metals Mobilization	Contaminated With
1	NE DOD Coastal Facility	DOD	Fine Sand	0.46	Yes: As	Petroleum; COCs: Benzene, Naphthalene
2	Navy Facility in California	Navy	Sand	0.59	unknown	Anticipated COCs: Cr(VI) and TCE
3	Navy Facility in California	Navy	Medium to Fine Sand	1.27	Yes: Cr, Cd	unknown
4	US Army Core Site in Mid Atlantic	USACE	Soil with Gravel	5.64	unknown	Anticipated COCs: Pb and Cr(VI)
5	Industrial Facility in NE	Confidential	Sand	0.65	unknown	TCE
6	Gasoline Station in NE	Confidential	Sand	0.67	unknown	Petroleum
7	Gasoline Station in NE	Confidential	Silts	0.53	unknown	Petroleum
8	Not used	USAF	Very hard clay	-	-	-
9	Navy Facility in the SE	DOD	Silty Sand	3.75	unknown	cVOCs
10	EPA Site in the S	EPA	Silty Clay	2.16	unknown	Heavy Petroleum/ Creosote; NAPL
11	Former Inductrial Facility in the SW	Confidential	Sand	1.14	unknown	unknown

All materials originated from contaminated sites where ISCO was the remedy of choice in the past, at the time of sampling, or planned for the future. Selected sites are spread across a wide array of geographic locations within the United States, and vary in soil type, organic carbon content and organic contaminants present. Metals mobilization has been observed at several of these sites. Additional sampling information for selected soils which were investigated in Tasks 3 and 4 are provided below.

Soil #1. Soil #1 was collected in acetate liners using direct push methods from approximately 8 to 14 ft bgs. Following collection, the soil material was placed into 5-gallon buckets and sealed.

Soil #2. On November 8-9, 2011, Battelle collected a total of four 5-gallon buckets of soil #2. A hollow-stem auger drill rig was used to penetrate down to the contaminated zone (15-20 feet bgs). At the contaminated interval, soil was removed from the auger flights and placed in 5-gallon buckets for shipment.

Soil #4. Soil 4 was collected using a track excavator. Soil was removed to a depth of 6 feet above the water table at areas with historically the highest metal and organic contamination. At final excavation depth, soil samples were collected using a stainless steel trowel and stored into 5-gallon buckets.

Groundwater. Groundwater was used to determine the oxidant demand of select soils and aquifer systems. It was also used in column testing to determine ISCO treatment effects to synthesized aquifer system for select soils. The source of the groundwater was from a well located on Battelle property that was installed in 1958 to a depth of 90 feet. An on-demand tap is located in the Environmental Restoration laboratory. Groundwater was further characterized as described in Section 3.1.4.

3.1.4 Material Characterization

Soils and groundwater were characterized prior to analysis using the following methods.

Soil Characterization

Soil characterization evaluations included acid neutralization capacity, cation exchange capacity, volatile organic carbon and synthetic preceipitation leaching procedure. The methods and laboratories used to determine these characteristics are provided below in Table 3.1.2.

Table 3.1.2 Preliminary Evaluation: Soil characterization methods

Parameters	Method	Minimum Sample Volume	Laboratory
Moisture Content	-	-	UNH
Synthetic Precipitation Leaching Procedure (SPLP)	EPA 1312	100 g	DHL Analytical, Round Rock, TX
Volatile Organic Compounds	SW8260C	4.0 oz	
Cation Exchange Capacity(CEC)	USDA Method 19	300 g Dried Soil	Energy Laboratories, Billings, MT
Total Acid Neutralizing Capacity (ANC)	USDA Method 23C		

Groundwater Characterization

Groundwater was characterized for pH, oxygen reduction potential, chloride, total iron, sulfate, sulfide, nitrate and total alkalinity. Methods used are described in Table 3.1.3.

Table 3.1.3 Preliminary Evaluation: Groundwater characterization methods

Parameters	Method
Temperature	-
pH	Electrode
ORP	Electrode
Chloride	Hach 8113
Total Iron	Hach 8008
Sulfate	Hach 8051
Sulfide	Hach 8131
Nitrate	Hach 8039
Total Alkalinity	Hach 10239

3.2 ISCO TREATMENT EFFECTS ON METALS MOBILIZATION

The ISCO treatment and metals mobilization portion of the study was designed to evaluate the response of ISCO site soils a range of ISCO treatments. This included a broad screening study to evaluate metals release and changes in geochemical properties of the soils due to the exposure of various oxidant/activator combinations at varying dosages; a detailed investigation to isolate the geochemical mechanism driving metals release from the soils; and geochemical modeling to further investigate the speciation and solid phase mineralogy controlling mobilization. The methods and materials used to conduct these evaluations are described below.

3.2.1 Initial Screening Evaluation

The initial screening evaluation was designed to measure the metals release and changes in geochemical properties for a large number of site soils exposed to a wide range of ISCO treatments. Specifically, the environmental response of 10 ISCO site soils exposed to 6 different ISCO treatment solutions were measured in 48 hour batch experiments. Following the initial screening, the effect of oxidant dosage was measured for a reduced number of soils and ISCO treatments. At the conclusion of the exposure period, ORP, pH and aqueous metal concentrations were measured.

Materials

Soils. All ten ISCO site soils received from outreach efforts were evaluated in the preliminary screening evaluation (Table 3.1.1). A more in depth description of each material is provided in Section 3.1.3. Briefly, all material originated from contaminated sites where ISCO was the remedy of choice in the past, at the time of sampling, or planned for the future. Soils originate from sites in various geographic locations of the United States, and vary in soil type, organic carbon content and organic contaminants present. Metals mobilization has been observed at several of these sites. Soils were evaluated at their natural moisture content and were not altered prior to evaluation.

Chemicals. *Oxidants*: hydrogen peroxide, potassium permanganate, sodium persulfate; *Activators:* citric acid, ferrous sulfate hepahydrate, sodium hydroxide; *Leaching Chemicals*: DI water, nitric acid, sodium hydroxide. A more in depth description of chemical properties and suppliers is included in Appendix B.

Experimental Design

Initial Screening. Ten soils were exposed to 6 ISCO treatment solutions and a control treatment (DI water) as described by Table 3.2.1 in 48 hour batch reactor leaching study. ISCO treatments included: potassium permanganate, iron-catalyzed sodium persulfate (with and without citric acid chelating agent), alkaline-activated persulfate, and iron-catalyzed hydrogen peroxide (with and without citric acid chelating agent). ISCO treatment solution concentrations were designed to mimic the upper range of oxidant reagent concentrations typically used in field applications. Catalyst and chelant concentrations were designed around typical field application ratios.

Table 3.2.1 Initial Screening: ISCO Treatment Details

ISCO Treatment	Oxidant	Activator		Oxidant Dose	Solution Conc.		Molar Ratio of Oxidant to Activator
		Catalyst	*Chelant*	*g/kg*	*g/L*	*mM*	*Oxidant:Catalyst:Citric Acid*
Control	-	-	-	*NA*	*NA*	*NA*	*NA*
PM	Potassium Permanganate	-	-	6.8	0.68	4.3	*NA*
IAP	Sodium Persulfate	Fe(II)	-	60.2	60.2	25.3	100:1
IAP+CA		Fe(II)	Citric Acid				100:1:2
AAP		NaOH	-				pH>11[a]
CHP	Hydrogen Peroxide	Fe(II)	-	300	30.0 (3%)	882	100:1
CHP+CA		Fe(II)	Citric Acid				100:1:2

[a] Base neutralization capacity of the soil +2:1= NaOH:Na2S2O8 molar ratio; soils tested include #1-#7 & #9-#11

Batch solutions were prepared by adding 5g (equivalent dry weight) of soil into 50 mL of the specified ISCO extraction solution (Table 3.2.1) resulting in a final liquid to solid (LS) ratio of 10:1 (ml/g). Because soils were used in their original wet form, any natural moisture content was included in the calculated final 50 mL final liquid volume. Components were added to 60 ml glass VOA vails and placed on an orbital shaker, at 125 rpm, for 48 hours. At the conclusion of the exposure period the pH and ORP of the samples were measured. Leachate was separated from the solids by filtration using a 0.45 µm mixed cellulose ester (MCE) membrane filter. All leachate was preserved using high purity nitric acid (to obtain pH<2) for metals analysis. Samples containing residual permanganate (as observed by the color of the solution) were quenched using L-ascorbic acid following the method described by Johnson et al. (2012).

Oxidant Dose Evaluation. An oxidant dose study was conducted following the initial screening to determine the impact of reagent dose on metals release. Soil #1 was exposed to 9 oxidation treatments ranging in oxidant exposure from 0.5 g/kg (mass oxidant/mass soil) to 500 g/kg as described by Table 2.3. All testing and analysis was conducted as described earlier in the preliminary screening evaluations.

Table 3.2.2 Initial Screening: Oxidant dosage evaluation

ISCO Treatment	Oxidant	Oxidant Dose *g oxidant/ kg soil*	Activator	Molar Ratio of Oxidant to Activator *Oxidant:Catalyst:Citric Acid*
Control	-	0	-	NA
PM	Potassium Permanganate	0.5, 0.9, 1.4, 6.8, 14, 15.8	-	NA
IAP	Sodium Persulfate	1.9, 7.6, 19, 60.2, 76.2	Fe(II)	100 : 1
		19, 76.2	Fe(II)	2.5 : 1
IAP+CA		1.9, 7.6, 19, 60.2, 76.2	Fe(II):CA	100 : 1 : 2
		19, 76.2	Fe(II):CA	12.5 : 5 : 1
AAP		1.9, 7.6, 19, 60.2, 76.2	NaOH	pH > 11[a]
HP	Hydrogen Peroxide	50, 500	-	NA
CHP		50, 150, 300, 500	Fe(II)	100 : 1
CHP+CA		50, 150, 300	Fe(II):CA	100 : 1 : 2

Analysis

Dissolved metal concentrations were determined using a Varian Vista AX Inductively Coupled Plasma Atomic Emission Spectrophotometer (ICP-AES) in accordance with EPA method 6010C. Samples were analyzed for 22 metals including: aluminum, antimony, arsenic, barium, beryllium, calcium, cadmium, cobalt, chromium, copper, iron, potassium, magnesium, manganese, sodium, silver, nickel, lead, selenium, thallium, vanadium, and zinc. pH and ORP were measured via electrometric measurements on an Accument XL50 meter. Probes were calibrated prior to measurement.

3.2.2 Detailed Evaluation

The detailed evaluation investigated a reduced number of soils and ISCO treatments in greater depth. Components included pH dependent leaching and hydrous ferric oxide (HFO) and aluminum oxide (AlO) extraction procedures. Specifically, 3 ISCO site soils were exposed to 4 different ISCO treatment solutions at controlled pH values ranging between 3 and 11 in a 48 hour batch experiment. At the conclusion of the exposure period ORP, pH, alkalinity, DOC and aqueous cationic and anionic concentrations were measured. HFO and AlO extractions were conducted on the same 3 soils.

Materials

Soils. Three soils, #1, #2, and #4, were evaluated in the detailed study. These soils were selected due to detectable metals release observed in the preliminary screening experiments (Section 3.2.1). A more in depth description of each material is provided in Section 3.1.3. Soils were evaluated at their natural moisture content and were not altered prior to evaluation.

Chemicals. *Oxidants*: hydrogen peroxide, potassium permanganate, sodium persulfate; *Activators:* citric acid, ferrous sulfate hepahydrate, sodium hydroxide; *Leaching Chemicals*: DI Water, nitric acid, sodium hydroxide. A more in depth description of chemical properties and suppliers is included in Appendix B.

Experimental Design

Three soils were exposed to 4 ISCO treatment solutions and a control treatment (DI water) as described by Table 3.2.3 at controlled pH ranges in 96 hour batch reactor leaching studies. ISCO treatments included: potassium permanganate, chelated iron-catalyzed sodium persulfate, alkaline-activated persulfate, and chelated iron-catalyzed hydrogen peroxide. ISCO treatment solutions were applied at the same concentration as in the screening study and were designed to mimic the upper range of oxidant reagent concentrations typically used in field applications. Catalyst and chelant ratios were designated around typical field application treatment ratios (oxidant: catalyst: chelant). The pH of the extract solution was controlled by acid/base addition at the end a 48hour. Five specific pH values were targeted: 3, 5, 7, 9 and 11.

Table 3.2.3 pH Dependent Leaching Study: ISCO Treatment Details

ISCO Treatment	Oxidant	Activator		Oxidant Dose	Solution Conc.		Molar Ratio of Oxidant to Activator
		Catalyst	*Chelant*	*g/kg*	*g/L*	*mM*	*Oxidant: Catalyst: Citric Acid*
Control	-	-	-	*NA*	*NA*	*NA*	*NA*
PM	Potassium Permanganate	-	-	6.8	0.68	4.3	*NA*
IAP+CA	Sodium Persulfate	Fe(II)	Citric Acid	60.2	6.02	25.3	100 : 1 : 2
AAP		NaOH	-				pH>11[a]
CHP+CA	Hydrogen Peroxide	Fe(II)	Citric Acid	34	3.4	100	100 : 1 : 2

Batch solutions were prepared by adding 20g (equivalent dry weight) of soil into 200 mL of the specified ISCO treatment extraction solution (Table 3.2.1) resulting in a final liquid to solid (LS) ratio of 10:1 (ml/g). Because soils were used in their original wet form, any natural moisture content was included in the final 200 mL final liquid volume. The batch study was conducted in two segments. First, soils were mixed with the ISCO treatment solution for 48 hours. This was conducted in an acid washed 250ml capped Erlenmeyer beaker on an orbital shaker (125 rpm). At the conclusion of the oxidant exposure period, the pH of leachate (treatment solution) was measured and adjusted to the specified pH and mixed for an additional 48 hours in an acid washed 250ml HDPE bottle on end over end standard TCLP mixer. At the conclusion of both exposure periods the pH and ORP of the samples were measured. The leachate was then separated from the solids by filtration using a 0.45 µm mixed cellulose ester (MCE) membrane filter and separated into four 50ml centrifuge vials for four different analysis: metals analysis, alkalinity, dissolved organic carbon, and major ion analysis. Samples designated for metals analysis were preserved using high purity nitric acid (to obtain pH<2); sample designated for alkalinity measurements were kept at 4°C and analyzed within 24 hrs; DOC and major ions samples were frozen and sent for analysis to a commercial laboratory if dissolved metal concentrations indicated that factors other than the pH caused metals release.

Samples containing residual permanganate (as observed by the color of the solution) were quenched using L-ascorbic acid following the method described by Johnson et al. (2012). All experiments were performed in duplicates.

Analysis
Dissolved metal concentrations were determined following the procedures described for Task 2.1. Alkalinity was determined by titration following Method 2320 in "Standard Methods for the Examination of Water and Wastewater". Samples for DOC and major ions analyses were sent to an outside laboratory.

3.2.3 Geochemical Modeling of Metals Release

Analytical results from the previously described laboratory studies were entered into the LeachXS database and modeling environment (ECN, The Netherlands), which is a leaching expert system developed for release of elements from a wide variety of wastes (over 600 materials and wastes are currently in the database). LeachXS provides the ability to conduct geochemical speciation and chemical reaction/transport modeling using the ORCHESTRA modeling environment. It permits the modeling of mineral dissolution/precipitation using an extended MINTEQ database, sorption on Fe- and Al-oxides, and DOC- and particulate organic matter interaction using the NICA-Donnan model. It has been used in the past to model the release of elements from wastes with a variety of redox potentials. LeachXS has been used to model the release of elements from a wide variety of materials in the past (Suer et al., 2009; Carter et al., 2008; Hyks et al., 2007), and was well suited for the task of determining controlling solid phases and elucidating the mechanisms of metals release in ISCO applications.

Model Input Parameters
Metals release results together with major ion and DOC concentrations obtained in the pH-dependent experiments were used as input parameters in the modeling study (Appendix B). The measured ORP values were also added to the model. The results of two ISCO treatments (alkaline-activated persulfate and catalyzed hydrogen peroxide) and the control (i.e., soil with no oxidant added) for Soil #1 were used as inputs in the modeling exercise. Table 2.7 summarizes the data and model assumptions used for the soil control simulations. Model inputs for the alkaline-activated persulfate and the catalyzed hydrogen peroxide simulations have been slightly modified to achieve a better model fit to the data. The dissolved humic acid (DHA) fraction in the catalyzed hydrogen peroxide simulation was kept at 100% below pH 7 and it was reduced to 10% above pH 7. In the alkaline-activated persulfate model, the DHA fraction was reduced to 20% in the pH range of 5 to 10, and the total amount of iron- and aluminum (hydr)oxides was reduced to 30% of the amount used in the control simulation (i.e. from 0.0006218 kg/kg to 0.00018654 kg/kg). In future work, determining the pH-dependent DHA fractions and the iron- and aluminum (hydr)oxide content in oxidant treated samples experimentally would increase confidence in the model simulations.

Table 3.2.4 Geotechnical Modeling: Data and model assumptions

Parameter	Value/Description	Source
Non-detect input data	Detection Limit/2	-
Mineral selection for materials	Included all minerals that were identified with the LeachXS default setting of saturation index (SI) range = ±0.15 and figure of merit (FOM) = 1	LeachXS database
Liquid to solid (LS) ratio	10 : 1 → corrected for actual average LS ratio	Determined by LeachXS
pH+pe	15 → oxidizing environment	Same assumption as in Dijkstra et al., 2004
Hydrous ferric oxide content	0.0000681 kg/kg (n = 3)	Obtained in Preliminary Characterization (Section 3.1.4); based on "ascorbic extraction" of Soil #1
Aluminum (hydr)oxide content	0.0005537 kg/kg (n = 3)	Obtained in Preliminary Characterization (Section 3.1.4); based on "oxalate extraction" of Soil #1
Clay content	0 kg/kg	Soil #1 is fine sand
Solid humic acid (HA)	0.002116 kg/kg (n = 4) → assumed 46% of soil total organic carbon (TOC) was HA; assumption based on Dijkstra et al., 2004	Soil TOC was determined in Preliminary Characterization (Section 3.1.4); (see Table 2.1)
Dissolved HA (DHA) fraction	Assumed that 100% of DOC was HA, i.e. DHA fraction = 1	Based on Dijkstra et al., 2004

Defining a Speciation Session

Prior to evaluating the pH-dependent leaching of elements, it is necessary to define speciation sessions for a material in LeachXS. A speciation session for all three materials has been defined. Relevant minerals were selected based on their saturation indices (SI); the default setting of ±0.15 was used.

Predicting Solid Phases that Control Metal Leaching

Leaching evaluation cases were defined based on the speciation sessions of each material. The "single material" – "pH-dependent (equilibrium) case" leaching prediction method was used in LeachXS to simulate metals release from the three materials evaluated in the modeling study. Once a reasonable fit has been achieved, solid phases controlling metals release under the different ISCO conditions were identified.

Adding New Materials into the LeachXS Database

Three new materials were added to the LeachXS database representing the two ISCO treatment conditions, catalyzed hydrogen peroxide and alkaline-activated persulfate, and the control for Soil #1. These conditions have been selected based on metals release results observed in Tasks 2.1 and 2.2; conditions that exhibited elevated metal levels post ISCO application compared to the control/background have been chosen for further study.

3.3 EVALUATION OF POST-ISCO RECOVERY/RETURN TO BASELINE CONDITIONS

Empirical data has shown that metals within the target area eventually return to near baseline conditions after ISCO application. However, the extent to which metals will migrate within the radius of influence of the applied ISCO reagents; beyond the radius of influence; as well as the geochemical properties of the aquifer matrix that govern the reversion to baseline conditions (pre-ISCO) are unknown. The goal of this study was to understand the post-remediation impact on groundwater quality and the factors influencing recovery and return to baseline conditions. Understanding the different geochemical factors which govern the spatial and temporal effects of ISCO application will aid in predicting the potential for migration of metals outside of the target area. This included determining the oxidant demand of three ISCO site soils, conducting batch reactor tests to evaluate the effects of oxidant dosage per mass of soil and a column test to evaluate the geochemistry and mobility of metals as ISCO treated site soils return to baseline conditions. The methods and materials used to conduct these evaluations are described below.

3.3.1 Oxidant Demand of Selected ISCO Site Soils for Column Studies

The oxidant demand is an important property of an oxidant/soil interaction and is critical to characterizing the area of influence of an ISCO treatment. This study was conducted to measure the natural oxidant demand (NOD) and total oxidant demand (TOD) of 3 ISCO site soils for 4 ISCO treatments.

Materials

Soils. Three soils, #1, #2, and #4, were selected due to detectable metals release observed in the preliminary screening experiments (Section 3.2.1). All soils were dried prior to evaluation. Additionally soil #4 was sieved to remove any particles larger than 2mm. Additional characterization and collection data for these materials is provided in Section 3.1.4.

Groundwater. The groundwater used in the NOD and TOD evaluations was collected from a 90 ft. deep maintained by Battelle. Additional groundwater attributes and collection procedures are provided in Section 3.1.4.

Chemicals. *Oxidants:* hydrogen peroxide, potassium permanganate, sodium persulfate; *Activators:* citric acid, ferrous sulfate hepahydrate, sodium hydroxide; *ROD Testing*: ammonium hydroxide, ammonium molybdate tetrahydrate, ammonium nitrate, potassium iodide, sodium bicarbonate, sodium thiosulfate, starch, sulfuric acid. *Other*: DI water, nitric acid. A more in depth description of chemical properties and suppliers is included in Appendix C.

Experimental Design

Natural and total oxidant demand was determined by independently measuring the residual oxidant demand (ROD) of 3 oxidant/soil/water configurations for 3 soils. The first configuration contained only oxidant in DI water (O), to measure the ROD of only the oxidant over time. The second configuration contained oxidant, activation agents (both catalysts and chelants) in DI water (OA) to determine the oxidant demand of all components of the ISCO treatments applied to the aquifer system. The third contained soil, oxidant and activation agents in groundwater (OAS) and measured the ROD of all components of the ISCO treated aquifer system, natural and applied. By independently analyzing the ROD of the three configurations, the NOD and TOD values of the ISCO treated aquifer system can be calculated (described later in further detail). Soil/oxidant/activator/water configurations are provided in Table 3.3.1. ISCO treatments included: potassium permanganate, chelated iron-catalyzed sodium persulfate, alkaline-activated persulfate, and chelated iron-catalyzed hydrogen peroxide. All oxidants were applied at the same concentration between the different configurations (H_2O_2 = 65g/L; $Na_2S_2O_8$ = 45 g/L; and $KMnO_4$= 20 g/L). Activating agent concentrations were based upon molar ratios of oxidant to activator, which were also consistent between the batch configurations (Fe(II) = 100:1; Citric Acid = 100:2; NaOH = 2:1). ISCO treatment solution concentrations were designed to mimic the upper range of oxidant reagent concentrations typically used in field applications. Catalyst and chelant concentrations were designated around typical field application ratios.

Table 3.3.1 Oxidant Demand Testing: Experimental Design

Config	**Sample ID**	**Batch Reactor Components (*concentrations*)**			
		Soil	**Water**	**Oxidant**	**Activators**
Oxidant Only	O(H_2O_2)	No Soil	DI Water	H_2O_2 *(65 g/L)*	-
	O($Na_2S_2O_8$)			$Na_2S_2O_8$ *(45 g/L)*	-
	O($KMnO_4$)			$KMnO_4$ *(20 g/L)*	-
Treatment (Oxidant & Activator)	OA(CHP)	No Soil	DI Water	H_2O_2 *(65 g/L)*	FeII *(1.07g/L)* Citric Acid *(7.34g/L)*
	OA(IAP+CA)			$Na_2S_2O_8$ *(45 g/L)*	FeII *(0.11g/L)* Citric Acid *(0.73g/L)*
	OA(AAP)			$Na_2S_2O_8$ *(45 g/L)*	NaOH *(16g/L)*
Total (Treatment & Natural System)	OAS(CHP)	Soil #1, #2 or #4	Groundwater	H_2O_2 *(65 g/L)*	FeII *(1.07g/L)* Citric Acid *(7.34g/L)*
	OAS(IAP+CA)			$Na_2S_2O_8$ *(45 g/L)*	FeII *(0.11g/L)* Citric Acid *(0.73g/L)*
	OAS(AAP)			$Na_2S_2O_8$ *(45 g/L)*	NaOH *(16g/L)*
	OAS(PM)			$KMnO_4$ *(20 g/L)*	-

Note: Activator concentration based upon oxidant:activator molar ratios

All treatments were prepared in sacrificial 40ml VOA vials batch reactors. Duplicate reactors were prepared for each treatment (10 treatments) for each sampling period (4 sampling times). *Oxidant* and *treatment* configurations (O and OA) did not contain soil and were prepared by diluting stock solutions of the designated oxidant and activating agents in DI. A total of 42 ml was applied to each vial to minimize headspace. *Total* configuration batches (OAS) did contain soil and were loaded at a LS ratio of 0.3 (pore volume ratio = 2:1) containing 59g of soil and 20 ml of solution which also minimized head space. Reactors were mixed on and end-over-end rotary mixer. Reactors containing sodium sulfate and potassium permanganate were sampled at 24hrs, 7d and 14d. Because hydrogen peroxide is consumed much faster, those reactors were sampled at 24hrs and 48hrs. At the conclusion of the designated exposure period the samples were centrifuged at 1,000 rpm for 10 min and immediately analyzed as described below.

Analysis

Determining the NOD and TOD of an ISCO treated aquifer system first requires measuring the ROD values of the *oxidant*, *treatment* and *total* oxidant/activator /soil configuration followed by calculations as described below.

Residual Oxidant Measurement. ROM evaluations were used to determine the remaining concentration of oxidant in each sample. The relative concentration between the test vials and controls can be used to determine the Natural Oxidant Demand (NOD) and the Total Oxidant Demand (TOD) for each ISCO soil and treatment. ROM methodology varies slightly between the different oxidants evaluated; however, each procedure uses an iodometric titration to determine the stoichiometric relationship between thiosulfate and the oxidant using an iodine indicator. Briefly, 0.25ml of supernatant from the centrifuged vial was added to an acidified iodide solution. The sample addition oxidizes the iodide in the solution to iodine and turns it a dark yellow. The solution is then titrated with thiosulfate colorimetrically until the iodine is reduced back to iodide (turning clear). Starch was added near the end of the titration to enhance the visual signal of trace amounts of iodine. The residual oxidant concentration can be determined by applying the molar concentration of thiosulfate added to stoichiometric ratio between thiosulfate to oxidant as described in equation 3.3.1. A detailed description of each SOP for the three oxidants is provided in Appendix C.

Equation 3.3.1 Residual Oxidant Concentration

$$C_{oxidant} = \frac{\left(V_{Na_2S_2O_3}\right)\left(C_{Na_2S_2O_3}\right)}{(MR)V_{sample}}$$

Where:

$C_{oxidant}$ → Molar concentration of oxidant (*M*)
$V_{Na2S2O3}$ → Volume of sodium thiosulfate titrated (*L*)
$C_{Na2S2O3}$ → Molar concentration of sodium thiosulfate titrated (*M*)
MR → Molar fraction of sodium thiosulfate to (over) oxidant (*unitless*)
V_{sample} → Volume of sample evaluated (*L*)

The molar fraction (R) is the number of moles of thiosulfate that react with the oxidant to balance the stoichiometric equation (*mol* $Na_2S_2O_3$/*mol* oxidant). A greater description of the stoichiometry is provided in Appendix C. R values for the three oxidants investigated are: hydrogen peroxide, sodium persulfate and potassium permanganate are 2, 2 and 5 respectively.

Calculation of NOD and TOD. The natural oxidant demand (NOD) and total oxidant demand (TOD) of the aquifer system and ISCO treatments were determined in this study. NOD is the oxidant demand of naturally occurring organic and inorganic components of the aquifer (soil and groundwater). This is calculated by the difference in ROM concentration between the treatment (OA) and total (OAS) batch samples, normalized to the soil mass tested (Eq. 3.3.2). TOD generally refers to all oxidant demands in the environment, including naturally occurring components as well as anthropogenic components, mainly contaminants and activators included in the treatment. The equations used to determine NOD and TOD are provided below (Eq. 3.3.2 and 3.3.3 respectively). Concentrations for each test and control were determined from the residual oxidant testing described previously.

Equation 3.3.2 Natural Oxygen Demand

$$NOD = \frac{((C_{ROM}^{OA}) - (C_{ROM}^{OAS}))V_{Batch}^{OAS}}{M_{Batch}^{Soil}}$$

Equation 3.3.3 Total Oxygen Demand

$$TOD = \frac{((C_{ROM}^{O}) - (C_{ROM}^{OAS}))V_{Batch}^{OAS}}{M_{Batch}^{Soil}}$$

Where:

NOD → Natural Oxidant Demand (*mg/kg*)
TOD →Total Oxidant Demand (*mg/kg*)
C_{ROM}^{OA} → Residual Oxidation Concentration in the *oxidant* (O) sample for that oxidant (*mg/L*)
C_{ROM}^{OAS} → Residual Oxidation Concentration in the *total* (OAS) sample for that oxidant (*mg/L*)
V_{Batch}^{OAS} → Volume of leachate solution in the *total* (OAS) sample batch (*L*)
M_{Batch}^{Soil} → Mass of soil test in *total* (OAS) sample batch (*kg*)

3.3.2 Batch Reactor Evaluation of Site Soils Exposed to ISCO Treatments

Batch studies were conducted to determine how geochemical properties and metals mobilization changed as ISCO treatments were exposed to additional soil mass over time. Specifically, 2 soils were exposed to 4 ISCO treatments in a cumulative series of batch studies where the same ISCO treatment solution was exposed to 3 iterations of fresh soil mass. Residual oxidant concentration, pH, ORP, conductivity and temperature were monitored.

Materials

Soils. Two site soils: #2 and #4 were evaluated in the bench scale evaluation. Soil #1 was not evaluated due to a limited amount of material. All soils were dried prior to evaluation.

Additionally soil #4 was sieved to remove any particles larger than 2mm. Additional characterization and collection data for these materials is provided in Section 3.1.4.

Chemicals. *Oxidants:* hydrogen peroxide, potassium permanganate, sodium persulfate; *Activators:* citric acid, ferrous sulfate hepahydrate, sodium hydroxide; *ROD Testing*: ammonium hydroxide, ammonium molybdate tetrahydrate, ammonium nitrate, potassium iodide, sodium bicarbonate, sodium thiosulfate, starch, sulfuric acid. *Other:* DI water, nitric acid;. A more in depth description of chemical properties and suppliers is included in Appendix C.

Experimental Design

Two soils were exposed to 4 ISCO treatments, in duplicate, in a series of batch experiments designed to monitor the decline in residual oxidant as the treatment solutions were exposed to additional mass of fresh soil. The experiment was conducted over 2 iterative batch tests. The first set of batch experiments were conducted in large reactor containers for 48hrs. At the conclusion of the exposure period the eluate was separtated from the soils, measured and then used as eluant in a second set of batch experiments as described below.

First Batch Test. Two-hundred and fifty milliliters of each ISCO treatment was exposed 750g of soil in the first batch series. ISCO treatments included: potassium permanganate, chelated iron-catalyzed sodium persulfate, alkaline-activated persulfate, and chelated iron-catalyzed hydrogen peroxide applied at the same concentrations as in Section 3.3.1 (65 g/L, 45 g/L, 45g/L and 20 g/L respectively). Oxidant to activator molar ratios were also consistent with the oxidant demand testing (Table 3.3.2).

Table 3.3.2 Oxidant Demand Batch Reactor Test: ISCO Treatment Details

ISCO Treatment	Oxidant	Activator		Oxidant Conc.		Molar Ratio of Oxidant to Activator
		Catalyst	*Chelant*	*g/L*	*mM*	*Oxidant:Catalyst:Citric Acid*
Control	-	-	-	*NA*	*NA*	*NA*
PP	Potassium Permanganate	-	-	20	126	NA
IAP+CA	Sodium Persulfate	Fe(II)	Citric Acid	45.0	189	100:1:2
AAP	Sodium Persulfate	NaOH	-			pH>11
CHP	Hydrogen Peroxide	Fe(II)	Citric Acid	65	1911	100:1:2

Eight reactors were prepared for the first series of batch experiments. The reactors consisted of 1 L wide mouth HDPE containers; to which 750 g of dried soil and 250 mL of ISCO treatment solution was added. Soil/solution additions were constituent with OD testing and resulted in a 2:1 PV ratio (0.3 LS ratio). The initial pH and ORP was measured in the reactors before they were placed on an end-over-end mixer and tumbled for 48 hours at 30 rpm. After mixing for 48 hours, the 1L containers were centrifuged at 200 rpm for 20 minutes. The overlaying liquid was measured to determine the pH and ORP. Overlaying liquid was then decanted from each duplicate container and combined to establish consistent solution baseline conditions for the second batch series.

Second Batch Test. The composite eluate was evenly split from each treatment and poured into 2 new 250 ml HDPE reactor bottles (approximately 50ml of eluent in each reactor, specific volumes are provided in Table 3.3.3). The reactors contained either 50g (*Batch A*) or 100g (*Batch B*) of clean wet soil, resulting in a LS ratio of 1 and 0.5 mL/g, respectively. The initial pH and ORP values were measured and the reactors were allowed to react over a 5d exposure period with only hand agitation applied daily. At the conclusion of the exposure period, pH, ORP, and residual oxidant measurements were conducted.

Table 3.3.3 Oxidant Demand Batch Reactor Test: Experimental Design

	Treatments			
	PM	**IAP+CA**	**AAP**	**CHP+CA**
First Batch Series				
Mass Soil (*Cumulative*)	750 (*750*) g			
Volume ISCO treatment (ml)	250 ml			
Batch (*Cumulative*) L:S	0.3 (*0.33*) ml/g			
Cumulative Dose (g/kg)	6.67	15	15	21.67
Second Batch – A (apply eluate from 1st batch to 50 g fresh soil)				
Mass Soil (*Cumulative*)	50 (*800*) g			
Volume ISCO treatment (ml)	62.5	56	61.5	47.5
Batch (*Cumulative*) L:S	1.25 (*0.080*)	1.12(*0.07*)	1.23 (*0.077*)	0.95(*0.059*)
Cumulative Dose (g/kg)	1.56	3.15	3.46	3.86
Second Batch – B (apply eluate from 1st batch to 100 g fresh soil)				
Mass Soil (*Cumulative*)	100 (*850*) g			
Volume ISCO treatment (ml)	62.5	56	61.5	47.5
Batch (*Cumulative*) L:S	0.63(*0.070*)	0.56(*0.066*)	.62 (*0.072*)	0.48(*0.056*)
Cumulative Dose (g/kg)	1.47	2.96	3.26	3.63

Analysis

Residual Oxygen Measurements. ROM was measured following an iodometric titration as described in section 3.3.1. ROM measurements were made by Battelle immediately following sampling.

pH, ORP. Electrometric readings were taken by Battelle using a Thermo Scientific probes. The pH probe was calibrated daily at pH values of 4, 7, and 10. An acceptable calibration slope was greater and 95.0 percent. The accuracy of the ORP probe was checked with quinhydrone solutions.

3.3.3 Column Studies

Column studies were conducted to determine the amount of time required for ISCO treated site soils to return to their original baseline following treatment (as measured by conductivity, pH & ORP). Additionally, the transport potential for various metals of concern was also evaluated over the reversion period. Specifically, 30 columns were constructed to evaluate 4 ISCO treatments (and one control) on 3 site soils. The columns consisted of 2 segments, the first contained ISCO treated soil followed by the second which contained untreated soil. Both sections were eluted with groundwater for 4 weeks until equilibrium of the pH and ORP occurred. Conductivity, pH, ORP, temperature and aqueous metals concentration were monitored throughout the study form sampling ports along the side of the columns.

Materials

Soils. Three site soils: #1, #2, and #4 were evaluated in the column study. All soils were dried prior to evaluation. Additionally soil #4 was sieved to remove any particles larger than 2mm. Additional characterization and collection data for these materials is provided in Section 3.1.4. the column experiment included both ISCO treated and virgin site soils. A description of the ISCO treatment application for the *up-gradient* column soils is included in the experimental design.

Groundwater. The groundwater used in the batch reactor evaluations was collected from a 90 ft. deep maintained by Battelle (same as previously used in Section 3.3). All groundwater was filtered prior to use in the experiment due to particulate iron observed in the reservoir. It was believed that the iron could potentially clog fittings and tubing within the experimental setup. To accomplish this, the groundwater was vacuum filtered with 0.45 µm pore size filter to remove particulate iron. Additional groundwater attributes and collection procedures are provided in Section 3.1.4.

Chemicals. *Oxidants:* hydrogen peroxide, potassium permanganate, sodium persulfate; *Activators:* citric acid, ferrous sulfate hepahydrate, sodium hydroxide; *Other:* DI water, nitric acid. A more in depth description of chemical properties and suppliers is included in Appendix C.

Experimental Design

The column study experimental design is described in 4 sections: ISCO soil treatment, column construction, column packing and column operation.

ISCO Soil Treatment. Each column reactor within the study included an *up-gradient* column and a *down-gradient* column. The *up-gradient* column contained ISCO treated soils while the *down-gradient* column contained virgin or untreated soils. ISCO treated soils were prepared in batch reactors prior to the start of the column evaluation by tumbling 2 kg of each respective soil in a 2 L HDPE container with the specified ISCO treatment (Table 3.3.4). The same ISCO treatments and treatment concentrations were applied to column soils as previously described in Section 3 with minimal exception. Soil #4 was air dried prior to mixing; however, soils #1 and #2 were applied at their natural moisture content. As a result, oxidant demand and similar calculations are on a wet soil basis (contrary to previous experiments where they were conducted on a dry mass basis). Soils treated with PM, IAP and AAP were mixed at 30rpm on an end-over-end mixer for 48 hrs. Soils treated with CHP were kept lightly capped in a fume hood instead of tumbled (due to the potential for gas evolution). The pH, ORP, conductivity, temperature, alkalinity, and residual oxidant were measured in the slurry after 48 hours.

Table 3.3.4 Column Experiment: ISCO Treatment Details

ISCO Treatment	Oxidant	Activator		Oxidant Conc.		Molar Ratio of Oxidant to Activator
		Catalyst	*Chelant*	*g/L*	*mM*	*Oxidant:Catalyst:Citric Acid*
Control	-	-	-	*NA*	*NA*	*NA*
PP	Potassium Permanganate	-	-	20.0	126	NA
IAP+CA	Sodium Persulfate	Fe(II)	Citric Acid	45.0	189	100:1:2
AAP	Sodium Persulfate	NaOH	-			pH>11
CHP	Hydrogen Peroxide	Fe(II)	Citric Acid	65.0	1,911	100:1:2

Column Construction. A total of 10 glass columns were set up for each column series. A series consisted of five column reactors (a control and four oxidants) with 2 column segments per reactor (*up-gradient* and *down-gradient*). The diameter of the glass columns (Ace Glass, Vineland, NJ) was 2 inches, and the column length was 2 feet. Three side ports were positioned along the length of the columns for sample collection. Two of the ports were positioned 4 inches from the column ends and another port was in the center of the column. Teflon® faced silicone septa were placed inside the ports and they were plugged with Teflon® threaded plugs. The end caps, at the top and bottom of the column, were fabricated to include a ¼-in NPT port and fitted with stainless steel unions (¼-in NPT x 1/8-in compression) to attach the influent, effluent or connecting lines. The columns were fastened to a 5ft x 6ft steel support structure with clamps to secure them during the construction and operation of the experiment. Additionally, acrylic sleeves were placed around the *up-gradient* and *down-gradient* columns exposed to peroxide as a safety precaution to protect laboratory staff in case a column were to crack due to excessive pressure build-up.

Each series of columns was outfitted with a dedicated FMI Q Pump (Model QG50MB). The FMI pumps had a maximum flowrate of 38 mL/min, but were only operated at a flowrate less than 1 mL/min for the study. Groundwater was pumped from a 5-gallon reservoir, through ¼-in Teflon tubing distribution manifold, to the influent ports of each of the 5 column reactors assembled within the series. Influent ports were located at the bottom of the *up-gradient* column. Groundwater was then pumped vertically through the *up-gradient* column followed by the *down-gradient* column which were connected by a 1/8-in Teflon® connection tube. An upward (upwelling) vertical flow dynamic was applied to both columns (despite their names which designate treatment exposure, not flow dynamics). Finally, groundwater exited the *down-gradient* column and was collected in a 2.5 gal HDPE effluent collection container.

Flow was controlled to each column reactor by a needle valve which was installed between each *up-gradient* influent port and the distribution manifold. The needle valves allowed for direct, reliable flow-control adjustments to be made for each reactor which was verified periodically by direct collection of effluent volume over a set amount of time. Additionally, one-way flow 1/8-in check valves were installed at immediately before the influent port of each column section (*up-gradient* and *down-gradient*) to prevent backflow of the feed lines from the water in the column.

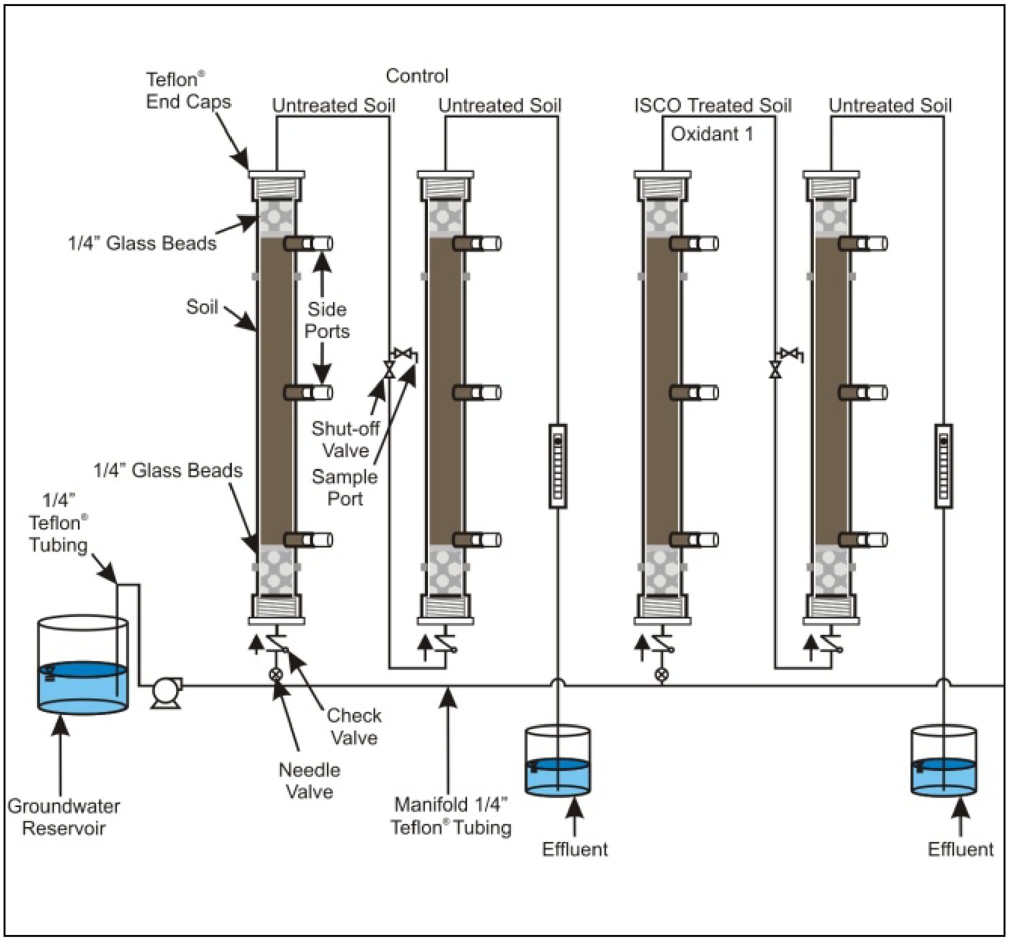


Figure 3.3.1 Column Experiment: Schematic

Sample ports were located along both *up-gradient* and *down-gradient* columns as previously described. Additionally a single effluent sampling port was installed along the collection line between each column segment. A shut off valve was also installed just below the sampling port.

All materials, including glass columns, Teflon® end caps, and fittings were first soaked overnight in an Alconox® soap solution and then rinsed with tap water prior to assembly. The materials were then soaked overnight in 10% nitric acid and followed by three rinses with DI water. Prior to loading the columns with soil, they system was flushed and checked for leaks. The five gallon reservoir was filled with DI water. The pumps were set at maximum flowrate (38 mL/min). DI water was pumped through each series of columns. Teflon® end caps and fittings were tightened with wrenches when leaks were found. The columns were flushed with DI water for 8 hours before packing with slurry from the batch study. Equipment blanks were collected from the effluent of each series of columns, preserved with nitric acid, and kept at 4°C. Equipment blanks were analyzed for metals by the University of New Hampshire.

Figure 3.3.2 Column Experiment: Experimental set-up

Column Packing. On September 24, 2012, June 24, 2013, and August 26, 2013, the 2 L HDPE soil #2, #4, and #1 batch containers (respectively) were weighted on a Mettler Toledo bench-top balance. The top Teflon® end cap was unscrewed. A thin layer of glass wool was placed at the bottom of the column using a glass stir rod. A sharpie was used to mark the outside of the column at 1-in from the bottom and top of the column. A l-in layer of 6 mm glass beads was added over the glass wool. The glass beads at the base of the column served to diffuse the upflowing groundwater. Another thin layer of glass wool was placed over the glass beads. A funnel was placed at the top of the column. The slurry in the 2 L containers were shaken and immediately poured into the column up to the marked 1-in line. 20-in of slurry were added into each column. A thin layer of glass wool was placed over the slurry followed by another 1-in layer of glass beads. The 1-in layer of glass beads at the top of the column prevented soil fines from eluting into the second column. Each series of columns were labeled. Series 1A and 1B were the controls, series 2A and 2B were the alkaline activated sodium persulfate (AAP) columns, series 3A and 3B were the iron/citric acid sodium persulfate (IAP) columns, 4A and 4B were the hydrogen peroxide (CHP) columns, and 5A and 5B were the potassium permanganate (PM) columns. Figure 2.6 shows the columns after soil packing. The 2 L HDPE containers were weighed after filling the columns to determine the amount of slurry added to each column. The mass of soil added into each column is shown in Table 2.23.

Table 3.3.4 Column Experiment: Soil Loading Details

Column	Description	Soil #2 (g)	Soil #4 (g)	Soil #1 (g)
1A	*Up-gradient* column, Untreated soil #2	2,167	1,302	1,838
1B	*Down-gradient* column, Untreated soil #2	1,911	1,219	1,879
2A	*Up-gradient* column, Groundwater, soil #2, 0.4 M NaOH, 45.0 g/L $Na_2S_2O_8$	2,009	1,230	1,949
2B	*Down-gradient* column, Untreated soil #2	1,854	1,273	1,675
3A	*Up-gradient* column, Groundwater, soil #2, 106 mg/L Fe(II), 726 mg/L citric acid, 45.0 g/L $Na_2S_2O_8$	1,903	1,420	1,993
3B	*Down-gradient* column, Untreated soil #2	1,926	1,418	1,978
4A	*Up-gradient* column, Groundwater, soil #2, 1,067 mg/L Fe(II), 7,344 mg/L citric acid, 65.0 g/L H_2O_2	2,047	1,456	1,980
4B	*Down-gradient* column, Untreated soil #2	1,922	1,329	1,879
5A	*Up-gradient* column, Groundwater, soil #2, 20.0 g/L $KMnO_4$	1,914	1,299	1,928
5B	*Down-gradient* column, Untreated soil #2	1,844	1,179	1,869

Column Study Operation. On September 25, 2012, June 25, 2013, and August 26, 2013, the pumps were turned on for soil #2, #4, and #1, respectively. The flow rate of filtered groundwater flowing up through the columns was adjusted to 0.3 mL/min (0.8 ft/day) using the needle valves. The flow rate was checked from the *up-gradient* column effluent sample tap. Groundwater was pumped continuously through the columns 24 hours-a-day for five days a week. During that time, flow was monitored on a daily basis by collecting effluent volumes in a 2 L graduated cylinder.

Sampling was conducted on a daily basis to determine pH, ORP, conductivity, temperature and dissolved metal concentrations changes over time. The samples were collected from the three side ports and effluent using a disposable 60 mL syringe with a 21 gauge needle. Care was made to avoid creating void spaces in the column soil during these events as shown in Figure 3.3.3. Fifteen mL of sample volume was collected from each side port sampling location as well as from the effluent equating to a total combined 60 ml volume removed from each column on a daily basis, 12% of the daily throughput. Samples were collected in 50 mL centrifuge vials and fractionated for water quality analysis or dissolved metals analysis. Five mL was designated for water quality analysis which was conducted immediately following the sampling event. The remaining 10 mL was designated for dissolved metals analysis which was filtered through 0.45

µm Mixed Cellulose Ester (MCE) filters, preserved with nitric acid and stored in 15 mL centrifuge vials at 4°C until analysis. Additionally, alkalinity and residual oxidant samples were also collected and analyzed twice-a-week from the column effluent.

`

Figure 3.3.3 Column Study: Sample collection from side ports

The pumps were turned off, approximately 4 weeks after startup as stabilization of pH and ORP was observed in the effluent of the *down-gradient* columns. The clamps were loosened and the columns were taken down from the rack. The remainder of the slurry was placed into a wide mouth 1 L container and kept at 4° C. This archived soil material from each column was analyzed for hydrous ferric and aluminum oxides.

Analysis

pH, Conductivity, ORP, Temperature. The water quality parameters were measured using Thermo Scientific probes and meters as shown in Figure 2.7. The pH probe was calibrated daily at pH values of 4, 7, and 10. An acceptable calibration slope was greater and 95.0 percent. The accuracy of the ORP probe was checked with quinhydrone solutions. The conductivity probe was calibrated using a 14.1 mS/cm standard. Measurements were made by Battelle following sampling events.

Alkilinity. The total alkalinity was analyzed using the HACH DR5000. The alkalinity Method 10239 (25-400 mg/L as $CaCO_3$) required only 0.5 mL of sample volume. Measurements were made by Battelle following sampling events.

Residual Oxidation Measurements. Sodium persulfate and potassium permanganate concentrations were determined following the idiometric titration method described in Section 3.3.1. Measurements were made by Battelle following sampling events.

Dissolved Metals. Dissolved metal concentrations were determined using a Varian Vista AX Inductively Coupled Plasma Atomic Emission Spectrophotometer (ICP-AES) in accordance with EPA method 6010C.

HFO and AlO. The hydrous ferric and aluminum oxide concentrations were determined by acid ammonium oxalate and dithionite-citrate extractions. The oxalate extraction will dissolve the amorphous iron and aluminum, whereas the dithionite extraction will dissolve the crystalline portion. The extractions were conducted at Battelle and the hydrous ferric and aluminum oxide analysis will be done by the University of New Hampshire.

3.4 MITIGATING THE MOBILIZATION OF METALS DUE TO ISCO APPLICATION

The metals mobilization mitigation portion of the study investigated if the addition of a chemical amendment would reduce the mobilization of metals in the subsurface. The effect of the amendment on the overall efficacy of the ISCO treatment to reduce COCs was also evaluated at the same time. Evaluations investigated the application of amendment prior to ISCO treatment; concurrent with treatment; and following the treatment application. The methods and materials used in this study are described below.

3.4.1 Pre-treatment Stabilization Evaluation

The pretreatment stabilization study evaluated the addition of reagents to treatment soils, prior to an ISCO treatment application, to reduce the mobility of metals. Specifically, 3 soils were pretreated with 5 pretreatment reagents (and 1 control) and then exposed to 4 ISCO treatments. The concentration of metals in the aqueous phase, residual oxidant, and geochemical parameters were assessed to determine the effectiveness of the treatment. Additional tests were included to determine any reduction ISCO treatment efficacy of VOCs.

Materials

Soils. Three soils, #1, #2, and #6, were selected due to detectable metals release observed in the preliminary screening experiments (Section 3.2.1) and material availability. Prior to the experiment, the moisture content of each soil type was determined based on the ASTM Test Method D2216. Moist soils were added to each experimental reactor based on dry weight, with moisture content taken into account. Soils were composited with material greater than 0.5 inches removed. Additional characterization and collection data for these materials is provided in Section 3.1.4.

Chemicals. *Oxidants:* hydrogen peroxide, potassium permanganate, sodium persulfate; *Activators*: citric acid, ferrous sulfate hepahydrate, sodium hydroxide; *Pretreatment Chemicals*: iron oxide, iron (III) sulfate hydrate, sodium phosphate, sodium sulfide; *Simulated Organic COCs:* benzene, carbon tetrachloride, trichloroethylene; *Other*: DI water, L-ascorbic acid and nitric acid. A more in depth description of chemical properties and suppliers is included in Appendix D.

Experimental Design

The potential for chemical pretreatment application to reduce metals mobilization during ISCO treatments was evaluated in 3 phases. Prior to evaluation, soils were pretreated with 5 stabilization reagents. The pretreated soils were then investigated in a series of screening evaluation to assess the pre-treatment effects. Based on the screening data, the most promising pre-treatment options were selected for investigation in a second detailed evaluation.

Soil Pretreatment. Three soils were pretreated with 5 stabilization reagents and a control (no treatment, DI water only) as described by Table 3.4.1. Treatments were selected to emulate common technologies used to stabilize specific metals. The ratio of 50 mM of each reagent was intended to be in excess of the demand for technologies and the metals they were intended to stabilize. Seven-hundred and fifty grams of each soil was placed in 1 L borosilicate reactors along with 110 mL of deionized water (to saturation) and the prescribed loadings of metal stabilization reagents. The reactors were allowed to sit in a dark incubator at 20°C for 7 days with periodic vigorous mixing. Following the 7-day contact period, the contents of the borosilicate reactors were poured into a Buchner funnel containing a 25 micron filter. The aqueous phase of the contents was vacuum extracted through the filter. Following this step, 250 mL of deionized water (greater than 2 pore volumes) was flushed through the system to remove residual aqueous phase reagents.

Table 3.4.1 Pretreatment Stabilization: Chemical Reagent Details

Pre-Treatment	**Chemical**	**Pretreatment Reagent Concentration**		**Pretreatment Reagent Dose**
		g/L	***mM***	$g_{oxidant}/kg_{soil}$
CNTL	Control	-	-	-
FeO	Ferric Oxide	54.44	340.9	7.98
FeS	Ferric Sulfate	136.2	340.9	19.99
NaP	Sodium Phosphate	55.89	340.9	8.20
NaS	Sodium Sulfide	26.61	340.9	3.90
NaP/S	Sodium Phosphate + Sodium Sulfide	27.9/13.3	170.5/170.5	4.10/1.95

ISCO Treatment Screening. Pretreated soils were exposed to 4 ISCO treatments, described by Table 3.4.2, for 2 days. ISCO treatments include: catalyzed hydrogen peroxide (with iron and citric acid), iron catalyzed persulfate (with a citric acid chelating agent), alkaline activated persulfate, and potassium permanganate. ISCO treatments were the same as those used in Sections 3.2 and 3.3; however, solution concentrations varied due to different soil to groundwater ratios and the type (batch or column) of reactor. The dosages of potassium permanganate (3 electrons per mole) and sodium persulfate (2 electrons per mole) were ended to be similar potential for electrons accepted during the reaction. The dose of hydrogen peroxide (2 electrons per mole), due to the auto decomposition, was dosed 10 times higher due to the autodecomposition that is typical of hydrogen peroxide reactions and this concentration was equivalent to approximately 6.7 percent hydrogen peroxide in a single pore volume, which is within the range of common injection concentrations used in the field.

Table 3.4.2 Pretreatment Stabilization: ISCO Treatment Details

ISCO Treatment	**Oxidant**	**Activator**		**Oxidant Conc.**		**Oxidant Dose**	**Molar Ratio of Oxidant to Activator**
		Catalyst	***Chelant***	***g/L***	***mM***	$g_{oxidant}/kg_{soil}$	***Oxidant:Catalyst:Citric Acid***
PM	Potassium Permanganate	-	-	3.48	22.0	3.48	NA
IAP+CA	Sodium Persulfate	Fe(II)	Citric Acid	7.62	32.0	7.61	100:1:2
AAP	Sodium Persulfate	NaOH	-				pH>11
CHP+CA	Hydrogen Peroxide	Fe(II)	Citric Acid	10.88	320	10.88	100:1:2

ISCO treatment solutions were prepared prior to the start of the screening test and added to the pretreated soils at a liquid to solids ratio of 1 (w/w). Pretreated soils with the ISCO reagents in the borosilicate reactors for the time specified for a 2 day exposure period. After this contact period the supernatant was extracted and filtered through a 0.45 micron filter. The filtered solution was treated with nitric acid until the pH decreased below 2.0, and then 4 moles of ascorbic acid was added for every mole of oxidant present in the initial dose.

Extended ISCO Treatment Evaluation. Between 1 and 3 pretreatments were observed to reduce metals mobility in the screening evaluation for each ISCO treatment. The extended study evaluated the select pretreated soils #2 and #6 over 3 extended exposure times (28d, 56d and 90d). Soil #1 was not evaluated due to limited quantities of material. Soils were evaluated under the same conditions, exposed to the same reagents and sampled in the same manner as in the ISCO Treatment Screening previously described. In addition, a single dedicated test reactor for each experimental condition was prepared and used exclusively to measure geochemical conditions and residual oxidant at the specified contact times.

Selected Extended Evaluation Treatments:

AAP → 3 Pretreatments Evaluated
- ◦ Ferric Sulfate (136 g/kg)
- ◦ Sodium Phosphate (56 g/kg)
- ◦ Sodium Sulfate (27 g/kg)

IAP+CA → 2 Pretreatments Evaluated
- ◦ Sodium Phosphate (56 g/kg)
- ◦ Sodium Sulfate (27 g/kg)

CHP+CA → 2 Pretreatments Evaluated
- ◦ Sodium Phosphate (56 g/kg)
- ◦ Sodium Sulfate (27 g/kg)

PM → 1 Pretreatments Evaluated
- ◦ Ferric Sulfate (136 g/kg)

ISCO Treatment Efficacy Evaluation. The impact of select pretreatment chemicals on the treatment efficacy of VOC reduction was evaluated for the same pretreatments evaluated in the extended study. All reagent loadings were the same as the above experiments with the aqueous phase of the probe compound reactors spiked with a stock solution containing carbon tetrachloride, benzene, and trichloroethene to a final reactor concentration of approximately 250 mg/L of each compound. Reactors with AAP, IAP, and $KMnO_4$ conditions, and associated control reactors, were left with zero headspace to minimize volatilization of VOCs. CHP reactors and associated control reactors were prepared in a similar way but with 20 mL of headspace to allow for evolution of gas common with the CHP reaction process. CHP and CHP control reactors were submitted for VOC analysis to Absolute Resource Associates after 2 days, while all other reactors were submitted after 28 days.

Analysis

Metals. Both screening and detailed evaluation aqueous samples were submitted to UNH for trace metals analysis using an ICP-AES system in accordance with EPA method 6010C. Samples were analyzed for 22 metals including: aluminum, antimony, arsenic, barium, beryllium, calcium, cadmium, cobalt, chromium, copper, iron, potassium, magnesium, manganese, sodium, silver, nickel, lead, selenium, thallium, vanadium, and zinc.

pH, ORP, T, mV. At each time point during the detailed evaluation, pH, ORP, temperature, and conductivity were measured using a Hach® sensION+ MM150 multi-parameter meter.. Geochemical measurements were collected from a dedicated, unfiltered, unpreserved test reactor.

VOC. Dedicated test reactors were submitted to Absolute Resource Associates for VOC analysis using Purge & Trap sample concentration and Gas Chromatography – Mass Spectrometry (GC-MS) in accordance with EPA Method 8260C/SW-846. Samples were analyzed for benzene, carbon tetrachloride, and trichloroethene. CHP reactors were submitted for VOC analysis to after 2 days of contact with ISCO reagents, while all other reactors were submitted after 28 days of contact.

ROM. Was ROM conducted for this, not mentioned. Residual oxidant was measured at each time point during the screening and detailed evaluation using the iodometric titration method described in Section 3.3.1. Oxidant measurements were collected at each time point from a dedicated, unfiltered, unpreserved test reactor.

3.4.2 Concurrent Biological Stabilization Evaluation

The concurrent biological stabilization study evaluated the addition of reagents to stimulate biological activity, during the addition of ISCO treatments, to reduce the mobility of metals. Several compounds that have a minimal to low reactivity with ISCO technologies can be used to stimulate biotic processes either as an electron donor or as a nutrient. As these compounds have a low reactivity with the ISCO technologies, they could be added with the ISCO reagents and eventually stimulate biotic activity following the application of ISCO. The biotic activity could help a site return to reducing conditions following the application of ISCO, as the ISCO reagents and other oxidized compounds would serve as electron acceptors. Specifically, this section evaluated the use of 6 biological stimulants to reduce metals mobility during 4 ISCO treatments on 3 site soils. The concentration of metals in the aqueous phase, residual oxidant, and geochemical parameters were assessed to determine the effectiveness of the treatment. Additional batches were also included to determine any reduction ISCO treatment efficacy of VOCs.

Materials

Soils. Three soils, #1, #2, and #6, were selected due to detectable metals release observed in the preliminary screening experiments (Section 3.2.1) and material availability. . Prior to the experiment, the moisture content of each soil type was determined based on the ASTM Test Method D2216. Moist soils were added to each experimental reactor based on dry weight, with moisture content taken into account. Additional characterization and collection data for these materials is provided in Section 3.1.4.

Chemicals. *Oxidants:* hydrogen peroxide, potassium permanganate, sodium persulfate; *Activators*: citric acid, ferrous sulfate hepahydrate, sodium hydroxide; *Biological Stimulants*: sodium acetate (anhydrous), sodium L-lactate, sodium nitrate, sodium phosphate, soybean oil, trisodium citrate (dehydrate), whey from bovine milk; *Simulated Organic COCs:* benzene, carbon tetrachloride, trichloroethylene; *Other*: DI water, L-ascorbic acid and nitric acid. A more in depth description of chemical properties and suppliers is included in Appendix D.

Experimental Design

The effect of biological stimulants on metals mobilization was evaluated in 2 phases. The first phase was a preliminary screening which evaluated 7 biological stimulant/ISCO treatment combinations over a single exposure period. Based on the screening level data, the most promising biological stimulants were selected to be evaluated in the second long term evaluation.

Screening Evaluation. Three soils were treated with 4 ISCO treatments and 6 biological co-treatments (and a control) in a 90d screening evaluation. ISCO treatments were consistent with those described previously in Section 3.4.1 (Table 3.4.2) and included: catalyzed hyrdrogen peroxide with iron and citric acid, iron catalyzed persulfate with citric acid, alkaline activated persulfate, and potassium permanganate. All biological co-treatments included sodium phosphate and sodium nitrate (except the control). The additional 5 treatments contained either sodium acetate, sodium lactate, soybean oil, trisodium citrate or whey as described in Table 3.4.3. These technologies were intended to emulate organic compounds either commonly used during ISCO applications or as electron donors used in creating anaerobic conditions for bioremediation.

Table 3.4.3 Biological Co-treatment: Biological Reagent Details

Biological Reagents *(g/kg soil)*	**Biological Treatments**						
	PN	APN	LPN	OPN	TPN	WPN	CNTL
Sodium Phosphate (0.02 g/kg)	X	X	X	X	X	X	
Sodium Nitrate (0.02 g/kg)	X	X	X	X	X	X	
Sodium Acetate (4.5 g/kg)		X					
Sodium Lactate (4.5 g/kg)			X				
Soybean Oil (4.5 g/kg)				X			
Trisodium Citrate (4.5 g/kg)					X		
Whey (4.5 g/kg)						X	

Screening tests were conducted in 100 ml borosilicate reactors. Forty grams of soil (dry weight) and 40 grams of reagent solution (1:1 liquid to solid ratio, w/w) were loaded into the reactor and capped with PTFE-lined septa cap. The experiments were conducted at 20 °C in duplicate sacrificial test reactors. One reactor was included for metals analysis and the second for heterotrophic plate counts (HPC) analyses. In addition, a single dedicated test reactor for each experimental condition was also prepared and used exclusively for collecting geochemical and residual oxidant measurements. Each reactor was vigorously mixed several times a week during the experiment. At the conclusion of the specified exposure period 90d exposure period, samples were prepared for the appropriate analysis. Reactor designated for metals analysis were filtered through a 0.45 micron filter and preserved with nitric acid until the pH decreased below 2.0.

Additionally, 4 moles of ascorbic acid were added for every mole of oxidant present in the initial dose. Reactors designated for HPC analysis remained unopened throughout the test period and were submitted to the laboratory unopened and unpreserved.

Extended Evaluation. Based on the screening level data, the most promising chemical co-treatments were selected for each ISCO technology to continue with additional evaluation for Soil 2 and Soil 6. Additional evaluations were not conducted for Soil 1 as the stock of Soil 1 had been depleted during the screening tests. The selected test conditions were evaluated (Table 3.4.5) for 3 additional time points (28d, 56d and 90d) using the same procedures as the original screening tests to measure the change in metals release over time. In addition, a single dedicated test reactor for each experimental condition was prepared and used exclusively to measure geochemical conditions and residual oxidant at the specified contact times.

Selected Extended Evaluation Treatments:

AAP → No Biological Treatments Evaluated

IAP+CA → 2 Biological Treatments Evaluated
- ◦ APN: Acetate, Phosphate, Nitrate
- ◦ TPN: Trisodium Citrate, Phosphate, Nitrate

CHP+CA → 2 Biological Treatments Evaluated
- ◦ APN: Acetate, Phosphate, Nitrate
- ◦ TPN: Trisodium Citrate, Phosphate, Nitrate

PM → 1 Biological Treatment Evaluated
- ◦ LPN: Lactate, Phosphate, Nitrate

ISCO Treatment Efficacy Evaluation. The impact of chemical co-treatment addition to ISCO treatments were evaluated to determine any reduced efficacy, for the reduction of VOCs, occurred. All methods were conducted as described in Section 3.4.1. All chemical co-treatments and reagent loadings were the same as described in the Detailed Evaluation with the aqueous phase of the probe compound reactors spiked with a stock solution containing carbon tetrachloride, benzene, and trichloroethene to a final reactor concentration of 250 mg/L of each compound. Reactors with AAP, IAP, and $KMnO_4$ conditions, and associated control reactors, were left with zero headspace to minimize volatilization of VOCs. CHP reactors and associated control reactors were prepared in a similar way but with 20 mL of headspace to allow for evolution of gas common with the CHP reaction process.

Analysis

Metals. Both screening and detailed evaluation aqueous samples were submitted to UNH for trace metals analysis using an ICP-AES system in accordance with EPA method 6010C. Samples were analyzed for 22 metals including: aluminum, antimony, arsenic, barium, beryllium, calcium, cadmium, cobalt, chromium, copper, iron, potassium, magnesium, manganese, sodium, silver, nickel, lead, selenium, thallium, vanadium, and zinc.

HPC Analysis: Samples were submitted to Absolute Resource Associates (subcontracted to Northeast Laboratory Services) for HPC analysis using Standard Methods (SM) 9215B (Pour Plate Method).

pH, ORP, T, mV. At each time point during the screening and detailed evaluation, pH, ORP, temperature, and conductivity were measured using a Hach® sensION+ MM150 multi-parameter meter.. Geochemical measurements were collected from a dedicated, unfiltered, unpreserved test reactor.

ROM. Residual oxidant was measured at each time point during the screening and detailed evaluations using the iodometric titration method described in Section 3.3.1. Oxidant measurements were collected from a dedicated, unfiltered, unpreserved test reactor.

VOC. Dedicated test reactors were submitted to Absolute Resource Associates for VOC analysis using Purge & Trap sample concentration and Gas Chromatography – Mass Spectrometry (GC-MS) in accordance with EPA Method 8260C/SW-846. Samples were analyzed for benzene, carbon tetrachloride, and trichloroethene. CHP reactors were submitted for VOC analysis to after 2 days of contact with ISCO reagents, while all other reactors were submitted after 28 days of contact.

3.4.3 Concurrent Chemical Stabilization Evaluation

The concurrent chemical stabilization study evaluated the addition of chemical reagents, during the addition of ISCO treatments, to reduce the mobility of metals. The chemical additives were intended to limit or reduce the concentrations of metals formed during ISCO by either buffering the pH or precipitating metals from the solution. Specifically, this section evaluated the use of 6 chemical reagents to reduce metals mobility during 4 ISCO treatments on 3 site soils. The concentration of metals in the aqueous phase, residual oxidant, and geochemical parameters were assessed to determine the effectiveness of the treatment. Additional batches were also included to determine any reduction ISCO treatment efficacy of VOCs.

Materials

Soils. Three soils, #1, #2, and #6, were selected due to detectable metals release observed in the preliminary screening experiments (Section 3.2.1) and material availability. Prior to the experiment, the moisture content of each soil type was determined based on the ASTM Test Method D2216. Moist soils were added to each experimental reactor based on dry weight, with moisture content taken into account.. Additional characterization and collection data for these materials is provided in Section 3.1.4.

Chemicals. *Oxidants:* hydrogen peroxide, potassium permanganate, sodium persulfate; *Activators*: citric acid, ferrous sulfate hepahydrate, sodium hydroxide; *Concurrent Chemical Reagents*: sodium bicarbonate, sodium iodate, sodium phosphate dibasic, sodium phosphate monobasic monohydrate, sodium sulfate; *Simulated Organic COCs:* benzene, carbon tetrachloride, trichloroethylene; *Other*: DI water, L-ascorbic acid and nitric acid. A more in depth description of chemical properties and suppliers is included in Appendix D.

Experimental Design

The effect of chemical stabilization amendment addition on the mobilization of metals was evaluated in 2 phases. The first phase, a preliminary screening, evaluated all chemical stabilization amendment/ISCO treatment combinations over a single exposure period. Based on the screening level data, the most promising biological stimulants were selected to be evaluated in the second detailed evaluation.

Screening Evaluation. Three soils were treated with 4 ISCO treatments and 6 chemical stabilization co-treatments (and a control) were evaluated over a 2d period. ISCO treatments were consistent with those described previously in Section 3.4.1 (Table X.X) and included: catalyzed hyrdrogen peroxide with iron and citric acid, iron catalyzed persulfate with citric acid, alkaline activated persulfate, and potassium permanganate. Chemical stabilization co-treatments included phosphate buffer, phosphate, bicarbonate buffer, bicarbonate, iodate and sulfate as described in Table 3.4.4. The concentration of the phosphate and bicarbonate "buffer"s were intended to be sufficient so that the pH would be consistent over the course of the experiment. The intent of the 5 mmole/Kg anions was to introduce these anions that are known to form precipitates with specific metals into the solution and assess their impact on the metals concentration.

Table 3.4.4 Chemical Co-treatment: Chemical Reagent Details

Chemical Stabilization Treatments (*g/kg soil*)	ISCO Treatments			
	AAP	IAP+CA	CHP+CA	PM
Control	DI Water, No Chemical Reagent			
Phosphate Buffer	100 mMol/kg disodium phosphate dibasic		50 mMol/kg disodium phosphate dibasic 50 mMol/kg Sodium phosphate dibasic	
Phosphate	5 mMol/kg disodium phosphate			
Bicarbonate Buffer	100 mMol/kg bicarbonate			
Bicarbonate	5 mMol/kg bicarbonate			
Iodate	5 mMol/kg idodate			
Sulfate	5 mMol/kg sulfate			

ISCO treatment solutions were prepared prior to the start of the screening test and added to the pretreated soils at a liquid to solids ratio of 1 (w/w). Pretreated soils with the ISCO reagents in the borosilicate reactors for the time specified for a 2 day exposure period. After this contact period the supernatant was extracted and filtered through a 0.45 micron filter. The filtered solution was treated with nitric acid until the pH decreased below 2.0, and then 4 moles of ascorbic acid was added for every mole of oxidant present in the initial dose. In addition a single dedicated test reactor for each experimental condition was prepared and used exclusively for collecting geochemical and residual oxidant measurements.

Extended Evaluation. Based on the screening level data, the most promising chemical co-treatments were selected for each ISCO technology to continue with additional evaluation for Soil 2 and Soil 6. Additional evaluations were not conducted for Soil 1 as the stock of Soil 1 had been depleted during the screening tests. The selected test conditions were evaluated (Table 3.4.5) for 3 additional time points (28d, 56d and 90d) using the same procedures as the original screening tests to measure the change in metals release over time. In addition a single dedicated test reactor for each experimental condition was prepared and used exclusively for collecting geochemical and residual oxidant measurements at the specified contact times.

Selected Extended Evaluation Treatments:

AAP → No Chemical Co-Treatments Evaluated

IAP+CA → 4 Chemical Co-Treatments Evaluated
◦ Phosphate Buffer ◦ Bicarbonate Buffer
◦ Phosphate ◦ Bicarbonate

CHP+CA → 2 Biological Treatments Evaluated
◦ Phosphate Buffer
◦ Phosphate

PM → 1 Biological Treatment Evaluated
◦ Bicarbonate

ISCO Treatment Efficacy Evaluation. The impact of chemical co-treatment addition to ISCO treatments were evaluated to determine any reduced efficacy, for the reduction of VOCs, occurred. All methods were conducted as described in Section 3.4.1. All chemical co-treatments and reagent loadings were the same as described in the Detailed Evaluation with the aqueous phase of the probe compound reactors spiked with a stock solution containing carbon tetrachloride, benzene, and trichloroethene to a final reactor concentration of 250 mg/L of each compound. Reactors with AAP, IAP, and $KMnO_4$ conditions, and associated control reactors, were left with zero headspace to minimize volatilization of VOCs. CHP reactors and associated control reactors were prepared in a similar way but with 20 mL of headspace to allow for evolution of gas common with the CHP reaction process. .

Analysis

Metals. Both screening and detailed evaluation aqueous samples were submitted to UNH for trace metals analysis using an ICP-AES system in accordance with EPA method 6010C. Samples were analyzed for 22 metals including: aluminum, antimony, arsenic, barium, beryllium, calcium, cadmium, cobalt, chromium, copper, iron, potassium, magnesium, manganese, sodium, silver, nickel, lead, selenium, thallium, vanadium, and zinc.

pH, ORP, T, mV. At each time point during the screening and detailed evaluations, pH, ORP, temperature, and conductivity were measured using a Hach® sensION+ MM150 multi-parameter meter.. Geochemical measurements were collected from a dedicated, unfiltered, unpreserved test reactor.

ROM. Residual oxidant measurements were made for each time point during the screening and detailed evaluations using the iodometric titration method described in Section 3.3.1. Oxidant measurements were collected at each time point from a dedicated, unfiltered, unpreserved test reactor.

VOC. Dedicated test reactors were submitted to Absolute Resource Associates for VOC analysis using Purge & Trap sample concentration and Gas Chromatography – Mass Spectrometry (GC-MS) in accordance with EPA Method 8260C/SW-846. Samples were analyzed for benzene, carbon tetrachloride, and trichloroethene. CHP reactors were submitted for VOC analysis to after 2 days of contact with ISCO reagents, while all other reactors were submitted after 28 days of contact.

3.4.4 Post-Treatment Stabilization Evaluation

The post-treatment stabilization study evaluated the addition of reagents, following the application of ISCO treatments, to reduce the mobility of metals. Specifically, 3 soils previously exposed to 4 ISCO treatments were treated with 6 post-treatments (and a control). The concentration of metals in the aqueous phase, residual oxidant, and geochemical parameters were assessed to determine the effectiveness of the treatment.

Materials

Soils. Three soils, #1, #2, and #6, were selected due to detectable metals release observed in the preliminary screening experiments (Section 3.2.1) and material availability. Prior to the experiment, the moisture content of each soil type was determined based on the ASTM Test Method D2216. Moist soils were added to each experimental reactor based on dry weight, with moisture content taken into account.. Additional characterization and collection data for these materials is provided in Section 3.1.4.

Chemicals. *Oxidants:* hydrogen peroxide, potassium permanganate, sodium persulfate; *Activators*: citric acid, ferrous sulfate hepahydrate, sodium hydroxide; *Post-Treatment Reagents*: hydrochloric acid, iron(III) sulfate hydrate, sodium bicarbonate, sodium hydroxide, sodium L-lactate, sodium phosphate monobasic monohydrate, sodium sulfide nonahydrate; *Other*: DI water, L-ascorbic acid and nitric acid. A more in depth description of chemical properties and suppliers is included in Appendix D.

Experimental Design

The effect of post-treatment chemical amendment addition on the mobilization of metals was evaluated in 3 phases. First, soils were exposed to four different ISCO treatments. Following the exposure, a preliminary screening was conducted to evaluate all post-treatment effects over a single time period. Based on the screening data, the most promising post-treatment options were selected to be evaluated in the second long term evaluation.

Preliminary ISCO Exposure. Three soils were treated with 4 ISCO treatments for 28 days prior to evaluating the post-treatment stabilization amendments. ISCO treatments were consistent with those described previously in Section 3.4.1 (Table 3.4.2) and included: catalyzed hyrdrogen peroxide with citric acid, iron catalyzed persulfate with citric acid, alkaline activated persulfate, and potassium permanganate. All experiments were conducted with 40 grams of soil (dry weight) and 40 grams of reagent solution (1:1 liquid to solid ratio, w/w) in 100 mL borosilicate reactors with PTFE-lined septa. ISCO reagents were added to each reactor and stored in a dark incubator at 20°C with periodic vigorous mixing for throughout the exposure period.

Screening Evaluation. Following the 28d ISCO exposure, 6 chemical stabilization post-treatments (and a control) were applied to soils in the designated reactors. Chemical stabilization post-treatments included bicarbonate, lactate, pH adjustment, phosphate, sulfate, and sulfide as described in Table 3.4.5. Bicarbonate and phosphate conditions were intended to assess the potential of metals precipitation with those anions. Lactate was intended stimulate and use biologic activity post ISCO to create reducing conditions at the site. The quantity of sulfide ws calculated as sufficient to reduce the mass of oxidant in the system and the pH modifiers were added until the desired pH was obtained. The reactors were then again stored in a dark incubator at 20°C with periodic vigorous mixing until the 2d exposure period was complete. At the conclusion of the exposure period, the supernatant was extracted, and filtered through both a 1.0 micron glass fiber and a PTFE 0.45 micron filter. The filtered solution was preserved with nitric acid until the pH decreased below 2.0, and then 4 moles of ascorbic acid was added for every mole of oxidant present in the initial dose. In addition a single dedicated test reactor for each experimental condition was prepared and used exclusively for collecting geochemical and residual oxidant measurements.

Table 3.4.5 Chemical Post-treatment: Chemical Reagent Details

Chemical Post-Treatments	ISCO Treatments			
	AAP	IAP+CA	CHP+CA	PM
Control	DI Water, No Chemical Reagent			
Bicarbonate	Sodium Bicarbonate (1mMol/kg soil)			
Lactate	Sodium lactate (10.0 mMol/kg soil) pH adjusted to between 6.5 &7.5			
pH Adjustment	Hydrochloric Acid (pH = 6.5-7.5)	Sodium Hydroxide (pH= 6.5-7.5)		
Phosphate	Sodium phosphate monobasic monohydrate (1.0 mMol/kg soil) pH adjusted to between 6.5 &7.5			
Sulfate	Sodium sulfate (1.0 mMol/kg soil) pH adjusted to between 6.5 &7.5			
Sulfide	Sodium sulfide monohydrate (48.0 mMol/kg soil) pH adjusted to between 6.5 &7.5			

Extended Evaluation. Based on the screening level data, the most promising chemical post-treatments were selected for each ISCO technology to continue with additional evaluation for Soil 2 and Soil 6. Additional evaluations were not conducted for Soil 1 as the stock of Soil 1 had been depleted during the screening tests. The selected test conditions were evaluated (Table 3.4.5) for 3 additional time points: 28d, 56d and 90d following the completion of the original 28d ISCO preliminary exposure (56d, 84d & 118d after the start of the experiment). The extended evaluations was conducted using the same procedures as the original screening tests to measure the change in metals release over time. In addition, a single dedicated test reactor for each experimental condition was prepared and used exclusively for collecting geochemical and residual oxidant measurements at the specified contact times. After each contact time period, the aqueous portion of the samples were processed as described above and submitted to UNH for metals analysis. No efficacy evaluation was included in the post-treatment study.

Selected Extended Evaluation Treatments:

AAP → 2 Chemical Post-Treatments Evaluated
- ◦ pH Neutralization
- ◦ Sulfide

IAP+CA → 2 Chemical Post-Treatments Evaluated
- ◦ pH Neutralization
- ◦ Sulfide

CHP+CA → 4 Chemical Post-Treatments Evaluated
- ◦ pH Neutralization
- ◦ Sulfide
- ◦ Lactate
- ◦ Bicarbonate

PM → 1 Chemical Post-Treatments Evaluated
- ◦ Sulfide

Analysis

Metals. Both screening and detailed evaluation aqueous samples were submitted to UNH for trace metals analysis using an ICP-AES system in accordance with EPA method 6010C. Samples were analyzed for 22 metals including: aluminum, antimony, arsenic, barium, beryllium, calcium, cadmium, cobalt, chromium, copper, iron, potassium, magnesium, manganese, sodium, silver, nickel, lead, selenium, thallium, vanadium, and zinc.

pH, ORP, T, mV. At each time point during the detailed evaluation, pH, ORP, temperature, and conductivity were measured using a Hach® sensION+ MM150 multi-parameter meter. Geochemical measurements were collected from a dedicated, unfiltered, unpreserved test reactor.

ROM. Residual oxidant measurements were made for each time point during the screening and detailed evaluations using the iodometric titration method described in Section 3.3.1. Oxidant measurements were collected at each time point from a dedicated, unfiltered, unpreserved test reactor.

4.0 RESULTS AND DISCUSSION

4.1 PRE-EXPERIMENTAL EVALUATION

The pre-experimental evaluation was conducted to collect data and material from ISCO remedial sites and the literature. This included the development and distribution of surveys to document metals mobilization from historic and existing ISCO sites; a scouring of state and federal databases to collect additional ISCO site data; the development of a new database to categorize and evaluate the collected information from the identified sites and literature; the collection of ISCO treated soils to conduct a series of metals mobilization laboratory experiments; and a preliminary characterization of the materials collected. The results of these evaluations are provided below.

4.1.1 ISCO Site Survey Compilation

Survey respondents were primarily consultants and Navy Environmental Restoration staff. Responses showed that groundwater was most often selected as the contaminated media and permanganate, persulfate, and hydrogen peroxide were all equally popular as oxidants of choice. Ozone and calcium peroxide based oxidants appear to be used infrequently. Chlorinated solvents and petroleum hydrocarbons were noted as contaminants of concern. Out of the 13 respondents, nine observed metals mobilization. Hexavalent chromium was listed specifically as a concern by the majority of the respondents for their sites. Several respondents included comments such as: "*For most current ISCO sites (all but one using permanganate and activated persulfate), regulators are not requesting that metals be monitored post-ISCO, as they feel fairly confident from past literature that oxidation will temporarily increase solubilization of select metals, but that these have been shown (literature) to return to background concentrations once oxidative conditions return to ambient conditions*" (CH2MHill response). This indicates that regulators assume that the return to ambient groundwater conditions will address any metals mobilized in situ.

As noted in the technical approach (Section 3.1.1), additional sources for data collection were undertaken and included searching the literature for published site information and utilizing remediation-specific databases. Across the literature, 100 sites were potentially identified. Site owner breakdown spanned four main categories: private, Department of Defense (DoD), Department of Energy (DOE), and the EPA. The majority of the literature search included published site information from on-line Web sites, state databases such as Oculus (Florida's Department of Environmental Protection) and GeoTracker (California Department of Toxic Substances Control). In addition, site data were collected from the in-progress reviewers for each agency and site managers for known ISCO sites. The following specific sources were used to populate the database:

1. The EPA's Contaminated Sites Clean-Up Information (Clu-In) Web site, which provides information on innovative remediation treatment techniques. As such, Clu-In was searched for relevant ISCO case studies. http://www.clu-in.org/.
2. The Interstate Technology and Regulatory Council (ITRC) Web site was utilized as it has published reports in which specific case study data are presented. http://www.itrcweb.org/
3. Reports issued by EPA were also utilized to generate the database. EPA has generated reports on the field application of chemical oxidation and within the report is an overview of several case studies.
4. Journal articles were identified through previously generated EndNote library databases. The EndNote libraries were populated by automatically searching through various databases for journal articles such as the Battelle Library, Science Direct, Pub Med, Elsevier, and Wiley Online Library.
5. State Coalition for Remediation of Drycleaners Web site provides site profiles for dry cleaning sites where ISCO was implemented as the remedial approach. http://www.drycleancoalition.org/
6. Web sites of environmental remediation practitioners were used as many provide information on case studies where ISCO has been implemented (e.g., Isotec, Environmental Assessment and Remediation, and US Peroxide).
7. General Web browsing via Google was also conducted as a means to uncover additional reports outside of the specific sources listed above.

The sites repeated across the references are entered into the database as one site with all references noted. Additionally, the installations gained through IPR representatives are cross checked against ISCO case studies found in the literature when populating the database. Table 4.1.1 provides a summary of ISCO sites incorporated into the database.

Table 4.1.1 Preliminary Evaluation: Summary of ISCO Sites in the Database (in the order of the sites in the Database)

No.	Site Name	City	State	Oxidant
1	Active Industrial Facility	Clifton	New Jersey	Hydrogen peroxide
2	Active Retail Gasoline Station	Kenton	Delaware	Ozone
3	Allegany Ballistics Laboratory-Solvent Disposal Pit Area of Site 1	Rocket Center	West Virginia	Sodium persulfate and Permanganate
4	American Cleaners	St. Peters	Missouri	Potassium permanganate
5	Anniston Army Depot	Anniston	Alabama	Hydrogen peroxide
6	Barb and Ron's Cleaners	Appleton	Wisconsin	Potassium permanganate
7	Beaches Laundry and Cleaners	Jacksonville Beach	Florida	Hydrogen peroxide
8	Butler Cleaners (#2)	Jacksonville	Florida	Potassium permanganate
9	Butler's Cleaners (#1)	Jacksonville	Florida	Potassium permanganate
10	Canadian Forces Base	Borden	Ontario, Canada	Potassium permanganate
11	Cottage Cleaners	Memphis	Tennessee	Potassium permanganate
12	Daisy Fresh Dry Cleaners	College Park	Georgia	Hydrogen peroxide
13	Demolished Retail Service Station	Suburban Philadelphia	Pennsylvania	Ozone
14	Denmark soil study		Denmark	Hydrogen peroxide
15	Denver Colorado Dry Cleaner	Denver	Colorado	Hydrogen peroxide
16	Dry Clean USA Orlando Florida	Orlando	Florida	Hydrogen peroxide
17	Essex Jamestown Site-UST Area	Jamestown	New York	Sodium persulfate
18	First Coast Laundry and Cleaners	Jacksonville Beach	Florida	Calcium peroxide
19	Former Alpine Cleaners	Friendswood	Texas	Permanganate and Hydrogen peroxide
20	Former Automobile Sales and Service Center	Bound Brook	New Jersey	Ozone
21	Former Cowboy Cleaners Site	Broomfield	Colorado	Permanganate
22	Former Electroplating and Manufacturing Plant			Hydrogen peroxide
23	Former Garden City Laundry and Cleaning Company (7th Street Site)	Garden City	Kansas	Ozone
24	Former Gasoline Station	New Castle	Indiana	Sodium persulfate
25	Former Heritage Cleaners (D-19-177)	Nashville	Tennessee	Permanganate
26	Former Isleta Chevron Filling Station	Albuquerque	New Mexico	Hydrogen peroxide
27	Former Manufacturing Facility	Quincy	Massachusetts	Permanganate
28	Former Market Place Shopping Center Site	Hilton Head Island	South Carolina	Ozone
29	Former MGP	Hartford	Connecticut	Sodium persulfate
30	Former MGP Site (South California Edison)	Long Beach	California	Ozone and Hydrogen peroxide
31	Former Modern Cleaners	Columbia	Tennessee	Sodium persulfate and Hydrogen peroxide
32	Former News Publisher Facility	Framingham	Massachusetts	Hydrogen peroxide
33	Former Oil Distribution Terminal	Ilion	New York	Ozone
34	Former Service Station	Commerce City	Colorado	Ozone
35	Former Service Station Site	Southeastern	Pennsylvania	Ozone
36	Former Sign Manufacturing Facility	Denver	Colorado	Hydrogen peroxide

Table 4.1.1(cont.) Preliminary Evaluation: Summary of ISCO Sites in the Database (in the order of the sites in the Database)

No.	Site Name	City	State	Oxidant
37	Former Wood Treatment Facility	Sonoma	California	Ozone
38	Foxy Cleaners and Tailoring	Aurora	Illinois	Permanganate
39	German Automotive Manufacturer Site	Sindelfingen	Germany	Permanganate
40	Hanner's Dry Cleaner	Pompano Beach	Florida	Hydrogen peroxide
41	Ineeda Cleaners-Dry Cleaning Facility	Hutchinson	Kansas	Ozone
42	Kansas City Plant	Kansas City	Missouri	Permanganate
43	LC 34 - Cape Canaveral Air Station	Cape Canaveral	Florida	Permanganate
44	Marine Corp Base Quantico; SWMU M-13	Prince William County	Virginia	Sodium persulfate
45	Marine Corps Base Camp Lejeune Site 88	Jacksonville	North Carolina	Permanganate
46	MidWest Gasoline Tanker Truck Crash Site			Hydrogen peroxide
47	Mixed Waste Site Bench and Pilot Scale Testing			Sodium persulfate
48	NAS Alameda Site 14	Alameda	California	Sodium persulfate
49	NAS Alameda Site 26	Alameda	California	Sodium persulfate & Hydrogen peroxide
50	Naval Submarine Base (NSB) Kings Bay- Site 11	Camden County	Georgia	Hydrogen peroxide
51	Nebraska Ordinance Plant	Mead	Nebraska	Permanganate
52	New York ISCO Project	New York	New York	Sodium persulfate
53	Niles Finest Cleaners (Site #1388)	Niles	Illinois	Permanganate
54	North Berwick	North Berwick	Maine	Sodium persulfate
55	North Island OU20	San Diego	California	Sodium persulfate
56	One Hour Cleaners	Chattanooga	Tennessee	Permanganate
57	One Hour Valet Cleaners	Chattanooga	Tennessee	Permanganate
58	Operable Unit 10 (OU-10), NAS Pensacola, FL	Pensacola	Florida	Hydrogen peroxide
59	OU4 Fort Ritchie Army Garrison	Washington County	Maryland	Permanganate
60	Paramount Cleaners	Florissant	Missouri	Permanganate
61	Park Avenue Cleaners	Richardson	Texas	Hydrogen peroxide
62	Park Between Commercial and Residential Area	Utrecht	The Netherlands	Ozone
63	Parkwood Former Dry Cleaner	Plano	Texas	Hydrogen peroxide
64	Paul's Classic Drycleaners		Wisconsin	Ozone
65	Pierce Service Station	Los Angeles	California	Hydrogen peroxide
66	Piketon OST/TMS ID 167	Piketon	Ohio	Permanganate
67	Polyester Manufacturing Plant, South Korea	Gumi City	South Korea	Hydrogen peroxide
68	Portsmouth Gaseous Diffusion Plant X701B	Piketon	Ohio	Permanganate
69	Quick-N-Easy Wash-O-Mat and Artistic Cleaners	Wichita	Kansas	Permanganate
70	Residential Fuel Oil Release		Connecticut	Hydrogen peroxide

Table 4.1.1(cont.) Preliminary Evaluation: Summary of ISCO Sites in the Database (in the order of the sites in the Database)

No.	Site Name	City	State	Oxidant
71	Residential Lake Front Property		New Jersey	Hydrogen peroxide
72	Retail Dry Cleaning in Edmonton, Canada	Edmonton	Alberta, Canada	Hydrogen peroxide & Permanganate
73	Retail Fueling Facility	Westport	Massachusetts	Hydrogen peroxide
74	Rummel Creek Shopping Center	Houston	Texas	Permanganate
75	Savannah River Site A/M Area	Aiken	South Carolina	Hydrogen peroxide
76	Service Station Site	Madison	Wisconsin	Hydrogen peroxide
77	Site 47 NSF Indian Head	Indian Head	Maryland	Sodium persulfate
78	Spin City Dry Cleaners	Plano	Texas	Hydrogen peroxide
79	Springvilla Dry Cleaners	Springfield	Oregon	Permanganate
80	Subsurface Chemical Injection Pilot Test Summary Report		New York	Hydrogen peroxide
81	Sun Belt Precision Products	Fort Lauderdale	Florida	Permanganate
82	Swift Cleaners -SVE and ISCO	Jacksonville	Florida	Hydrogen peroxide
83	Tinker Site CG038	Tinker AFB	Oklahoma	Permanganate
84	U.S. Army Cold Regions Research and Engineering Laboratory	Hanover	New Hampshire	Permanganate
85	Union Chemical Company Superfund Site	South Hope	Maine	Permanganate
86	USG Corporation Facility	La Mirada	California	Permanganate
87	Vandenberg Air Force Base IRP Site 50		California	Hydrogen peroxide
88	Warehousing Facility	Union County	New Jersey	Hydrogen peroxide
89	Washland Cleaners	Dickson	Tennessee	Permanganate

4.1.2 ISCO Site Database Observations

Eighty-nine case studies were identified from over 100 potential ISCO sites to populate the ISCO Site Database. Selection was based upon two major components, a primary focus on the field implementation of ISCO treatments (not solely batch studies) and a comprehensiveness data set able to fully populate the required database fields. Of the 89 sites (Figure 4.1.1), the majority of the sites were commercial (47 sites), mostly drycleaner sites; followed by the Navy (7 sites); DOE (5 sites); Army (4 sites) and Air Force (2 sites). The “other” category includes all sites that are outside the U.S. and with undefined site responsibility.

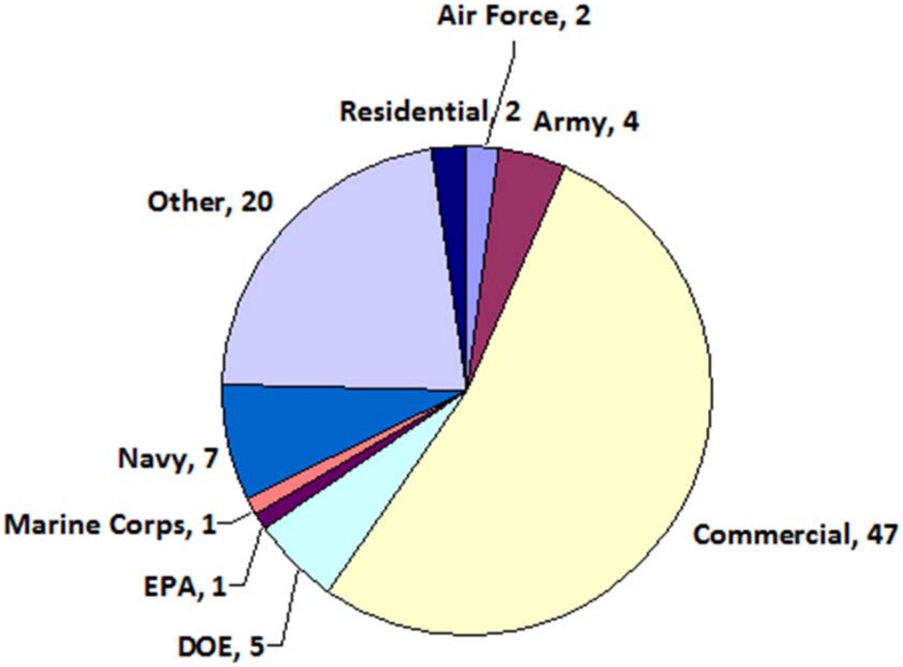


Figure 4.1.1 Preliminary Evaluation: Site Responsible Party

The most commonly observed oxidant in the database was permanganate (56 sites), followed by hydrogen peroxide (55 sites); sodium persulfate (19 sites); ozone (15 sites) and calcium peroxide (1 site) as illustrated in Figure 4.1.2. In some of the sites, treatment involved the use of multiple oxidant types. Table 4.1.2 shows the range of operation dates for the different types of oxidants. Hydrogen peroxide was observed to be implemented as early as 1995, followed by permanganate in 1996.

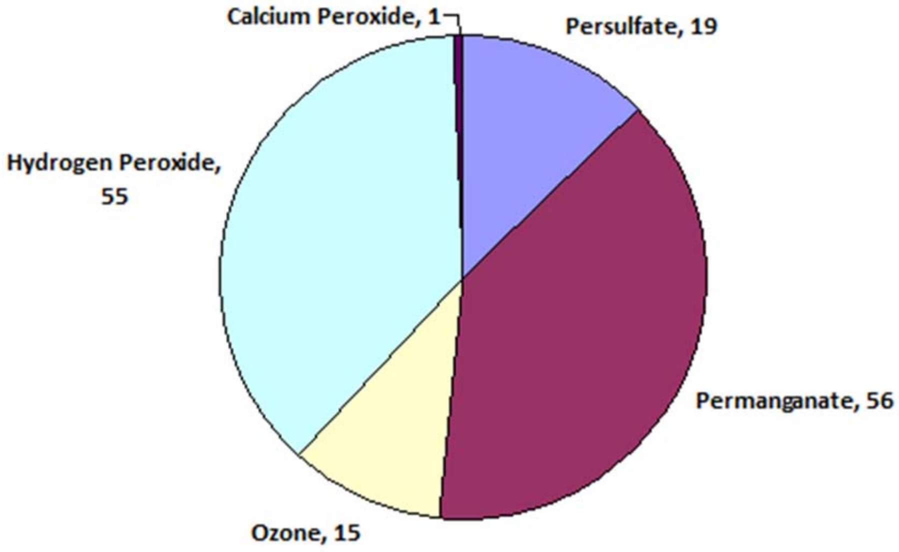


Figure 4.1.2 Preliminary Evaluation: Oxidant Breakdown

Table 4.1.2 Preliminary Evaluation: Operation Dates for the Oxidants

Oxidant	Operation Date Range	
Calcium peroxide*	November 2007	November 2007
Hydrogen Peroxide	January 1995	May 2012
Ozone	April 1997	June 2002
Permanganate	May 1996	October 2010
Persulfate	December 2003	October 2009

***Among the 89 sites, one site used calcium peroxide as an oxidant. (First Coast Laundry, Jacksonville, Florida)**

Among the different delivery methods, the most common oxidant delivery method was direct injection (85 sites) as shown in Figure 4.1.3. Direct push (12 sites) and recirculation (11 sites) were methods employed less frequently. The other category included the use of trenches, gravity feeding, garden sprayers, soil mixing techniques and pneumatic fracturing for injection methods. There were no sites that used push-pull technique.

The number of sites using temporary wells, permanent wells and direct push technology for injection by oxidant is listed in Table 4.1.3. Several sites used multiple injection strategies for the injection event to maximize the subsurface distribution of the oxidant (e.g., a combination of recirculation and permanent wells or a combination of direct push technology and direct injection using temporary wells). The majority of injections for persulfate, permanganate, ozone and hydrogen peroxide were performed using permanent wells.

The median values for injection radius for persulfate was 12.5ft (information in database report titled “rptDesignParamsStats”). Similarly, the median of injection radius of influence for permanganate, ozone and peroxide was observed to be 20ft, 33.5ft and 16ft, respectively. Several sites did not report information on the injection radius of influence. The duration of injection event ranged between 4 to 195 days for the different oxidants.

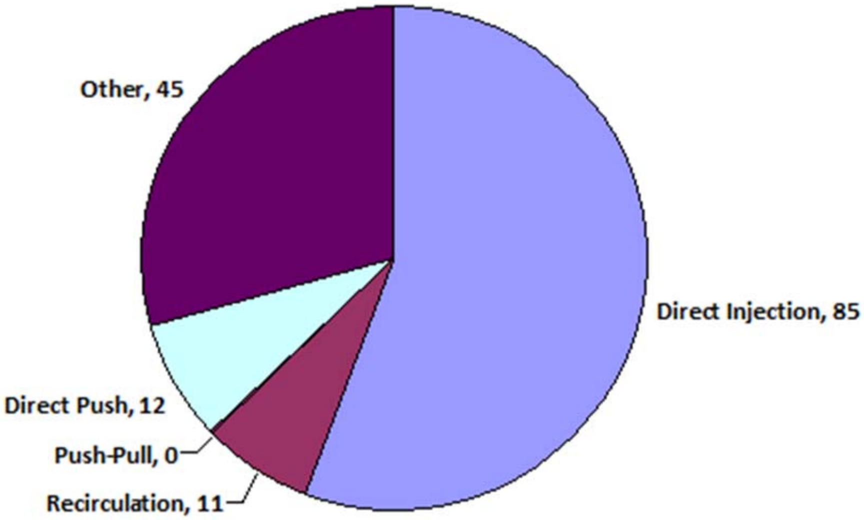


Figure 4.1.3 Preliminary Evaluation: Oxidant Delivery Methods

Table 4.1.3 Preliminary Evaluation: Design Parameters for Oxidants

Design Parameters	Persulfate	Permanganate	Ozone	Hydrogen Peroxide	Calcium Peroxide
Injection radius of influence (ft) (Median value)	12.5	20	33.5	16	NA
Duration of delivery events (days)* (Median value)	14	42	195	7	4
No. of sites using Direct push technology	1	10	0	5	0
No. of sites using Permanent wells	11	30	10	35	1
No. of sites using Temporary wells	4	1	0	1	0

***In case studies where duration was specified in months, the data were converted to days (assuming 30 days per month)**
NA- Not available

Metals were monitored in a total of 19 sites out of the 89 sites (21%). An increase in metal concentration was observed in 12 sites out of these 19 sites (63%). Table 4.1.4 lists the 12 sites that observed metals mobilization. In several cases where metal was monitored, the concentration of metal was not reported in the documents available.

Persulfate and permanganate were the two commonly used oxidants where metals mobilization was observed (Figure 4.1.5). Out of the 12 sites, direct injection was the most frequent method of implementation (nine sites) as shown in Figure 4.1.6. In some cases (e.g., Marine Corp Base Quantico SWMU M-13) both direct push technology and direct injection using temporary well were used during ISCO implementation.

Table 4.1.4 Preliminary Evaluation: Sites with Mobilized Metals

Site	Oxidant	Injection Strategy	Mobilized Metals
Denmark Soil Study	Hydrogen peroxide	Direct injection	Copper, iron, lead, manganese, nickel
LC-34- Cape Canaveral Air Station	Permanganate	Direct push technology	Chromium, Nickel, Thallium
Marine Corp Base Quantico SWMU M-13	Persulfate	Direct push technology; Direct injection using temporary well	Arsenic, chromium, iron, manganese
Marine Corps Base Camp Lejeune Site 88	Permanganate	Direct injection	Chromium
NAS Alameda Site 14	Persulfate	Recirculation	Arsenic, chromium, iron, manganese
North Berwick	Persulfate	Direct injection	Aluminum, arsenic, cadmium
North Island OU20	Persulfate	Recirculation	Arsenic, chromium, iron, vanadium
OU4 Fort Richie Army Garrison	Permanganate	Gravity feeding	Chromium, iron, manganese
Savannah River Site A/M Area	Hydrogen Peroxide	Direct injection	Copper, manganese
Site 47 NSF Indian Head	Persulfate	Direct injection	Aluminum, arsenic, chromium, iron, vanadium
Sun Belt Precision Products	Permanganate	Direct push technology	Iron, manganese
Tinker Site CG038	Permanganate	Pneumatic fracturing and liquid atomized injection	Chromium, lead, selenium

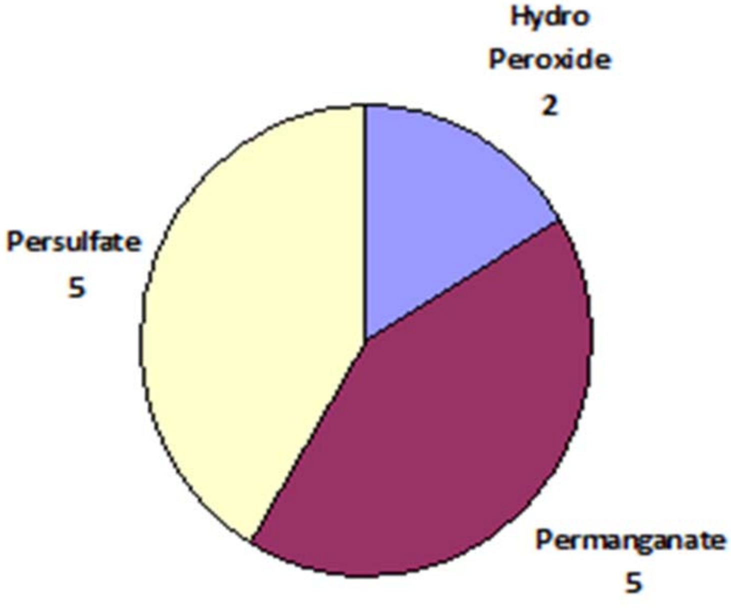


Figure 4.1.4 Preliminary Evaluation: Breakdown by type of Oxidant Breakdown

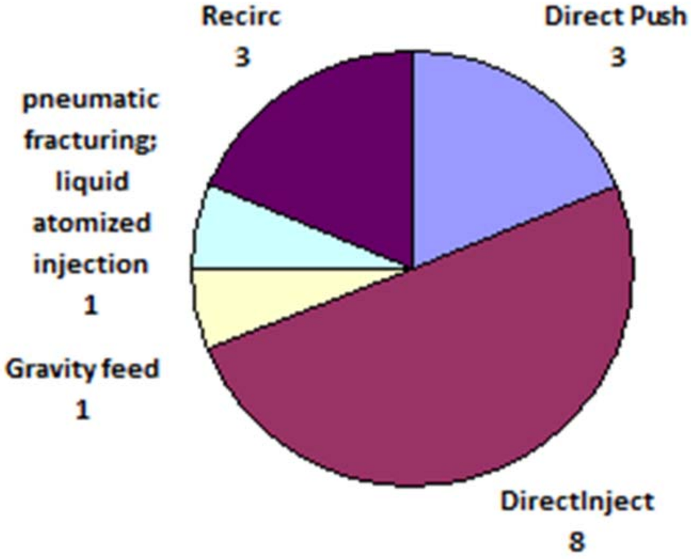


Figure 4.1.5 Preliminary Evaluation: Breakdown of Oxidant Delivery in 12 sites

Chromium (total and hexavalent), iron, manganese and arsenic were the four most frequently observed mobilized metals in these 12 sites as shown in Figure 4.1.6. A total of 10 sites out of the 12 sites had metals that exceeded the maximum contaminant levels (MCLs). Table 4.1.5 lists the MCLs for both Resource Conservation and Recovery Act (RCRA) metals and priority pollutants (PP). This MCL list was used to compare the concentrations of metals in the database. The metals that exceeded the MCLs were primarily chromium (total and hexavalent), arsenic, copper, lead, thallium, cadmium and selenium.

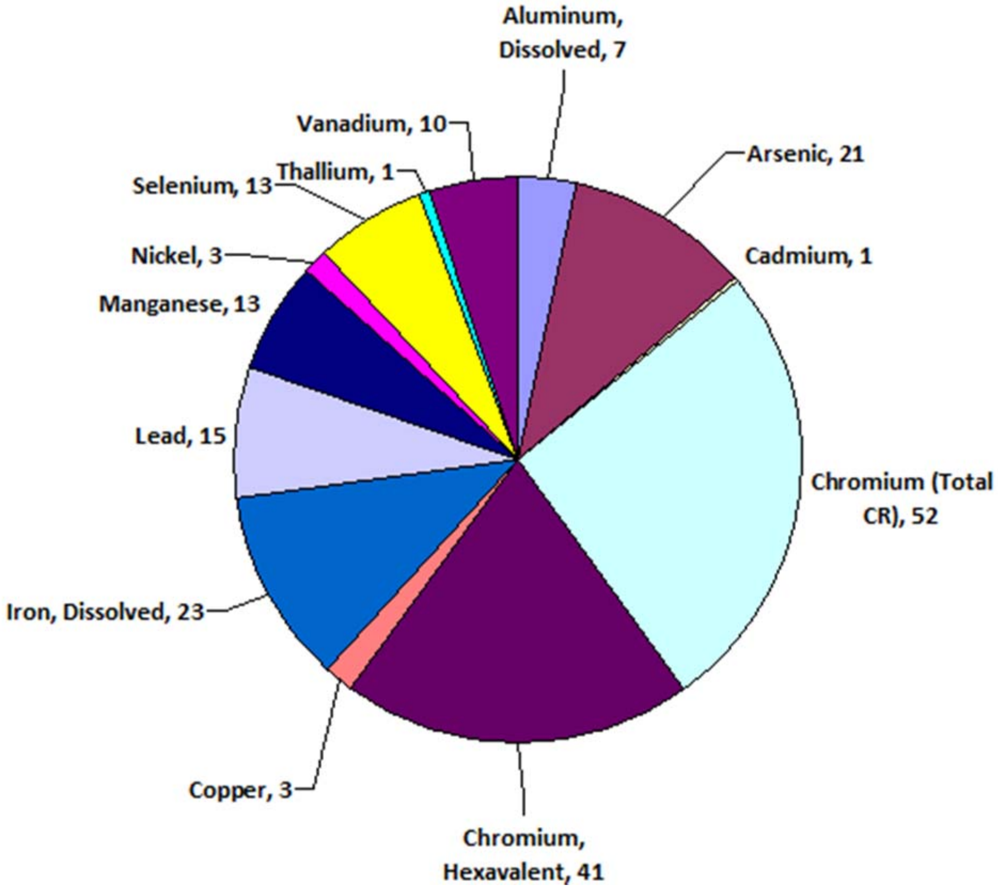


Figure 4.1.6 Preliminary Evaluation: Frequently Observed Mobilized Metals

Table 4.1.5 MCLs for RCRA Metals and Priority Pollutants

Contaminant	RCRA Metals	Priority Pollutants	Maximum Contaminant Level (mg/L)
Arsenic	X	X	0.01
Barium	X		2.0
Cadmium	X	X	0.005
Chromium (total)	X	X	0.1
Lead	X	X	0.015
Mercury (inorganic)	X	X	0.002
Selenium	X	X	0.05
Silver[(a)]	X	X	0.1
Antimony		X	0.006
Beryllium		X	0.004
Copper		X	1.3
Thallium		X	0.002
Nickel[(b)]		X	None
Zinc[(a)]		X	5.0

Note : [a]Secondary Maximum Contaminant Level (SMCL)
[b]There is no current MCL for Nickel. It has been remanded back to EPA for further regulation. Previously, the MCL was 0.1 mg/L.

Most of the monitoring events performed for the 12 sites with mobilized metals ranged from one month to three years after the injection event. Among the 12 sites with mobilized metal data, there were seven sites with two or more monitoring events.

There were four sites with two monitoring events each. Among these, only two sites (Site 47 NSF Indian Head and North Island OU20) showed increasing trends for chromium and arsenic.

Monitoring events at Site 47 NSF Indian Head were performed at three months and six months. Overall metals solubilization at the site appeared to be temporary and showed that most of the metals were at baseline or returning towards baseline concentrations after 6 months. Aluminum, arsenic, iron and vanadium concentrations continued to increase in some wells and remained above baseline conditions.

Monitoring events at North Island OU20 were performed at one and three months. At the end of 90 days post treatment at the site, geochemical parameters, such as DO, pH, ORP had returned close to their pre-treatment equilibrium levels. However, trace metals, such as chromium, arsenic, and vanadium continued to remain at substantially elevated levels. It was recommended to track the metals for a few more quarters. Additional long-term monitoring in both these sites could determine whether the metals concentrations returned to baseline. It is also important to note that the two data points in the range of two to six months are not adequate to understand a concentration trend.

Three sites (NAS Alameda Site 14, OU4 Fort Ritchie Army Garrison, and Tinker Site CG038) had three or more monitoring events (three) tracking the metal concentrations. OU4 Fort Ritchie Army Garrison had the highest number of monitoring events- five.

Tinker Site CG038 had three monitoring events performed at two-week, one month and three months after injection. Chromium concentration (Figure 4.1.7) shows overall decreasing trends in four months after the injection event. Small amounts of dissolved lead and selenium were liberated but they showed signs of decreasing concentrations (see Figure 4.1.8). It was recommended to collect additional longer term monitoring to assess whether the chromium concentrations would return to baseline conditions. Follow-on sampling at the Tinker Base indicated the presence of chromium in some monitoring wells but the data were not available for this effort.

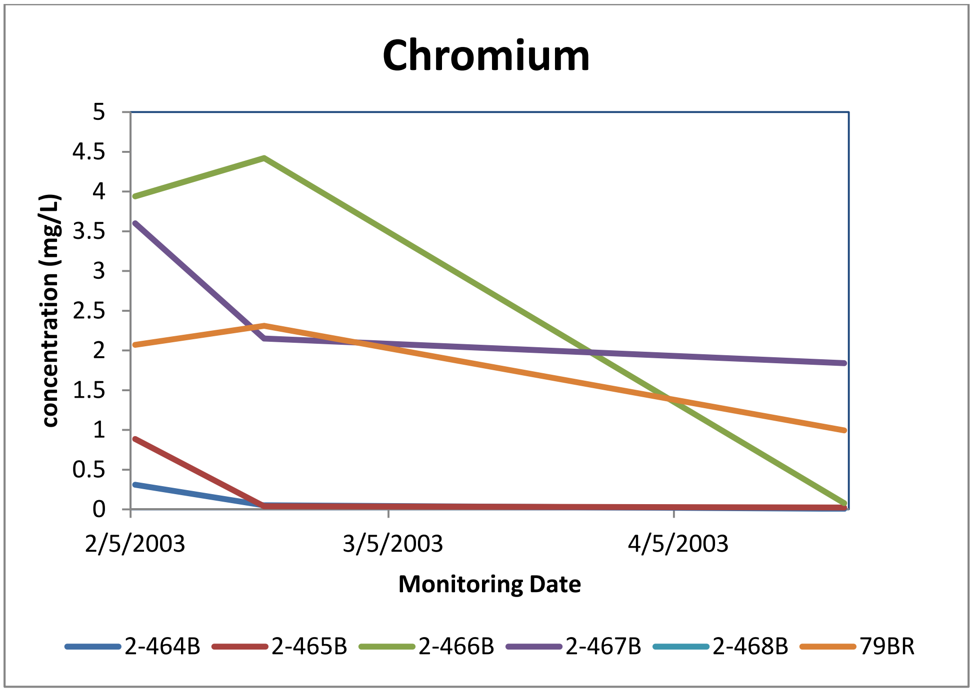


Figure 4.1.7 Preliminary Evaluation: Tinker - Cr Concentration Post-injection

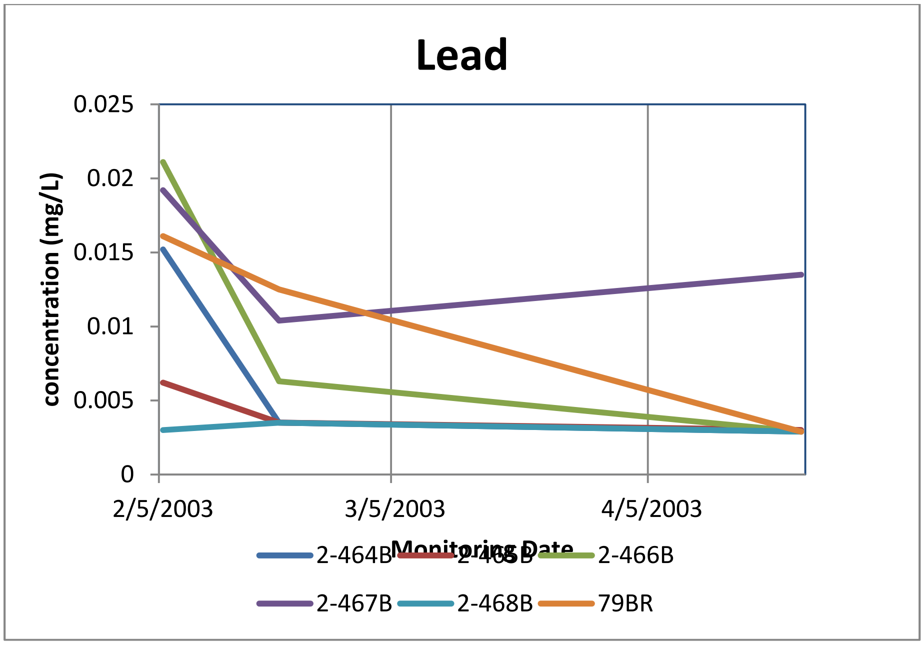


Figure 4.1.8 Preliminary Evaluation: Tinker- Pb concentration post-injection

At NAS Alameda Site 14, chromium, iron and manganese were monitored at three monitoring events after persulfate injection (Phase I injection, Phase 2 injection and Phase 3 [polishing]). Figures 4.1.9 and 4.1.10 illustrate the decreasing trend of chromium and arsenic concentrations post-injection of persulfate, respectively.

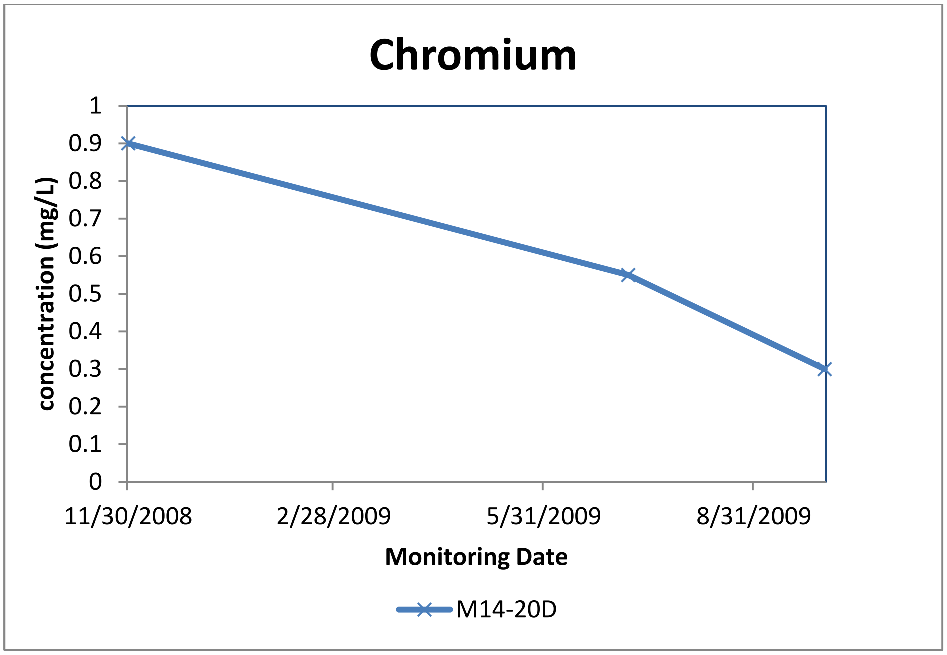


Figure 4.1.9 Preliminary Evaluation: NAS Alameda Site 14- Cr concentration post-injection

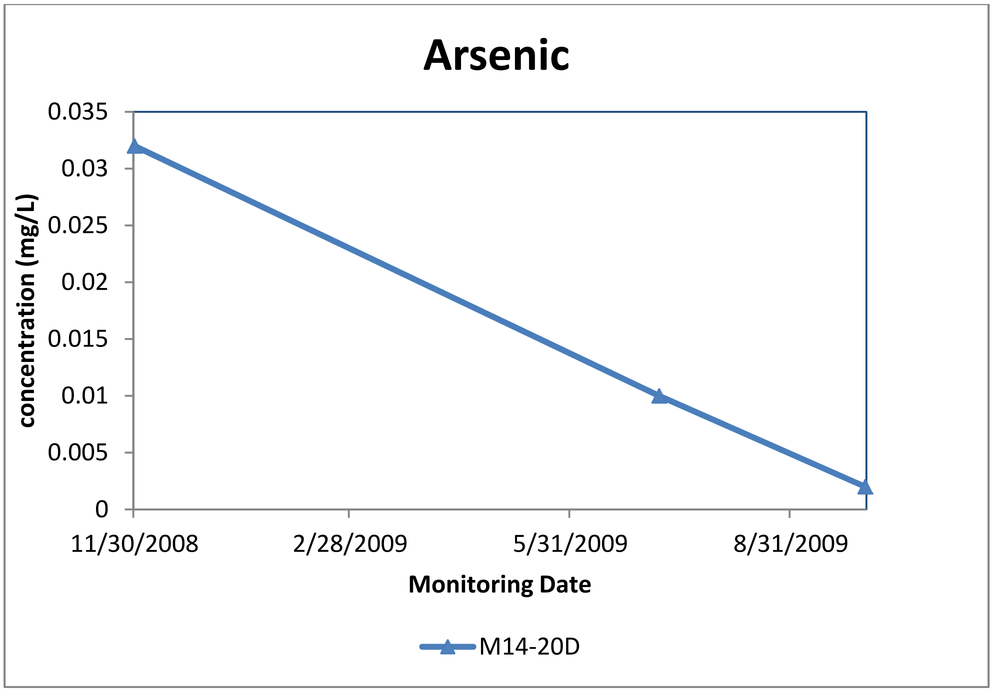


Figure 4.1.10 Preliminary Evaluation: NAS Alameda Site 14- As concentration post-injection

Similarly, chromium was monitored at OU4 Fort Ritchie Army Garrison during five monitoring events post injection of sodium permanganate. The delivery strategy involved gravity feed into injection wells. There were three injection events at the site. Chromium concentrations were decreasing even though they exceeded MCLs in all five monitoring events (Figure 4.1.11). After five monitoring events, it was recommended that a remedial investigation (RI)/Feasibility Study (FS) be completed for OU4 to evaluate whether additional active remedies are necessary or whether contamination in the aquifer will attenuate naturally to below MCLs in a reasonable length of time.

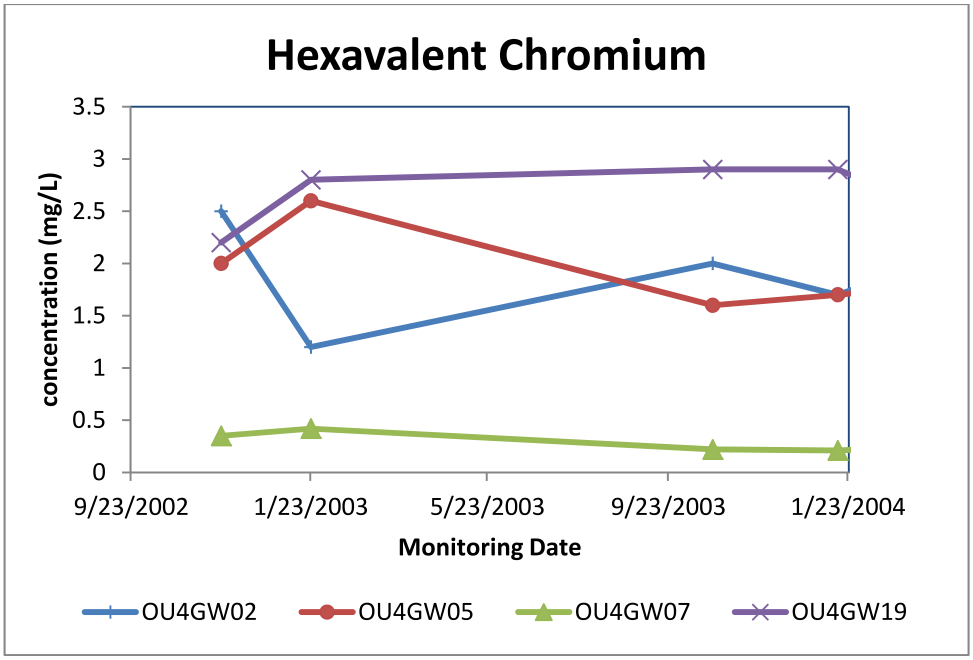


Figure 4.1.11 Preliminary Evaluation: OU4 Fort Ritchie Army Garrison- Cr concentration post-injection

4.1.3 Material Characterization

Select ISCO soils and groundwater used in this study were characterized at the start. Soils #1,#2 and #4 were selected due to material availably and measureable levels of mobile metal determined in preliminary screening of the materials. Attributes included: moisture content, synthetic precipitation leaching potential, volatile organic carbon content, acid neutralization capacity and cationic exchange capacity. Groundwater was also characterized prior to the start of the study. Attributes included: pH of the study

Moisture Content. MC was measured by Battelle at the beginning of the study. Soils were dried for 24 hrs. at 105°C in duplicate. Soil moisture ranged from 12.4% to 18.8%. Average moisture contents were fairly consistent between the three soils. Results are provided in Table 4.1.6.

Table 4.1.6 Initial Screening: Percent Moisture of Soils #1, #2, and #4

Sample ID	Crucible *(g)*	Wet Soil *(g)*	Wet Soil & Crucible *(g)*	Dried Soil & Crucible *(g)*	% Moisture	Average % Moisture
Soil #1-1	10.6	6.3	17.0	16.2	12.4%	16.3%
Soil #1-2	9.4	8.2	17.6	15.9	20.2%	
Soil #2-1	9.8	15.8	25.5	22.6	18.5%	18.7%
Soil #2-2	9.7	13.8	23.5	20.9	18.8%	
Soil #4-1	9.8	7.1	16.9	15.8	14.9%	15.0%
Soil #4-2	9.8	7.9	17.7	16.5	15.1%	

Synthetic Precipitation Leaching Procedure. SPLP testing was conducted by DHL Analytical, Round Rock, TX, for seven of the primary regulated metals (ITRC, 2015). Testing found no evidence of leachable metals from soils #1 and #2. Soil #4 contains detectable levels of leachable antimony, chromium, copper and lead (Table 4.1.7). Of these, lead concentrations were detected above the national primary drinking water levels.

Table 4.1.7 Initial Screening: Leaching of Aquifer Materials by SPLP

Metals	Soil #1 *(ug/L)*	Soil #2 *(ug/L)*	Soil #4 *(ug/L)*
Antimony	<2.50	<2.50	0.809
Arsenic	<6.00	<6.00	<6.00
Beryllium	<1.00	-	<1.00
Cadmium	<1.00	<1.00	<1.00
Chromium	-	-	2.62
Copper	-	-	8.14
Lead	<1.00	-	63.4

Acid Neutralization Capacity and Cationic Exchange Capacity. ANC and CEC were measured Energy Laboratories, Billings, MT. These parameters are indicative of the native aquifer material's capacity to retard metals transport through electrostatic attenuation of positively charged metals (CEC), and the capacity of each aquifer material to neutralize acid (ANC). Materials with low concentrations of organic matter, low abundance of 2:1 double layered clay minerals, and high in sand (quartz) would be expected to contain low CEC and low ANC. In contrast materials high in CEC and ANC may contain organic carbon, high activity clay minerals, and possibly carbonate minerals. Analysis found similar ANC and CEC values between Soils #1 and #2 which are both coarse textured and primarily comprised of sand. Soil #4 is much higher in organic matter and exhibited a much higher ANC and CEC values (13x and 3x, respectively). Results are shown in Table 4.1.8.

Table 4.1.8 Initial Screening: Characterization of Aquifer Materials for ANCand CEC

Analysis	Soil #1	Soil #2	Soil #4
Acid -Base Accounting (t/kt)			
Neutralization Potential	4	4	52
Acid Potential	0	0	2
Acid/Base Potential	4	3	50
Chemical Characteristics (meq/100 g)			
Cation Exchange Capacity	4.2	4.4	13.4

t/kt = tons/kiloton = parts per thousand

Volitile Organic Carbon. No detectable VOCs were present in the aquifer materials as received (Table 4.1.9). These soils were taken from sites with active remediation, where a presence of VOCs has previously been documented. The absence of any detectable VOCs may be a consequence of volatilization during prolonged exposure to the atmosphere.

Table 4.1.9 Initial Screening: VOCs Present in Aquifer Materials

VOCs	Soil #1	Soil #2	Soil #4
	mg/Kg-dry	mg/Kg-dry	mg/Kg-dry
1,1,1,2-Tetrachloroethane	<0.00560	<0.00549	<0.00529
1,1,1-Trichloroethane	<0.00560	<0.00549	<0.00529
1,1,2,2-Tetrachloroethane	<0.00560	<0.00549	<0.00529
1,1,2-Trichloroethane	<0.00560	<0.00549	<0.00529
1,1,2-Trichlorotrifluoroethane	<0.0168	<0.0165	<0.0159
1,1-Dichloroethane	<0.00560	<0.00549	<0.00529
1,1-Dichloroethene	<0.00560	<0.00549	<0.00529
1,1-Dichloropropene	<0.00560	<0.00549	<0.00529
1,2,3-Trichlorobenzene	<0.00560	<0.00549	<0.00529
1,2,3-Trichloropropane	<0.00560	<0.00549	<0.00529
1,2,4-Trichlorobenzene	<0.00560	<0.00549	<0.00529
1,2,4-Trimethylbenzene	<0.00560	<0.00549	<0.00529
1,2-Dibromo-3-chloropropane	<0.00560	<0.00549	<0.00529
1,2-Dibromoethane	<0.00560	<0.00549	<0.00529
1,2-Dichlorobenzene	<0.00560	<0.00549	<0.00529
1,2-Dichloroethane	<0.00560	<0.00549	<0.00529
1,2-Dichloropropane	<0.00560	<0.00549	<0.00529
1,3,5-Trimethylbenzene	<0.00560	<0.00549	<0.00529
1,3-Dichlorobenzene	<0.00560	<0.00549	<0.00529
1,3-Dichloropropane	<0.00560	<0.00549	<0.00529
1,4-Dichlorobenzene	<0.00560	<0.00549	<0.00529

Table 4.1.9 (cont.) VOCs Present in Aquifer Materials

VOCs	Soil #1	Soil #2	Soil #4
	mg/Kg-dry	mg/Kg-dry	mg/Kg-dry
1-Chlorohexane	<0.00560	<0.00549	<0.00529
2,2-Dichloropropane	<0.00560	<0.00549	<0.00529
2-Butanone	<0.0168	<0.0165	<0.0159
2-Chlorotoluene	<0.00560	<0.00549	<0.00529
2-Hexanone	<0.0168	<0.0165	<0.0159
4-Chlorotoluene	<0.00560	<0.00549	<0.00529
4-Methyl-2-pentanone	<0.0168	<0.0165	<0.0159
Acetone	<0.0560	<0.0549	<0.0529
Benzene	<0.00560	<0.00549	<0.00529
Bromobenzene	<0.00560	<0.00549	<0.00529
Bromochloromethane	<0.00560	<0.00549	<0.00529
Bromodichloromethane	<0.00560	<0.00549	<0.00529
Bromoform	<0.00560	<0.00549	<0.00529
Bromomethane	<0.00560	<0.00549	<0.00529
Carbon disulfide	<0.00560	<0.00549	<0.00529
Carbon tetrachloride	<0.00560	<0.00549	<0.00529
Chlorobenzene	<0.00560	<0.00549	<0.00529
Chloroethane	<0.00560	<0.00549	<0.00529
Chloroform	<0.00560	<0.00549	<0.00529
Chloromethane	<0.00560	<0.00549	<0.00529

Table 4.1.9 (cont.) VOCs Present in Aquifer Materials

VOCs	**Soil #1**	**Soil #2**	**Soil #4**
	mg/Kg-dry	**mg/Kg-dry**	**mg/Kg-dry**
cis-1,2-Dichloroethene	<0.00560	<0.00549	<0.00529
cis-1,3-Dichloropropene	<0.00560	<0.00549	<0.00529
Cyclohexane	<0.0168	<0.0165	<0.0159
Dibromochloromethane	<0.00560	<0.00549	<0.00529
Ethylbenzene	<0.00560	<0.00549	<0.00529
Hexachlorobutadiene	<0.00560	<0.00549	<0.00529
Isopropylbenzene	<0.00560	<0.00549	<0.00529
m,p-Xylene	<0.00560	<0.00549	<0.00529
Methyl Acetate	<0.00560	<0.00549	<0.0159
Methyl tert-butyl ether	<0.00560	<0.00549	<0.00529
Methylcyclohexane	<0.0168	<0.0165	<0.0159
Methylene chloride	<0.00560	<0.00549	<0.00529
n-Butylbenzene	<0.00560	<0.00549	<0.00529
n-Propylbenzene	<0.00560	<0.00549	<0.00529
Naphthalene	<0.0168	<0.0165	<0.0159
o-Xylene	<0.00560	<0.00549	<0.00529
p-Isopropyltoluene	<0.00560	<0.00549	<0.00529
sec-Butylbenzene	<0.00560	<0.00549	<0.00529
Styrene	<0.00560	<0.00549	<0.0159

Table 4.1.9 (cont.) VOCs Present in Aquifer Materials

VOCs	Soil #1	Soil #2	Soil #4
	mg/Kg-dry	mg/Kg-dry	mg/Kg-dry
tert-Butylbenzene	<0.00560	<0.00549	<0.00529
Tetrachloroethene	<0.00560	<0.00549	<0.00529
Toluene	<0.00560	<0.00549	<0.00529
trans-1,2-Dichloroethene	<0.00560	<0.00549	<0.0159
trans-1,3-Dichloropropene	<0.00560	<0.00549	<0.00529
Trichloroethene	<0.00560	<0.00549	<0.00529
Trichlorofluoromethane	<0.0168	<0.0165	<0.0159
Vinyl chloride	<0.00560	<0.00549	<0.00529

Groundwater

Groundwater was used for NOD tests, reactor tests (Task 3.2), and the soil #2 batch and column study (Tasks 3.2 and 3.3, respectively). The source of the groundwater was from a well located on Battelle property that was installed in 1958 to a depth of 90 feet. An on-demand tap is located in the Environmental Restoration laboratory. The chemical profile of the groundwater is presented in Table 4.1.10. The groundwater was characterized for chloride, iron, sulfate, sulfide, nitrate, and total alkalinity. The groundwater tap was flushed at a high flowrate for 10 minutes before collecting a sample for characterization.

Table 4.1.10 Initial Screening: Battelle Groundwater Characterization

Parameters	Method	Range	Unit	Result
Temperature	-	-	°C	20.5
pH	Electrode	-	S.U.	8.3
ORP	Electrode	-	mV	339
Chloride	Hach 8113	0.1-25.0 mg/L Cl^-	mg/L	123
Total Iron	Hach 8008	0.02-3.0 mg/L	mg/L	0.06
Sulfate	Hach 8051	2.0-70.0 mg/L	mg/L	90.0
Sulfide	Hach 8131	5.0-800 µg/L	µg/L	15.0
Nitrate	Hach 8039	0.3-30.0 mg/L	mg/L as NO_3-N	0.6
Total Alkalinity	Hach 10239	25.0-400 mg/L $CaCO_3$	mg/L as $CaCO_3$	64.7

4.2 EVALUATION OF ISCO TECHNOLOGIES AND MOBILIZATION OF METALS

The ISCO treatment and metals mobilization portion of the study was designed to evaluate the response of ISCO site soils a range of ISCO treatments. This included a broad screening study to evaluate metals release and changes in geochemical properties of the soils due to the exposure of various oxidant/activator combinations at varying dosages; a detailed investigation to isolate the geochemical mechanism driving metals release from the soils; and geochemical modeling to further investigate the speciation and solid phase mineralogy controlling mobilization. The results of these evaluations are provided in the following 3 sections.

4.2.1 Initial Screening Evaluation

The initial soil screening evaluation was designed to measure the metals release and changes in geochemical properties for a large number of site soils exposed to a wide range of ISCO treatments. Specifically, the environmental response of 10 ISCO site soils exposed to 6 different ISCO treatment solutions were measured in 48 hour batch experiments. Following the initial screening, the effect of oxidant dosage was measured for a reduced number of soils and ISCO treatments. At the conclusion of the exposure period, ORP, pH and aqueous metal concentrations were measured. This section will provide the results of the initial screening followed by the results of the dosage study. All results from the preliminary screening evaluation will then be discussed in a summary.

INITIAL SCREENING

Nine of the 10 site soils were screened for metals release using 6 different oxidant treatments. The tenth soil was tested under only four ISCO chemistries. In these experiments, each oxidant was added at one dose that, with the exception of hydrogen peroxide, was in agreement with the higher range of reagent concentrations typically used in field applications . This allowed the evaluation of potential “worst case” metal release scenarios from the selected site soils. Eh and pH results are presented first, followed by the effects each oxidant and activation agent has on the mobilization of metals into solution.

Eh and pH Results. Oxidants were applied at different concentrations in the initial screening based upon typical field applications (Table 3.2.1). At the conclusion of the contact period, the Eh and pH of the aqueous solutions (eluant) was measured. Eh values are presented in Figure 4.2.1. ORP was primarily dependent upon the ISCO treatment applied but did vary between the 11 soils evaluated. Iron activated persulfate, permanganate and IAP+CA resulted in the solutions with the highest oxidant potential after 48hrs (avg. values 600, 587 & 570mV, respectively). Alkaline activated persulfate resulted in the most reducing potential (80 mV).

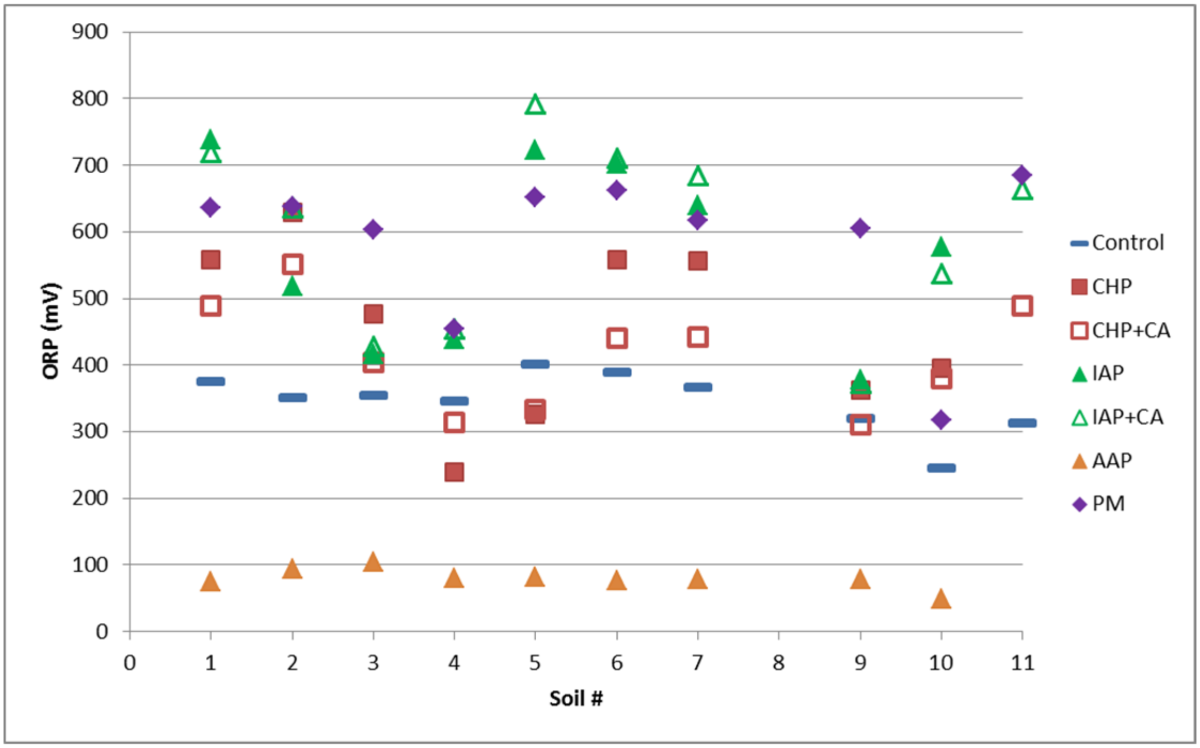


Figure 4.2.1 Initial Screening: ORP Values

In all experiments, the pH of the batch solutions was driven by the ISCO treatment applied and, with the exception of permanganate, pH was significantly different from the natural pH of the soils (see Figure 4.2.2). Permanganate only caused a slight increase in the natural pH of the soils, while alkaline-activated persulfate raised the pH to greater than 11. Conversely, iron-activated persulfate and catalyzed hydrogen peroxide caused the pH to drop between 2 and 4, which is significantly lower than the ambient pH of the untreated soils. Exceptions to this phenomenon were soils with good buffering capacity such as soil #9. Soils #3 and #4 also demonstrated buffering capacity for iron activated persulfate treatments and, to a lesser degree, catalyzed hydrogen peroxide.

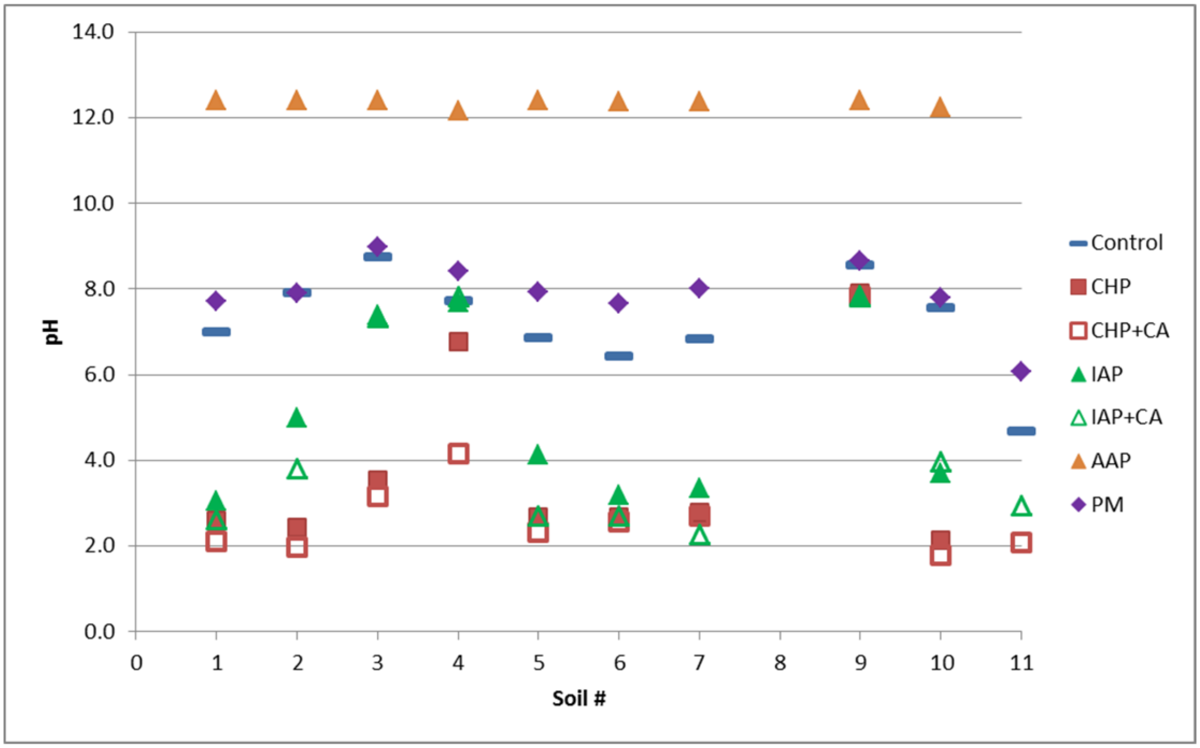


Figure 4.2.2 Initial Screening: pH Values

Effects of ISCO Treatments on Metals Release. Aqueous metal concentrations of 22 elements were measured following the previously described 48hr batch experiment. The concentration of 9 metals mobilized in each of the 6 oxidant chemistries is shown in Figure 4.2.3 (additional results are provided in Appendix B). Metals release depended on the characteristics of the soil to be treated (TOC, grain size), the ISCO treatment (i.e., oxidant type, activation method, and presence or absence of a chelating agent, all of which determine the pH and the Eh of the system), and the individual metal. Overall, catalyzed hydrogen peroxide with citric acid caused the highest level of metals release across most soils. This was followed by iron-activated hydrogen peroxide without the citric acid chelating agent and the various activated persulfate reagents. The application of permanganate resulted in the least metals release, with most of the observed metals mobilization originating from the reagent itself in the form of impurities.

The leaching of several cations (Be, Cd, Co, Ni, Pb, and Zn) and oxyanions (As, Cr, and V) were selected due to their different chemistries, environmental toxicity, and interpretability of their results. All additional aqueous metal concentrations from the batch studies are provided in Appendix B. The highest amount of Cd cation leached was in the iron-activated hydrogen peroxide system when citric acid was present, followed by the same chemistry without the chelating agent (Figure 4.2.3). In the presence of chelated and unchelated iron-activated persulfate, some release was observed, but in smaller amounts and for a fewer number of soils. Finally, no Cd leached when permanganate was present, and only a small amount of this metal was released in the alkaline-activated persulfate system in soil #4. Most of the Cd release was observed in cases when the oxidant and other reagents lowered the pH of the soil below 4 (Figure 4.2.4). This is in agreement with the observation that metal cations (such as Cd, Cu, Ni, Pb, and Zn) present in soils tend to mobilize at the two pH extremes (Dijkstra et al., 2004). In the present study, soils #3, 4, and 9 exhibited a high buffering capacity by counteracting the pH reducing effect of the reagents, resulting in less Cd mobilization. Part of the high buffering capacity of soils #4 and 9 was due to their high TOC content. The organic matter content is also an important contributor to the soil NOD. The pH stabilizing affect most likely occurred because the high NOD of these soils consumed the oxidants, as indicated by the lower ORP values compared to the rest of the soils, and therefore prohibited the formation of pH lowering acidic compounds in the iron-activated hydrogen peroxide and persulfate systems. Besides the pH effect, Cd in the permanganate system could also have been mitigated by $MnO_{2(S)}$ formed during the oxidation reaction (Crimi and Siegrist, 2004; Siegrist et al., 2002). Furthermore, the presence of the citric acid chelating agent significantly increased Cd leaching in the catalyzed hydrogen peroxide system of the present study. This impact was also observed in the presence of iron-activated persulfate but to a lesser extent. Finally, the TOC content and the grain size of the soils did not seem to have a clear correlation with the amount of Cd leached due to any of the ISCO chemistries tested.

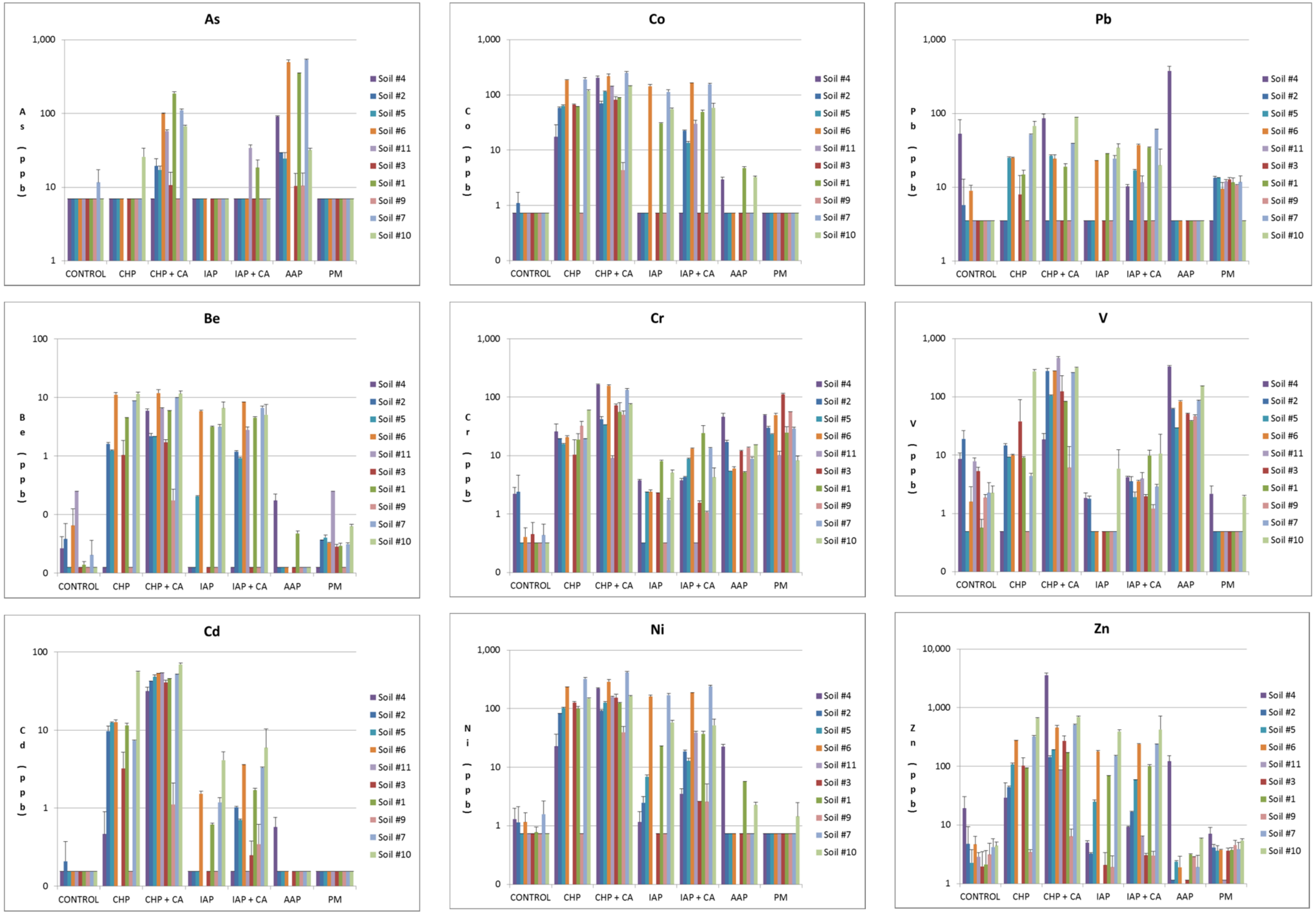


Figure 4.2.3 Initial Screening: Metals mobilization from ISCO treatments of 10 ISCO site soils.

Note: Soils are shown in order of coarse to fine grain size

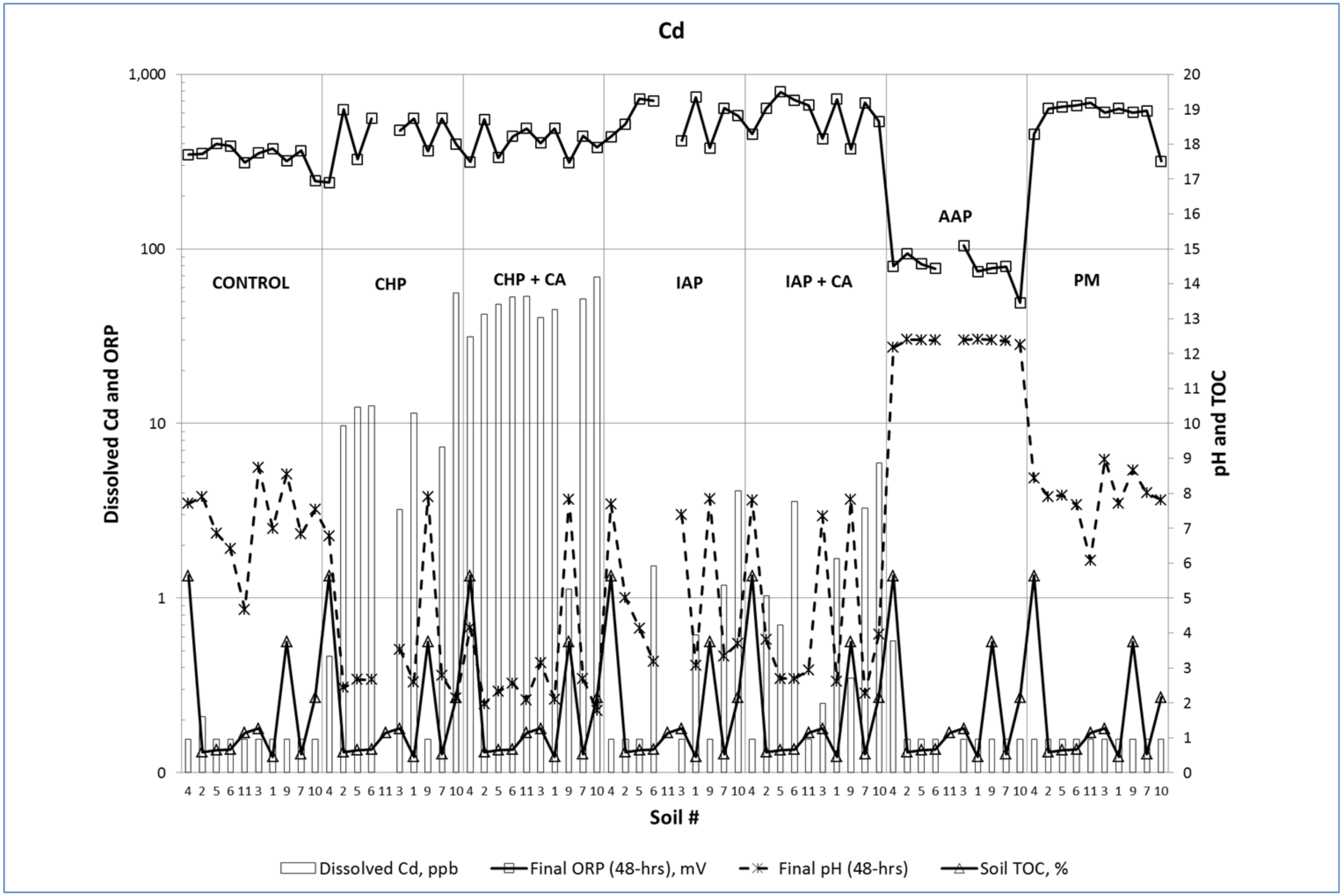


Figure 4.2.4 Initial Screening: Soil TOC, pH, ORP, and Cd release from ten site soils

Metals release trends similar to Cd were observed for other divalent cations such as Be, Co, Ni, Pb, and Zn (Figure 4.2.3), with metals mobilization occurring in most soils in the catalyzed hydrogen peroxide system, followed by the iron-activated persulfate chemistry that resulted in similar amounts released, but only for select soils. Some release was also observed in the alkaline-activated persulfate system, primarily in soils #1 and 4, but only Ni and Zn leached from these soils at comparable levels to the iron-activated chemistry, i.e. at both high and low pH values. In addition, Pb release was highest in the presence of alkaline-activated persulfate in soil #4. There was no significant Be, Co, Ni, Pb, and Zn leaching in the presence of permanganate; dissolved Pb concentrations observed under this oxidant chemistry originated from the reagent (Table 4.2.1). The presence of metal impurities in permanganate is a known concern for field applications of this oxidant (Siegrist et al., 2011). Furthermore, Pb, Ni, and Zn have been reported to adsorb to $MnO_{2(S)}$ formed during permanganate oxidation (Al et al., 2006; Crimi and Siegrist, 2004; Nelson et al., 2001). As in the case of Cd, most Be, Co, Ni, Pb, and Zn release occurred at pH values at or below 4 (Appendix B), indicating that the interplay of the pH lowering affect of the reagents and the soil buffering capacity determine the amount of metals leached. Teel et al. (2008a, b) also observed increased Cd and Pb mobilization in the presence of catalyzed hydrogen peroxide at pH 3 compared to pH 7 from soils with high organic content; the increased metal mobilization was attributed to the destruction of the soil organic matter that previously contained the metals by hydroxyl radicals formed during the oxidation reaction. This theory is further supported by the observation that cations such as Cd, Cu, Ni, Pb, and Zn tend to associate with the organic matter phase of soils (Dijkstra et al., 2004). A few exceptions in the present study occurred in soil #4, where Co, Ni, Pb, and Zn leached in higher amounts even at intermediate pH levels (between pH 7 and 8), a phenomenon also observed for Ni in soil #9 (Appendix B). Another exception was observed for Pb, as this metal did not mobilize even below pH 4 from select soils (i.e., primarily from soil #2, but also from soils #3, 5, and 11) in either the iron-activated hydrogen peroxide or persulfate systems. Similarly to Cd, the TOC content and the grain size of the soils did not seem to have a clear correlation with the amount of other cations leached due to any of the ISCO chemistries tested.

ISCO chemistries had similar effects on the leaching of oxyanions compared with cations, but some differences were also observed. Similarly to cations, the application of the iron-activated chelated hydrogen peroxide chemistry resulted in the highest Cr, Sb, and V release for the majority of the soils (Figures 4.2.3). On the other hand, alkaline-activated persulfate mobilized similar or even higher amounts of As and V, while this oxidant chemistry did not cause significant cation release in most soils. Iron-activated hydrogen peroxide without the chelating agent only caused mobilization of Cr and V for most soils, and of As and Sb in soil #10. Similarly, iron-catalyzed persulfate (both with and without citric acid) only mobilized Cr from most soils and As and V from select materials. Finally, while the presence of permanganate did not result in significant cation release, Cr leaching has been significantly impacted by this oxidant. It should be noted that a portion of dissolved Cr, 4.3 to 58.5% depending on the soil, originated from the reagent itself (see Figure 4.2.3 Table 4.2.1).

Table 4.2.1 Metals Present in the Permanganate Reagent

Metal	**Metal Concentration** *ppb*
Ag	8.59
As	BDL
Ba	2.31
Be	0.03
Cd	BDL
Co	BDL
Cr	4.80
Cu	BDL
Ni	BDL
Pb	10.65
Sb	BDL
Se	60.91
V	1.19
Zn	BDL

Chromium was highly impacted by all of the oxidant chemistries tested (Figure 4.2.3). This is an important finding, since the release of Cr in the form of highly soluble Cr(VI) is a potential concern for contaminated site managers (Gardner, 2012); this issue has been reported as a concern at both permanganate (Crimi and Siegrist, 2003) and hydrogen peroxide ISCO sites (Rock et al., 2001; Villa et al., 2008). In the present study, the leaching of V was primarily caused by catalyzed hydrogen peroxide (both with and without citric acid) and alkaline-activated persulfate (Figure 4.2.3). Arsenic was mainly mobilized by chelated iron-catalyzed hydrogen peroxide and alkaline-activated persulfate, and the former oxidant also caused the most Sb release. There was no significant Se release observed in the ISCO systems tested, but Se was among the metals that were observed in the permanganate system due to metal impurities in the reagent. The fact that not all ISCO conditions resulted in significant As, Sb, and V release implies that mobilization of these oxyanions can be prevented or minimized by careful oxidant chemistry selection at contaminated sites. In the case of Cr, mobilization could be minimized by selecting the oxidant condition that resulted in the least release. It should be noted that while the present paper evaluated metals release that occurred after 48 hours of oxidant exposure, longer-term release behavior in the field will be affected by the subsurface persistence of the oxidants. For example, persulfate and permanganate persist longer in the environment than peroxide and as a result these two oxidants could continue to mobilize metals over time. Finally, similarly to cations, the TOC content and the grain size of the soils did not seem to have a clear correlation with the amount of oxyanions leached due to any of the ISCO chemistries tested.

Effect of chelating agents and activation method. The effect of different activation chemistries on metals release from using the same oxidant was also evaluated. For example, metals like As, Cd, Cr, Zn, and (except for soil #3) V, always leached in higher amounts in the presence of citric acid in the catalyzed hydrogen peroxide system (Figure 4.2.3); and so did Be, Co, and Ni from most soils. Chelating agents such as EDTA and citric acid have been long used to extract heavy metals from contaminated soils (Peters, 1999). As the chelating agents assist the leaching of metals, their presence could result in a potential metals mobilization pathway in ISCO applications (Siegrist et al., 2011). On the other hand, Bennedsen et al. (2012) reported that the presence of chelating agents, including citric acid, did not increase As, Cu, Ni, Pb, and Zn release in the presence of hydrogen peroxide when a 183 : 1 : 1 = oxidant : Fe(II) : citric acid molar ratio was used. A different reagent molar ratio was applied in the present study (i.e., 100 : 1 : 2) and this could have contributed to the observed differences. Furthermore, there were also instances in the present study when a given metal would leach in equal quantities from the chelated and unchelated catalyzed hydrogen peroxide systems from certain soils, indicating that this phenomenon might be both soil and metal specific. For example, there was no significant difference in Co and Ni leaching in the presence and absence of citric acid in soils #2 and 3. Similarly, Be mobilization was the same for both the chelated and unchelated chemistry in soils #3, 6, and 10. Finally, Pb was the only metal that exhibited a more varied release chemistry; with smaller (soils #3 and 7), equal (soils #1, 5, and 6), and higher (soils #4 and 10) release in the presence of citric acid.

Similar trends were observed for the chelated and unchelated iron-activated persulfate chemistries, where most metals leached in higher quantities in the presence of citric acid (Figure 4.2.3); this was the case for As, Cd, Co, and with the exception of soil #10, for Be, Ni, Pb, and V. Additional exceptions have been observed for Cr and Zn in soils #3, 4, and 10. This indicates that while the effect of citric acid on release is still metal specific, soil characteristics seems to have a more significant impact in the persulfate than in the hydrogen peroxide oxidant system.

When comparing the two iron-activated and the alkaline-activated persulfate chemistries, iron-activation typically resulted in higher release of Be, Cd, Co, Ni, Pb, and Zn in all soils except for soil #4 (Figure 4.2.3). On the other hand, alkaline-activation stimulated As and V release the most, as well as the mobilization of all metals from soil #4. Chromium leaching has also been elevated at higher pH values in select soils (i.e., soils #2, 3, 4, 9, and 10). This seems to suggest that with the exception of soil #4, the most cation release occurred at low pH and oxyanions were mobilized to a greater extent at high pH. Metal leaching behavior in soil #4 was most likely impacted by the fact that acidic pH conditions have never been achieved in the iron-activated persulfate chemistries due to the high buffering capacity of this soil. Furthermore, one of the oxyanions, Cr exhibited more complex release chemistry. While alkaline-activation resulted in Cr release in most soils, the leaching of this metal was higher under acidic conditions in soil #1, and pH conditions did not seem to have a clear impact in soils #5 to 7.

Oxidant Dose-Response Curves

The effect of oxidant dose on metals release was evaluated for one site soil (soil #1) and the same six ISCO chemistries that were tested in the screening experiments but at multiple oxidant doses (see Table 3.2.2). In addition, the dose-response relationship of uncatalyzed hydrogen peroxide, and the iron-activated persulfate chemistry with two different molar ratios of oxidant : iron(II) : citric acid has also been tested. pH and Eh results are presented first followed by metals results which are organized categorically by the oxidant used in the ISCO treatment.

Eh and pH. ORP increased or decreased immediately with the initial application of each ISCO treatment (Figure 4.2.5). However, increased applications consistently resulted in a reduced ORP change at higher dosages. Similar trends were observed with pH change.

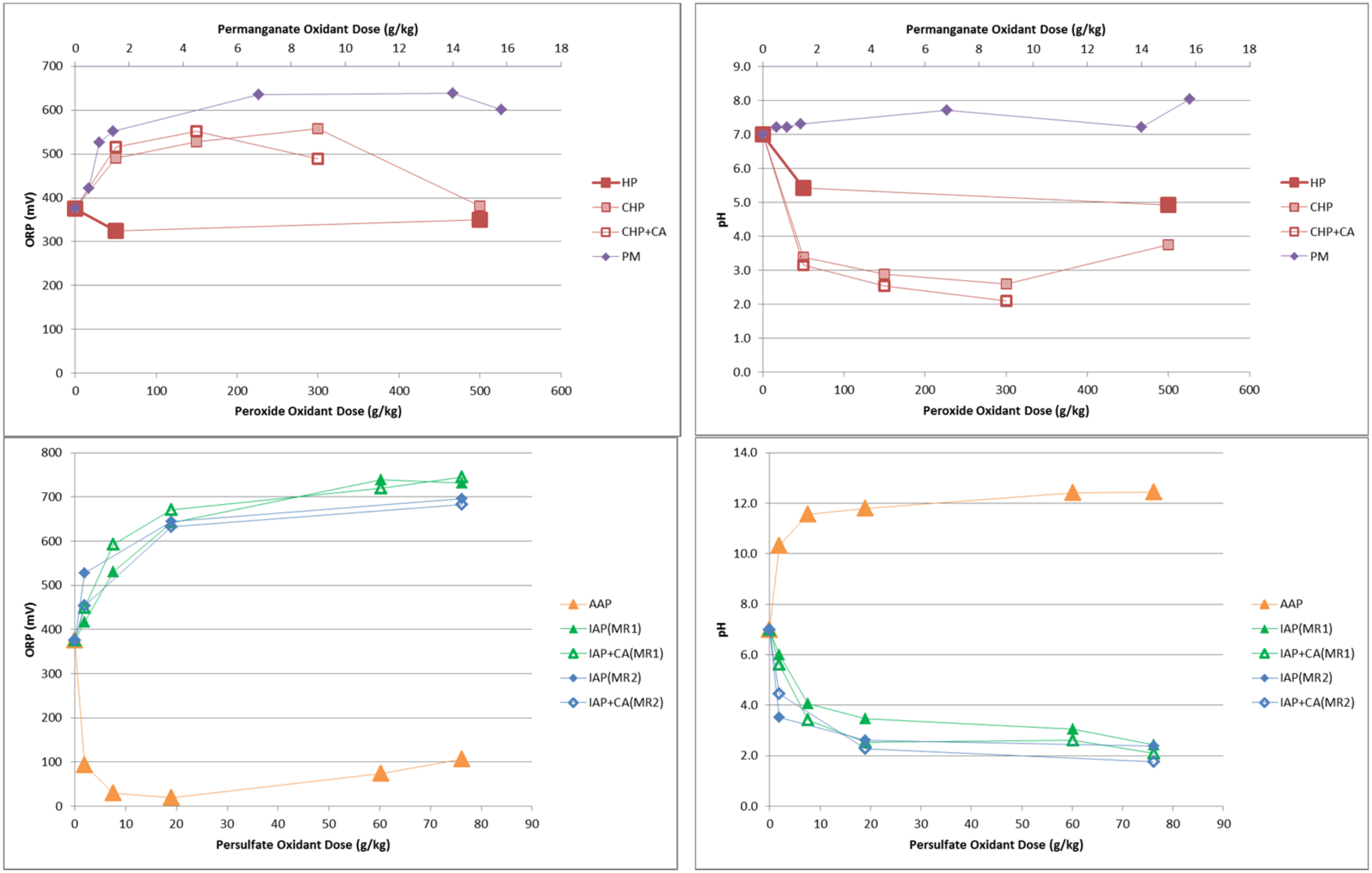


Figure 4.2.5 Initial Screening: Eh and pH changes due to increasing ISCO treatment dosage

Hydrogen peroxide. Unchelated and chelated iron-activated hydrogen peroxide, and the oxidant by itself were evaluated at four, three, and two different oxidant doses, respectively (see Table 3.2.2). The amount of metals mobilized in the presence of various hydrogen peroxide chemistries generally increased with rising oxidant dose (Figure 4.2.6; see also Appendix B). This increase followed two general shapes: (1) a sharp increase in dissolved metal concentrations at lower oxidant doses with less pronounced change at higher reagent concentrations (e.g. for Be, Co, Cr, Cu, Ni, and Zn), and (2) a more gradual increase over the range of oxidant doses tested (for As, Cd, and Sb). It should be noted, that since the pH in the oxidant dosing experiments was not controlled and since the final pH was determined by the amount of reagents added (Figure 4.2.5), both changes in pH and ORP could have contributed to the oxidant dose effect in metals release. For most metals, the highest amount of metals mobilization in the presence of hydrogen peroxide occurred in the chelated iron-catalyzed system, followed by the unchelated iron-catalyzed condition, and finally the uncatalyzed reagent. This is the same trend in which the pH of the same oxidant dose batches increased from one treatment to the other ((Figure 4.2.5) indicating the potential impact of pH conditions. As previously noted, the presence of a chelating agent could also provide a potential metal mobilization pathway during ISCO applications. Furthermore, the addition of citric acid decreased the pH of the soil potentially contributing to increased metals release. Similarly, the Fe catalyst also lowered the ambient pH, which resulted in elevated post-ISCO metal concentrations. Metals like As, Be, Cd, Pb, and Sb did not mobilize in the presence of the uncatalyzed oxidant (Figure 4.2.6), and similarly no Se release has been observed under any of the three hydrogen peroxide conditions (not shown). Finally, the difference in the amount of metals released in the unchelated and chelated iron-catalyzed oxidant system varied between slight and more highly significant for the various metals. For example, As and Sb were released in much higher amounts in the presence of citric acid, while the level of Be, Cu, and Ni mobilization was similar in both the presence and absence of the chelating agent. The above results indicate that both hydrogen peroxide dose and chemistry had a significant impact on metals release from soil #1.

Persulfate. Three persulfate activation chemistries were evaluated in the oxidant dosing experiments for their effect on metals mobilization: alkaline-activated persulfate, and iron-catalyzed persulfate with and without citric acid chelating agent. These chemistries were tested using five oxidant doses (see Table 3.2.2). The iron-activated persulfate systems were tested at two molar ratios of oxidant : iron(II) : citric acid; first with 100:1:2 (MR1) and then with 12.5:5:1 (MR2). These MRs represent values commonly used in ISCO site remediation projects and in research studies published in the literature, respectively. Under the MR1 condition there is less iron relative to the amount of oxidant and more citric acid relative to the iron present in the system compared to the MR2 scenario. Similarly to hydrogen peroxide, the amount of most metals released also increased with rising persulfate dose (Figure 4.2.7). Suthersan and Horst (2008) observed the same for Cr in the presence of alkaline-activated persulfate, and for As, Cd, Cr, and Ni when iron-activated persulfate was applied. The shape of the persulfate dose-response curves in the present study either showed a gradual increase over the range of oxidant doses tested, or a rapid initial increase in observed metal concentrations with smaller amount of additional release. The type of oxidant dose-response curve observed depended on both the individual metal and on the oxidant chemistry. Similarly to hydrogen peroxide, metal leaching in the presence of persulfate could have been impacted by both the pH and the ORP of the system that was determined by the amount of reagents added (Table 3.2.2).

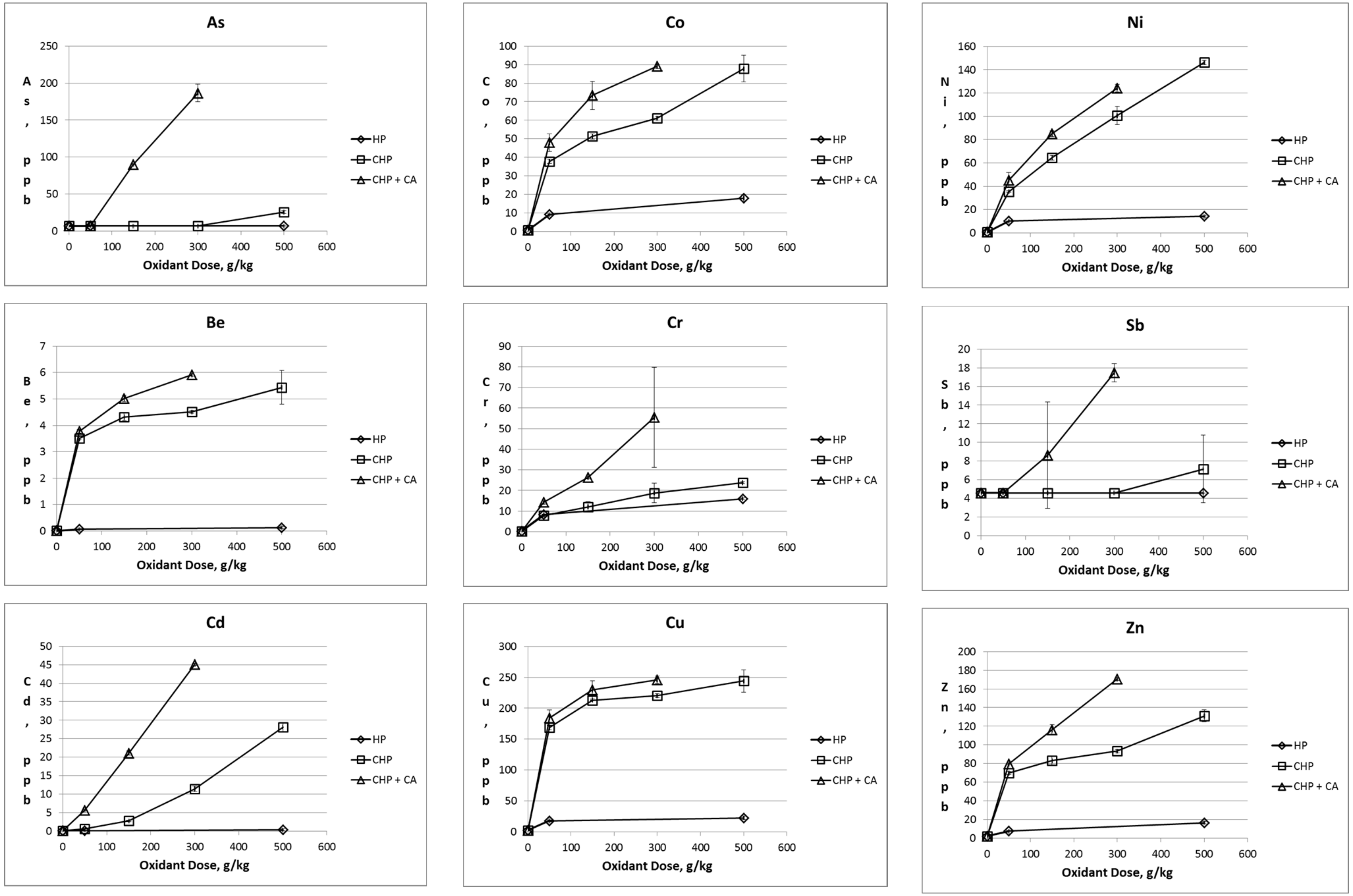


Figure 4.2.6 Initial Screening: Metals mobilization as a function of peroxide dose for soil#1

(HP = hydrogen peroxide; CHP = iron-activated hydrogen peroxide; CA = citric acid chelating agent)

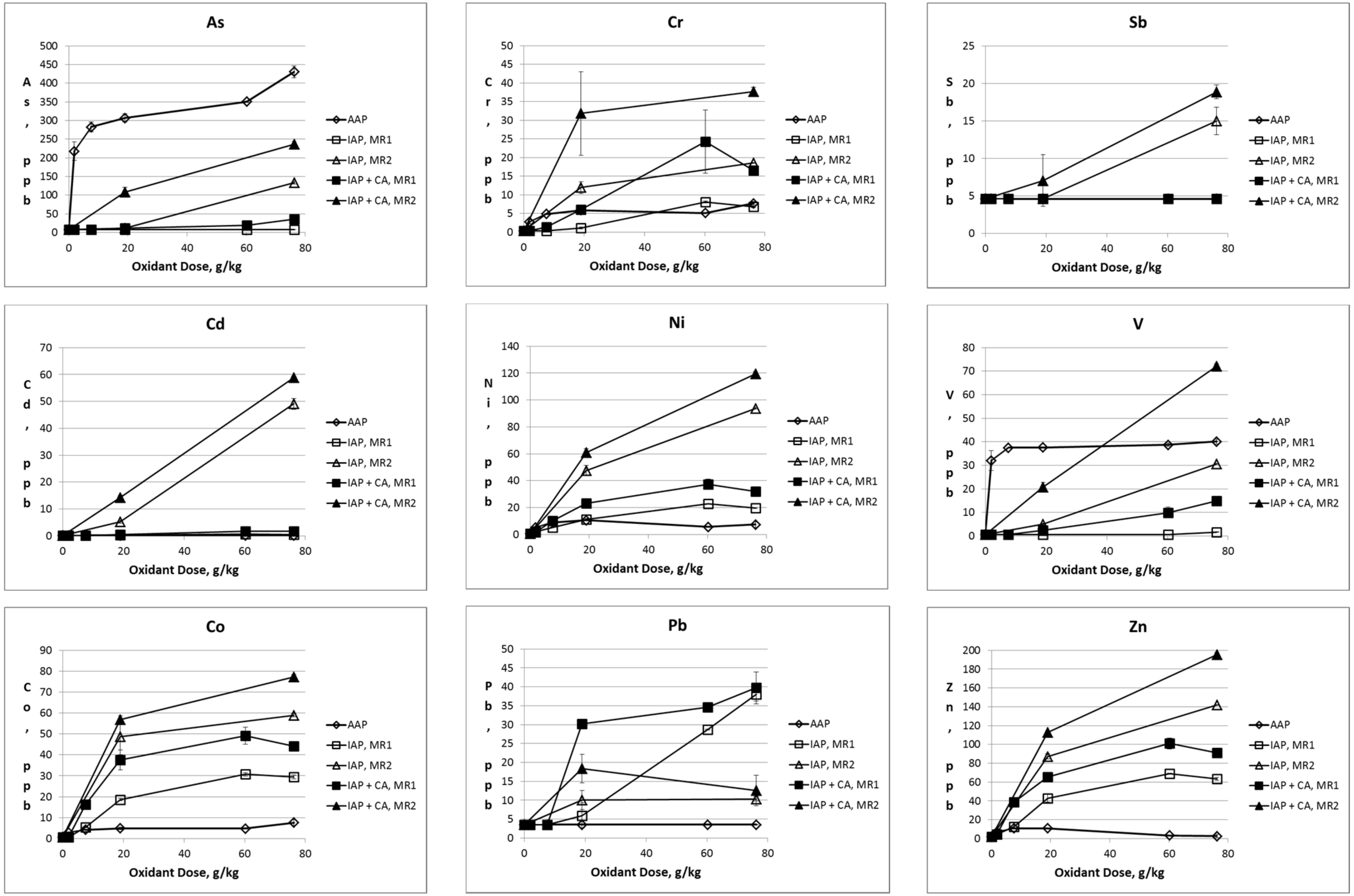


Figure 4.2.7 Initial Screening: Metals mobilization as a function of persulfate dose for soil#1

(AAP = alkaline-activated persulfate; IAP = iron-catalyzed persulfate; CA = citric acid chelating agent; MR = molar ratio; MR1 = 100:1:2 and MR2 = 12.5:5:1)

Alkaline-activation represented the only basic pH condition among the three persulfate chemistries tested. The application of this ISCO chemistry resulted in the highest As release and the most V leaching below 40 g/kg oxidant added (Figure 4.2.7). On the other hand, several other metals such as Ba, Be, Cd, Co, Pb, Ni, and Zn have been released at the lowest levels at alkaline pH conditions (Figure 4.2.7). In the iron-catalyzed systems, the MR2 condition generally resulted in higher metal release (e.g. for As, Cd, Co, Cu, Ni, Sb, V, Zn and except for one oxidant dose for Cr), the same condition that resulted in lower pH values for all oxidant doses tested (Table 3.2.2), indicating that the pH of the system could have influenced the amount of metals leached. Exceptions were Ba and Pb, where the MR1 condition resulted in more metal mobilization at most oxidant doses. When comparing metals release in the presence and absence of citric acid in the iron-catalyzed persulfate system, the use of the chelating agent generally increased the amount of metals mobilized for all oxidant doses and for both reagent MRs tested. The only metal that exhibited a different type of behavior was Ba; the release of this metal was about the same in both the presence and absence of citric acid under the MR2 condition, and was oxidant dose dependent under the MR1 scenario (i.e., in the presence of the chelating agent, Ba leaching decreased and increased above and below 40 g/kg persulfate, respectively). A similar oxidant dose-dependent behavior was observed for Pb when comparing the effect of reagent molar ratios on metal release. In the presence of citric acid, a higher amount of Pb was released in the MR1 system between 10 and 60 g/kg of persulfate applied, while below 10 g/kg persulfate Pb mobilization was higher under the MR2 condition. Ba and Pb also behaved differently when comparing release at various Fe catalyst additions. In general, metal leaching increased with higher amounts of Fe(II) added (i.e. under the MR2 scenario); while the opposite was observed for Ba and Pb. It should be noted that the difference in the Fe(II) : citric acid application ratio in the MR1 and MR2 scenarios might have also contributed to this metal leaching behavior. In addition, the pH of the soil decreased with increased Fe(II) addition (Table 2.5) and that could have also resulted in increased metal release. Metals that have not been mobilized in the presence of persulfate included Se for all three conditions (not shown), and As, Cd, Pb, Sb, and V for select persulfate chemistries (Figure 4.2.7). These are the same metals (with the exception of V) that did not mobilize in the presence of uncatalyzed hydrogen peroxide.

Permanganate. Finally, metals mobilization was tested at six different permanganate doses in soil #1 (see Table 3.2.2). Most metals were released in significantly lower quantities in the presence of this oxidant compared to both hydrogen peroxide and persulfate. An exception to this was Cr that was mobilized in the presence of permanganate at levels comparable to select persulfate and hydrogen peroxide chemistries (see Figures 4.2.6, 4.2.7 and 4.2.8). As noted above, Cr was one of the metal impurities found in permanganate (Table 4.2.1), however, most of the observed release in the present study originated from the soil. Crimi and Siegrist (2003) suggested that permanganate could oxidize Cr(III) into the more soluble Cr(VI) form resulting in increased mobilization of this metal; a concept previously proven at the laboratory scale by Li and Schwartz (2004) and Chambers et al. (2000a). Furthermore, Cr concentration in the present study increased with rising oxidant dose, a finding similar to the observation made by Luhrs et al. (2006) for metals in general for this oxidant. Additional metals that were detected in the presence of permanganate in the present study included Be, Pb, and Se; post-ISCO dissolved concentrations of these three metals originated from the reagent (results not shown). Several metals were mobilized in only small quantities in the presence of permanganate (e.g. Ba, Cu, V, and Zn, results not shown), and others like Cd, Co, Ni, and Sb were not detected in the dissolved phase. The above results indicate that most of the dissolved metals observed in soil #1 in the presence of permanganate originated from the oxidant itself, and that Cr was the only metal that was mobilized well above levels found in the reagent.

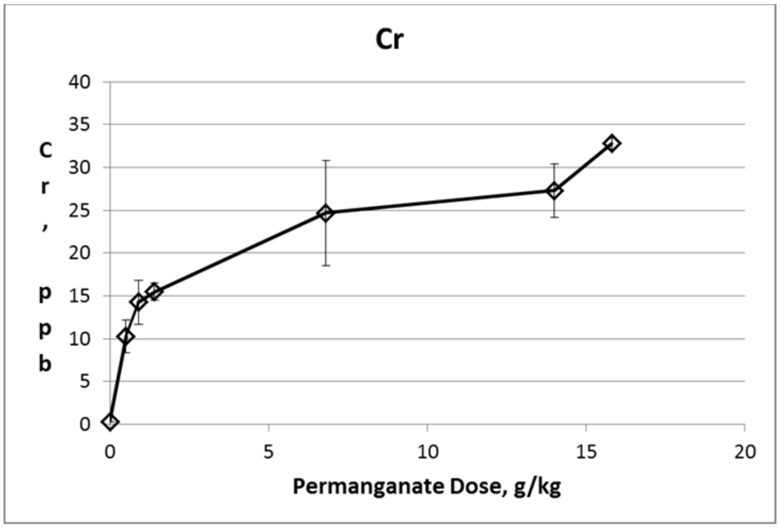


Figure 4.2.8 Initial Screening: Cr mobilization as a function of permanganate dose in soil#1

Summary of ISCO site soil screening experiments.

Results of the above screening studies have been summarized in Tables 4.2.2 and 4.2.3. Table 4.2.2 lists all metals that have been mobilized compared to the background (i.e. when no oxidant was present) for each soil and ISCO condition tested. In addition, based on the amount of metal release, the following categories have been defined: 1) exceeded regulatory limits (i.e. regulated under the Safe Drinking Water Act (SDWA) or the Resource Conservation and Recovery Act (RCRA)), 2) did not exceed regulatory limits, and 3) unregulated. This categorization was simply carried out to provide an example of how metals release results could be interpreted in a regulatory framework; a similar evaluation could be performed for any ISCO site using the applicable regulatory limits for that particular site. In addition, Table 4.2.3 shows the frequency of metals mobilization in the ten ISCO site soils tested in this study; release above both the maximum contaminant level (MCL) and the background is shown. Priority metal contaminants that exceeded the MCL in over two thirds of the site soils tested included As, Be, Cd, Pb, and Sb (highlighted in red). This release was ISCO chemistry specific. For example, As only mobilized at levels above the MCL in the alkaline-activated persulfate and the chelated catalyzed hydrogen peroxide systems, and Cd and Sb were only released in excess of the MCL in the presence of hydrogen peroxide. On the other hand, Pb release exceeded the MCL in the presence of both chelated and unchelated catalyzed hydrogen peroxide and iron-activated persulfate, and with the exception of the unchelated iron-activated persulfate, so did Be when the same ISCO chemistries were applied. In general, catalyzed hydrogen peroxide seemed to have the biggest impact on metals release in terms of number of metals mobilized in over one third of the soils tested, followed by the various persulfate chemistries. When comparing the impact of the various persulfate chemistries, iron activation resulted in more metals release than alkaline activation. Finally, permanganate only mobilized Cr and Ba above background levels in over one third of the sites tested. There were no MCL exceedances in the presence of this oxidant in any of the site soils. In summary, as stated previously, the types and concentrations of metals released depended on both treatment (i.e. oxidant chemistry) and soil type.

Table 4.2.2 Initial Screening: Metals Mobilization in for ISCO Site Soils [a]

Oxidant:	**Hydrogen Peroxide**		**Persulfate**			**Permanganate**
ISCO Treatment:	**CHP**	**CHP+CA**	**IAP**	**IAP+CA**	**AAP**	**PM**
Oxidant Dose (g/kg)	300	300	60.2	60.2	60.2	6.8
Oxid. Aqueous Conc. (g/L)	30	30	6.02	6.02	6.02	0.68
Molar Ratio (*Oxidant:Fe(II):CA)*	100 : 1	100 : 1 : 2	100 : 1	100 : 1 : 2	1 : 0 : 2	na
Soil #1 (NE DOD Facility)						
Exceeded regulatory limits	Be, Cd	As, Be, Cd, Pb, Sb	Pb	As, Be, Pb	As	Se
Did not exceed regulatory limits	Ba, Cr, Cu, Pb	Ba, Cr, Cu	Ag, Ba, Be, Cd, Cr, Cu	Ag, Ba, Cd, Cr, Cu	As, Cu	Ag, Be, Cr, Pb
Unregulated	Co, Ni, V, Zn	Co, Ni, V, Zn	Co, Ni, Zn	Co, Ni, V, Zn	Co, Ni, V	none
Soil #2 (Navy facility in California)						
Exceeded regulatory limits	Cd	As, Cd, Sb	none	none	As	Se
Did not exceed regulatory limits	Ba, Be, Cr, Cu	Ag, Ba, Be, Cr, Cu	Ag, Ba	Ag, Ba, Be, Cd	Ag	Ag, Ba, Cr, Pb
Unregulated	Co, Ni, Zn	Co, Ni, V, Zn	none	Co, Ni, Zn	V	none
Soil #3 (Navy facility in California)						
Exceeded regulatory limits	none	As, Cd, Sb	none	none	As	Cr, Se
Did not exceed regulatory limits	Ag, Ba, Be, Cd, Cr, Cu, Pb,	Ag, Ba, Be, Cr, Cu	Ag, Ba, Cr	Ba, Cd, Cr	Cu	Ag, Ba, Be, Pb
Unregulated	Co, Ni, V, Zn	Co, Ni, V, Zn	none	Ni	V	none
Soil #4 (US Army Core site in Mid Atlantic)						
Exceeded regulatory limits	none	Be, Cd, Cr, Sb	none	none	As, Pb	none
Did not exceed regulatory limits	Ag, Cd, Cr, Cu	Ag, Ba, Cu	Ba, Cr	Ba, Cr, Cu	Be, Cd, Cu	Cr, Cu
Unregulated	Co, Ni	Co, Ni, V, Zn	none	Ni	Co, Ni, V, Zn	none
Soil #5 (Industrial Facility in New England)						
Exceeded regulatory limits	Cd, Pb	As, Cd, Pb, Sb	none	none	As	Se
Did not exceed regulatory limits	Ag, Ba, Be, Cr, Cu	Ag, Ba, Be, Cr, Cu	Ba, Be, Cr, Cu	Ba, Be, Cd, Cr, Cu	Cu	Ag, Ba, Be, Cr, Pb
Unregulated	Co, Ni, V, Zn	Co, Ni, V, Zn	Ni, Zn	Co, Ni, V, Zn	V	none

Note: Regulatory Limits under SDWA or RCRA8 primary MCLs

Table 4.2.2 (cont.) Initial Screening: Metals Mobilization in for ISCO Site Soils [a]

Oxidant:	**Hydrogen Peroxide**		**Persulfate**			**Permanganate**
ISCO Treatment:	**CHP**	**CHP+CA**	**IAP**	**IAP+CA**	**AAP**	**PM**
Oxidant Dose (g/kg)	300	300	60.2	60.2	60.2	6.8
Oxid. Aqueous Conc. (g/L)	30	30	6.02	6.02	6.02	0.68
Molar Ratio (*Oxidant:Fe(II):CA)*	100 : 1	100 : 1 : 2	100 : 1	100 : 1 : 2	1 : 0 : 2	na
Soil #6 (Gasoline Station in New England)						
Exceeded regulatory limits	Be, Cd, Pb	As, Be, Cd, Cr, Pb, Sb	Be, Pb	Be, Pb	As	Se
Did not exceed regulatory limits	Ba, Cr, Cu	Ba, Cu	Ba, Cd, Cr, Cu	Ba, Cd, Cr, Cu	Cu	Ag, Cr, Pb
Unregulated	Co, Ni, V, Zn	Co, Ni, V, Zn	Co, Ni, Zn	Co, Ni, V, Zn	V	none
Soil #7 (Gasoline Station in New England)						
Exceeded regulatory limits	Be, Cd, Pb	As, Be, Cd, Cr, Pb, Sb	Pb	Be, Pb	As	Se
Did not exceed regulatory limits	Ba, Cr, Cu	Ag, Ba, Cu	Ba, Be, Cd, Cr, Cu	Ba, Cd, Cr, Cu	Cu	Ag, Ba, Cr, Pb
Unregulated	Co, Ni, V, Zn	Co, Ni, V, Zn	Co, Ni, Zn	Co, Ni, Zn	V	none
Soil #9 (Navy Facility in the Southeast)						
Exceeded regulatory limits	none	none	none	none	As	Se
Did not exceed regulatory limits	Ag, Ba, Cr, Cu	Ag, Ba, Be, Cd, Cr, Cu, Se	Ba	Ba, Cr	Cu	Ag, Cr, Cu, Pb
Unregulated	none	Co, Ni, V	none	Ni	V	none
Soil #10 (EPA Site in the South)						
Exceeded regulatory limits	As, Be, Cd, Pb, Sb	As, Be, Cd, Pb, Sb	Be, Pb	Be, Cd, Pb	As	none
Did not exceed regulatory limits	Ag, Cr, Cu	Ag, Cr, Cu	Cd, Cr, Cu	Cr, Cu	Cu	Be, Cr, Cu
Unregulated	Co, Ni, V, Zn	Co, Ni, V, Zn	Co, Ni, Zn	Co, Ni, V, Zn	Ni, V	Ni
Soil #11 (Former Industrial Facility in the Southwest)						
Exceeded regulatory limits	*Not evaluated*	As, Be, Cd, Sb	*Not evaluated*	As	*Not evaluated*	Se
Did not exceed regulatory limits		Ag, Ba, Cr, Cu		Ag, Ba, Be, Pb		Ag, Ba, Cr, Pb
Unregulated		Co, Ni, V, Zn		Co, Ni		none

Table 4.2.3 Initial Screening: Frequency of Metals Mobilization in ISCO Site Soils

	Dissolved Metals										
	Ag[1]	**As**	**Ba**	**Be**	**Cd**	**Cr**	**Cu**	**Pb**	**Sb**	**Se**	**Zn[1]**
MCL (ug/L):	***100***	***10***	***2000***	***4***	***5***	***100***	***1300***	***15***	***6***	***50***	***5000***
Background (10 Sites Evaluated)											
Site Max Conc. > MCL	0	10%	0	0	0	0	0	0	0	0	0
AAP - Alkaline Activated Persulfate (9 Sites Evaluated)											
Site Max Conc. > Background	22%	100%	22%	22%	11%	100%	88%	11%	0	0	33%
Site Max Conc. > MCL	0	100%	0	0	0	0	0	11%	0	0	0
CHP - Catalyzed Hydrogen Peroxide (9 Sites Evaluated)											
Site Max Conc. > Background	55%	11%	77%	77%	88%	100%	100%	66%	11%	0	88%
Site Max Conc. > MCL	0	11%	0	44%	66%	0	0	55%	11%	0	0
CHP+CA - Catalyzed Hydrogen Peroxide with Citric Acid (10 Sites Evaluated)											
Site Max Conc. > Background	80%	80%	90%	100%	100%	100%	100%	60%	90%	10%	100%
Site Max Conc. > MCL	0	80%	0	60%	90%	30%	0	60%	90%	0	0
IAP – Iron Activated Persulfate (9 Sites Evaluated)											
Site Max Conc. > Background	33%	0	88%	55%	44%	77%	55%	44%	0	0	55%
Site Max Conc. > MCL	0	0	0	22%	0	0	0	44%	0	0	0
IAP+CA – Iron Activated Persulfate with Citric Acid (10 Sites Evaluated)											
Site Max Conc. > Background	30%	20%	90%	70%	80%	80%	80%	60%	0	0	70%
Site Max Conc. > MCL	0	20%	0	40%	10%	0	0	50%	0	0	0
PM – Permanganate (10 Sites Evaluated)											
Site Max Conc. > Background	20%	0	40%	20%	0	100%	30%	0	0	20%	0
Site Max Conc. > MCL	0	0	0	0	0	10%	0	0	0	0	0

Note: 1- Metal regulated by secondary MCL; **Red** highlight indicates >66% of sites are above threshold, **yellow** highlight indicates greater than 33% of sites are above threshold.

4.2.2 Detailed Evaluation

Experiments conducted in the initial screening evaluated metal leaching from ISCO site soils at the "natural pH" of these materials (i.e. the native pH of the soil material impacted by the pH of the oxidant applied). While results of these studies are useful observations in terms of metals mobilization at the tested ISCO sites, causes of the release cannot be fully elucidated from these data; e.g. metal leaching could be caused by pH or redox conditions or other factors. To rule out pH effects, pH-dependent leaching studies on Soils #1, 2, and 4 were performed in the Detailed Evaluation using 4 ISCO treatments: permanganate, iron-activated hydrogen peroxide, and iron- and alkaline-activated persulfate. In these studies, metals release has been evaluated both in the presence and absence of the oxidant at pH ranges between 3 and 11. Soils and ISCO treatments were selected based upon previous metal release observations in the screening experiments (Section 4.2.1). The pH dependent metals release of 14 elements is organized and discussed below in relation to the ISCO treatment applied. A summary is then provided comparing the four ISCO treatments.

pH Dependent Leaching Results

Permanganate. Several metals were released at higher concentrations in the permanganate system in soils #1 and #2 than from the soil by itself (i.e., without the oxidant, see Figures 4.2.9 and 4.2.10): Cr, Pb, Se, Ag, and Th. However, with the exception of Cr, these metals originated from the oxidant. Cr release has been observed at significantly higher levels in both soils than the amount present in the reagent at all pH values. Ba was another metal that was released at slightly higher levels in soil #2 in the presence of permanganate between pH 5 and 6 (Figure 4.2.9). On the other hand, As and V mobilized in lower amounts in soil #1 in the presence of permanganate between pH 6.5 and 9.5 (Figure 4.2.9). Similarly, the leaching of Co below pH 3 and of Cu, V and Zn above pH 6 was reduced in the presence of this oxidant in soil #2 (Figure 4.2.10). Finally, the pH-dependent leaching of most metals (such as Ag, As, Ba, Be, Cd, Cu, Ni, Pb, Se, Tl, V, and Zn) was not impacted by the presence of permanganate in soil #4 (Figure 4.2.11), indicating that pH was the controlling factor of the observed release in this particular soil. The two exceptions in soil #4 were Cr and Co that leached in higher and lower amounts in the presence of permanganate between pH 5 and 11 and below pH 6, respectively.

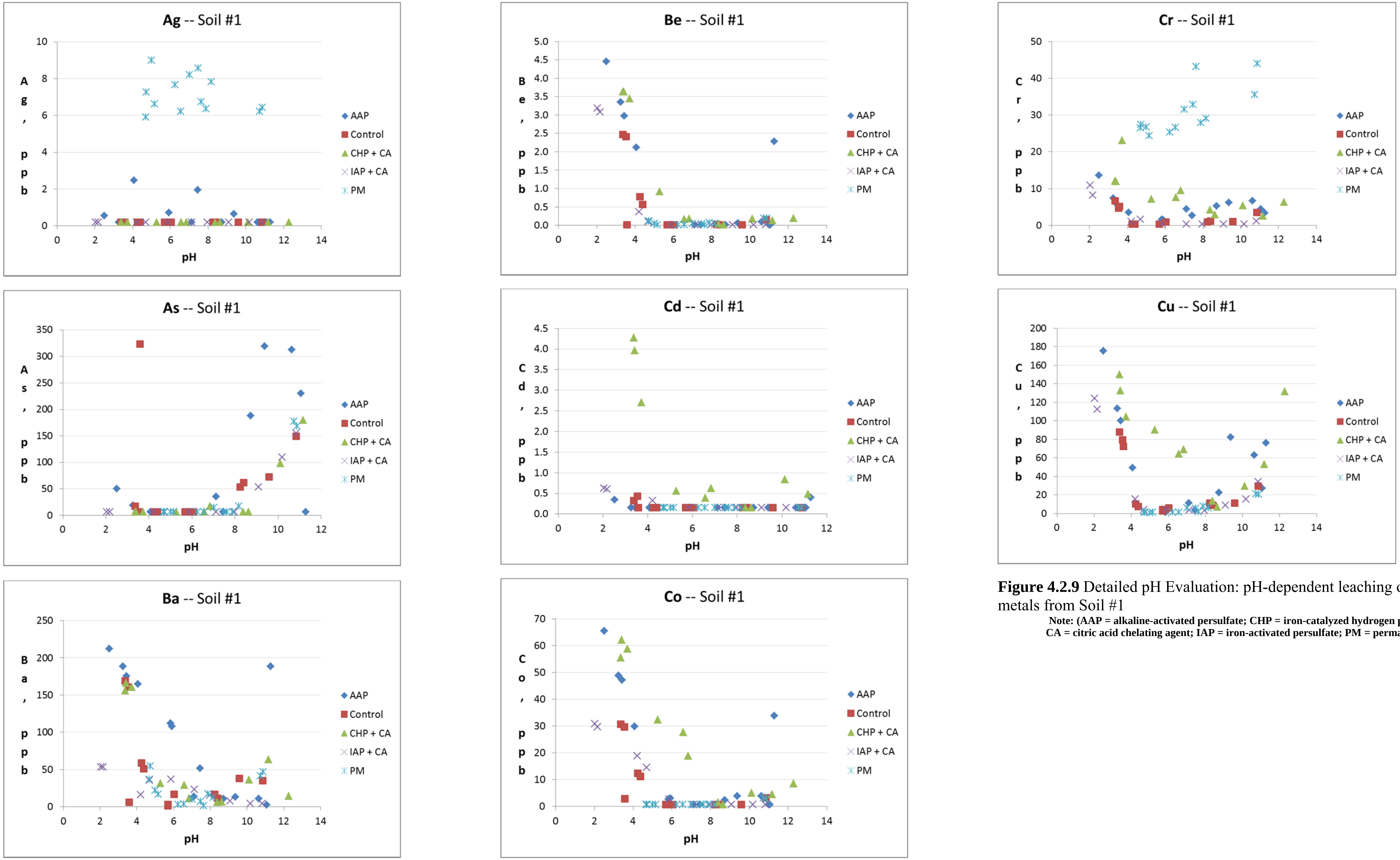


Figure 4.2.9 Detailed pH Evaluation: pH-dependent leaching of metals from Soil #1

Note: (AAP = alkaline-activated persulfate; CHP = iron-catalyzed hydrogen peroxide; CA = citric acid chelating agent; IAP = iron-activated persulfate; PM = permanganate)

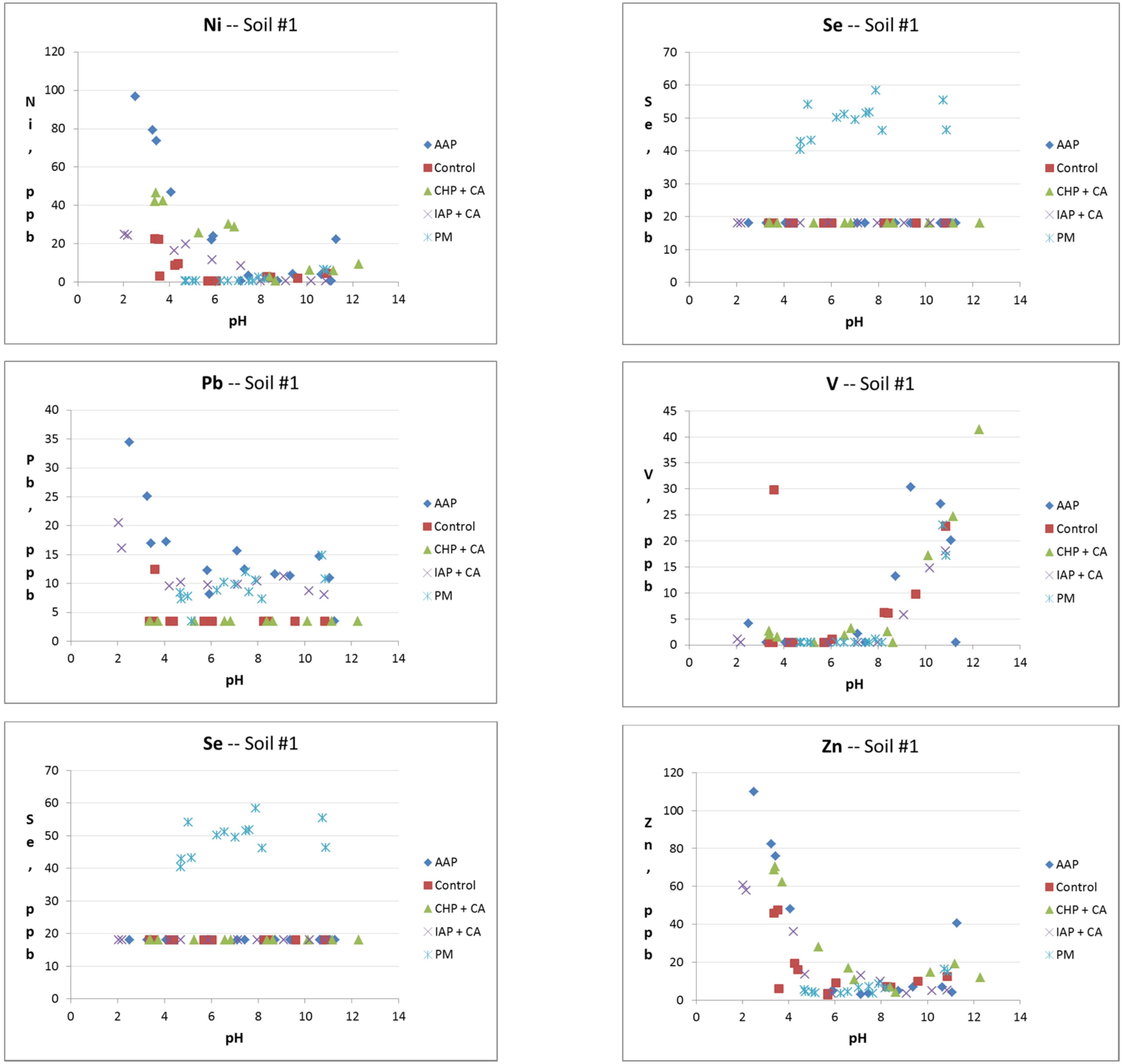


Figure 4.2.9 (cont) Detailed pH Evaluation: pH-dependent leaching of metals from Soil#1

Note: (AAP = alkaline-activated persulfate; CHP = iron-catalyzed hydrogen peroxide; CA = citric acid chelating agent; IAP = iron-activated persulfate; PM = permanganate)

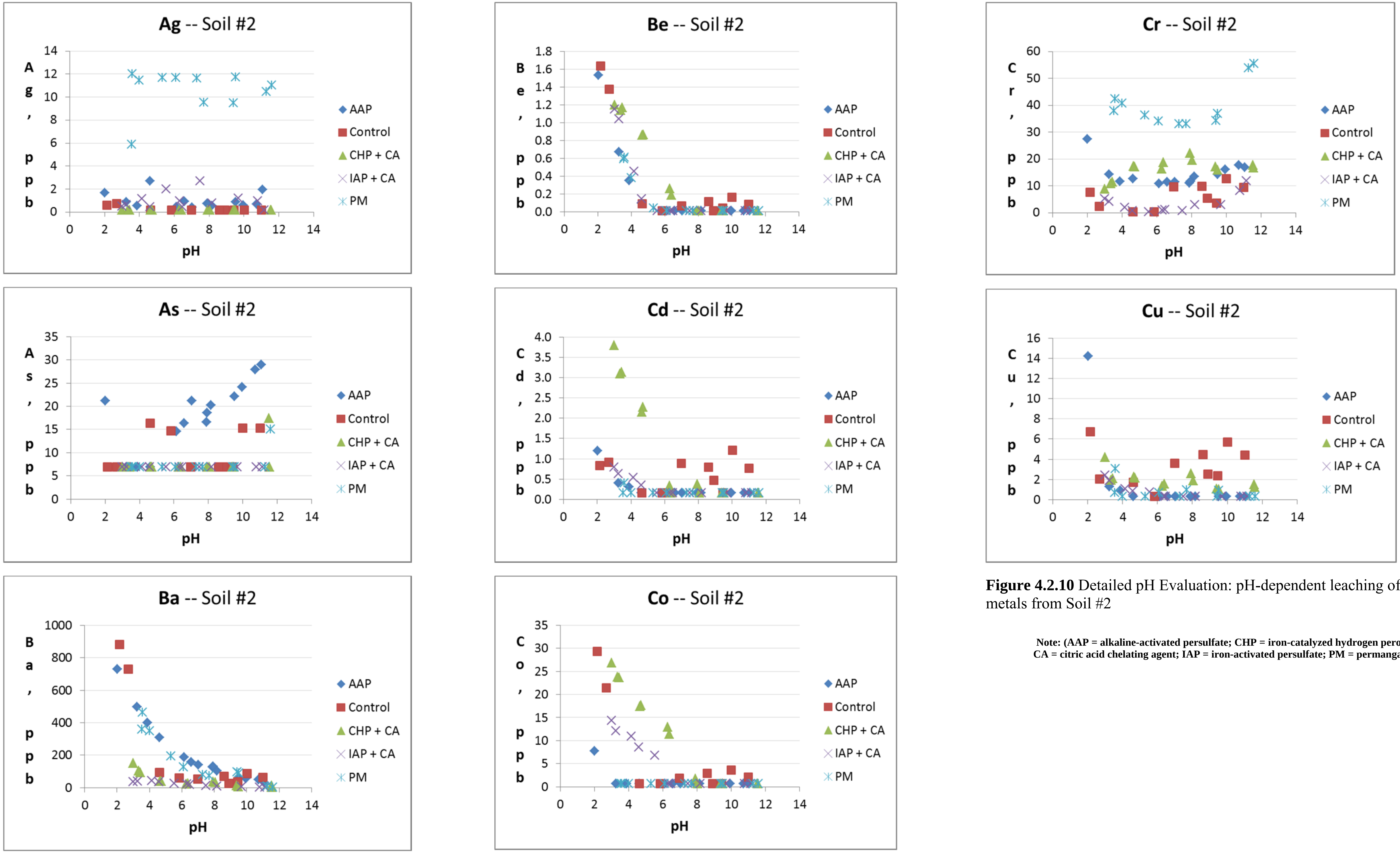


Figure 4.2.10 Detailed pH Evaluation: pH-dependent leaching of metals from Soil #2

Note: (AAP = alkaline-activated persulfate; CHP = iron-catalyzed hydrogen peroxide; CA = citric acid chelating agent; IAP = iron-activated persulfate; PM = permanganate)

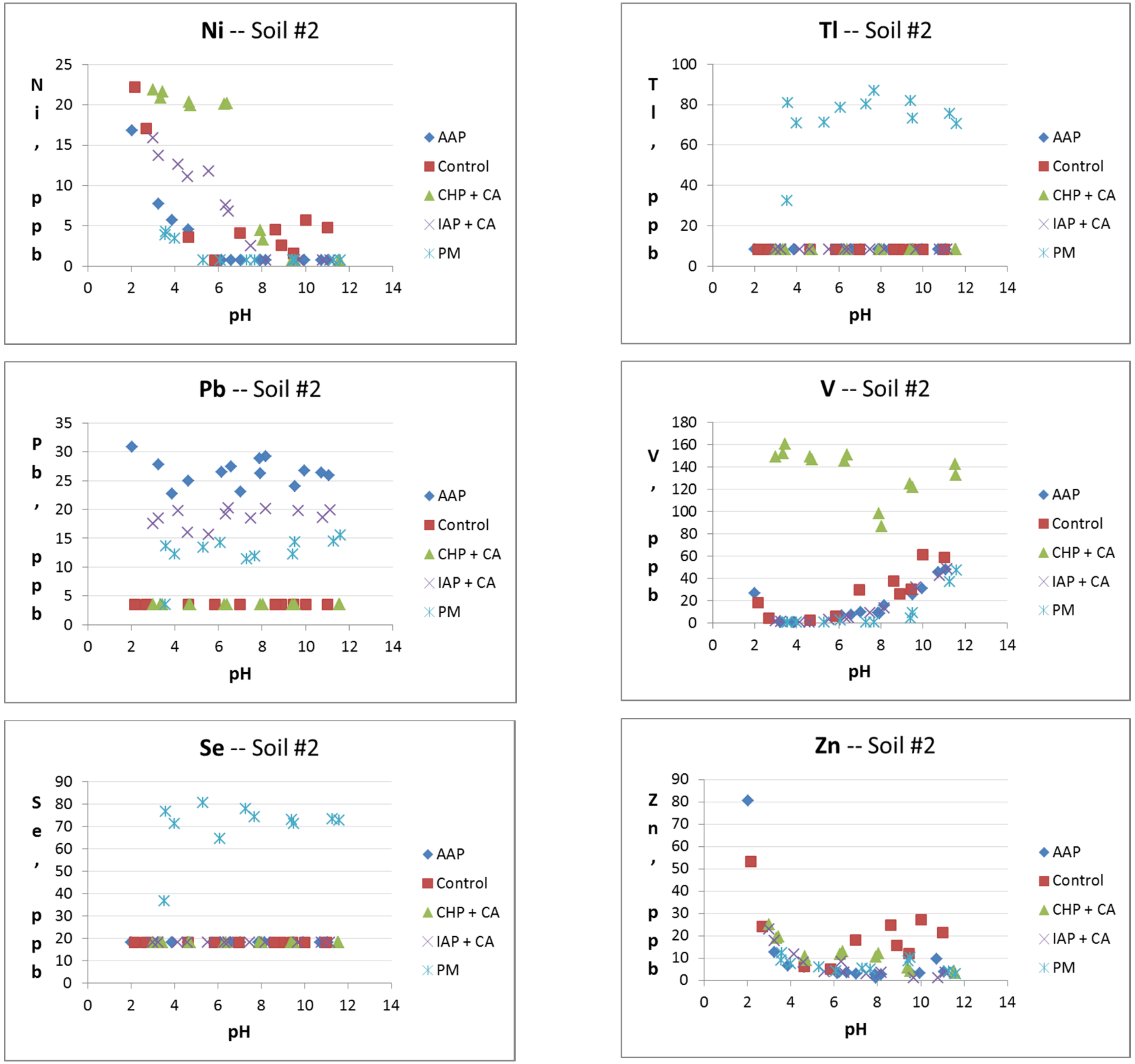
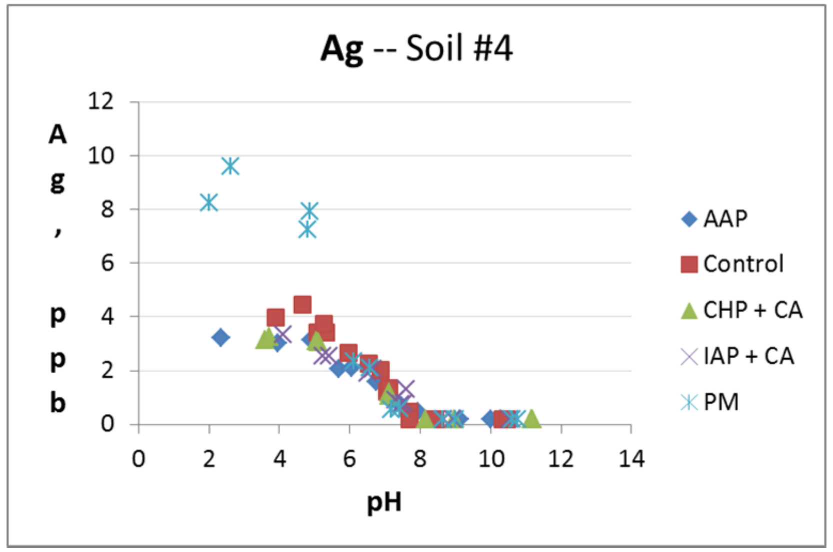
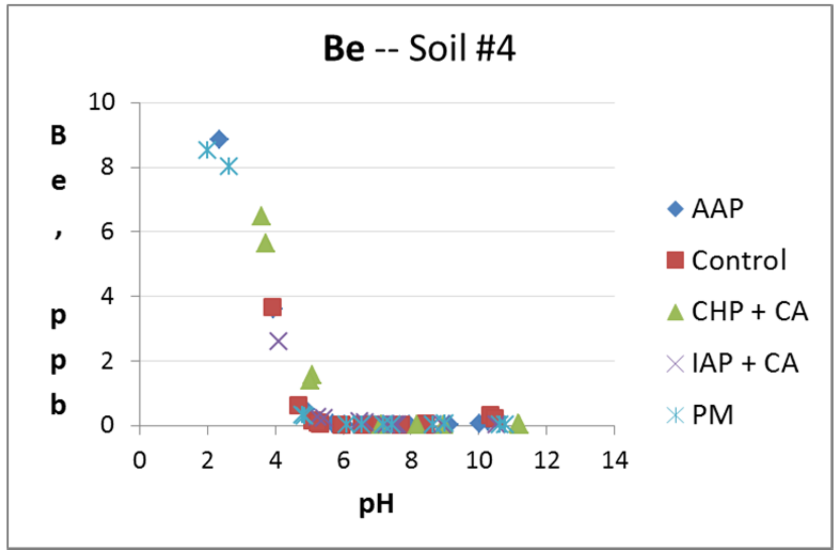
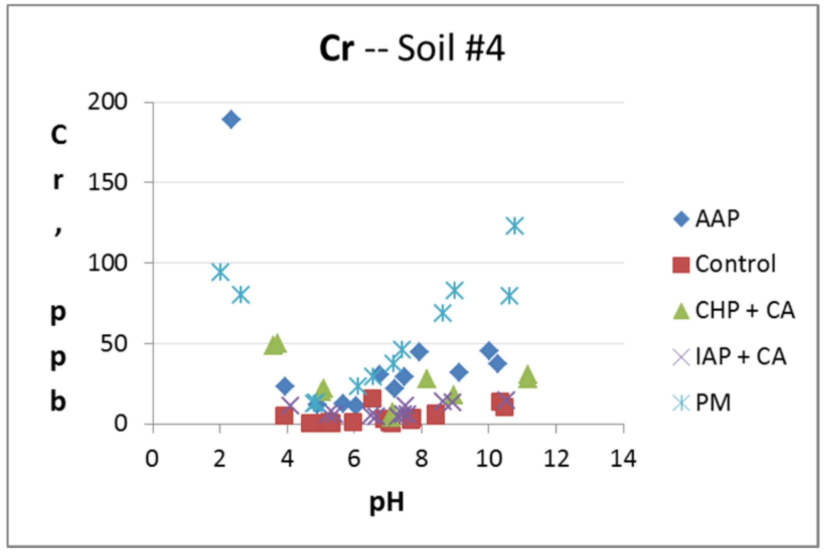


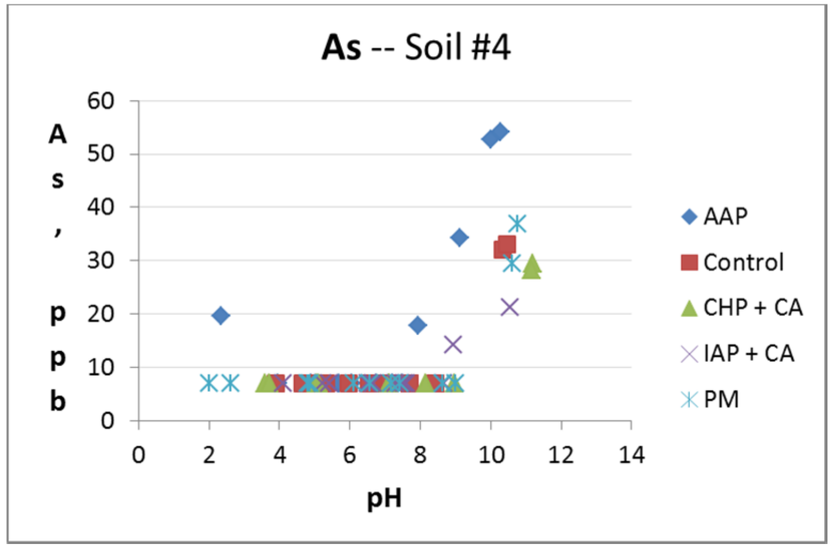
Figure 4.2.10 (cont.) Detailed pH Evaluation: pH-dependent leaching of metals from Soil #2

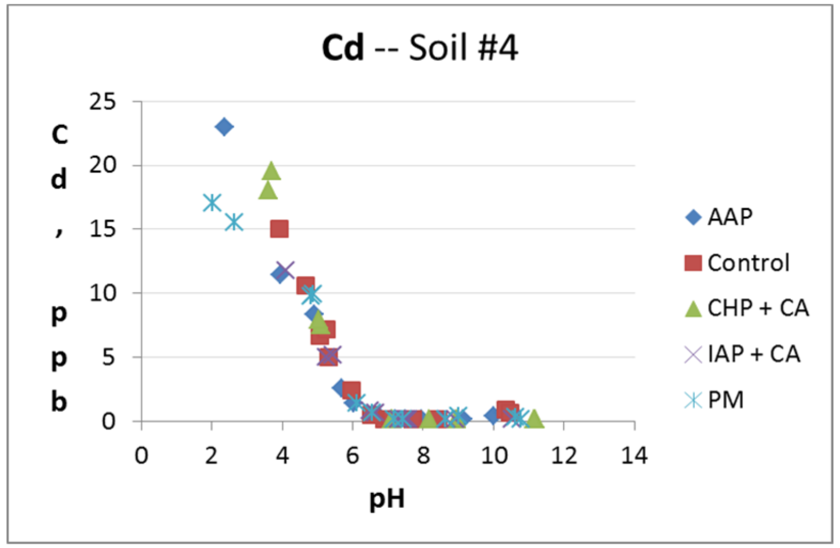
Note: (AAP = alkaline-activated persulfate; CHP = iron-catalyzed hydrogen peroxide; CA = citric acid chelating agent; IAP = iron-activated persulfate; PM = permanganate)

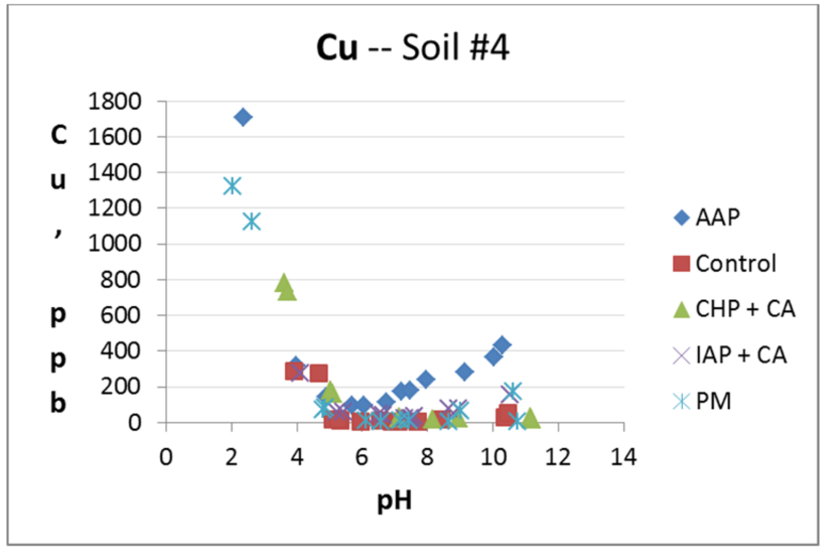


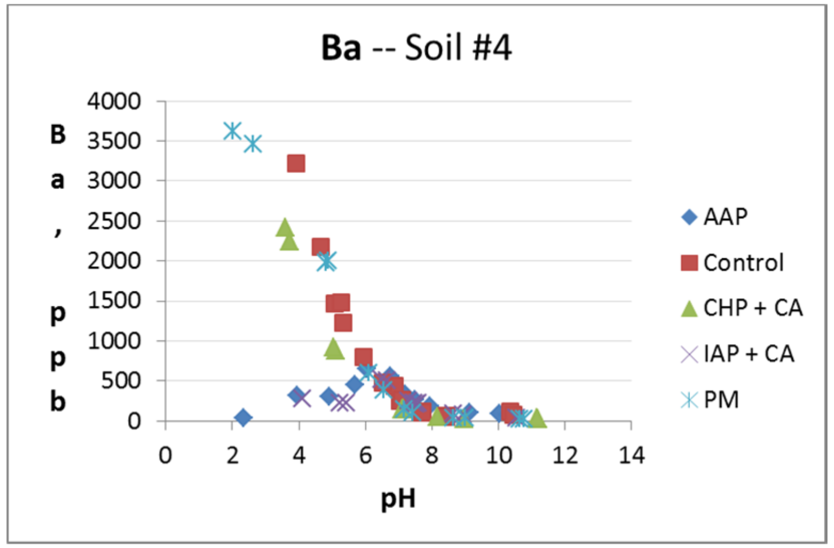












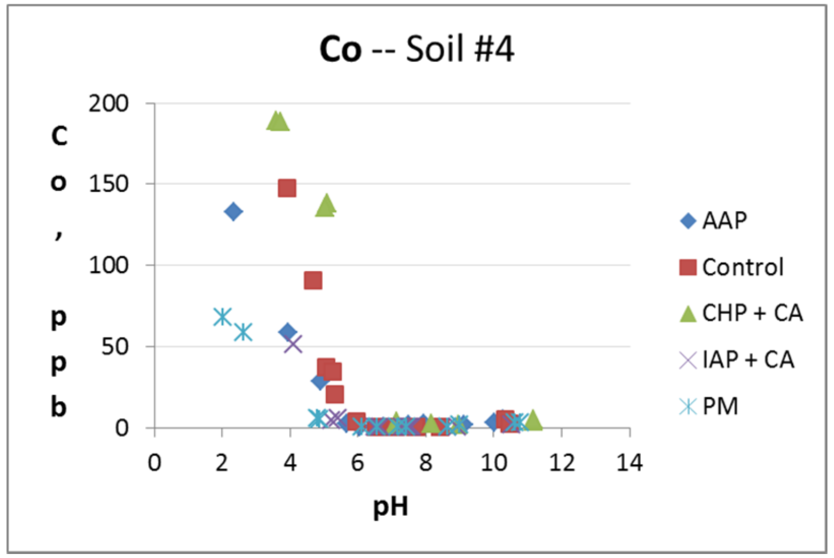


Figure 4.2.11 Detailed pH Evaluation: pH-dependent leaching of metals from Soil #4

Note: (AAP = alkaline-activated persulfate; CHP = iron-catalyzed hydrogen peroxide; CA = citric acid chelating agent; IAP = iron-activated persulfate; PM = permanganate)

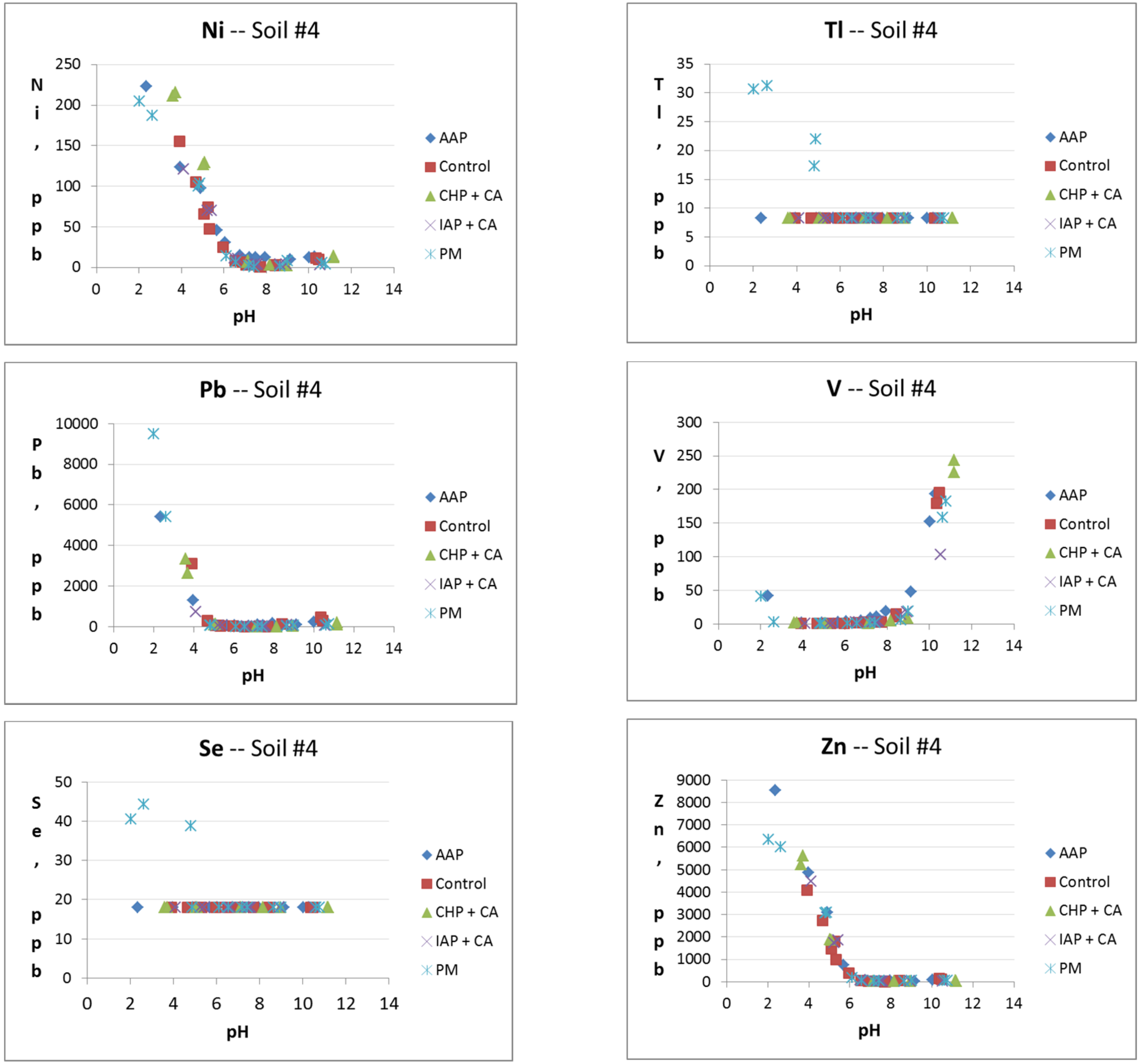


Figure 4.2.11 (cont.) Detailed pH Evaluation: pH-dependent leaching of metals from Soil #4

Note: (AAP = alkaline-activated persulfate; CHP = iron-catalyzed hydrogen peroxide; CA = citric acid chelating agent; IAP = iron-activated persulfate; PM = permanganate)

Catalyzed Hydrogen Peroxide. Dissolved metal concentrations in the catalyzed hydrogen peroxide system exceeded the controls (i.e. soils without the oxidant) in soil #1 for Be at pH < 6.5, Co, Cu and Ni for pH < 8, and Cr for pH < 10 (Figure 4.2.9). Furthermore, Cd was released at higher levels than the control at both pH < 7 and in the pH range of 8.5 to 11. Similar observations were made in soil #2 for Be between pH 4 ad 6, Co and Ni between pH 3 and 7, Cd below pH 6, and Cr and V at all pH values (Figure 4.2.10). On the other hand, As and V were mobilized in smaller quantities in soil #1 in the presence of this oxidant in the pH range of 7 to 9 (Figure 4.2.9). Similarly, Cu and Zn were mobilized in smaller quantities in soil #2 in the presence of this oxidant above pH 6.5 (Figure 4.2.10). Both these observation were very similar to what had been seen in the permanganate system. Finally, similarly to permanganate, the release of most metals in soil #4 in the catalyzed hydrogen peroxide system was controlled by the pH (Figure 4.2.11). The only metal that leached in higher amounts in the presence of catalyzed hydrogen peroxide in this soil was Cr in the pH range of 2 to 11. Furthermore, As, and Ag and Ba mobilized in lower quantities in the presence of this oxidant above pH 9 and below pH 6, respectively.

Iron-Activated Persulfate. In the presence of iron-activated persulfate a number of metals were mobilized at lower concentrations than the control in soils #1 and #2 (Figures 4.2.9 and 4.2.10). In soil #1, these included As and V between pH 6 and 9 (again, similarly to the permanganate and hydrogen peroxide systems), Co and Cu below pH 4, Be below pH 6, Ba below pH 4.5 and above pH 9, and Cr and Ni below pH 3.5 and above pH 8 (Figure 4.2.9). Similar observations were made in soil #2 for Cu and Zn above pH 6 and Ba below pH 3 (Figure 4.2.10). On the other hand, Ni was released in higher amounts than the control in soil #1 in the pH range of 3.5 to 8, and Pb at all pH values (Figure 4.2.9). Similarly, in soil #2 Ag mobilized in excess of background levels above pH 3, Co between pH 4 and 6, Ni between pH 3 and 7, and Pb at all pH values (Figure 4.2.10). Finally, in soil #4 the release of Be, Cd, Co, Ni, Se, Tl, and Zn was controlled by pH conditions in the iron-activated persulfate chemistry (Figure 4.2.11). Exceptions were observed for As, Pb, and V, the leaching of which metals decreased in the presence of this oxidant above pH 9, indicating that oxidant chemistry played an important role in the observed release. Similarly, Ag and Ba release was lower below pH 6 when the oxidant was present in soil #4. Metals that were mobilized in higher amounts in the iron-catalyzed persulfate system in this soil included Cr and Cu between pH 5 and 11.

Alkaline-Activated Persulfate. In general, alkaline-activation resulted in higher levels of metal mobilization in both soils #1 and #2 compared to the control for several metals (Figures 4.2.9 and 4.2.10), which is an opposite trend to what was observed for the iron-activated persulfate system. In soil #1, alkaline activation resulted in increased mobilization of Ba between pH 4 and 8, Be below pH 6, Co below pH 5.5, Cr between pH 4 and 11, Cu in the pH ranges of 4 to 5 and 8 to 10.5, Ni below pH 7, and Pb below pH 11 (Figure 4.2.9). In addition, several metals (Ba, Be, Cd, Co, and Ni) were released at higher concentration in this oxidant system when the pH was above 11.3. Furthermore, both As and V were mobilized at higher concentrations than the control in the pH range of 8 to 11 and 8.5 to 11, respectively. This was contrary to what have been observed in the other three oxidant systems for these two oxyanions. In soil #2, alkaline activation resulted in increased mobilization of Cu, V, and Zn at pH 2, As at pH 2 and above pH 6, Ba between pH 4 and 7, and Cr, Pb, and Ag at all pH values (Figure 4.2.10). On the other hand, lower release has been observed for both As and V in soil #1 above pH 11.2 and 11, respectively, in the presence of the oxidant (Figure 4.2.9). Other metals that mobilized at lower concentrations in the presence of alkaline-activated persulfate in soil #1 included Ba below pH 4 and in the pH range of 8 to 11, and Cd below pH 4. Metals that mobilized at lower concentrations in soil #2 included Co below pH 3 and Cu, Ni, V, and Zn above pH 6 (Figure 4.2.10). Finally, similarly to the other oxidant chemistries, the release of most metals in soil #4 was controlled by the pH in the alkaline-activated persulfate system (Figure 4.2.11). Exceptions were As, and Cr and Cu that mobilized in higher amounts in the presence of the oxidant above pH 8 and between pH 5 and 11, respectively. On the other hand, Ag and Ba leaching reduced in soil #4 in the presence of alkaline-activated persulfate below pH 6.

Summary Comparison of the Four Oxidant Systems

Metals release above background has been observed in all three soils (i.e. soils #1, 2, and 4) and in all four ISCO systems. However, the highest number of metals released at greater concentrations than the control was observed in the alkaline-activated persulfate system in all three soils, followed by catalyzed hydrogen peroxide in soils #1 and 2, and iron-activated persulfate in soil #4. The most significant metal mobilization (i.e. at least five metals mobilized) occurred in soils #1 and 2 in the alkaline-activated persulfate and the iron-catalyzed hydrogen peroxide systems. The application of permanganate resulted in the least metals release in all three soils however, this oxidant contained impurities that caused elevated metal concentrations in the treatment area.

In some instances, the application of the oxidant resulted in reduced metals release compared to background levels. This phenomenon was most significant (i.e. the release behavior of at least five metals was impacted) in the presence of iron-activated persulfate in soils #1 and 4, and in the alkaline-activated persulfate system in soil #2.

In summary, alkaline-activated persulfate had the greatest impact on metals release (in terms of number of metals whose release behavior deviated from the control, either as an increase or a decrease) in soils #1 and 2, and was the second most influential oxidant chemistry in soil #4. The application of permanganate resulted in the least metals release in all three soils, but metal impurities found in the reagent caused elevated metal concentrations. Both iron-activated persulfate and catalyzed hydrogen peroxide impacted metals mobilization, and with the exception of soil #4 (for which soil this was the most influential oxidant), the number of metals impacted by these two oxidant chemistries was between that of alkaline-activated persulfate and permanganate.

4.2.2 Geochemical Modeling of Metals Release

Analytical results of the Task 2.2 pH-dependent leaching experiments were entered into the LeachXS database and geochemical modeling environment (ECN, the Netherlands) to study controlling solid phases and elucidate processes responsible for the release of metals in instances when pH was not the controlling factor. Metals release from soil #1 in the presence and absence of alkaline-activated persulfate and catalyzed hydrogen peroxide has been evaluated. With an understanding of which phases or aqueous species are controlling metals release, suitable alterations to the ISCO process may be developed and tested. The more fundamental understanding of controlling solid phases enables prediction of successful chemical additives that would likely reduce aqueous phase concentrations; this testing was the focus of Task 4.

The utility of combining pH-dependent leaching studies with geochemical speciation modeling to elucidate the fate of metals in contaminated soils was demonstrated by Dijkstra et al. (2004). This study revealed the pH-dependent (pH range of 0.4 to 12) distribution of Cd, Cu, Pb, Ni, and Zn in eight contaminated soils in the solution (free and complexed with DOC or inorganics) and solid (adsorbed on soil organic matter, clay, or iron and aluminum (hydr)oxides) phases. The current study used a similar approach to evaluate the impact of oxidizing agents on metals release in contaminated soils in order to elucidate the mechanisms that were responsible for the observed release with the ultimate goal to understand the extent to which commonly used remedial technologies such as ISCO could lead to increased human exposure of a variety of naturally occurring metals.

Model results show reasonable estimate of metals release from the untreated soil (i.e., the control); Figure 4.2.12 shows that the model captured well the pH-dependent behavior of most metals. The difference in simulated and measured values might be due to the fact that estimated instead of measured HA fractions of the soil and dissolved organic matter (SOM and DOM) were used as model inputs; all assumptions were made based on published literature (see Table 2.7).

In the control simulation of the present study, the liquid-solid partitioning of Ba, Cd, Cr, Cu, Ni, Pb, and Zn was primarily determined by both the SOM and DOM (shown as particulate organic matter (POM) and DOC in Figure 4.2.12), indicating that it is important to understand the way natural organic matter phases and characteristics change in the presence of oxidizing agents. As earlier results revealed (see the Task 2.1 and 2.2 results), changes in pH is one of the driving factors of metals release in ISCO applications. Changes in pH can also impact natural organic matter. Figure 4.2.13 shows that with the addition of alkaline-activated persulfate and catalyzed hydrogen peroxide, that represent pH conditions significantly higher and lower than the control, respectively, the amount of DOC present in the reactors significantly increased compared to the background. This indicates that the oxidants destroyed part of the SOM, resulting in increased DOC release and an increased potential for metal complexation with DOC, which is a likely pathway for metals release. Destruction of the SOM can also result in the direct release of associated metals

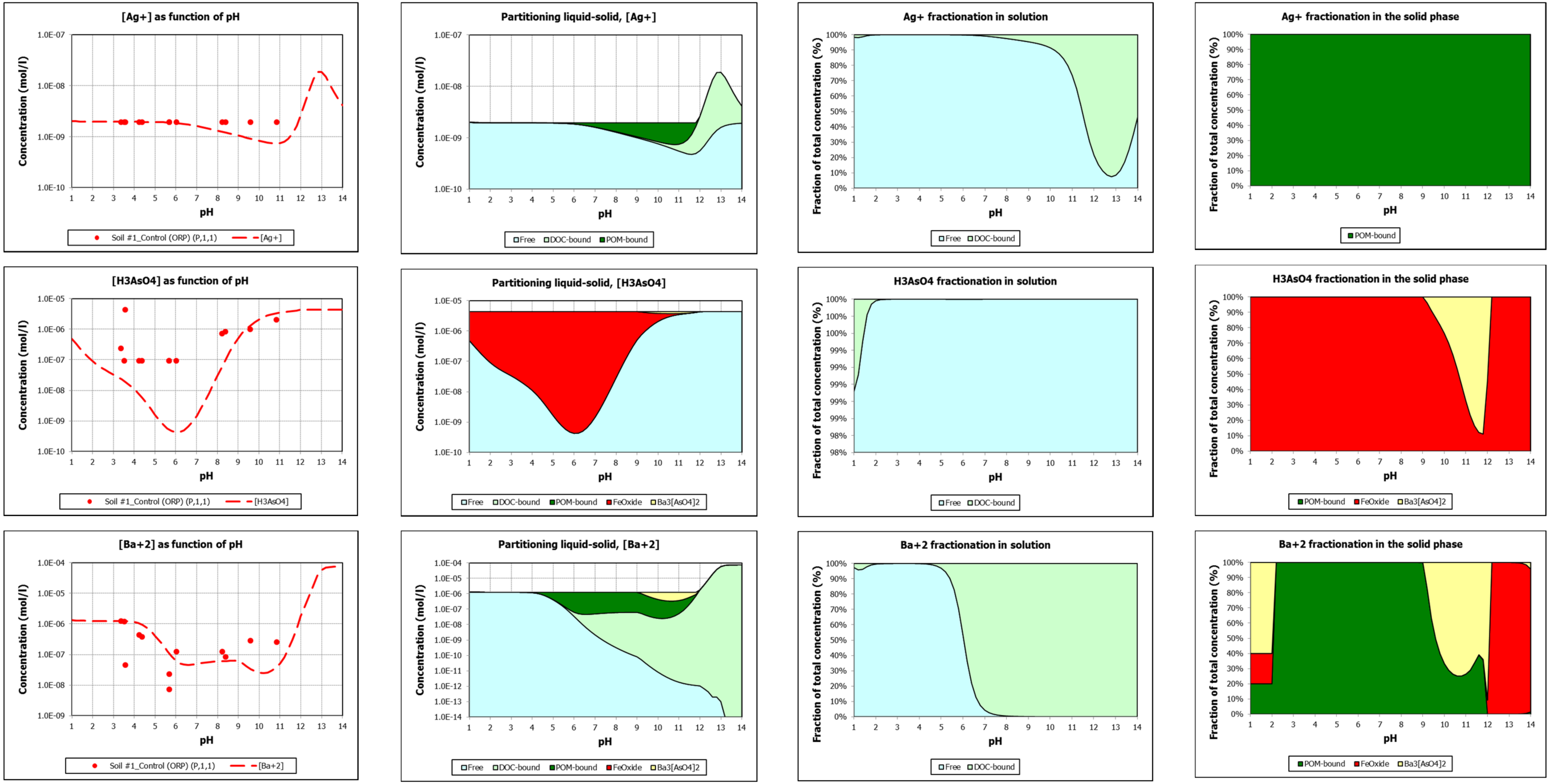


Figure 4.2.12 Geotechnical Modeling: Metal release and partitioning in Soil #1.

The first graph in each row depicts the solubility of a given metal (symbols and line represent experimental data and model prediction, respectively). The subsequent graphs in the row show the liquid-solid partitioning and the solution and solid phase fractionation of the same metal.

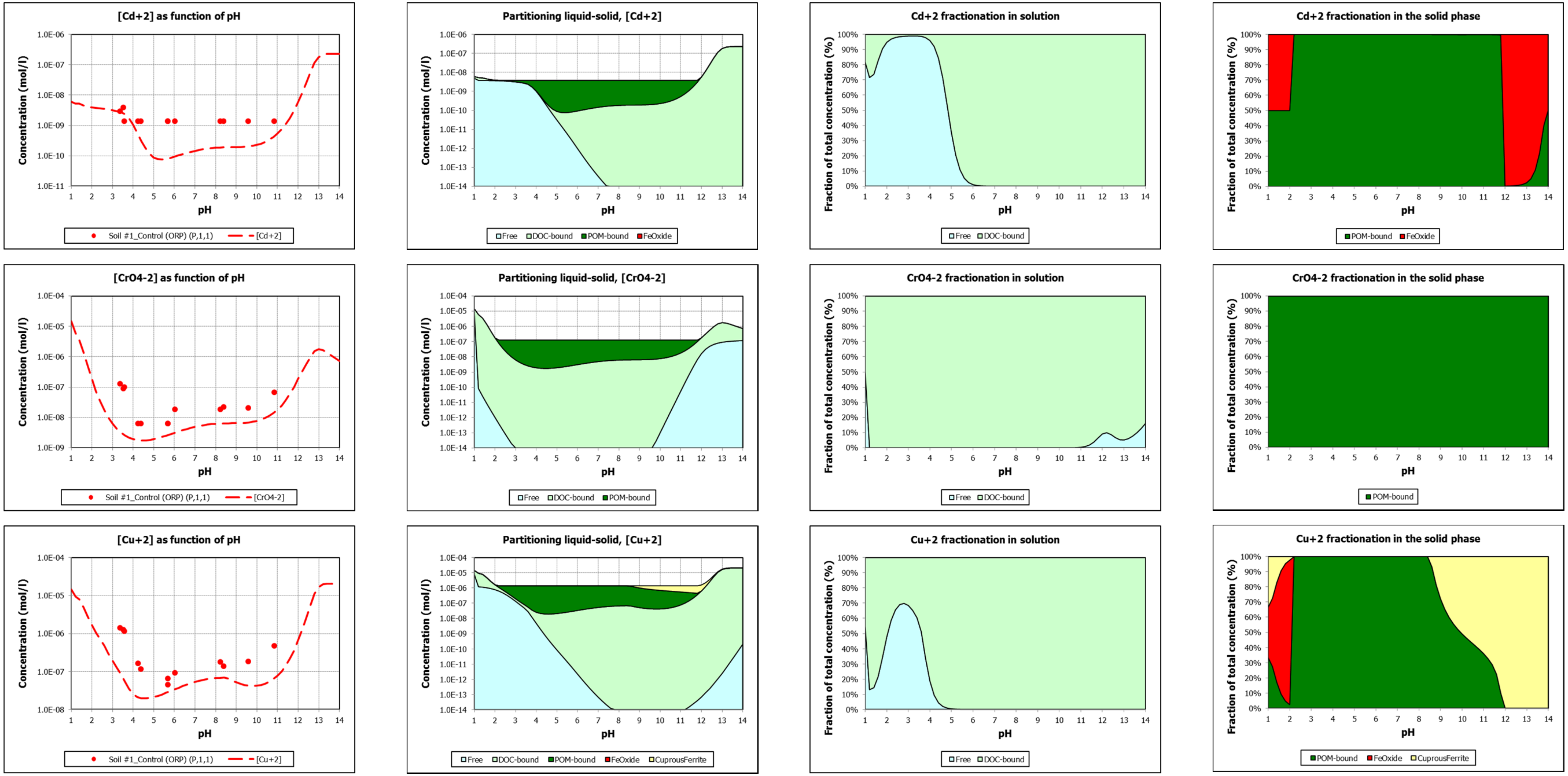


Figure 4.2.12 (cont.) Geotechnical Modeling: Metal release and partitioning in Soil #1.

The first graph in each row depicts the solubility of a given metal (symbols and line represent experimental data and model prediction, respectively). The subsequent graphs in the row show the liquid-solid partitioning and the solution and solid phase fractionation of the same metal.

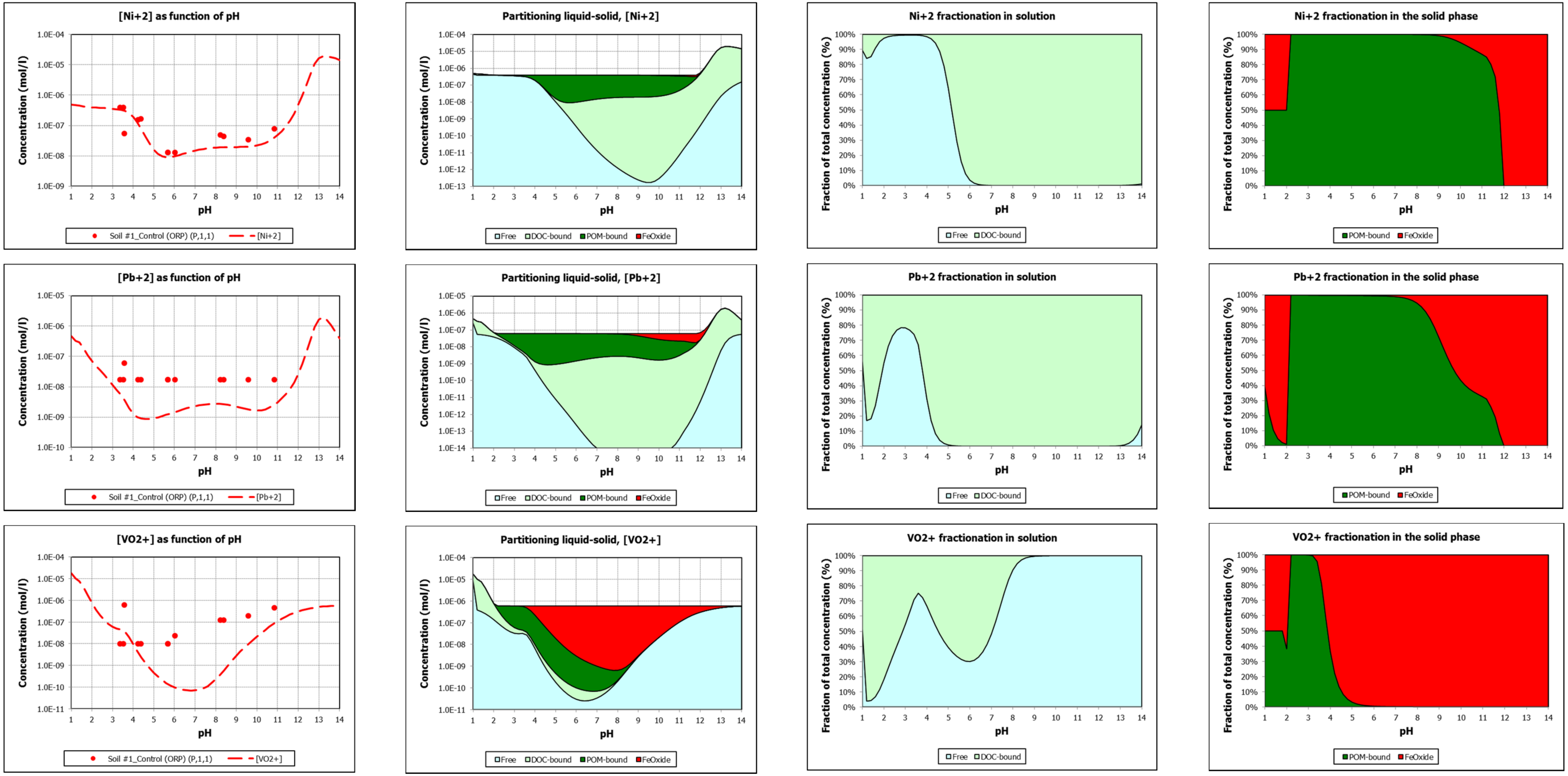


Figure 4.2.12 (cont.) Geotechnical Modeling: Metal release and partitioning in Soil #1.

The first graph in each row depicts the solubility of a given metal (symbols and line represent experimental data and model prediction, respectively). The subsequent graphs in the row show the liquid-solid partitioning and the solution and solid phase fractionation of the same metal.

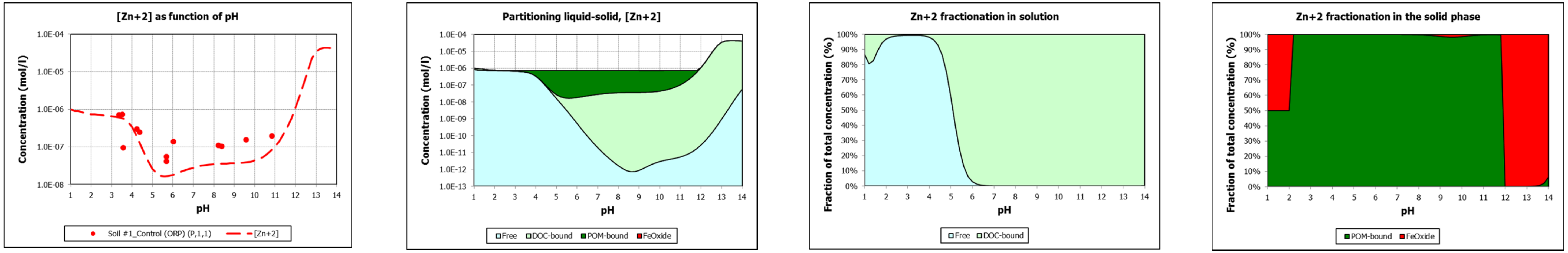


Figure 4.2.12 (cont.) Geotechnical Modeling: Metal release and partitioning in Soil #1.

The first graph in each row depicts the solubility of a given metal (symbols and line represent experimental data and model prediction, respectively). The subsequent graphs in the row show the liquid-solid partitioning and the solution and solid phase fractionation of the same metal.

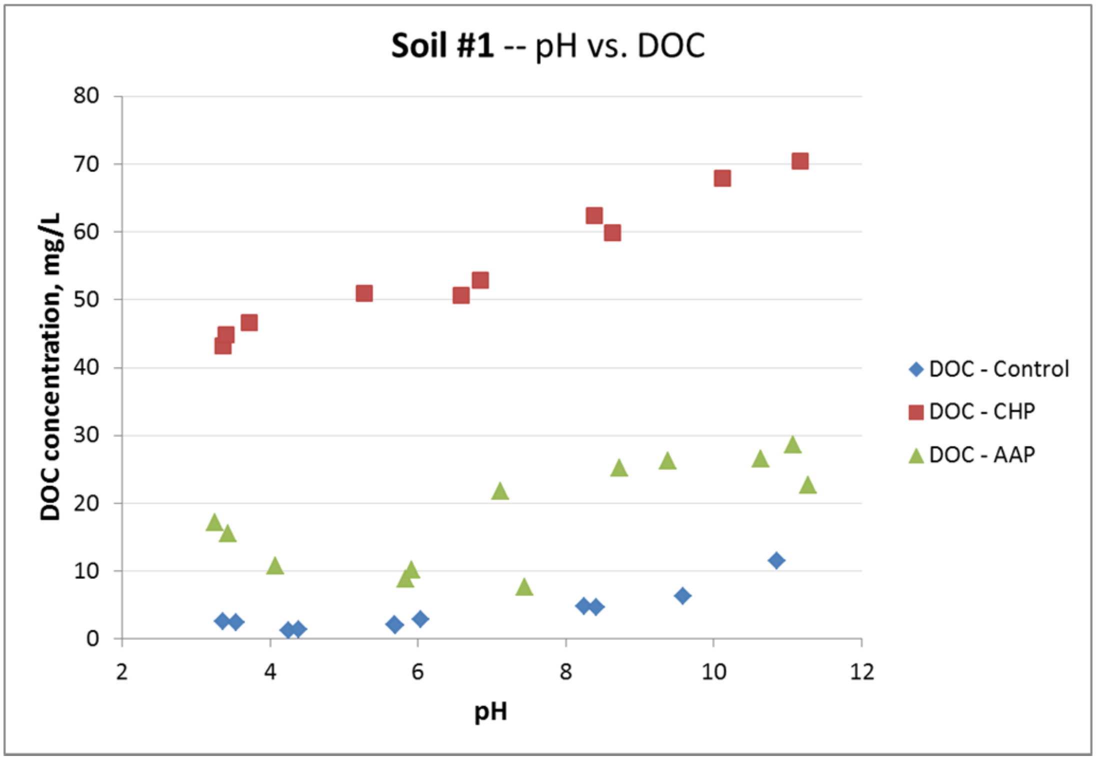


Figure 4.2.13 Soil #1DOC concentration vs. pH for CHP and AAP systems

Note: AAP = alkaline-activated persulfate, CHP = catalyzed hydrogen peroxide

On the other hand, As and V partitioning in background samples was primarily determined by iron oxide minerals (Figure 4.2.12), highlighting the importance of mineral phases in the fate of select metals. Other metals where mineral phases played a role in partitioning Ba, Cu, and Pb in the pH range of 9 to 12; the specific minerals were barium arsenate, cuprous ferrite, and ironoxide, respectively. Barium arsenate also impacted the solid phase fractionation of As in the same pH range.

While the leaching of several metals increased in the presence of alkaline-activated persulfate and catalyzed hydrogen peroxide in certain pH ranges (see the Task 2.2 results), DOC and POM were still the major controlling phases in the liquid-solid partitioning of most of these metals in soil #1 treated with the oxidants (Figures 4.2.14 and 4.2.15). For example, the addition of alkaline-activated persulfate resulted in increased Cr and Ni release above and below pH 6, respectively, in soil #1 (Figure 4.2.9), but partitioning of both metals was still determined by the POM and DOC content (Figure 4.2.14), indicating that the main release mechanism occurred through the destruction of POM by oxidation and the subsequent formation of DOC complexes. Similarly, the release of Cd, Cr, Cu, and Ni was dominated by the dissolution of the SOM and the subsequent formation of DOC complexes in the presence of catalyzed hydrogen peroxide (Figure 4.2.15).

In the presence of alkaline-activated persulfate, Cu partitioning was also controlled by DOC and POM, but the main release mechanism of this metal in the alkaline-activated persulfate chemistry was the dissolution of mineral phases, i.e. cuprous ferrite, in the pH range of 9 to 11. The mobilization of Pb occurred due to both the dissolution of iron oxides (pH > 9) and the SOM (all pH values); Pb was also present in the sodium hydroxide reagent that was used for alkaline activation. On the other hand, the partitioning of As and V was primarily controlled by iron oxide minerals in both the untreated and treated soils (Figures 4.2.12 and 4.2.14). For example, the leaching of As increased in the presence of alkaline-activated persulfate in the pH range of 9-11 (Figure 4.2.9); the main mechanism of As release was the dissolution of barium arsenate mineral (Figures 4.2.12 and 4.2.14). Similarly, the leaching of V increased in the presence of alkaline-activated persulfate in the pH range of 9 to 11 (Figure 4.2.9), but the release occurred due to the dissolution of iron oxides (Figures 4.2.12 and 4.2.14).

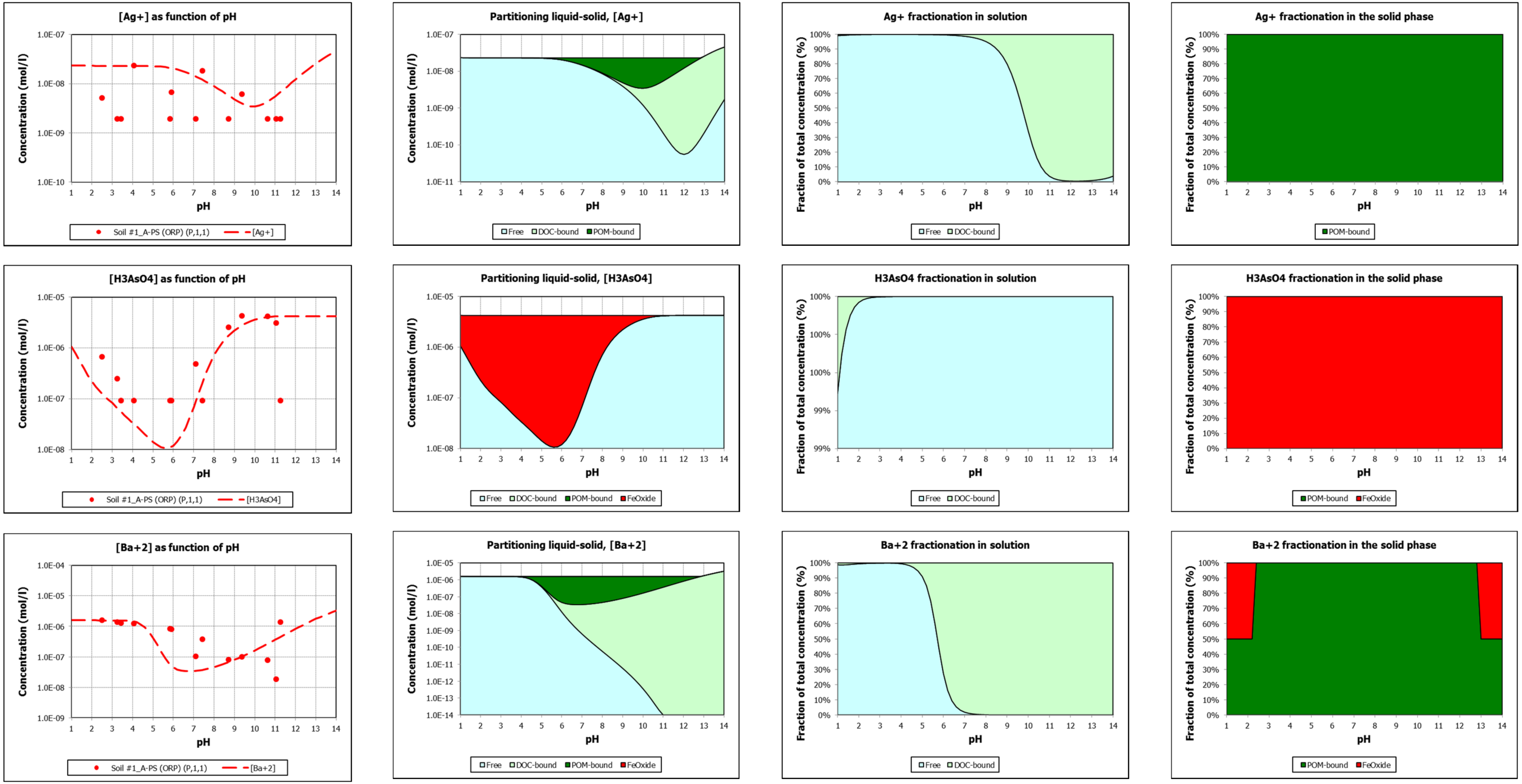


Figure 4.2.14 Geotechnical Modeling: Metal release and partitioning in the presence of AAP in Soil #1.

The first graph in each row depicts the solubility of a given metal (symbols and line represent experimental data and model prediction, respectively)
The subsequent graphs in the row show the liquid-solid partitioning and the solution and solid phase fractionation of the same metal.

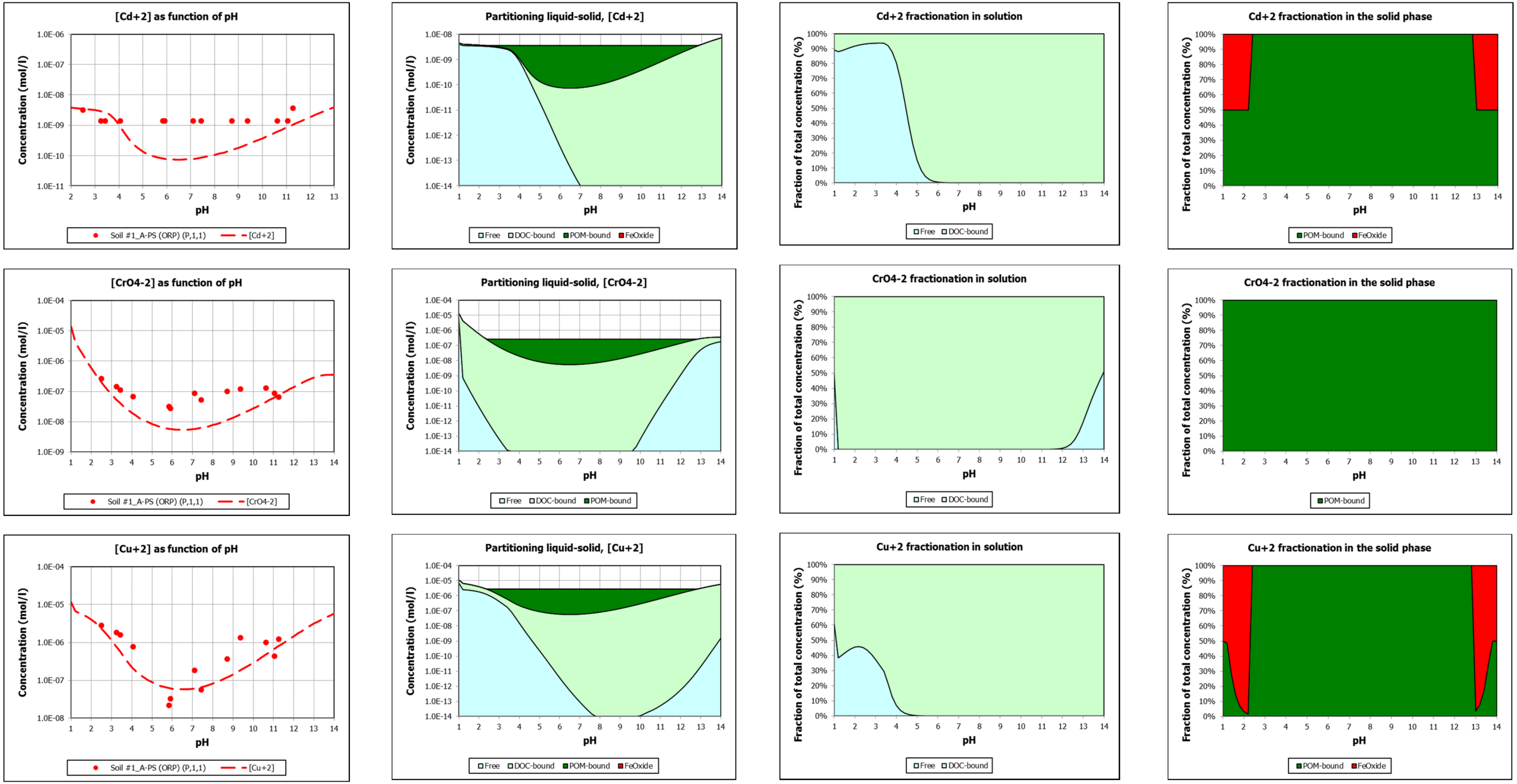


Figure 4.2.14 (cont.) Geotechnical Modeling: Metal release and partitioning in the presence of AAP in Soil #1.
The first graph in each row depicts the solubility of a given metal (symbols and line represent experimental data and model prediction, respectively) The subsequent graphs in the row show the liquid-solid partitioning and the solution and solid phase fractionation of the same metal.

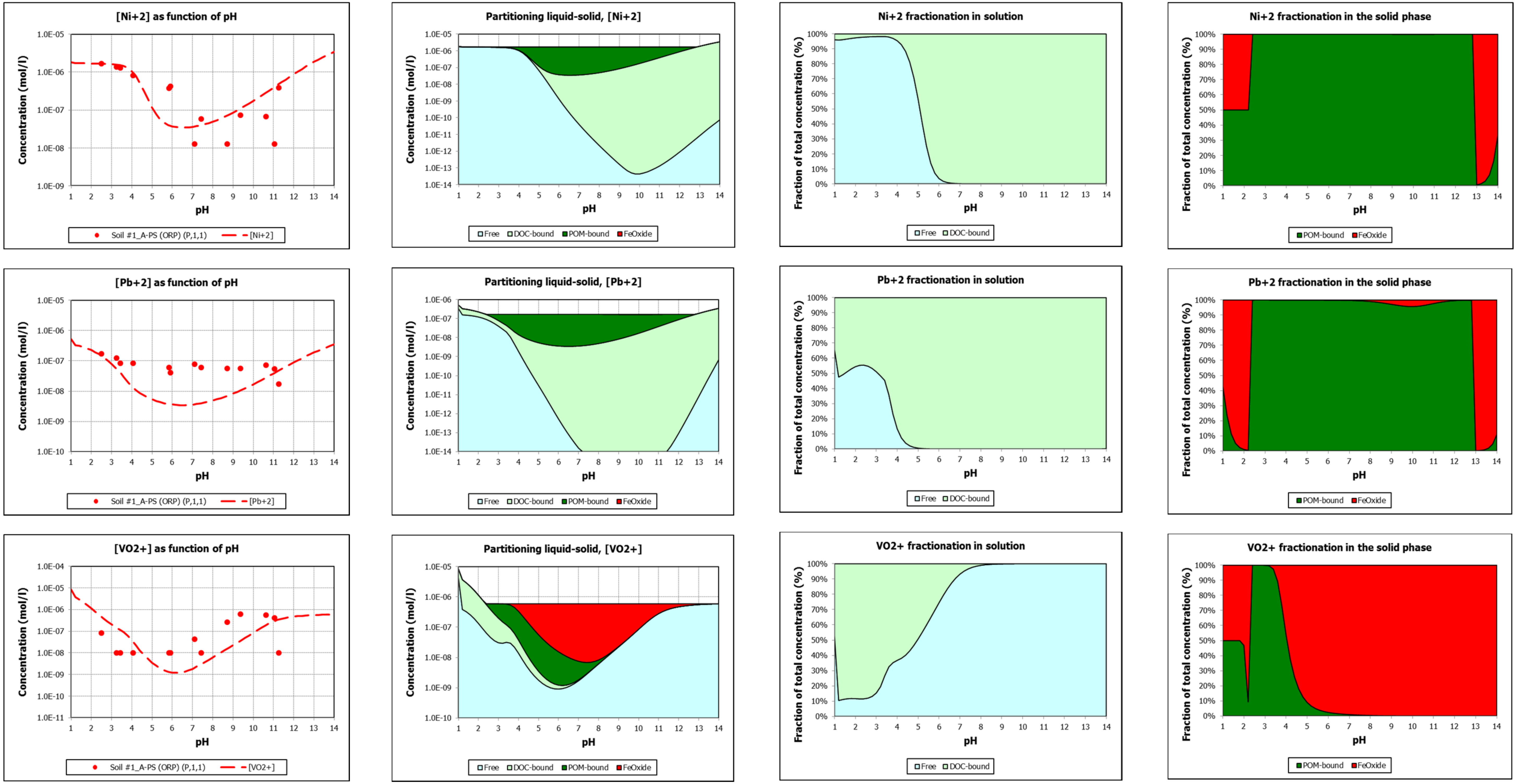


Figure 4.2.14 (cont.) Geotechnical Modeling: Metal release and partitioning in the presence of AAP in Soil #1.

The first graph in each row depicts the solubility of a given metal (symbols and line represent experimental data and model prediction, respectively)
The subsequent graphs in the row show the liquid-solid partitioning and the solution and solid phase fractionation of the same metal.

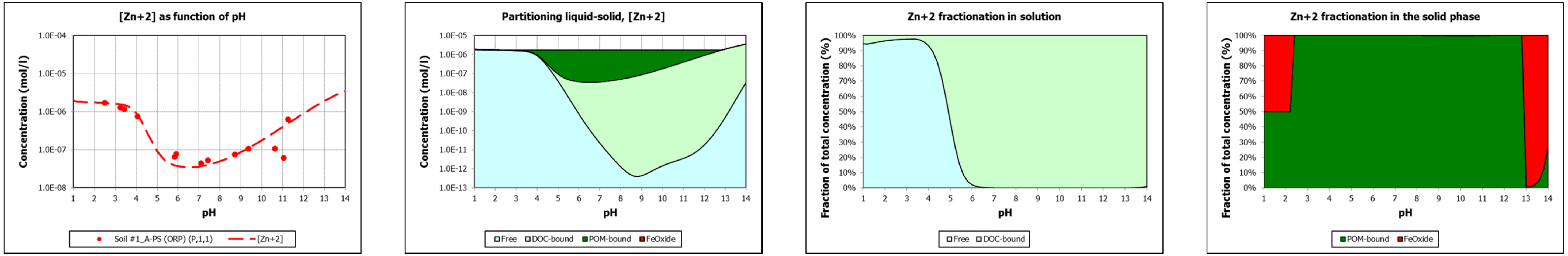


Figure 4.2.14 (cont.) Geotechnical Modeling: Metal release and partitioning in the presence of AAP in Soil #1.

The first graph in each row depicts the solubility of a given metal (symbols and line represent experimental data and model prediction, respectively)
The subsequent graphs in the row show the liquid-solid partitioning and the solution and solid phase fractionation of the same metal.

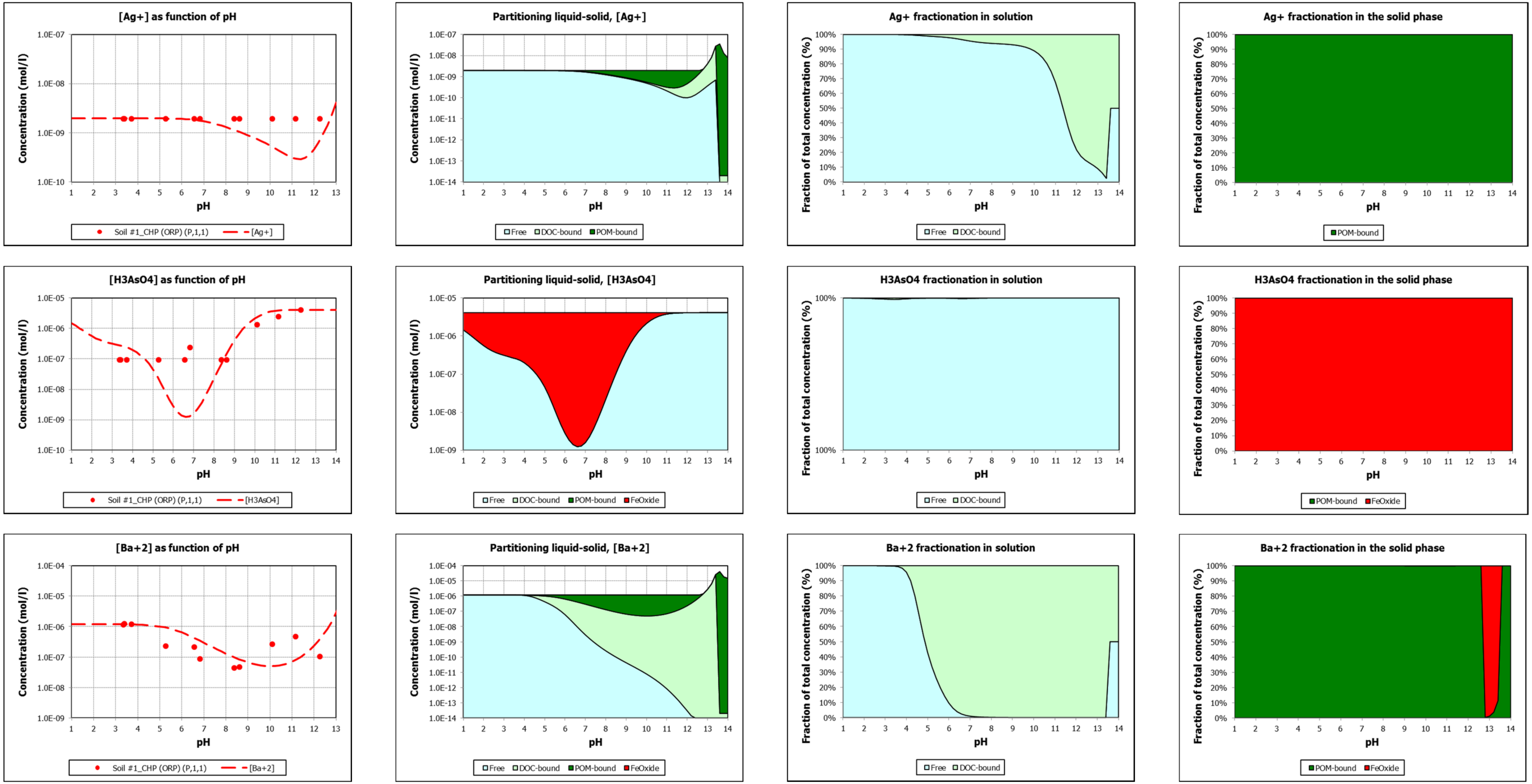
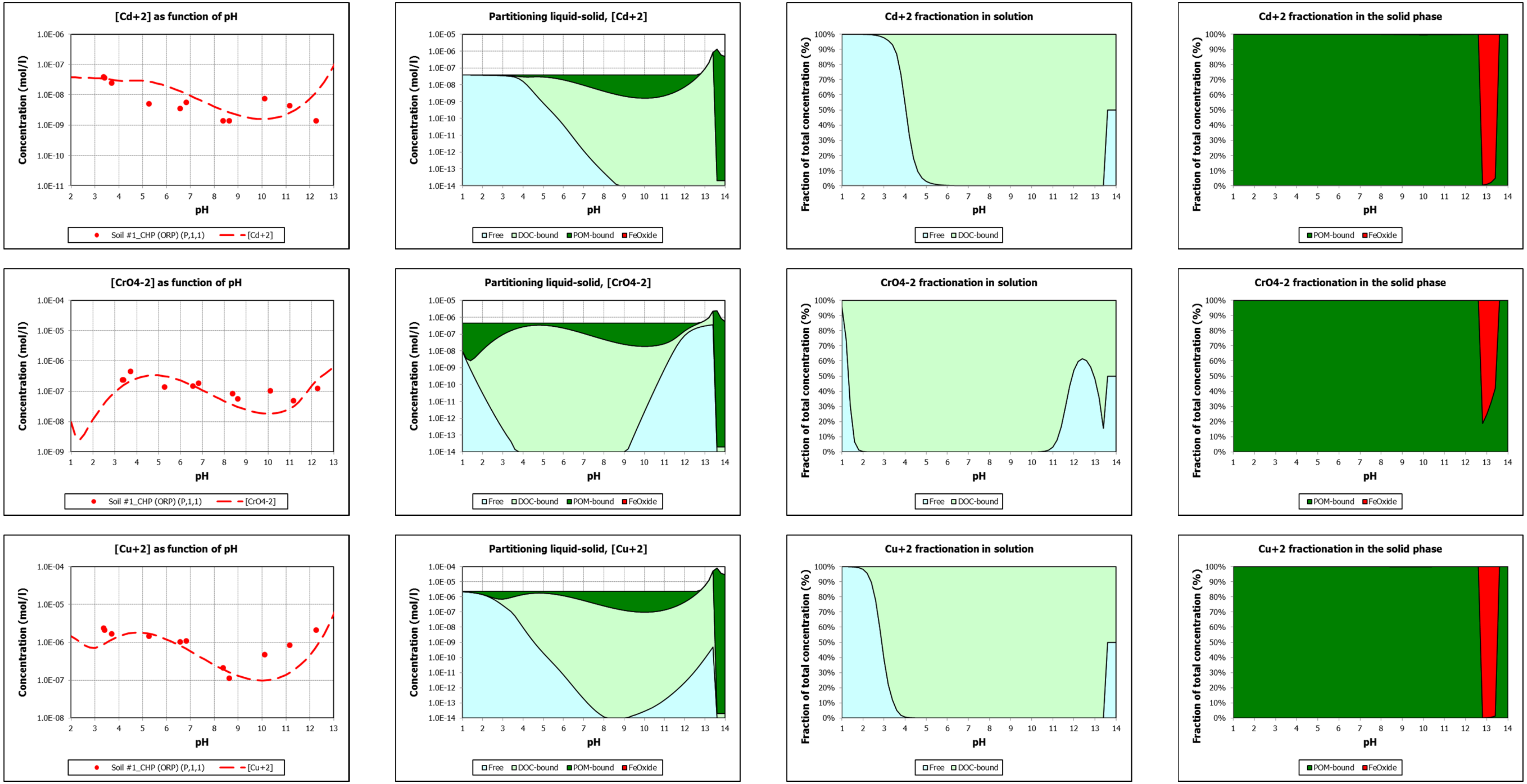


Figure 4.2.15 Geotechnical Modeling: Metal release and partitioning in the presence of CHP in Soil #1.
The first graph in each row depicts the solubility of a given metal (symbols and line represent experimental data and model prediction, respectively)
The subsequent graphs in the row show the liquid-solid partitioning and the solution and solid phase fractionation of the same metal.


[Cd+2] as function of pH

Partitioning liquid-solid, [Cd+2]

Cd+2 fractionation in solution

Cd+2 fractionation in the solid phase

[CrO4-2] as function of pH

Partitioning liquid-solid, [CrO4-2]

CrO4-2 fractionation in solution

CrO4-2 fractionation in the solid phase

[Cu+2] as function of pH

Partitioning liquid-solid, [Cu+2]

Cu+2 fractionation in solution

Cu+2 fractionation in the solid phase

Figure 4.2.15 (cont.) Geotechnical Modeling: Metal release and partitioning in the presence of CHP in Soil #1.
The first graph in each row depicts the solubility of a given metal (symbols and line represent experimental data and model prediction, respectively)
The subsequent graphs in the row show the liquid-solid partitioning and the solution and solid phase fractionation of the same metal.

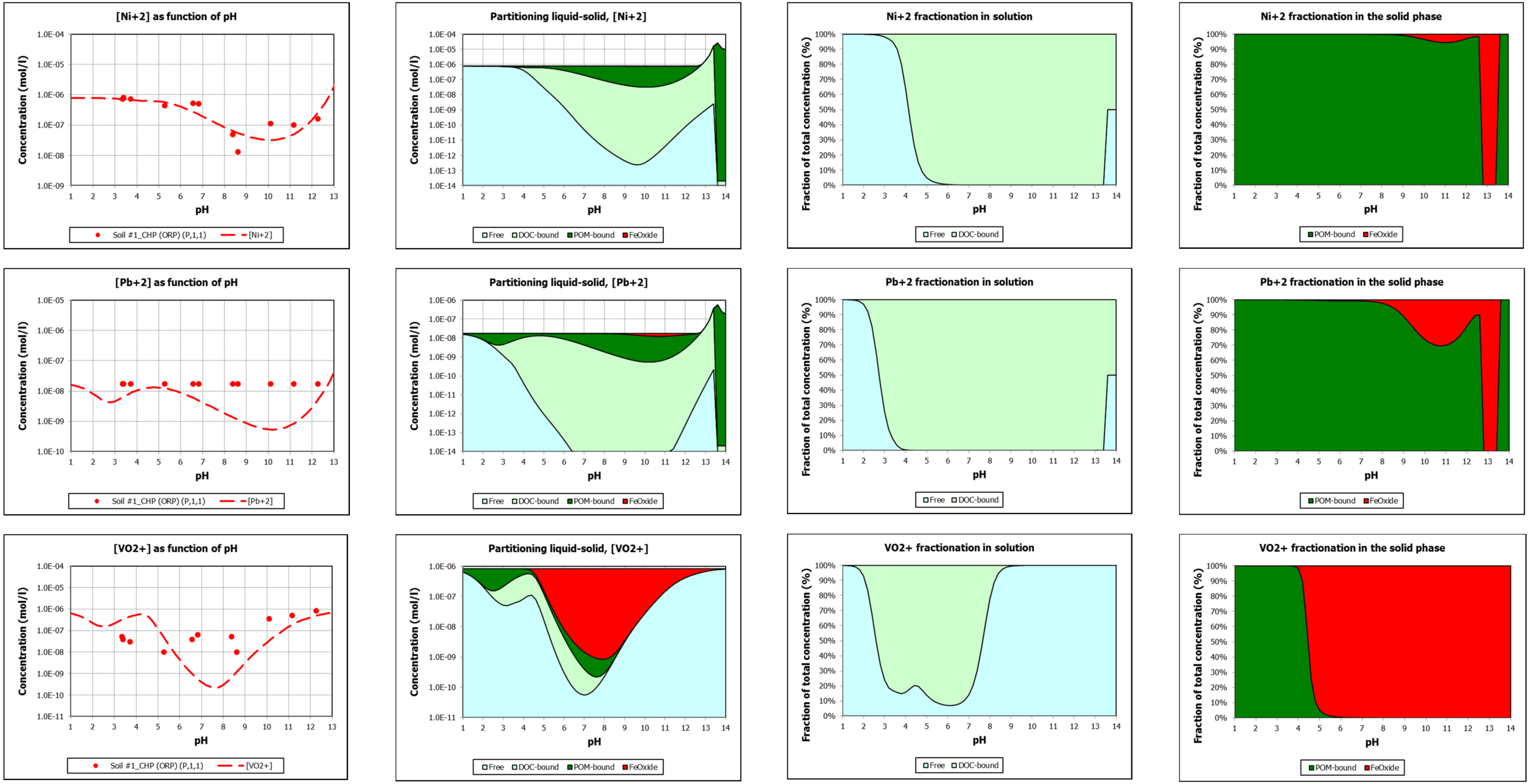


Figure 4.2.15 (cont.) Geotechnical Modeling: Metal release and partitioning in the presence of CHP in Soil #1.

The first graph in each row depicts the solubility of a given metal (symbols and line represent experimental data and model prediction, respectively)
The subsequent graphs in the row show the liquid-solid partitioning and the solution and solid phase fractionation of the same metal.

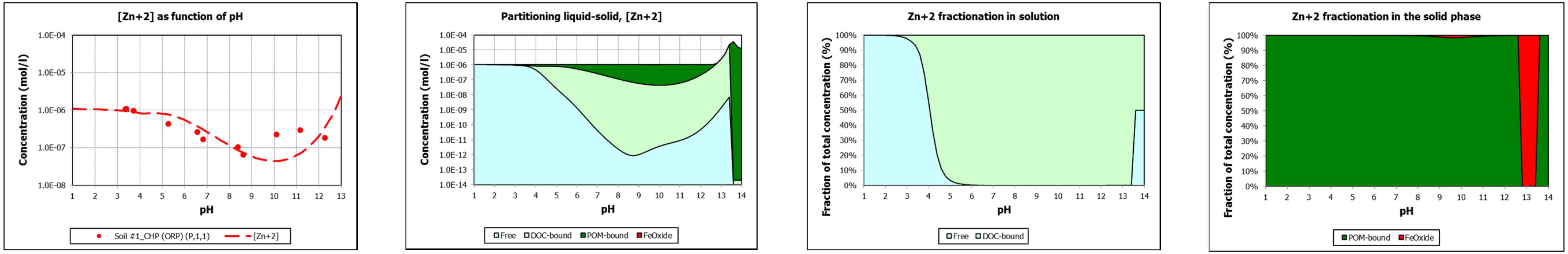


Figure 4.2.15 (cont.) Geotechnical Modeling: Metal release and partitioning in the presence of CHP in Soil #1.

The first graph in each row depicts the solubility of a given metal (symbols and line represent experimental data and model prediction, respectively) The subsequent graphs in the row show the liquid-solid partitioning and the solution and solid phase fractionation of the same metal.

4.3 EVALUATION OF POST-ISCO RECOVERY/RETURN TO BASELINE CONDITIONS

Application of ISCO to treat solvent-impacted groundwater can have the unintended consequence of mobilizing metal contaminants that were previously attenuated onto the aquifer matrix. Empirical data has shown that metals within the target area eventually return to near baseline conditions after ISCO application. However, the extent to which metals will migrate within the radius of influence of the applied ISCO reagents, beyond the radius of influence, and the geochemical properties of the aquifer matrix that govern the reversion to baseline conditions (pre-ISCO) are unknown. The goal of this task is to understand post-remediation impact on groundwater quality and the factors influencing recovery and return to baseline conditions. Understanding the different geochemical factors which govern the spatial and temporal effects of ISCO application will aid in predicting the potential for migration of metals outside of the target area. Furthermore, these results can be used to make predictive estimates of the rates required to re-establish baseline conditions and narrow the range of possible mechanisms for site recovery.

4.3.1 Natural Oxidant Demand of Selected ISCO Site Soils

The oxidant demand of a soil and/or aquifer system is a critical value to characterizing the area of influence of an ISCO treatment. This study was conducted to measure the natural oxidant demand (NOD) and total oxidant demand (TOD) of 3 ISCO site soils for 4 ISCO treatments. NOD is defined as the oxidant demand from the natural system (soil and groundwater), TOD includes natural and applied oxidant demands when applying ISCO treatments.

Results of Soil Analysis

Figure 4.3.1 provides the TOD an NOD for the three soils evaluated. The TOD and NOD results in the plot are after 14 days of contact, which represented equilibrium values. The NOD and TOD are highest for soil #1 which had the highest organic content (5%). Soil #2 and #1 were sandy soils with a similar organic content, around 0.5%. H_2O_2 reacts very quickly and unfortunately due to the experimental design, all oxidant reacted with the treatment prior to exposure to the soil; therefore, NOD results for the CHP+CA treatment does not reflect the NOD of the soils and is not applicable.

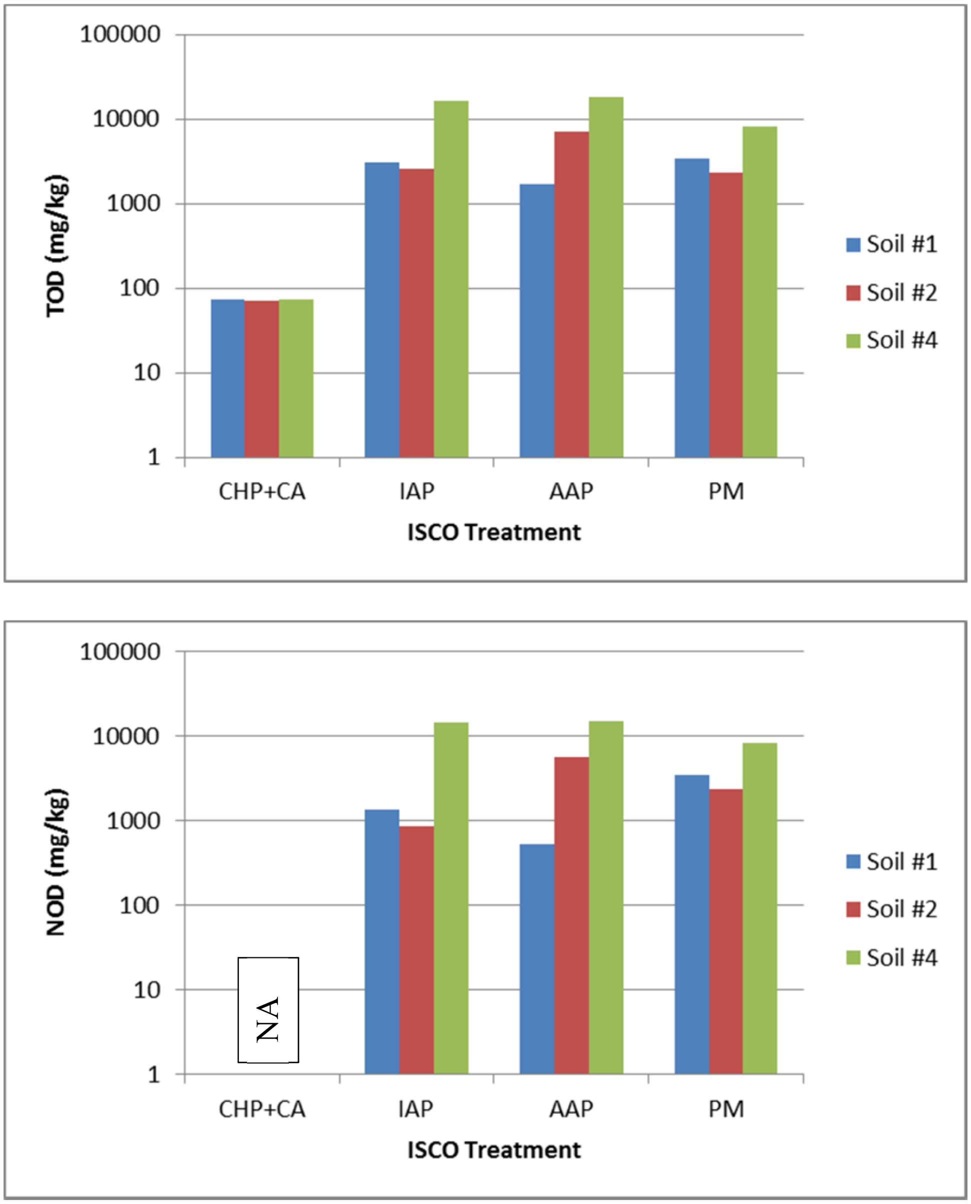


Figure 4.3.1 TOD and NOD of 3 ISCO Soils

Note: CHP measurements taken at 48 hrs. CHP+CA results not applicable for NOD results.

3.3.2 Batch Reactor Evaluation of Site Soils Exposed to ISCO Treatments

Batch studies were conducted to determine how geochemical properties and metals mobilization changed as ISCO treatments were exposed to additional soil mass over time. Specifically, 2 soils were exposed to 4 ISCO treatments in a cumulative series of batch studies where the same ISCO treatment solution was exposed to 3 iterations of fresh soil mass. PH, ORP, conductivity and temperature were monitored.

Results of Soil Analysis

In Figure 4.3.2, the pH and ORP are presented for soil #2 and #4 for the batch reactor test after 5 days of contact with ISCO treatments for various liquid to solid ratios (LS). The purple line represents the control pH and ORP of the groundwater (sourced from a well at Battelle) and soil without ISCO treatment.

For Soil #2, the pH was much lower for ISCO treatments CHP+CA and IAP+CA relative to the control (pH of 8). Furthermore, the pH for AAP was around 13. Large shifts to the pH for Soil #2 were expected with the addition of the ISCO treatments as it was a sandy soil with a low buffering capacity. Soil #4 showed more buffering capacity due to the higher organic content, so the pH for all the ISCO treatments was similar to the control value.

For Soil #2, the ORP values for IAP+CA and PM were around 700 mV for all LS ratios. As Soil #2 had a low organic content, a high percentage of the residual oxidant remained in the reactors after 5 days, with the exception of CHP+CA which had no residual remaining. The ORP values for Soil #4 showed a high degree of variability across the LS ratios and ISCO treatments. We believe this variability is due to the high organic content of this soil.

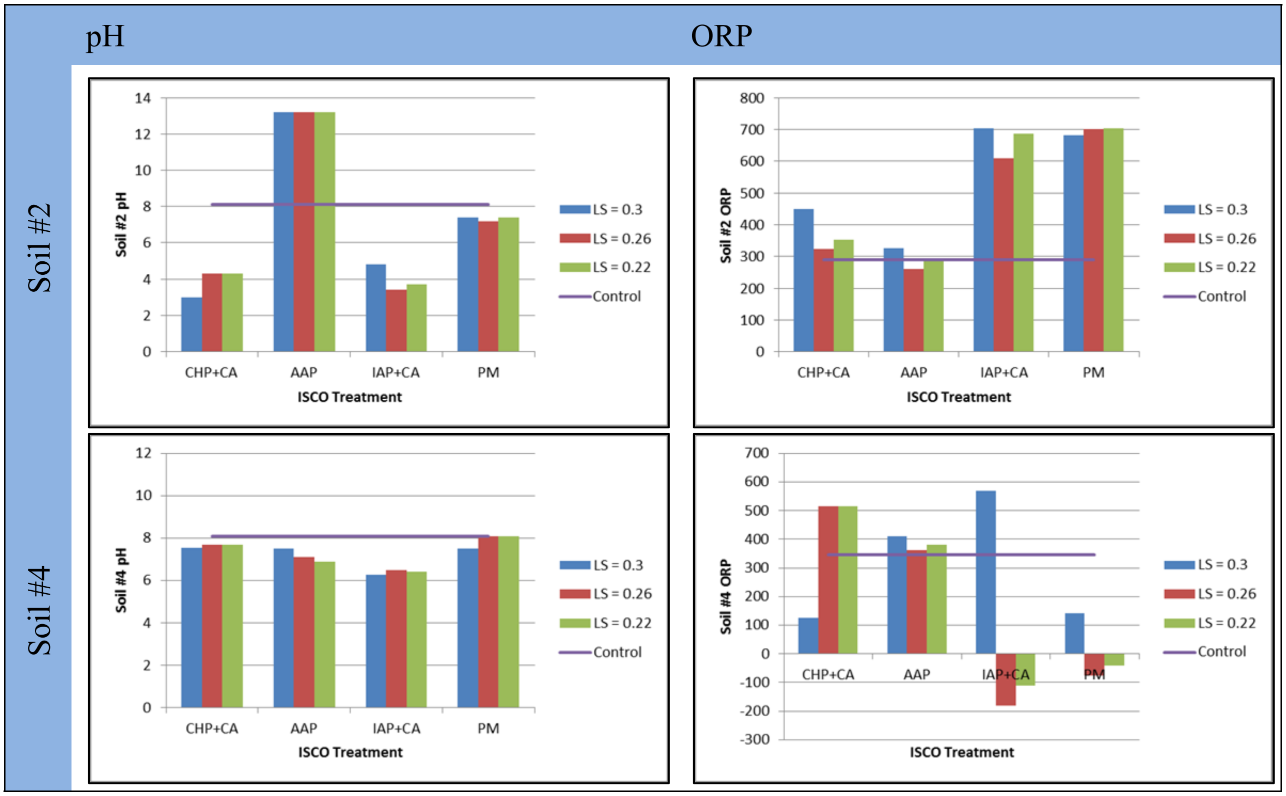


Figure 4.3.2 pH and ORP Readings for Soils #2 and #4

Note: Peroxide measurements taken at 48 hrs.

3.3.3 Column Studies

Column studies were conducted to determine the amount of time required for ISCO treated site soils to return to their original baseline following treatment (as measured by conductivity, pH & ORP). Additionally, the transport potential for various metals of concern was also evaluated over the reversion period. Specifically, 30 columns were constructed to evaluate 4 ISCO treatments (and one control) on 3 site soils. The columns consisted of 2 segments, the first contained ISCO treated soil followed by the second which contained untreated soil. Both sections were eluted with groundwater for 4 weeks until equilibrium of the pH and ORP occurred. Results of the study are discussed in 4 section below which, describe the initial baseline conditions of ISCO treated soils loaded into the columns; the changes in the background geochemistry of the soil over 4 weeks of groundwater elution; the mobilization of metals in and out of the aqueous phase during the same operation period; and a summary of the results.

Baseline Geochemistry of ISCO Soils Evaluated

Aquifer material from soils #1, #2, and #4 were equilibrated with either Battelle groundwater (control) or one of the four ISCO treatments (Table 3.3.4) for 48 hours as described in Section 3.3.3. At the conclusion of the mixing, pH, Eh, conductivity, temperature and ROM measurements were recorded to establish a baseline of the ISCO treated soil prior to the start of the column study. The results are provide below in Table 4.3.1

Changes in Background Geochemistry due to ISCO reagents.

After the ISCO treated soils were prepared, the soils were loaded into each column segment as described in Section 3.3.3. Briefly, the first column (*up-gradient*) of the 2-column series was loaded with ISCO treated soil and a second (*down-gradient*) column (Figure 4.3.1) contained aquifer material equilibrated with Battelle groundwater. Once the aquifer materials were loaded into each column, groundwater was used to elute both columns, which were hydraulically connected and arranged in series. Columns were sampled from ports alongside the column as well as from the effluent port at both the up-gradient and down-gradient columns. This experimental arrangement allowed for a kinetic investigation of the system reversion to baseline conditions.

Results of the conductivity, pH and ORP analyses for all samples acquired over a 4 week time period for the controls and four treatments (5 series total) are presented in Figures 4.3.2 through 4.3.6 for soil #2, Figures 4.3.7 through 4.3.11 for soil #4, and Figures 4.3.12 through 4.3.16 for soil #1. These data clearly demonstrate the migration and neutralization of the various ISCO reagents through the columns over the course of these experiments. Only slight changes in conductivity and pH can be observed in the Control Treatment columns (Figures 4.3.2, 4.3.7 and 4.3.11) as the groundwater equilibrates with the aquifer material.

Alkaline Activated Persulfate. The conductivity, pH and ORP data for AAP treatment is shown in Figures 4.3.3, 4.3.8 and 4.3.13. Like other treatments, the addition of reagent increases the conductivity, which declines back to baseline conditions after approximately 4 pore volumes (PVs). Furthermore, due to the mechanism of activation, the initial pH is rather high (pH ~ 13). In the *up-gradient* (treated) column of soil #2 the pH drops from an initial value of ~13 as it declines asymptotically to the pH of the groundwater, approximately 8 over approximately 11 PVs. This same trend is also seen in soil #1 (Figure 4.3.13). In contrast, in soil #4 (Figure

4.3.8) the pH effect is almost non-existent with the initial time point showing an elevated pH of nearly 8.5. This is presumably due to the high concentration of organic carbon in this soil, effectively neutralizing the alkaline activator. Even though an effect of pH was not seen in soil #4 with AAP, the effect of the added reagent is clearly seen in elevated conductivity, which persisted for approximately 10 PVs in the *up-gradient* column and 12 PVs in the *down-gradient* column.

Table 4.3.1 ISCO Treated Soil Parameters Prior to Column Study

Sample ID	pH	ORP *(mV)*	Conductivity *(mS/cm)*	Temperature *(°C)*	Alkalinity *(mg/L)*	Residual Oxidant *(g/L or % if noted)*
Soil #1						
Control	7.3	226.8	1.418	20.8	83.0	NA
AAP	13.0	245.9	64.5	20.5	over range	39.0
IAP+CA	5.6	465.9	30.1	20.9	73.7	39.5
CHP	4.2	326	3.98	20	47.0	4.08%
PM	7.1	609.3	11.8	20.7	Error	13.8
Soil #2						
Control	7.7	289	0.8	21.5	166	NA
AAP	13.2	296	89.3	21.4	Over range	49.6
IAP+CA	4.8	712	10.9	20.3	61.1	49.7
CHP	2.3	493	4.7	19.7	Under range	0.1%
PM	7.0	691	14.5	20.1	Error	22.7
Soil #4						
Control	7.6	223.1	0.724	23.1	387	NA
AAP	7.2	352.7	11.59	21.7	Over range	6.1
IAP+CA	6.1	536.9	3.83	21.4	Over range	23.1
CHP	6.8	217	1.703	21.8	Over range	0.06%
PM	7.5	280.7	1.704	21.7	Over range	0.3

Note: Alkalinity range: Over >500mg/L, Under <45mg/L

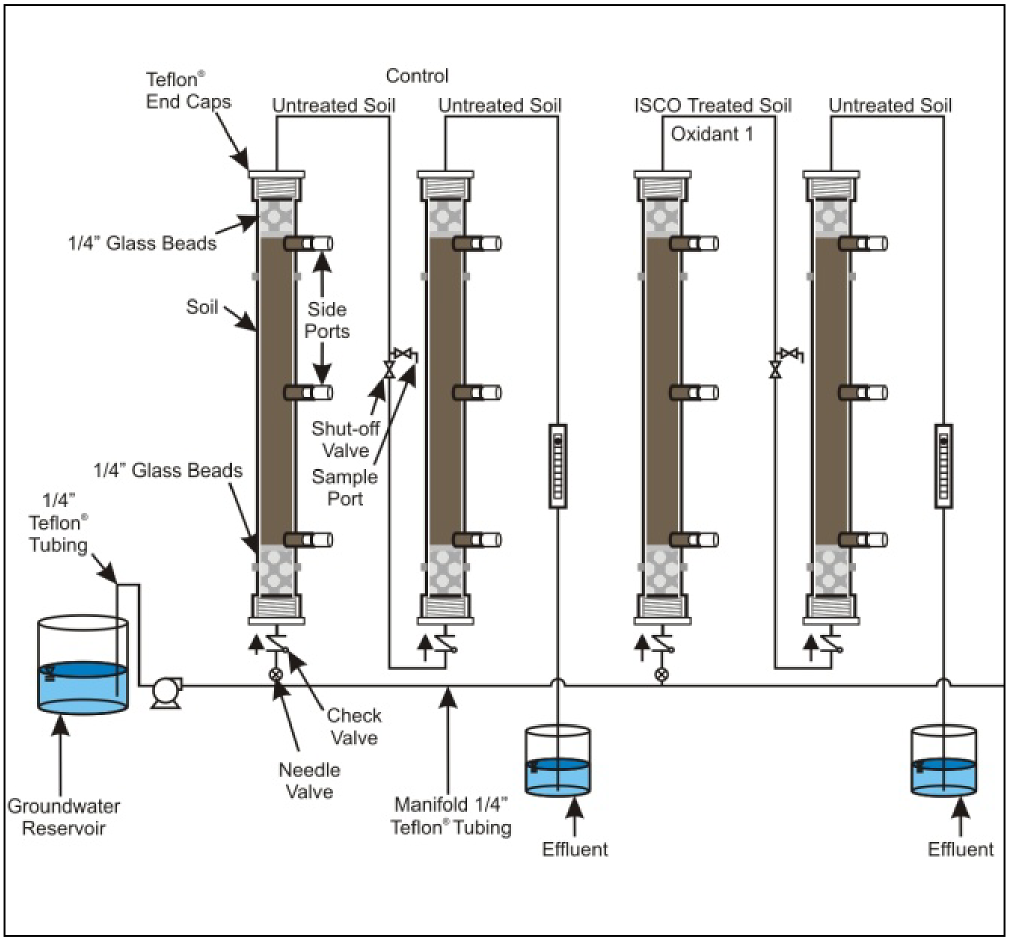


Figure 4.3.1 Column Experiment Schematic

Iron Activated Persulfate. IAP treatments did not cause dramatic shifts in pH as seen with AAP. The main effect seen in the IAP treatments is with ORP in Soil #2. The ORP value for soil #2 with IAP treatment was an initial value of approximately 500 mV (Figure 4.3.4), with a steady decline to baseline conditions (approximately 250-300 mV) over the duration of this experiment. IAP showed variable effects on measured ORP values for the other two soils (Figure 4.3.9, soil #4; Figure 4.3.14, soil #1).

Catalyzed Hydrogen Peroxide. The peroxide treatment for soil #2 was shows an initial decline in pH, followed by a relatively rapid re-equilibration to the native pH of the groundwater. There is also evidence for oxidant consumption as seen in the changes in the ORP data, however not to the same extent as the changes seen in the samples treated with iron activated persulfate (Figure 4.3.4).

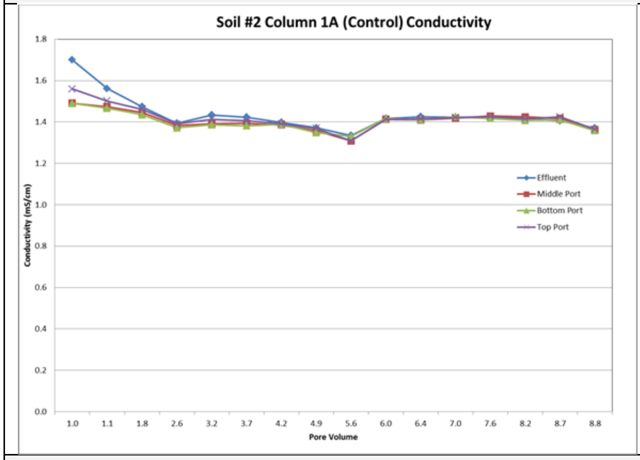
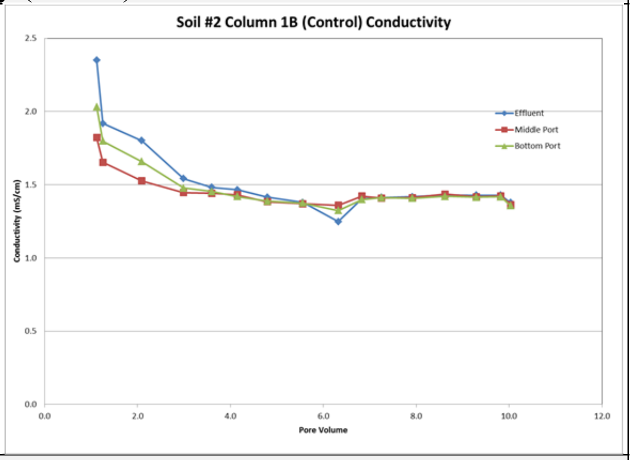
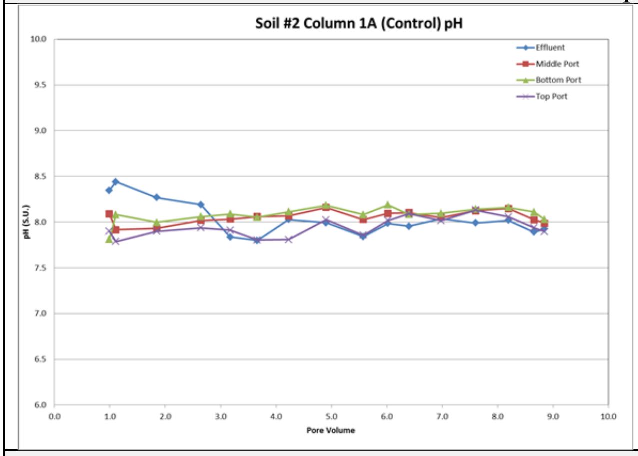
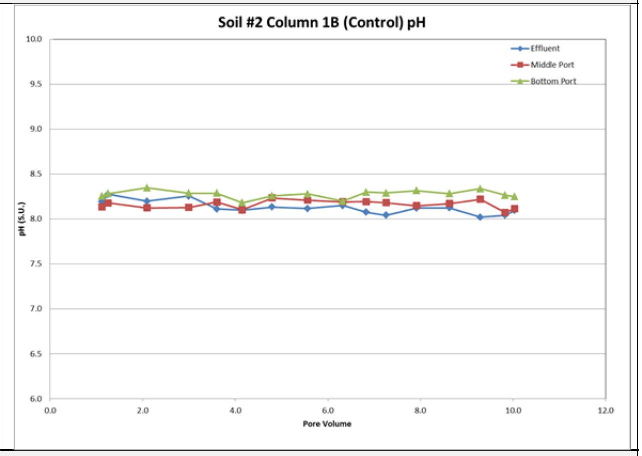
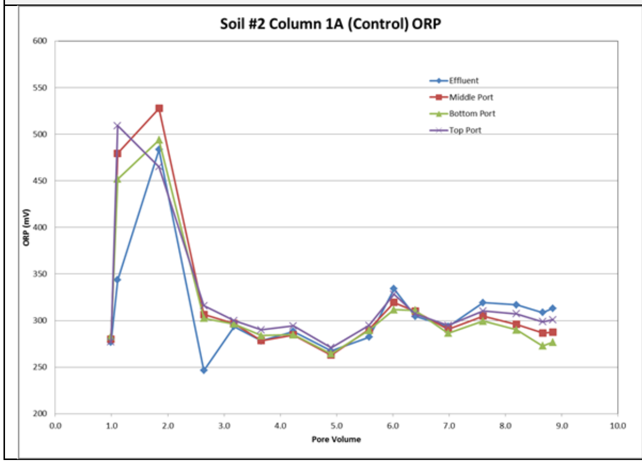
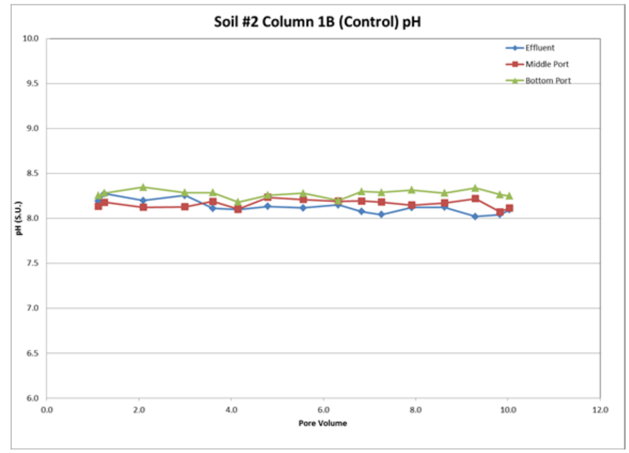
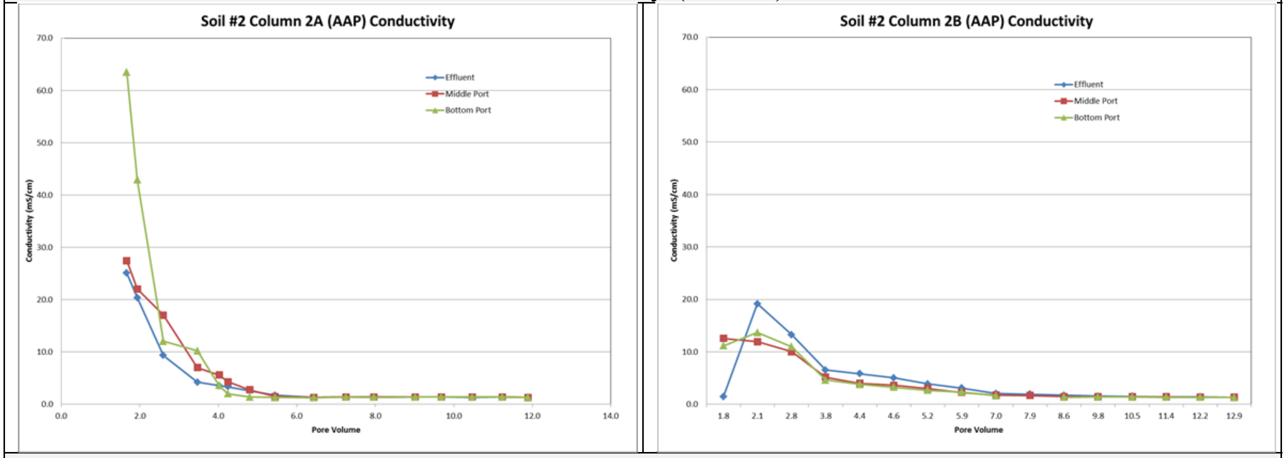
<table>
<tr><th>Up-gradient Column</th><th>Down-gradient Column</th></tr>
<tr><td colspan="2">Conductivity (mS/cm)</td></tr>
<tr><td>
</td><td>
</td></tr>
<tr><td colspan="2">pH</td></tr>
<tr><td>
</td><td>
</td></tr>
<tr><td colspan="2">ORP (mV)</td></tr>
<tr><td>
</td><td>
</td></tr>
</table>

Figure 4.3.2 Column Experiment: Soil #2 with Control Treatment (groundwater only) – Geochemical variation with increasing groundwater PV.

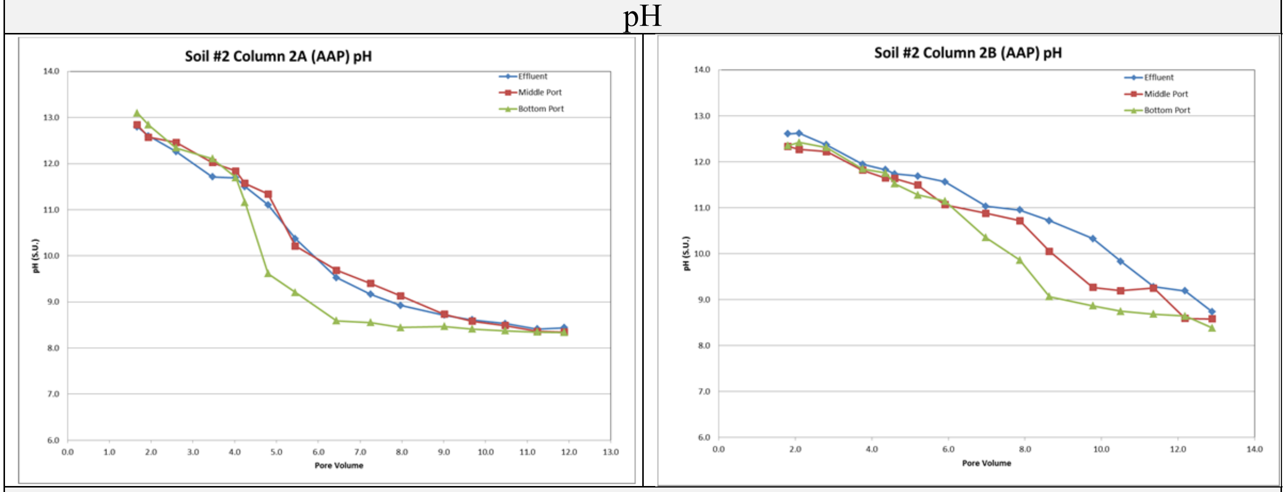
Up-gradient Column | ***Down-gradient Column***

Conductivity (mS/cm)


Soil #2 Column 2A (AAP) Conductivity

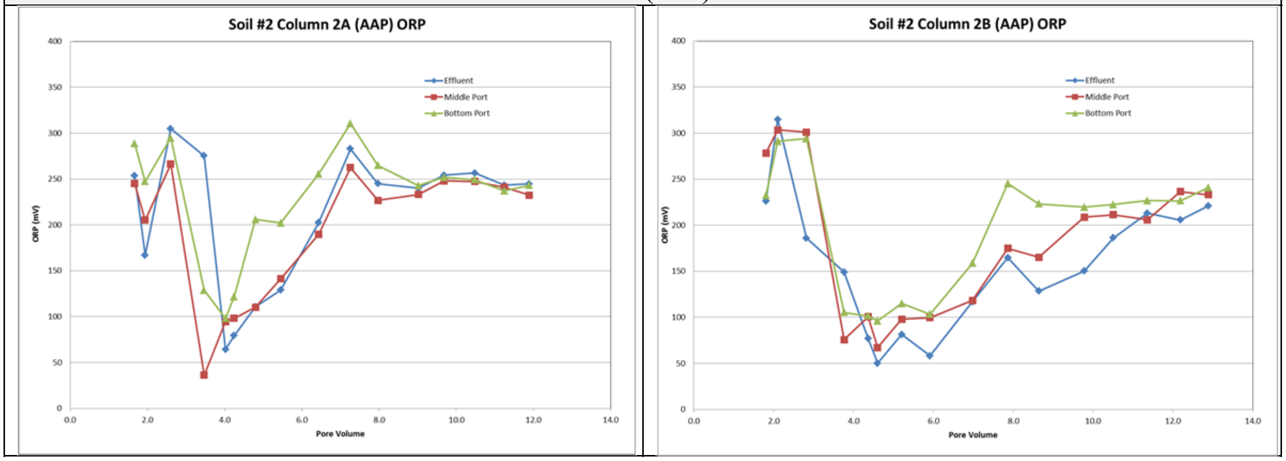
Soil #2 Column 2B (AAP) Conductivity

pH


Soil #2 Column 2A (AAP) pH

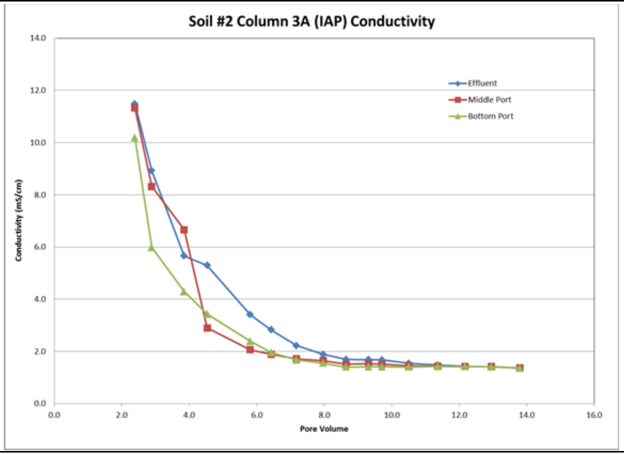
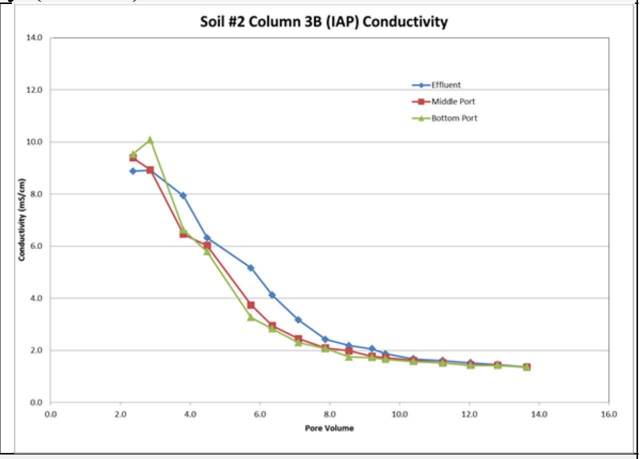
Soil #2 Column 2B (AAP) pH

ORP (mV)


Soil #2 Column 2A (AAP) ORP

Soil #2 Column 2B (AAP) ORP

Figure 4.3.3 Column Experiment: Soil #2 with AAP Treatment – Geochemical variation with increasing groundwater PV.

<table>
<tr><th>Up-gradient Column</th><th>Down-gradient Column</th></tr>
<tr><td colspan="2">Conductivity (mS/cm)</td></tr>
<tr><td>
Soil #2 Column 3A (IAP) Conductivity
</td><td>
Soil #2 Column 3B (IAP) Conductivity
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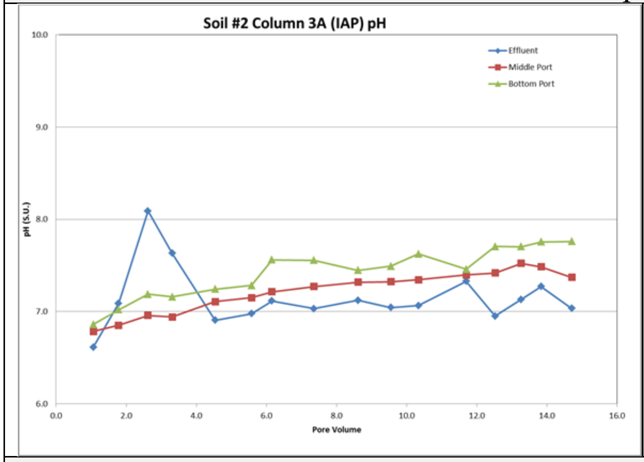
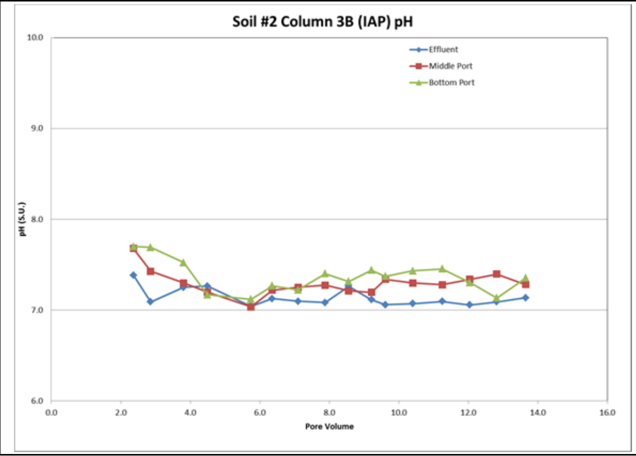
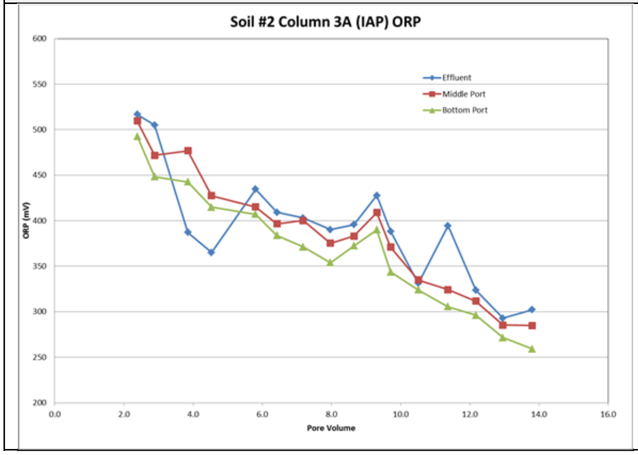
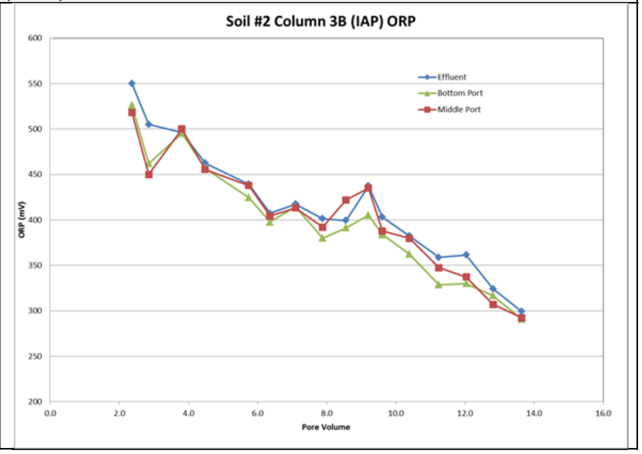
<tr><td colspan="2">pH</td></tr>
<tr><td>
Soil #2 Column 3A (IAP) pH
</td><td>
Soil #2 Column 3B (IAP) pH
</td></tr>
<tr><td colspan="2">ORP (mV)</td></tr>
<tr><td>
Soil #2 Column 3A (IAP) ORP
</td><td>
Soil #2 Column 3B (IAP) ORP
</td></tr>
</table>

Figure 4.3.4 Column Experiment: Soil #2 with IAP Treatment – Geochemical variation with increasing groundwater PV.

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<tr><th><i>Up-gradient Column</i></th><th><i>Down-gradient Column</i></th></tr>
<tr><td colspan="2">Conductivity (mS/cm)</td></tr>
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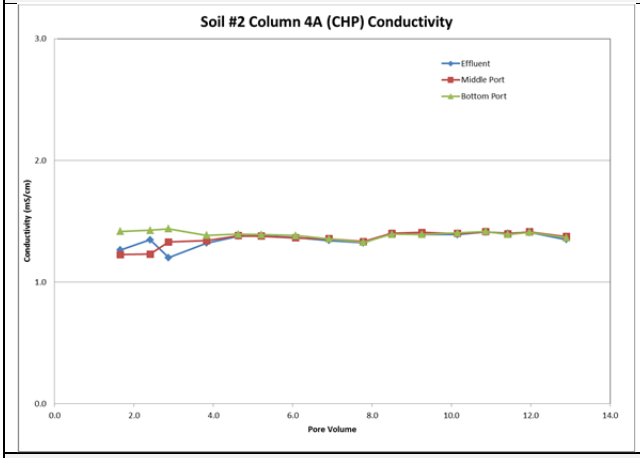

Soil #2 Column 4A (CHP) Conductivity

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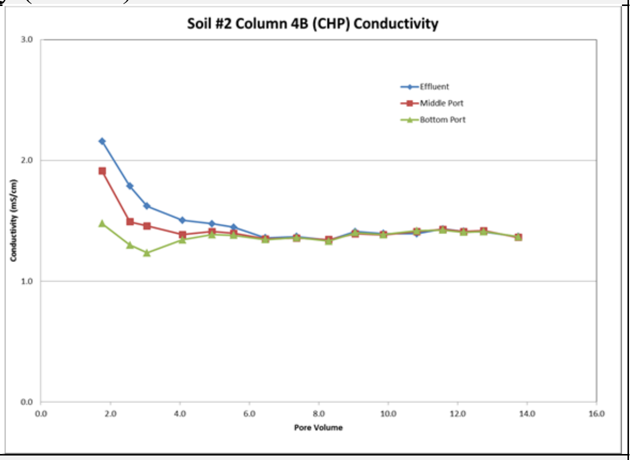

Soil #2 Column 4B (CHP) Conductivity

</td></tr>
<tr><td colspan="2">pH</td></tr>
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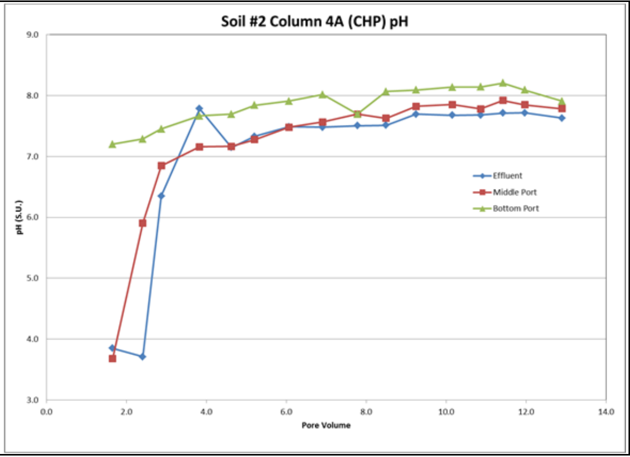

Soil #2 Column 4A (CHP) pH

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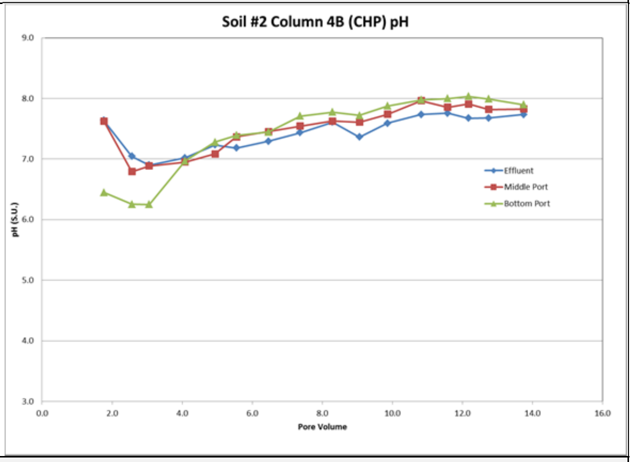

Soil #2 Column 4B (CHP) pH

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<tr><td colspan="2">ORP (mV)</td></tr>
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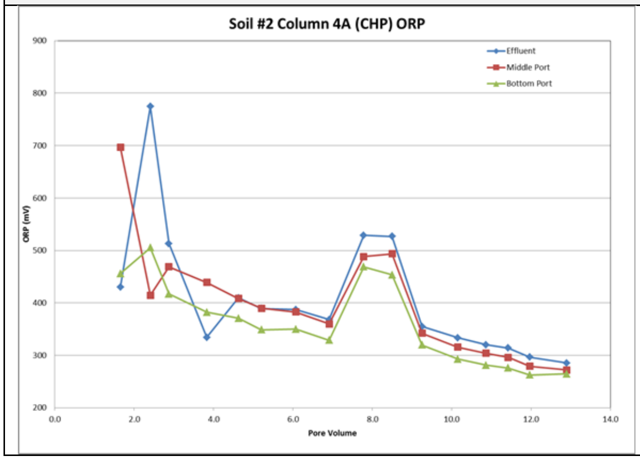

Soil #2 Column 4A (CHP) ORP

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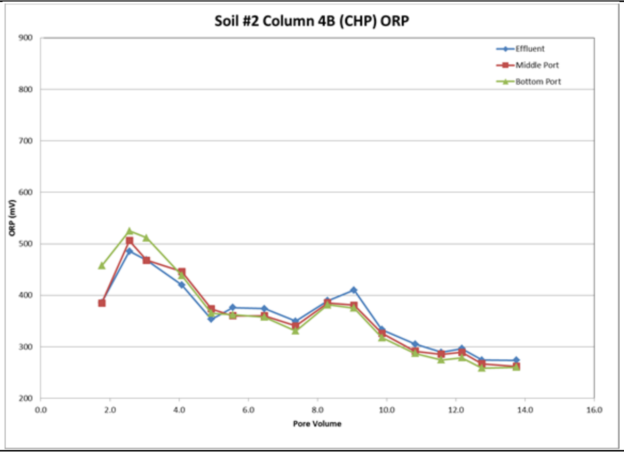


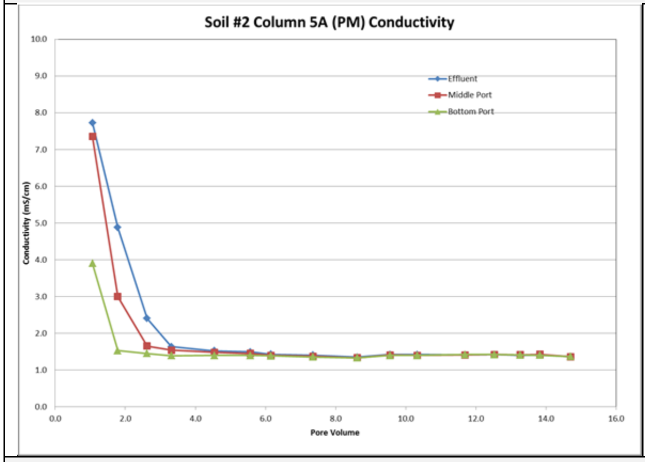
Soil #2 Column 4B (CHP) ORP

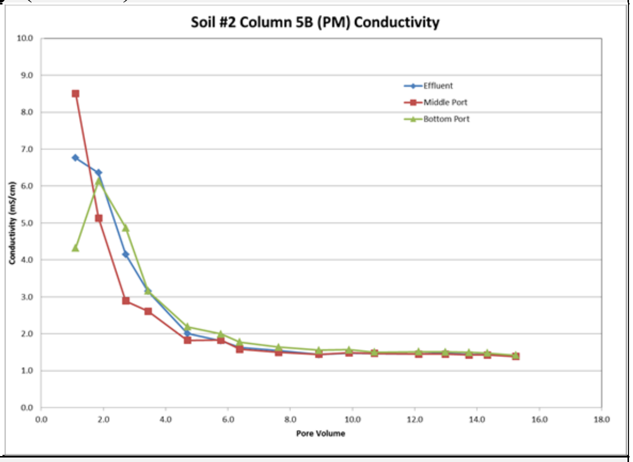
</td></tr>
</table>

Figure 4.3.5 Column Experiment: Soil #2 with CHP Treatment – Geochemical variation with increasing groundwater PV..

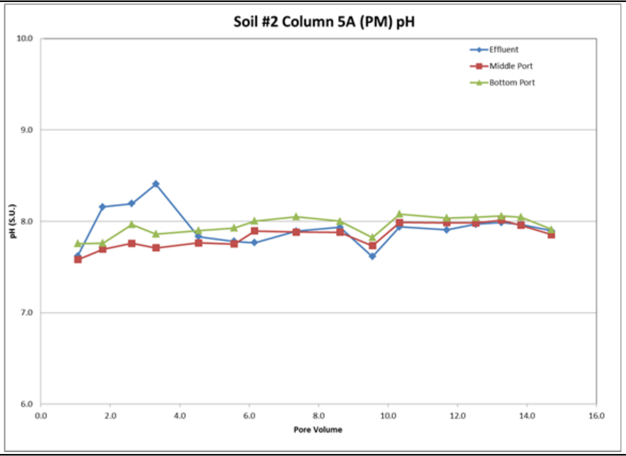
Up-gradient Column | ***Down-gradient Column***

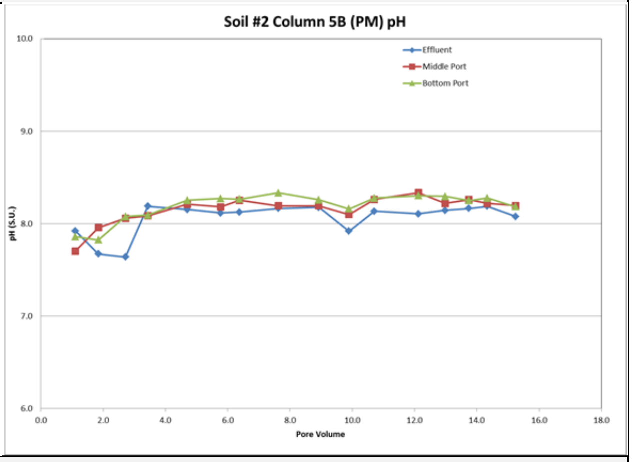
Conductivity (mS/cm)



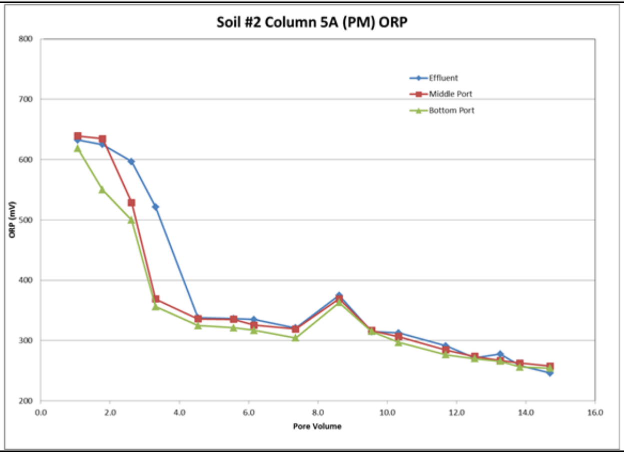


pH





ORP (mV)



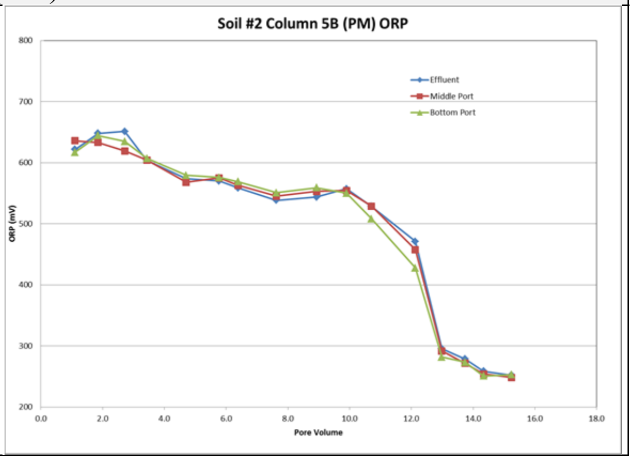


Figure 4.3.6 Column Experiment: Soil #2 with PM Treatment – Geochemical variation with increasing groundwater PV.

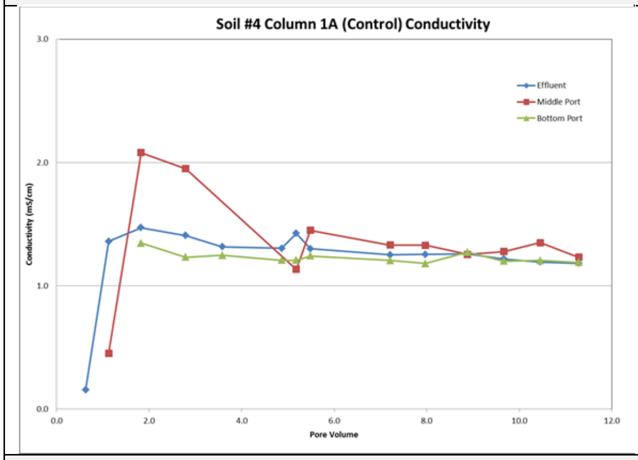
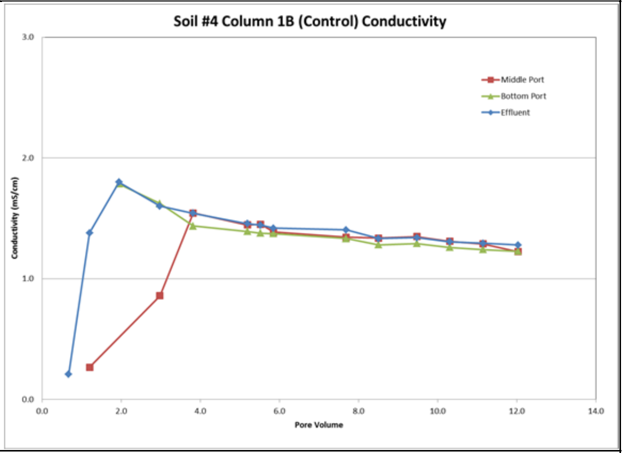
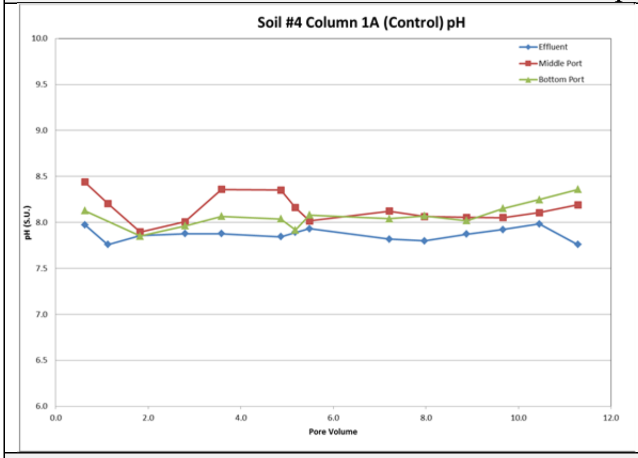
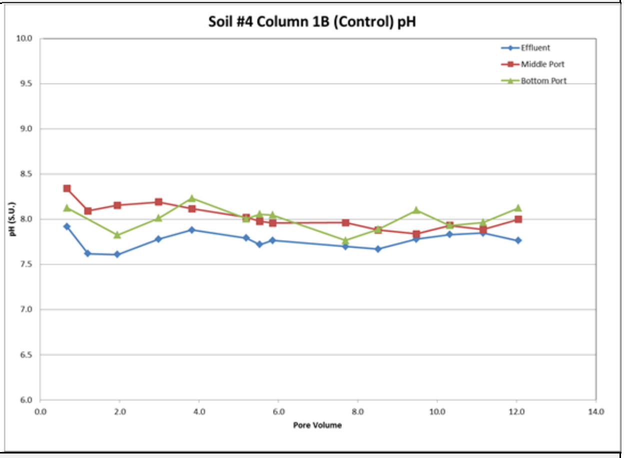
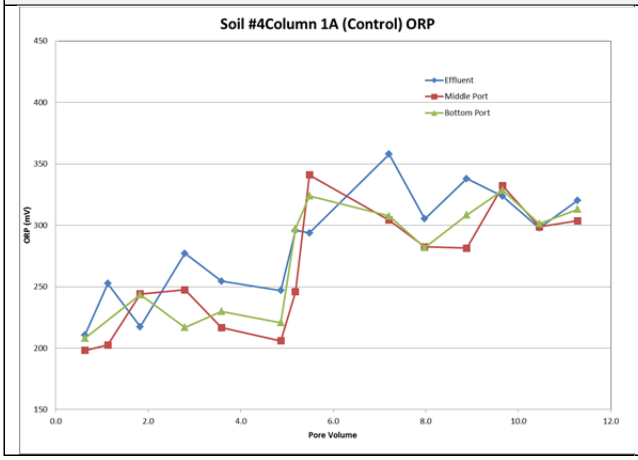
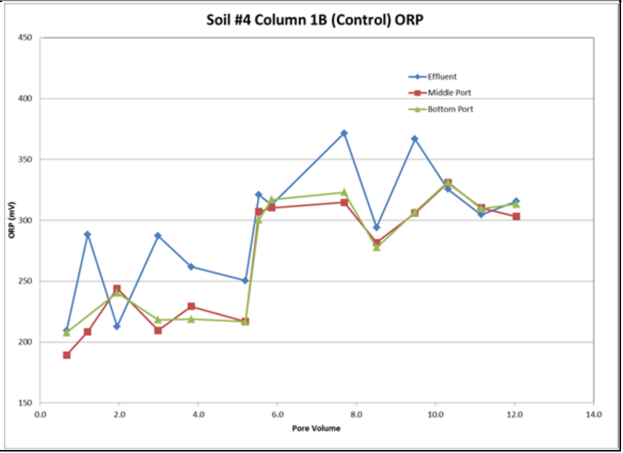
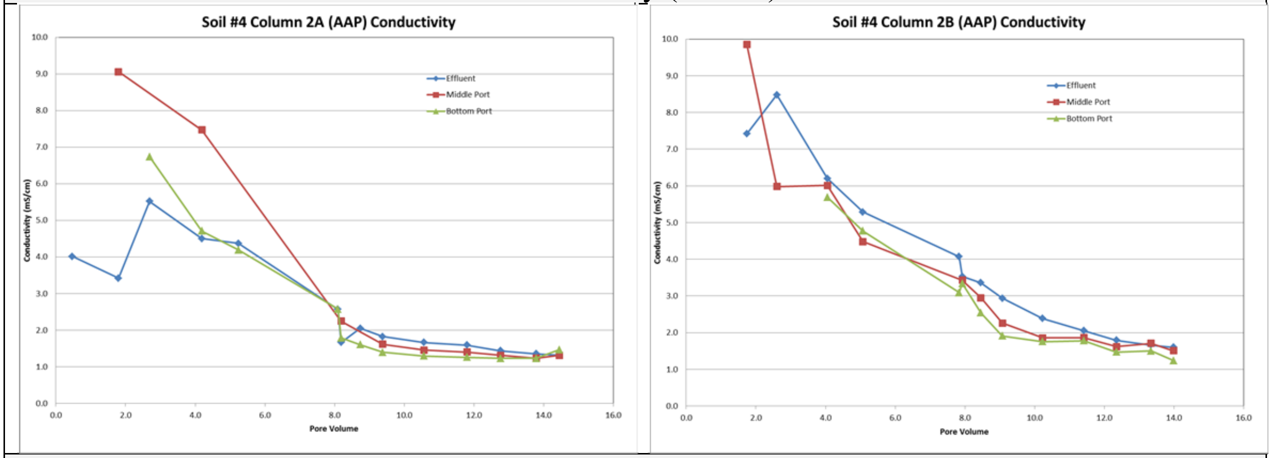
Up-gradient Column	***Down-gradient Column***
Conductivity (mS/cm)	
	
pH	
	
ORP (mV)	
	

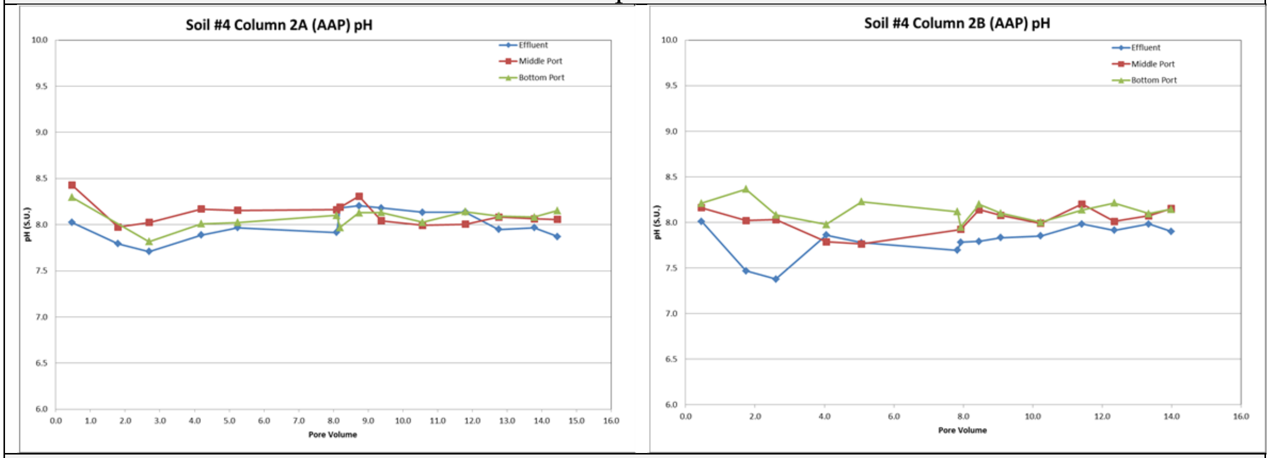
Figure 4.3.7 Column Experiment: Soil #4 with Control Treatment (groundwater only) – Geochemical variation with increasing groundwater PV.

Up-gradient Column	***Down-gradient Column***

Conductivity (mS/cm)



pH



ORP (mV)

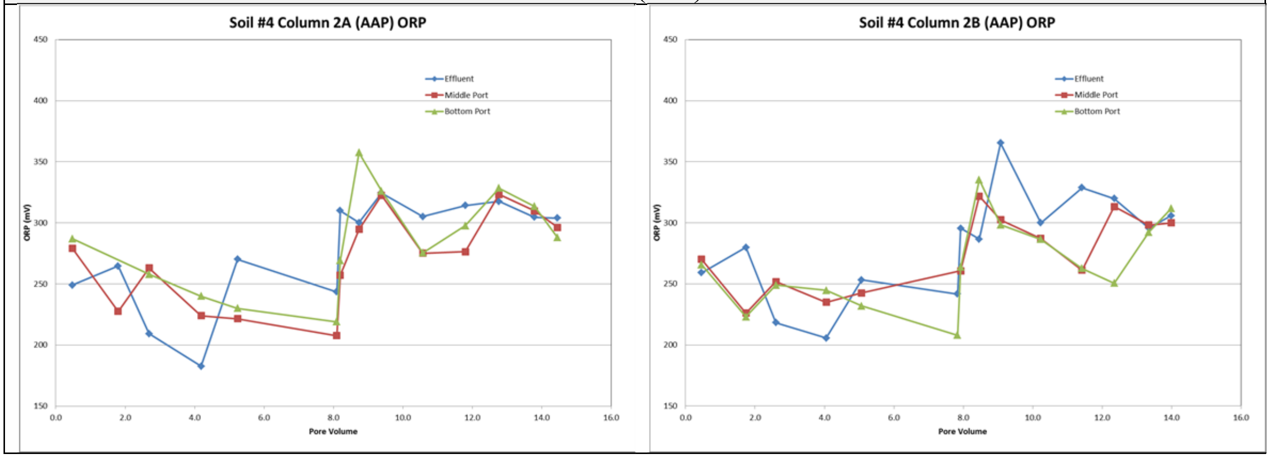


Figure 4.3.8 Column Experiment: Soil #4 with AAP Treatment – Geochemical variation with increasing groundwater PV.

Up-gradient Column	***Down-gradient Column***
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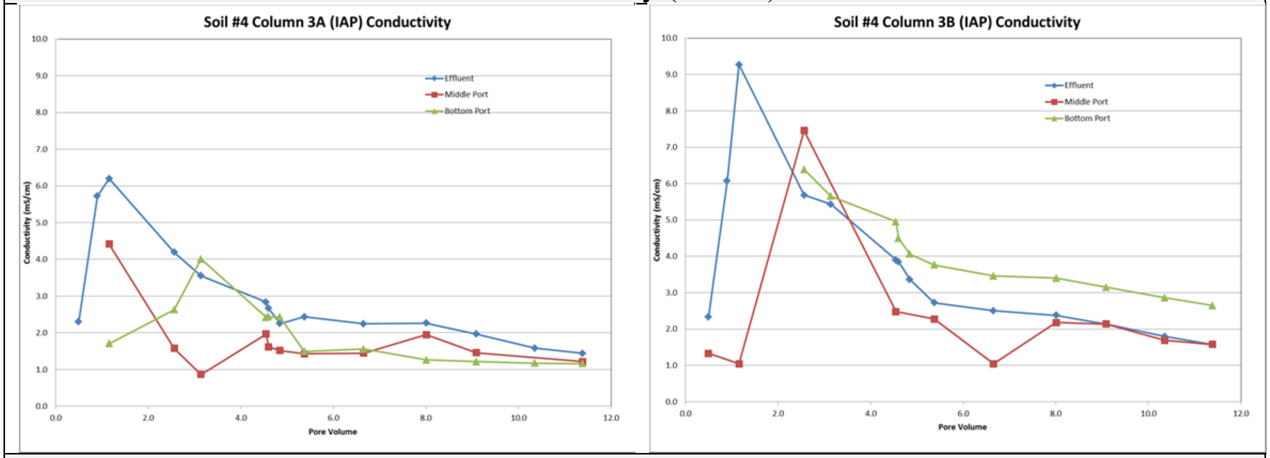
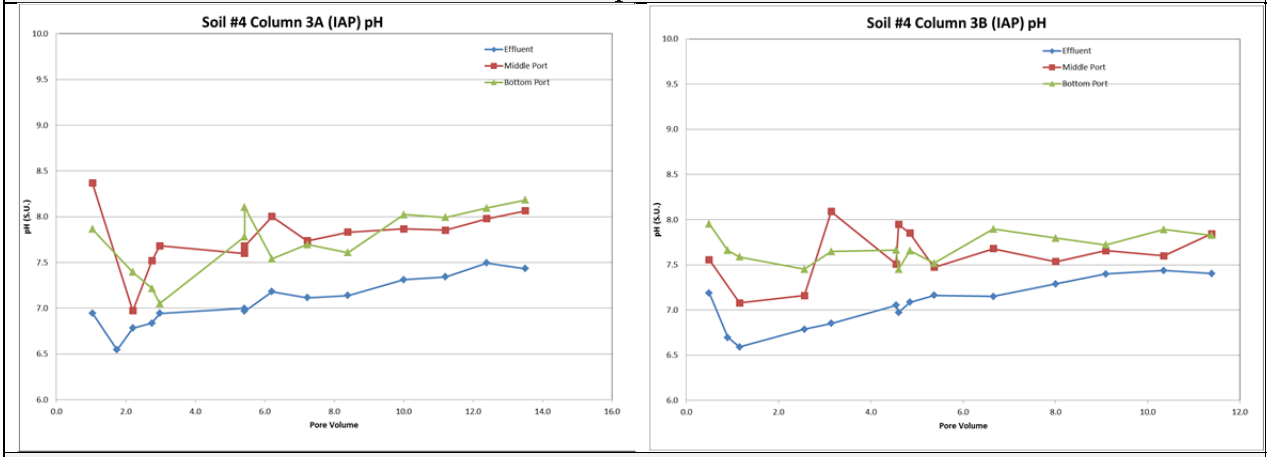
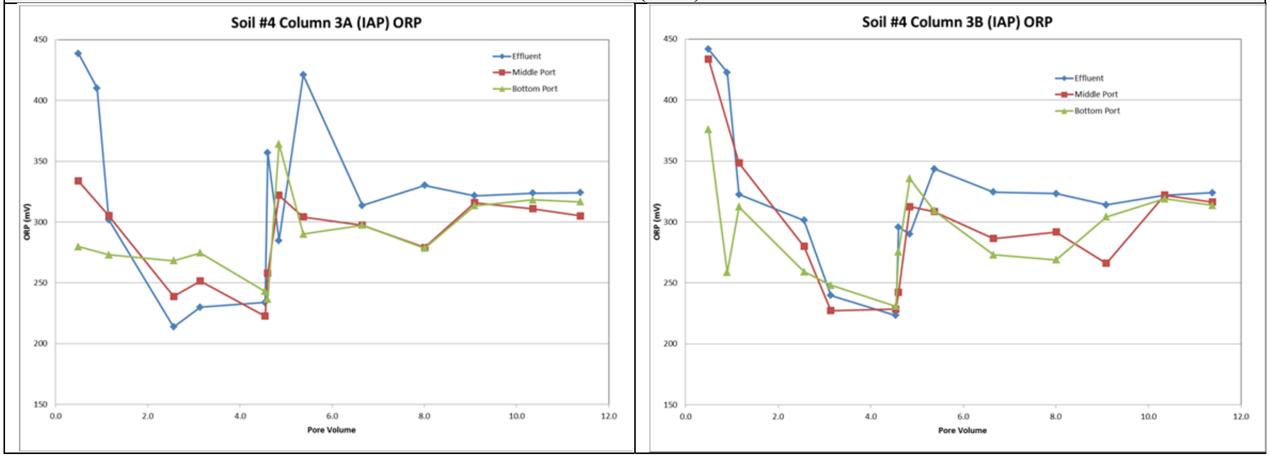
	
pH	
	
ORP (mV)	
	

Figure 4.3.9 Column Experiment: Soil #4 with IAP Treatment – Geochemical variation with increasing groundwater PV.

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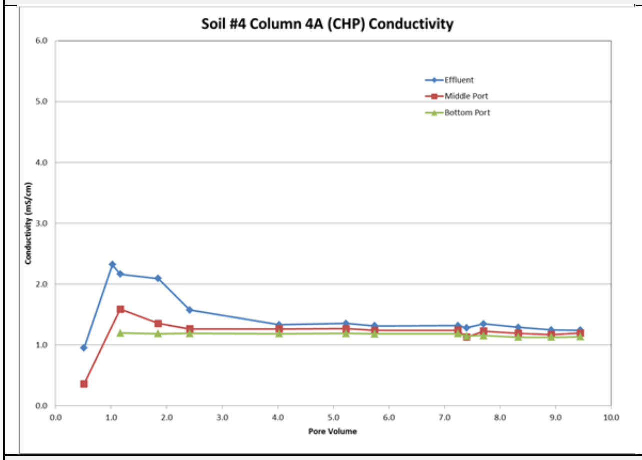
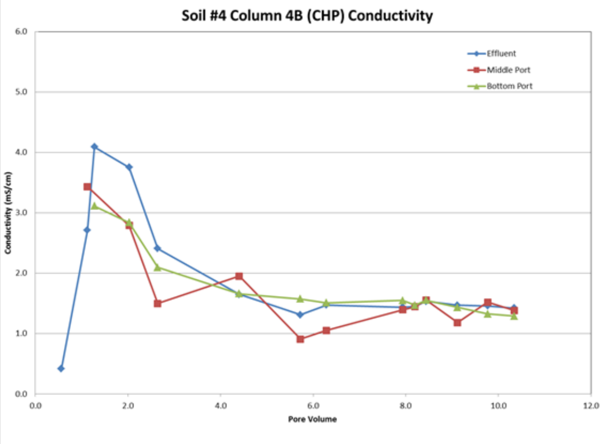
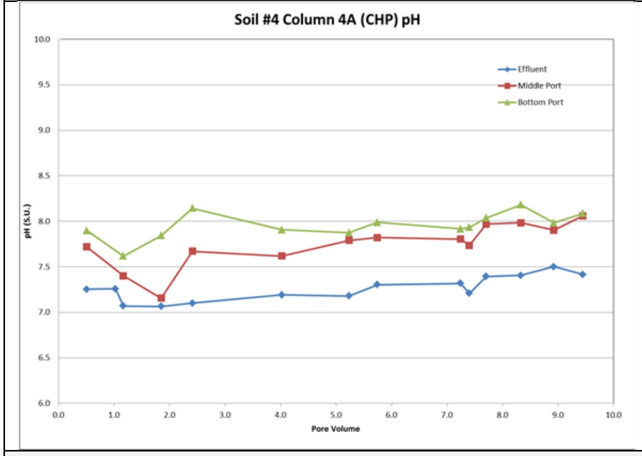
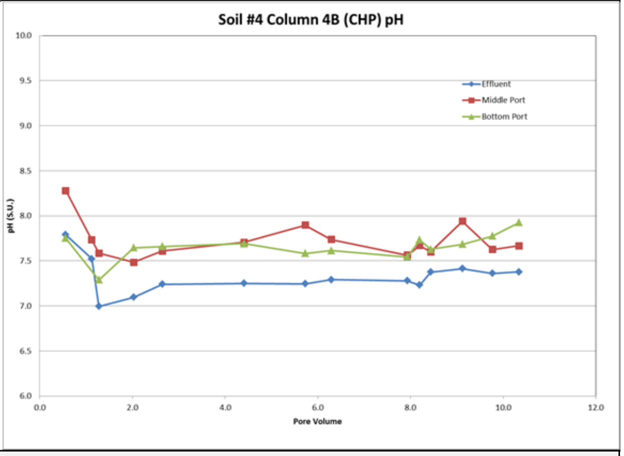
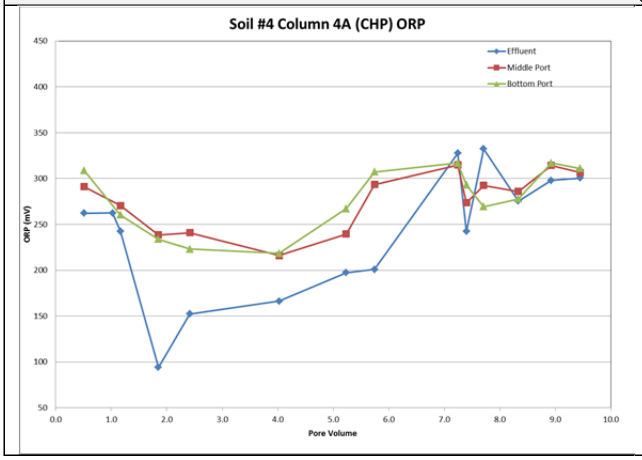
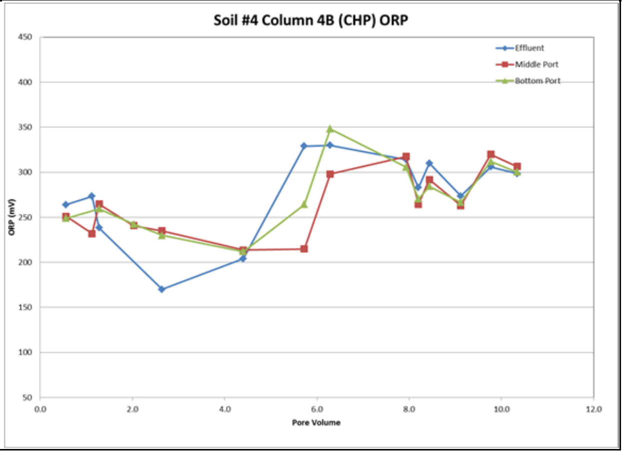
Conductivity (mS/cm)	
	
pH	
	
ORP (mV)	
	

Figure 4.3.10 Column Experiment: Soil #4 with CHP Treatment – Geochemical variation with increasing groundwater PV.

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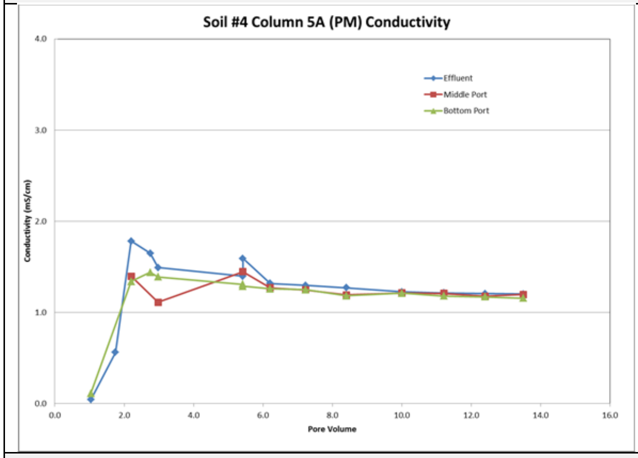
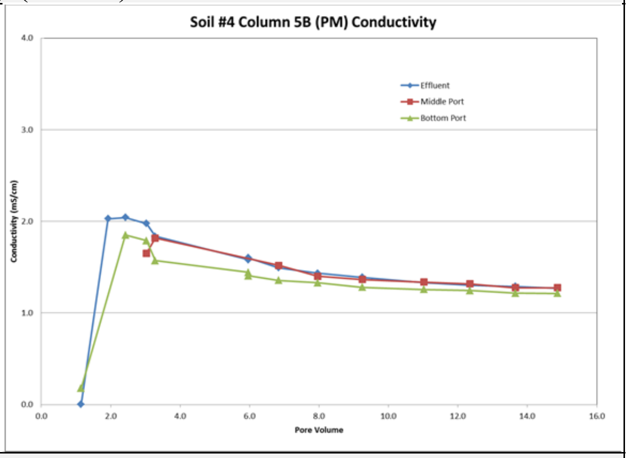
<tr><td>
</td><td>
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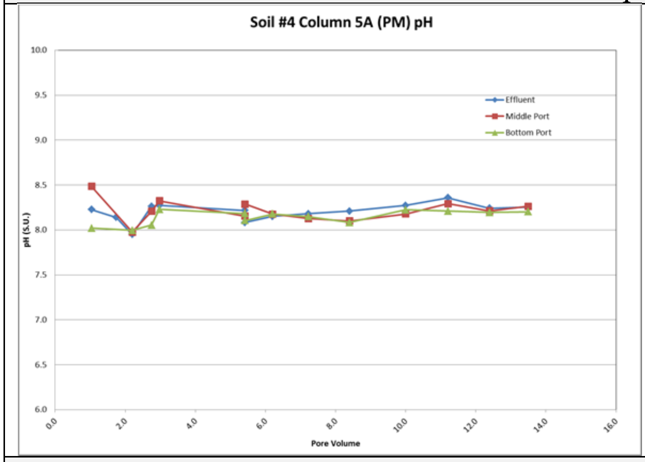
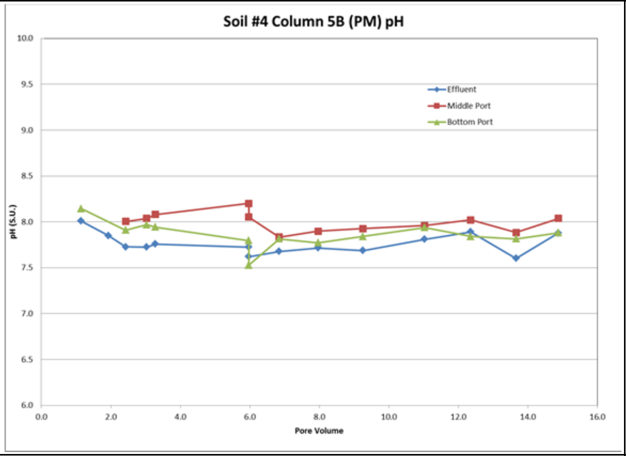
<tr><td>
</td><td>
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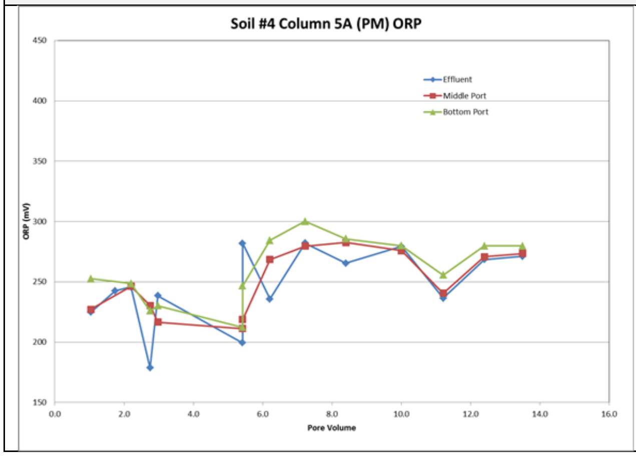
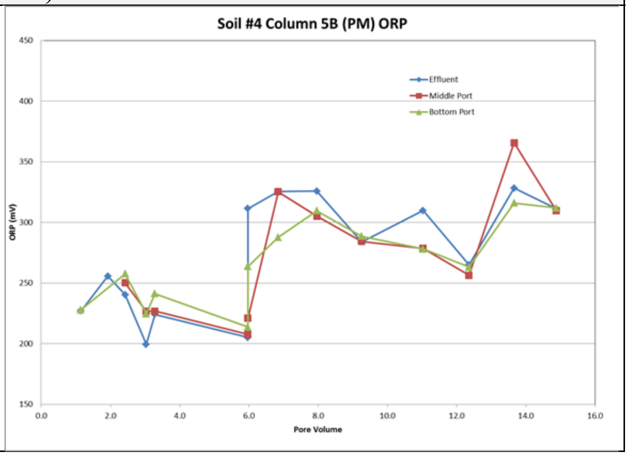
<tr><td>
</td><td>
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Figure 4.3.11 Column Experiment: Soil #4 with PM Treatment – Geochemical variation with increasing groundwater PV.

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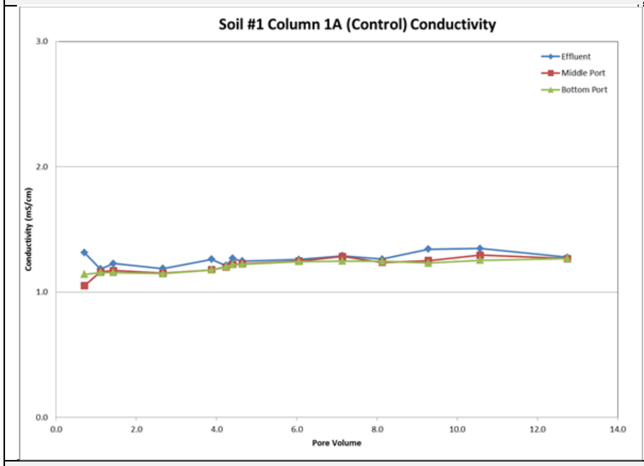
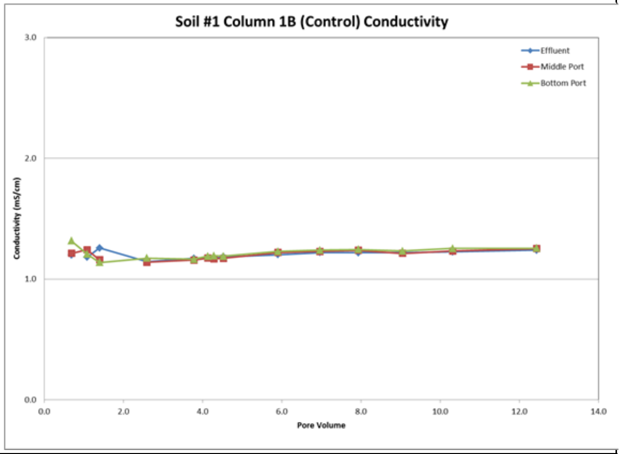
<tr><td> </td><td> </td></tr>
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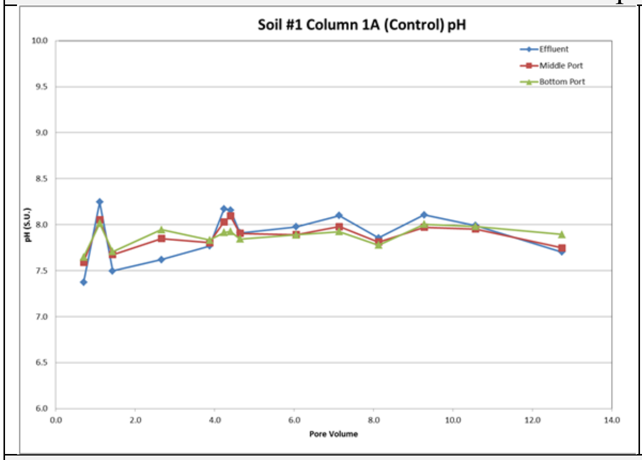
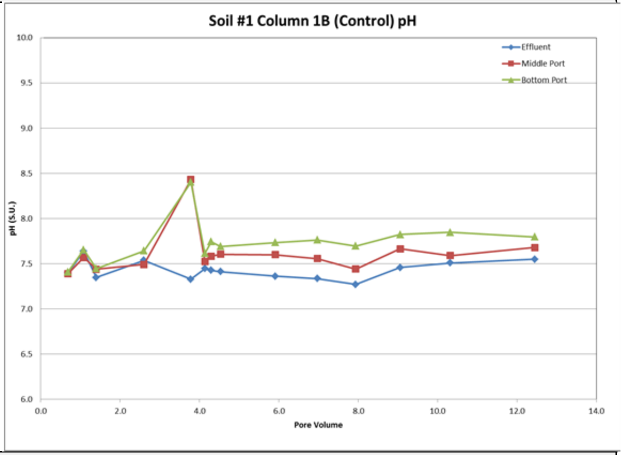
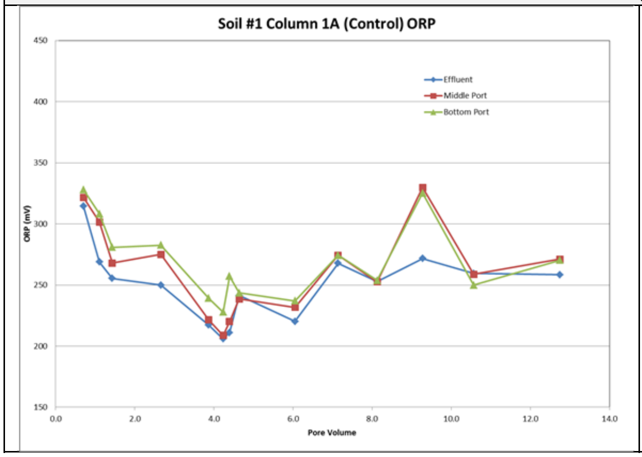
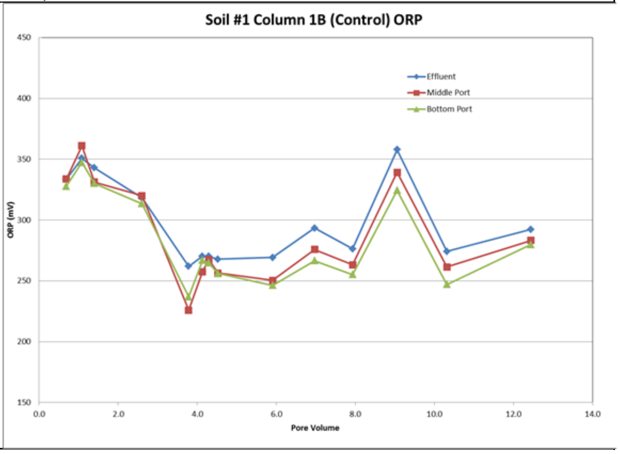
<tr><td> </td><td> </td></tr>
<tr><td colspan="2">ORP (mV)</td></tr>
<tr><td> </td><td> </td></tr>
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Figure 4.3.12 Column Experiment: Soil #1 with Control Treatment (groundwater only) – Geochemical variation with increasing groundwater PV..

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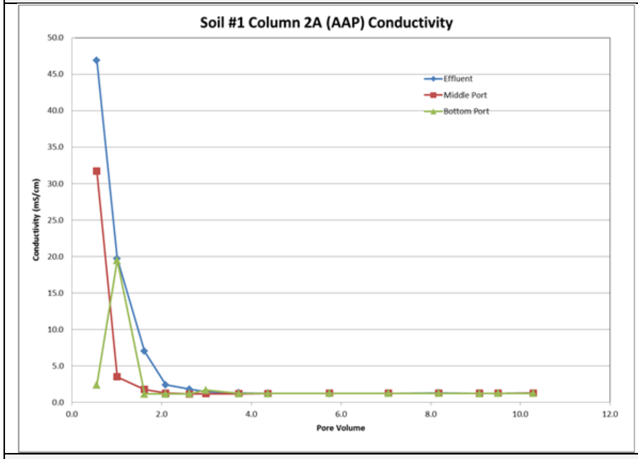

Soil #1 Column 2A (AAP) Conductivity

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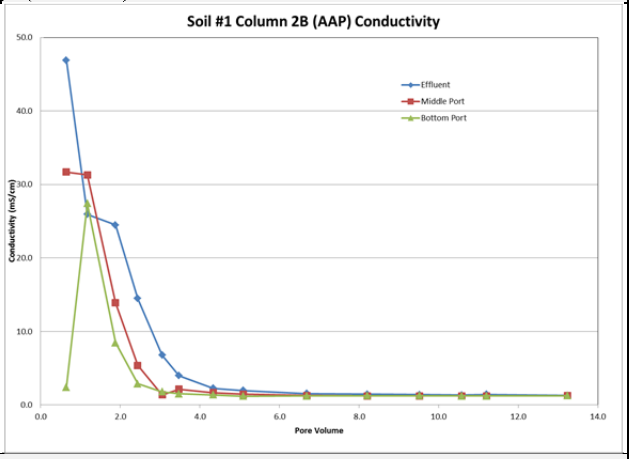

Soil #1 Column 2B (AAP) Conductivity

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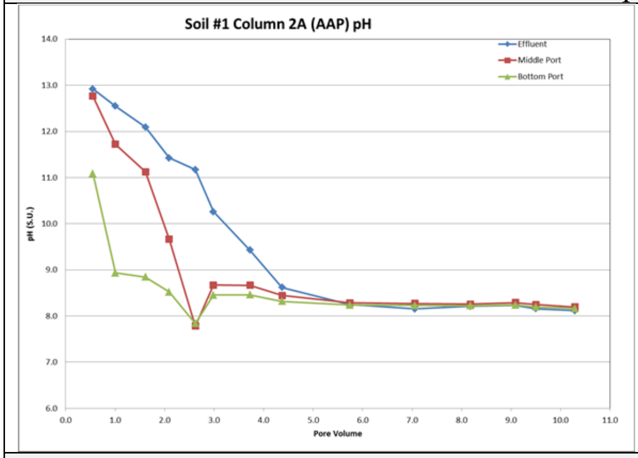
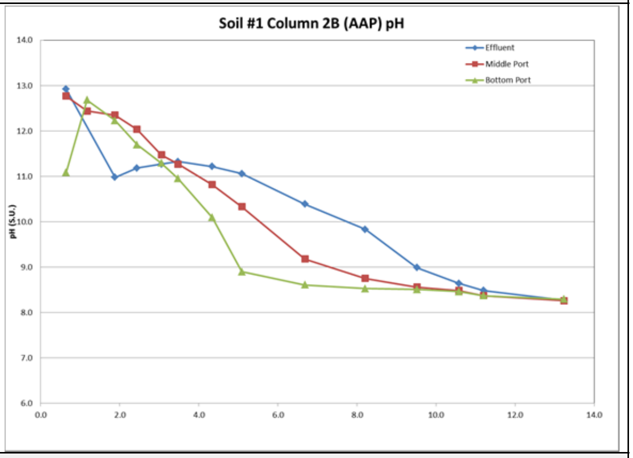
<tr><td>



Soil #1 Column 2A (AAP) pH

</td><td>



Soil #1 Column 2B (AAP) pH

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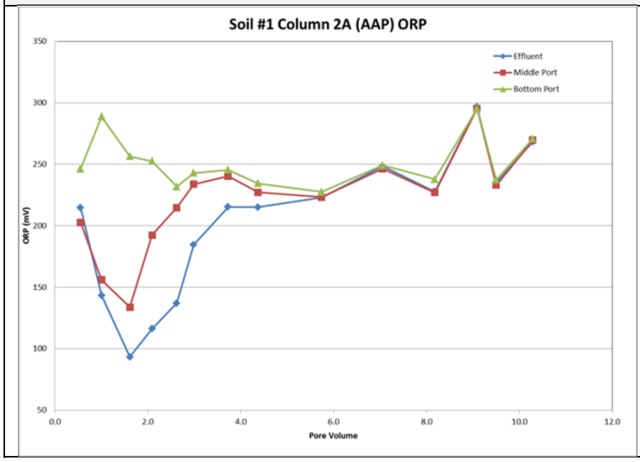
<tr><td colspan="2">ORP (mV)</td></tr>
<tr><td>



Soil #1 Column 2A (AAP) ORP

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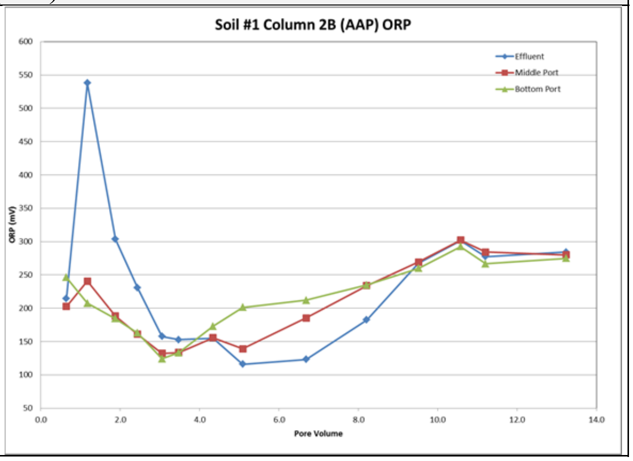

Soil #1 Column 2B (AAP) ORP

</td></tr>
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Figure 4.3.13 Column Experiment: Soil #1 with AAP Treatment – Geochemical variation with increasing groundwater PV.

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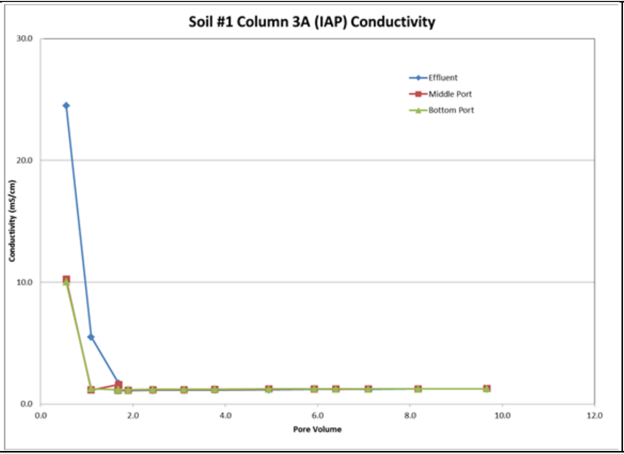
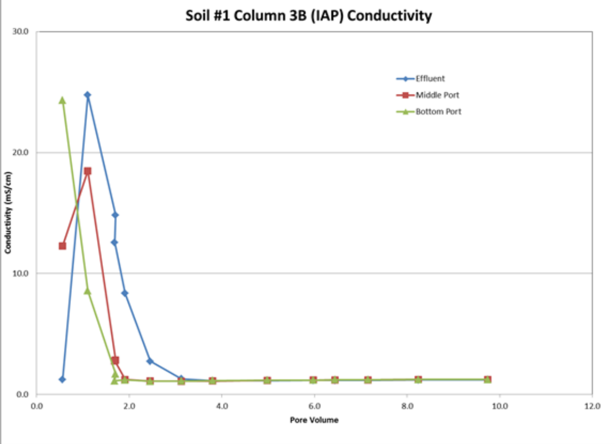
<tr><td>
</td><td>
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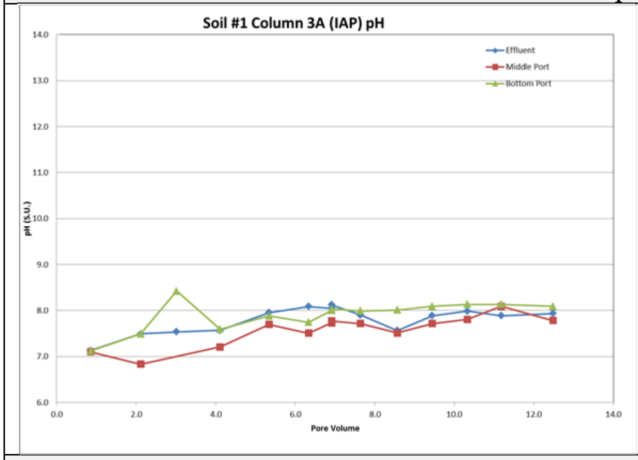
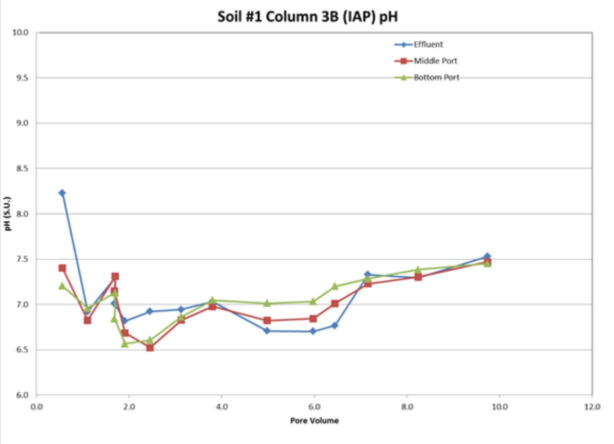
<tr><td>
</td><td>
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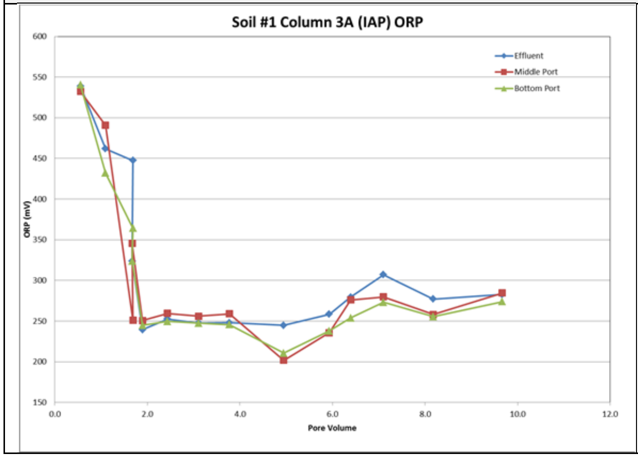
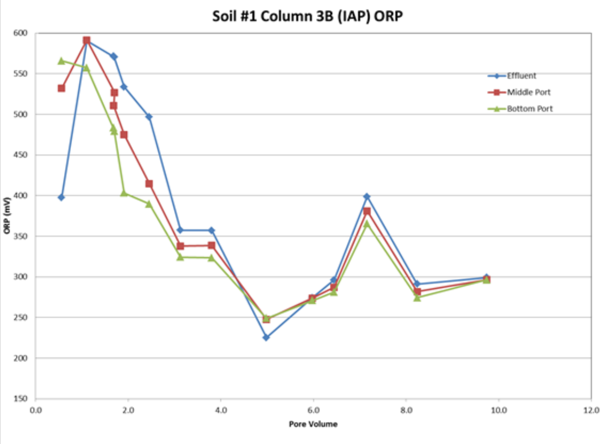
<tr><td>
</td><td>
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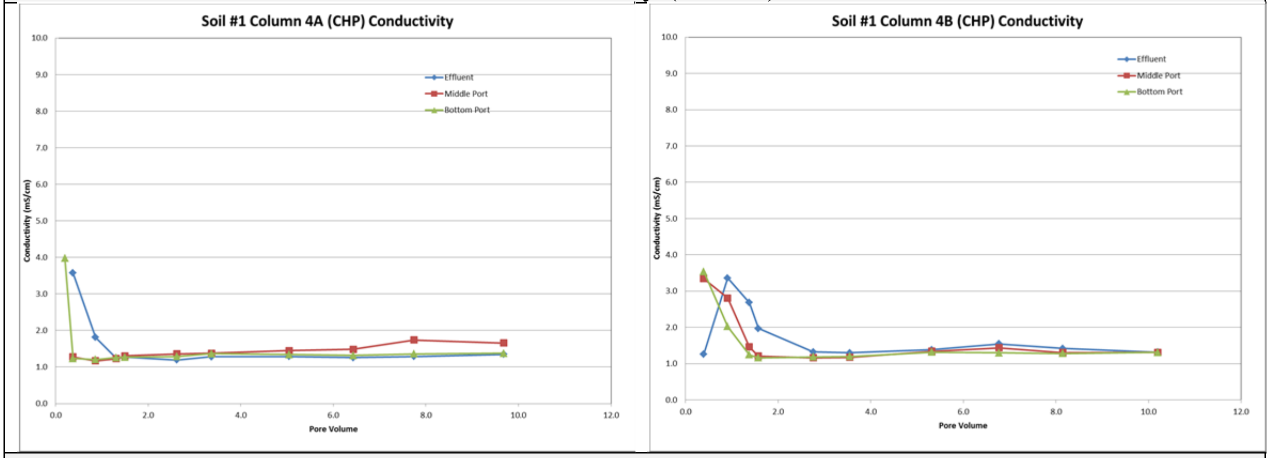
Figure 4.3.14 Column Experiment: Soil #1 with IAP Treatment – Geochemical variation with increasing groundwater PV.

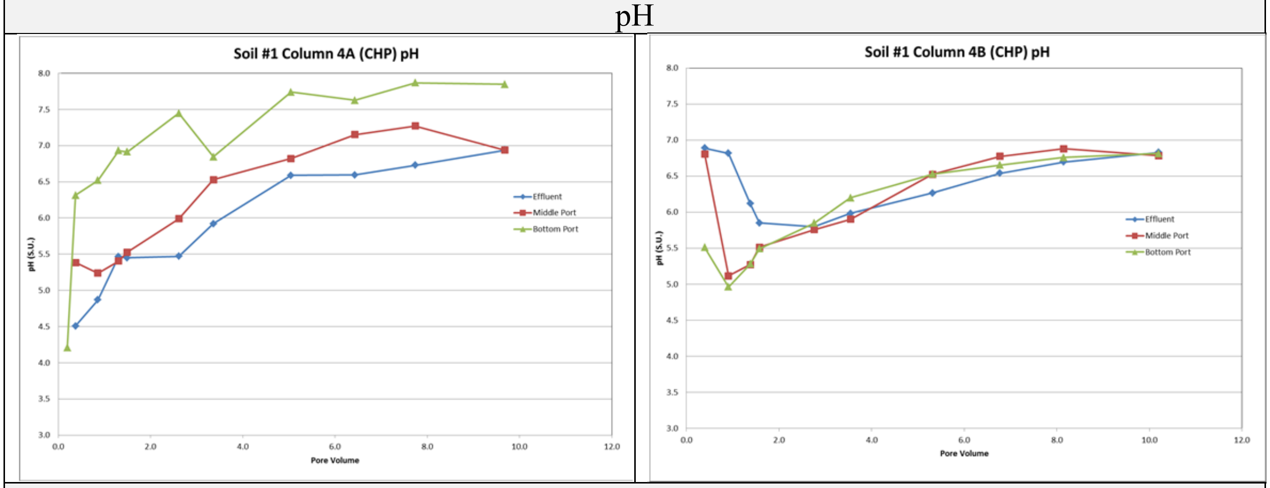
Up-gradient Column | ***Down-gradient Column***

Conductivity (mS/cm)


Soil #1 Column 4A (CHP) Conductivity

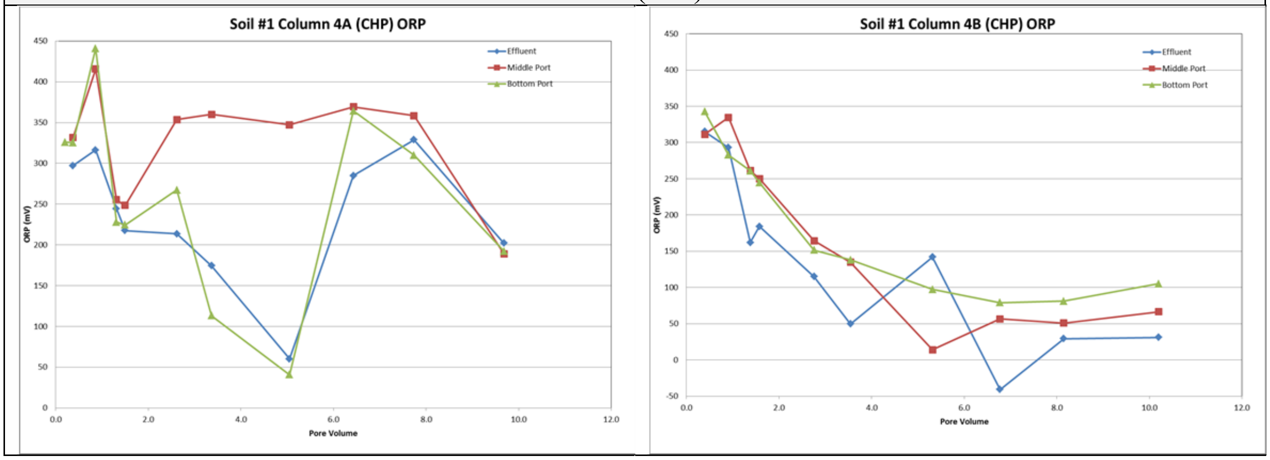
Soil #1 Column 4B (CHP) Conductivity

pH


Soil #1 Column 4A (CHP) pH

Soil #1 Column 4B (CHP) pH

ORP (mV)


Soil #1 Column 4A (CHP) ORP

Soil #1 Column 4B (CHP) ORP

Figure 4.3.15 Column Experiment: Soil #1 with CHP Treatment – Geochemical variation with increasing groundwater PV.

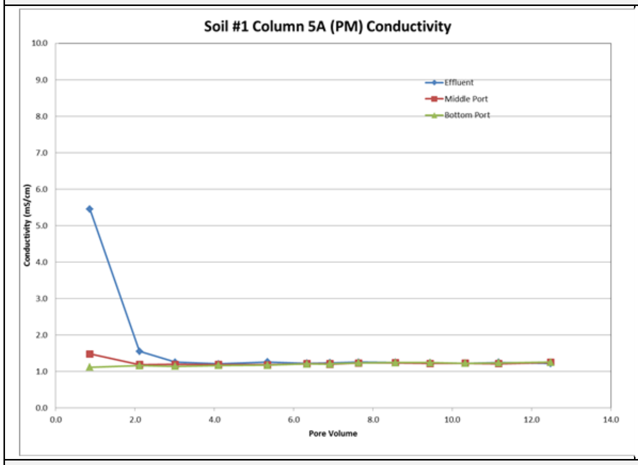
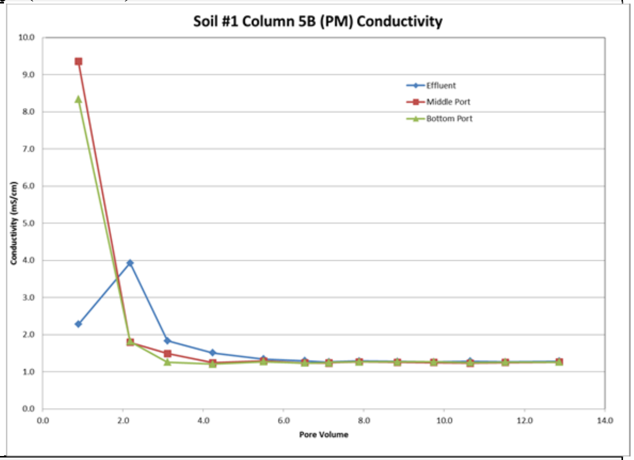
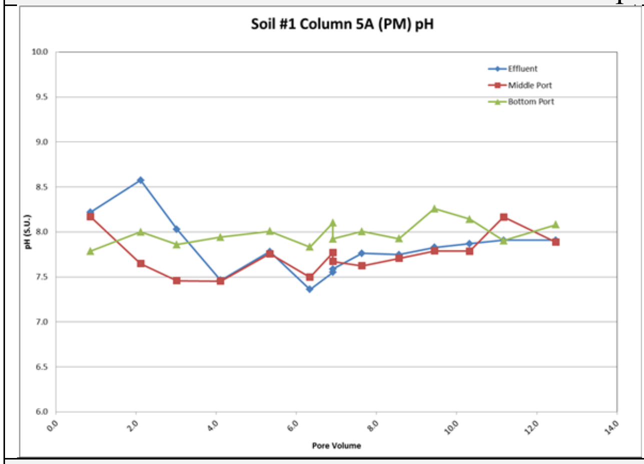
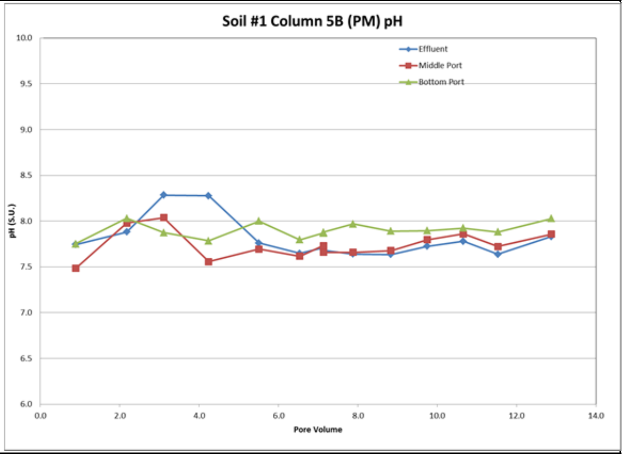
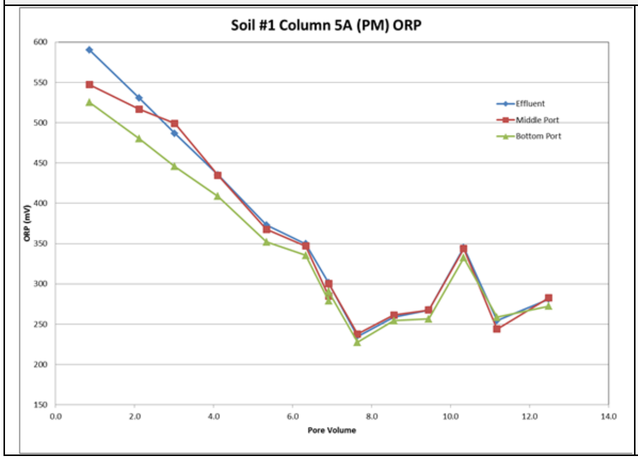
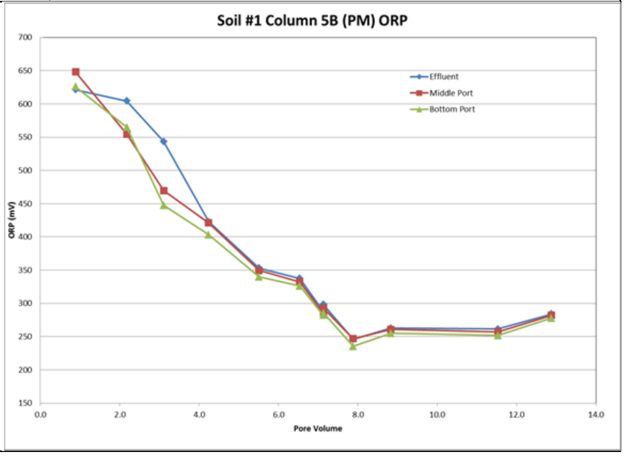
<table>
<tr><th><i>Up-gradient Column</i></th><th><i>Down-gradient Column</i></th></tr>
<tr><td colspan="2">Conductivity (mS/cm)</td></tr>
<tr><td>Soil #1 Column 5A (PM) Conductivity </td><td>Soil #1 Column 5B (PM) Conductivity </td></tr>
<tr><td colspan="2">pH</td></tr>
<tr><td>Soil #1 Column 5A (PM) pH </td><td>Soil #1 Column 5B (PM) pH </td></tr>
<tr><td colspan="2">ORP (mV)</td></tr>
<tr><td>Soil #1 Column 5A (PM) ORP </td><td>Soil #1 Column 5B (PM) ORP </td></tr>
</table>

Figure 4.3.16 Column Experiment: Soil #1 with PM Treatment – Geochemical variation with increasing groundwater PV.

Permanganate. The permanganate treatment was visibly striking, as the typical purple color of this reagent was clearly seen migrating through the columns as the purple color front passed through the first column and slowly bled through the second column. The ORP data mirror the trend that was visible in the laboratory, with a continuous decline in ORP values in both columns, reflecting the visible observations of the purple color decreasing in intensity as the oxidant moved through the columns.

Metals Mobilization due to ISCO Reagents.
Analyses focused upon metals common to remedial sites: arsenic, chromium, copper, nickel, lead and zinc. This suite of metals was also chosen in order to capture metals that are among the RCRA list, and also to capture metals that would be expected to behave differently, such as oxyanions (As, Cr) and divalent cations (Cu, Ni, Pb, and Zn).

Aside from the site-specific nature of the findings, there are two valuable observations that can be made from a consideration of the results. First, even though all ISCO technologies combine to dramatically raise the redox potential, not all ISCO reagents release metals to the same extent. Secondly, in those cases where two or more reagents were found to mobilize the same metal from the same aquifer material, not all reagents maintain metals in solution for equal time. Essentially, once the ISCO reagent is effectively neutralized by the aquifer material and/or influent groundwater, most metals revert back to their original attenuated (non-aqueous, non-mobile) condition. These points are elaborated below.

In the graphical series shown in Figure 4.3.19, copper leaching from Soil #2 is used to illustrate the effect of ISCO reagents on metals mobilization. As can be seen, only two of the four ISCO reagents were able to mobilize copper from these aquifer materials – AAP and CHP. Even though AAP and CHP were both able to generate concentrations of soluble copper as high as 0.3 mg/L for AAP and 2 mg/L for CHP, the other two ISCO reagents (IAP and PM) did not release copper to any extent greater than the groundwater control. Therefore, it is conceivable to select an ISCO technology that will effectively treat the target organic contaminant and also not affect the mobilization of metals; assuming that the nature of the metals within the aquifer designated for ISCO treatments is known *a priori*.

Secondly, the plots in Figure 4.3.19 illustrate that copper released from Soil #2 due to CHP treatment is initially highly mobile, with the entire volume of mobilized copper moving through both columns with nearly conservative transport (1 pore volume), whereas the copper mobilized from AAP requires approximately 5 pore volumes to migrate through the two columns. Thus, not all reagents mobilize metals with equal propensity to migrate at the same velocities as site groundwater. This effect is more dramatic when considering the results from soil #4 (Figure 4.3.25) and the contrasting effect of alkaline persulfate mobilization of copper. In the more organic-rich and finer textured aquifer material of aquifer Soil #4, elevated levels of dissolved copper are maintained for many more pore volumes relative to Soil #2 (more sandy, less organic carbon). Where the copper concentrations in the dissolved phase return to pre-ISCO (AAP) conditions after < 5 pore volumes for Soil #2, the levels of copper in the experiment with Soil #4 require > 5 pore volumes to return to baseline conditions. Thus, different ISCO treatments not only determine the extent to which metals are released, but also have an important influence on the length of time they will remain mobilized. Longer time frames of mobilization correspond to greater number of pore volumes, and therefore distance from ISCO application that the metals will migrate.

Where copper is a divalent metal, arsenic is an oxyanion and is expected to demonstrate different behavior. In many instances where arsenic is found associated co-mingled with organic contaminants, sorption onto iron oxides is an important mechanism of arsenic retention onto aquifer solids. At alkaline pH, arsenic is known to be de-sorbed from iron oxides (presumably due to electrostatic repulsion and competition between hydroxide and arsenate for available sorption sites). Indeed, this was the case for our treatments, where arsenic was mobilized to concentrations exceeding 0.35 mg/L (Soil #2, Figure 4.3.17) and 5 mg/L (Soil #1; Figure 4.3.29) after treatment with AAP. Desorption from iron oxides and re-absorption onto iron oxides is considered to be an important mechanism for arsenic attenuation. As such, amorphous iron oxides (extracted with ascorbic acid) were characterized from treated and untreated columns for soil #1 (Figure 4.3.35). It can be seen that iron oxides were mobilized from the *up-gradient* (treated column) and re-precipitated in the *down-gradient* column (untreated). The re-precipitation of iron oxides *down-gradient* from the treatment zone offers an attenuation mechanism for those metals that are known to have strong affinity for sorption onto iron oxides.

Adsorption is a common mechanisms for metals attenuation in the subsurface, often enhanced by the presence of iron oxides (as described above) and also organic matter. In this study, soil #4 contains appreciable quantities of organic carbon, from which evaluation of partitioning to the solid organic phase can be made for metals mobilized due to ISCO application. In this soil, chromium was found to be mobilized (Figure 4.3.24). Similar to soils #1 and #2, the mobilized chromium, an oxyanion, was seen to revert to baseline conditions after 5 pore volumes. Thus, the higher presence of organic matter was found not to have an appreciable effect on the attenuation of chromium. Other divalent metal cations were also found to be mobilized from soil #4. Using copper as an example, the results from soil #4 demonstrate that copper was released due to reaction with AAP, CHP, and PM, and was elevated in concentration above control conditions for over 10 pore volumes. In contrast, the copper mobilized from the other soils in approximately 5 pore volumes. Although the finer textured material will have lower pore volumes per column, the greater reactivity of the organic phases was thought to contribute to a faster return to baseline conditions. This was not observed in the daily measurements, especially for AAP (Figure 4.3.10) where conductivity readings show elevated conductivity for approximately 10 pore volumes. However, the organic phase was effective at neutralizing the effect of pH; which indicates that other mechanisms aside from a large shift in pH in the AAP treatment is responsible for the mobilization of metals from this soil material.

In general, data represented in Figures 4.3.17 through 4.3.33 shows that metals from each site respond differently to the different ISCO reagents. Given the range of metals and concentrations that were observed to be released from these three soils, the primary conclusion is that these results will be most useful to those sites where the presence of metals within the aquifer subject to ISCO treatment is known. Therefore, for sites where metals have not been characterized, it is highly recommended that aquifer solids and groundwater be submitted for metals analysis prior to selection of ISCO reagent for use at a particularly site. This is critical to strategic selection of an ISCO technology that will minimize the mobilization of a particularly metal.

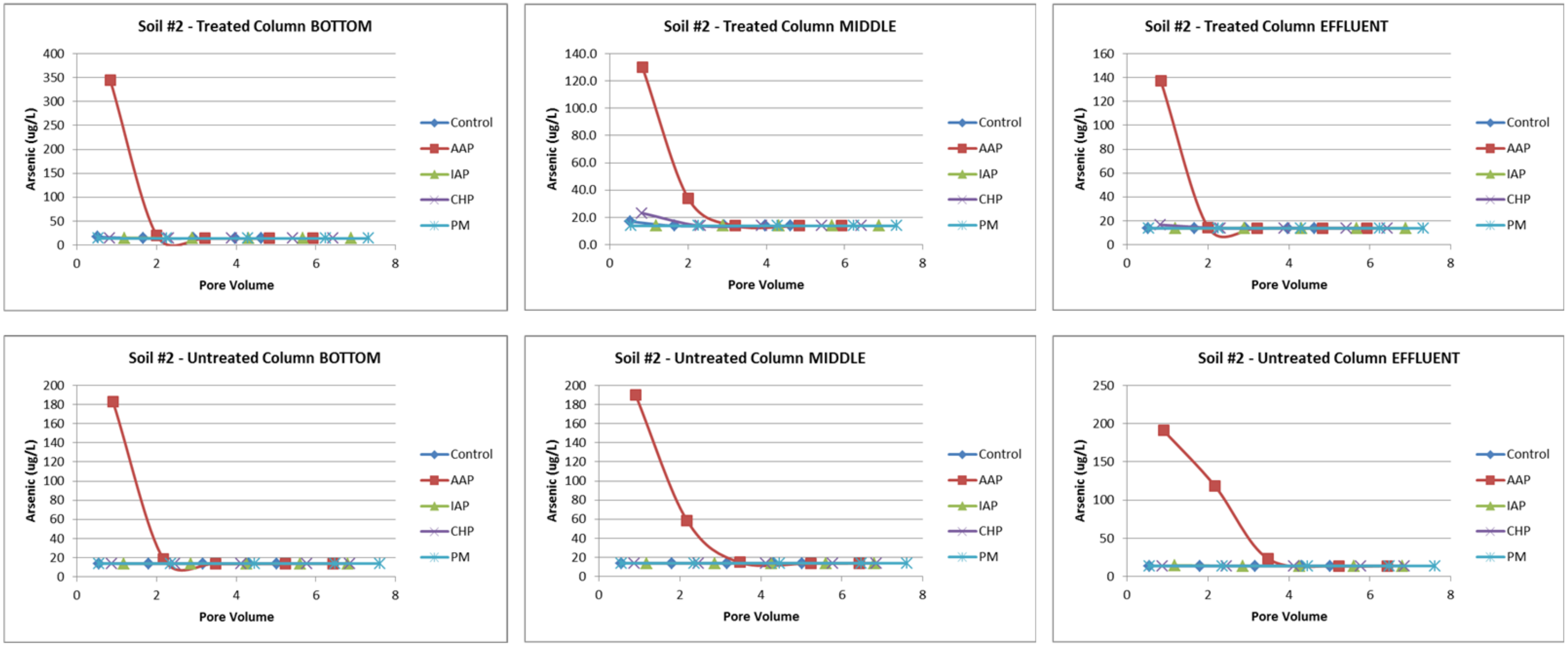


Figure 4.3.17 Column Experiment: Soil #2 - Arsenic mobilization

Note: Upper three panels are *up-gradient* column, lower three panels are *down-gradient* column. Left panels are bottom ports. Center panels are middle ports. Right panels are effluent ports. Columns were operated in upflow direction.

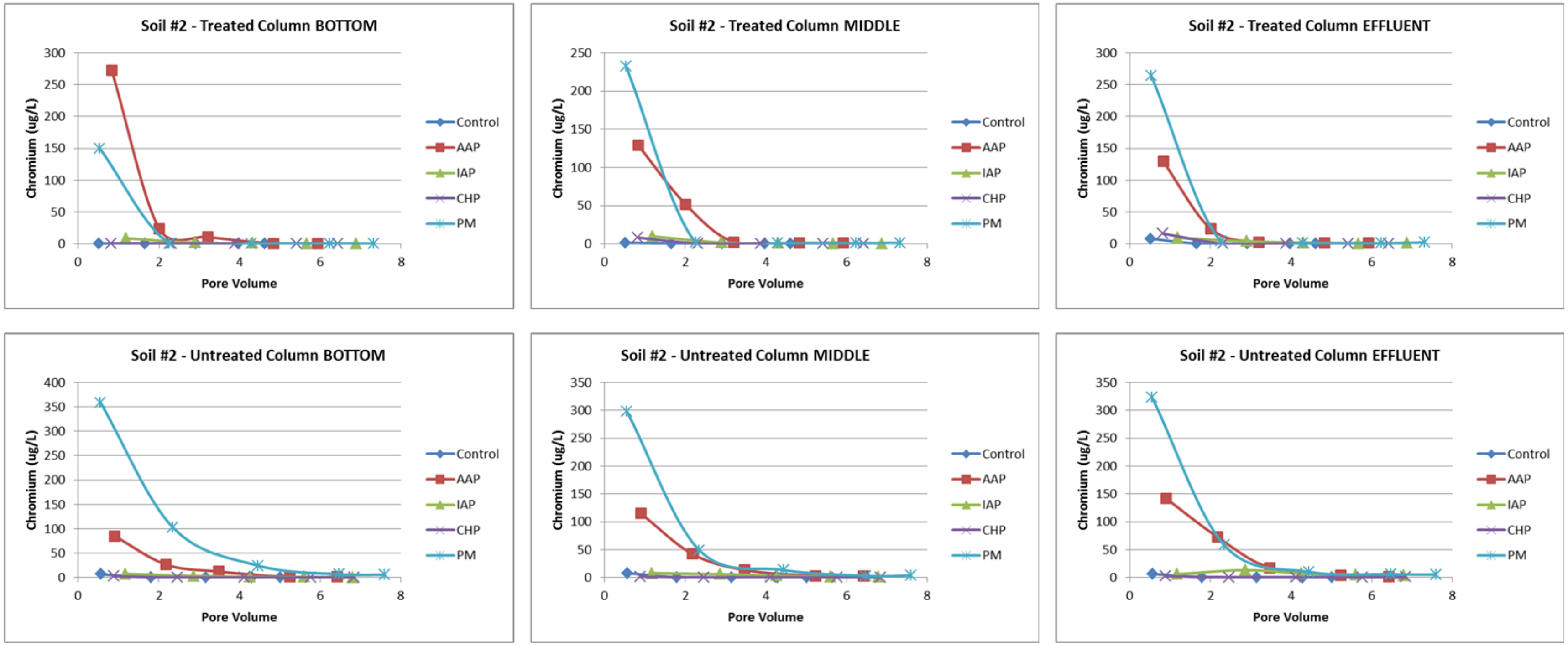


Figure 4.3.18 Column Experiment: Soil #2 - Chromium mobilization

Note: Upper three panels are *up-gradient* column, lower three panels are *down-gradient* column. Left panels are bottom ports. Center panels are middle ports. Right panels are effluent ports. Columns were operated in upflow direction.

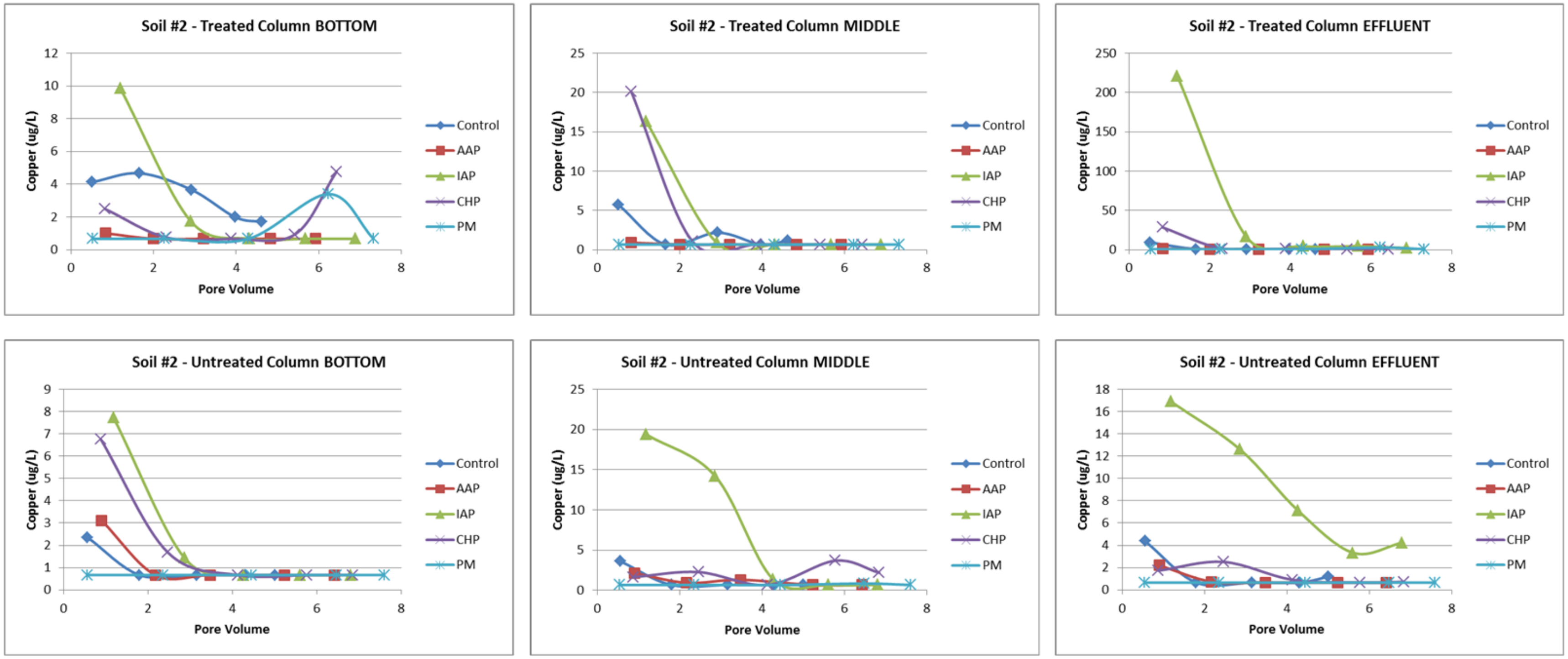


Figure 4.3.19 Column Experiment: Soil #2 – Copper mobilization

Note: Upper three panels are *up-gradient* column, lower three panels are *down-gradient* column. Left panels are bottom ports. Center panels are middle ports. Right panels are effluent ports. Columns were operated in upflow direction.

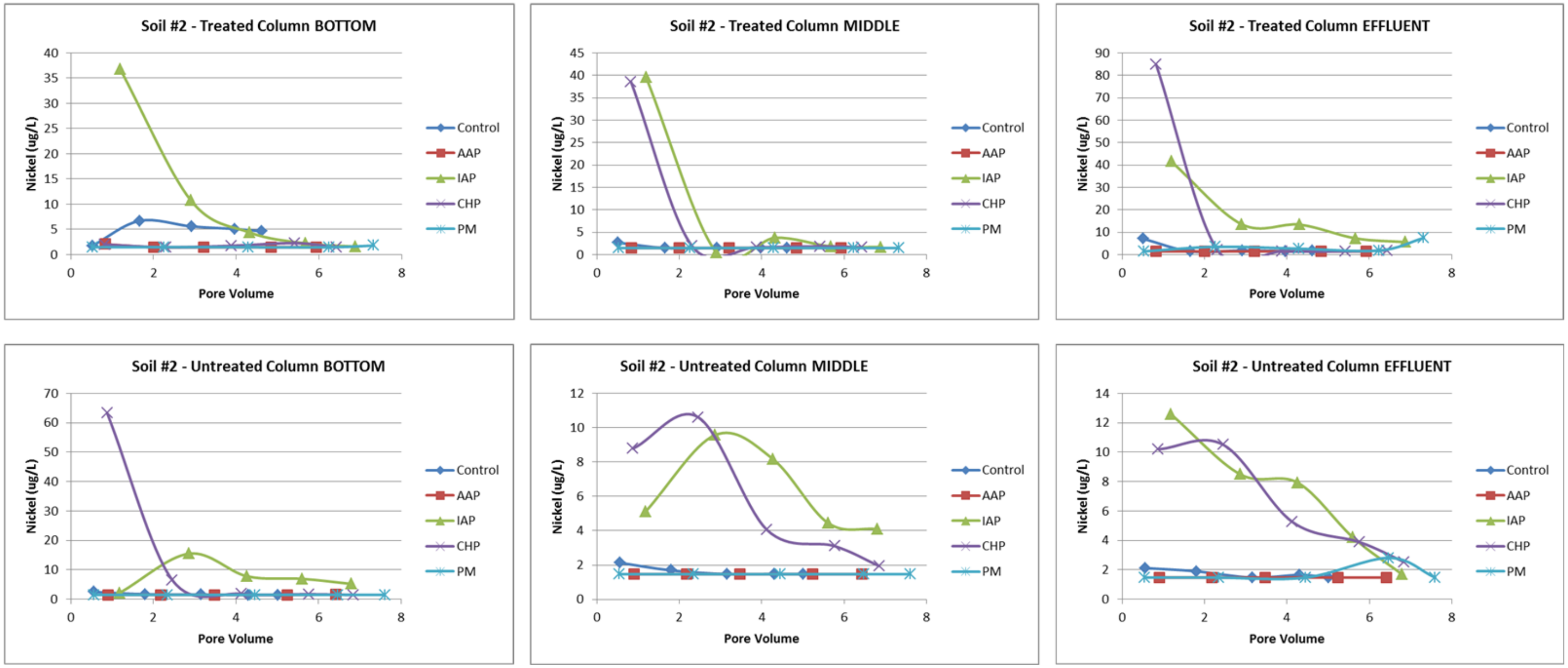


Figure 4.3.20 Column Experiment: Soil #2 – Nickel mobilization

Note: Upper three panels are *up-gradient* column, lower three panels are *down-gradient* column. Left panels are bottom ports. Center panels are middle ports. Right panels are effluent ports. Columns were operated in upflow direction.

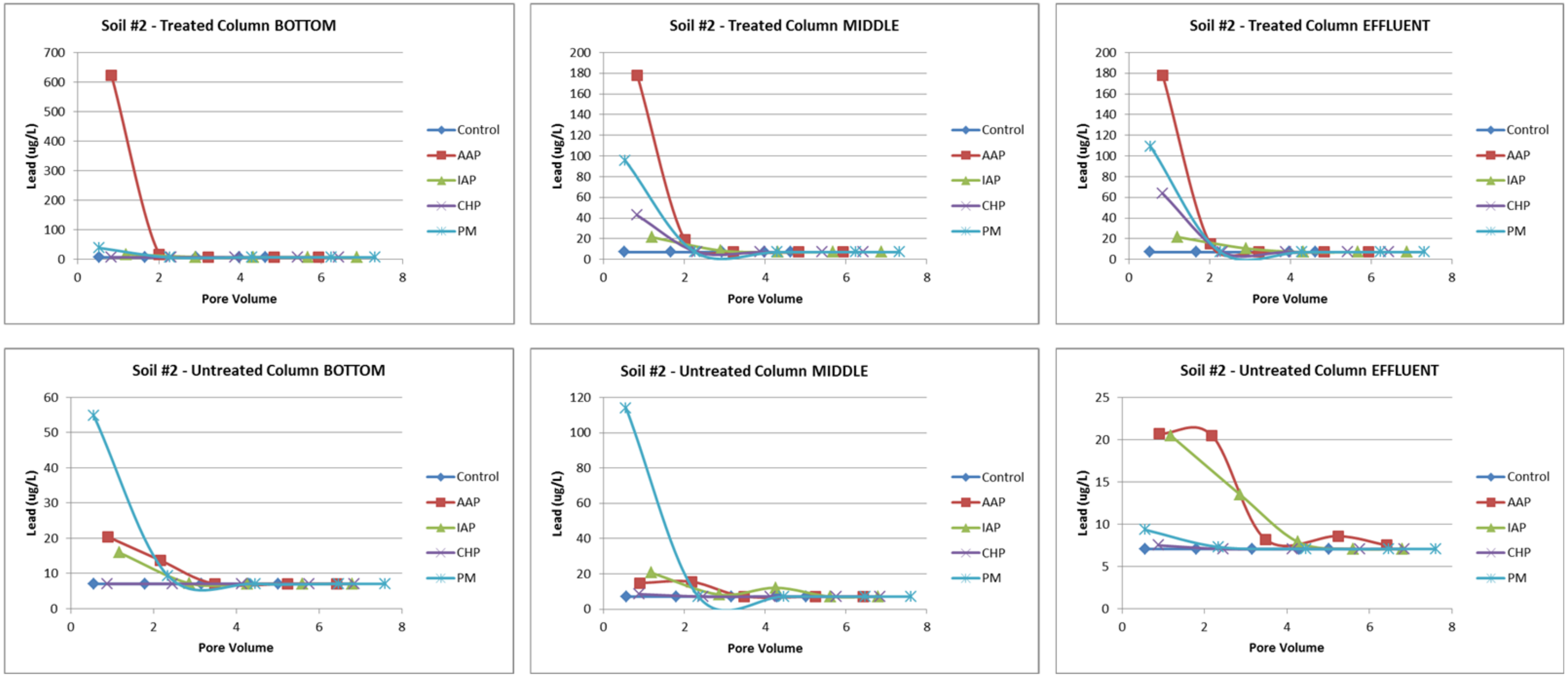


Figure 4.3.21 Column Experiment: Soil #2 – Lead mobilization

Note: Upper three panels are *up-gradient* column, lower three panels are *down-gradient* column. Left panels are bottom ports. Center panels are middle ports. Right panels are effluent ports. Columns were operated in upflow direction.

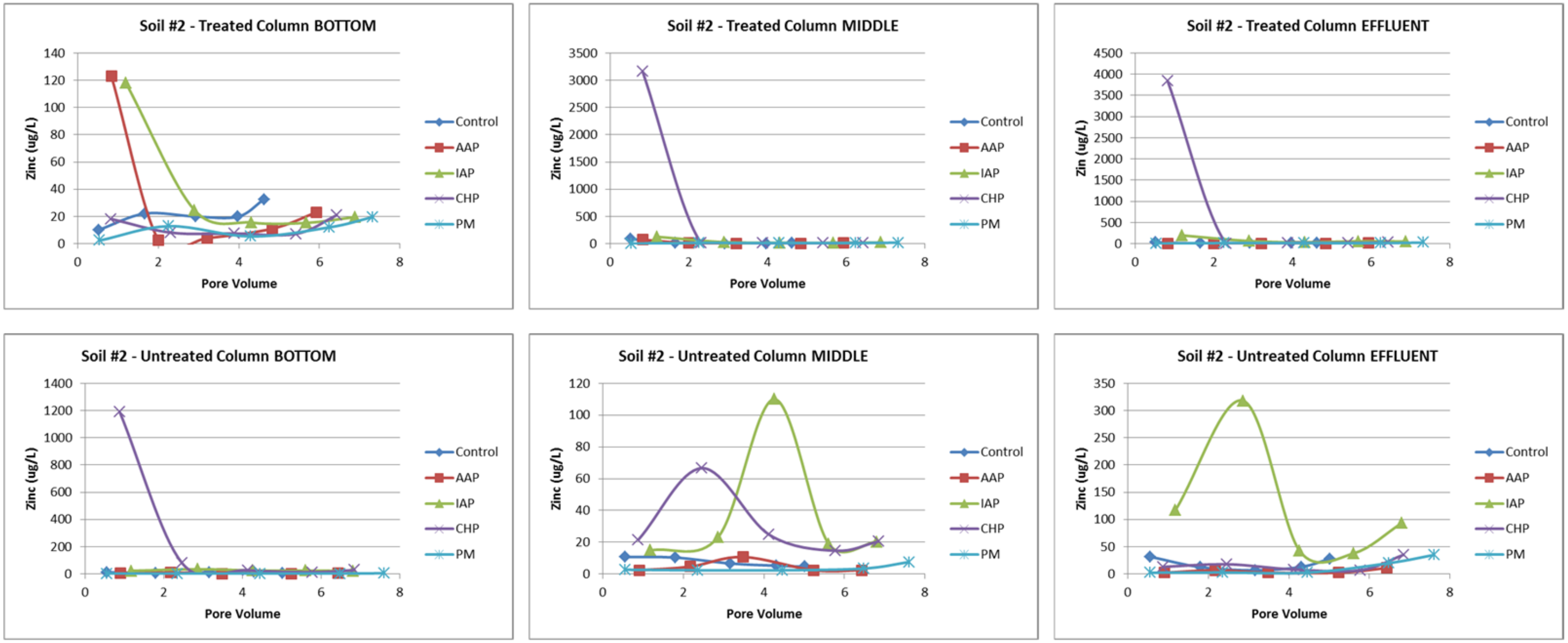


Figure 4.3.22 Column Experiment: Soil #2 – Zinc mobilization

Note: Upper three panels are *up-gradient* column, lower three panels are *down-gradient* column. Left panels are bottom ports. Center panels are middle ports. Right panels are effluent ports. Columns were operated in upflow direction.

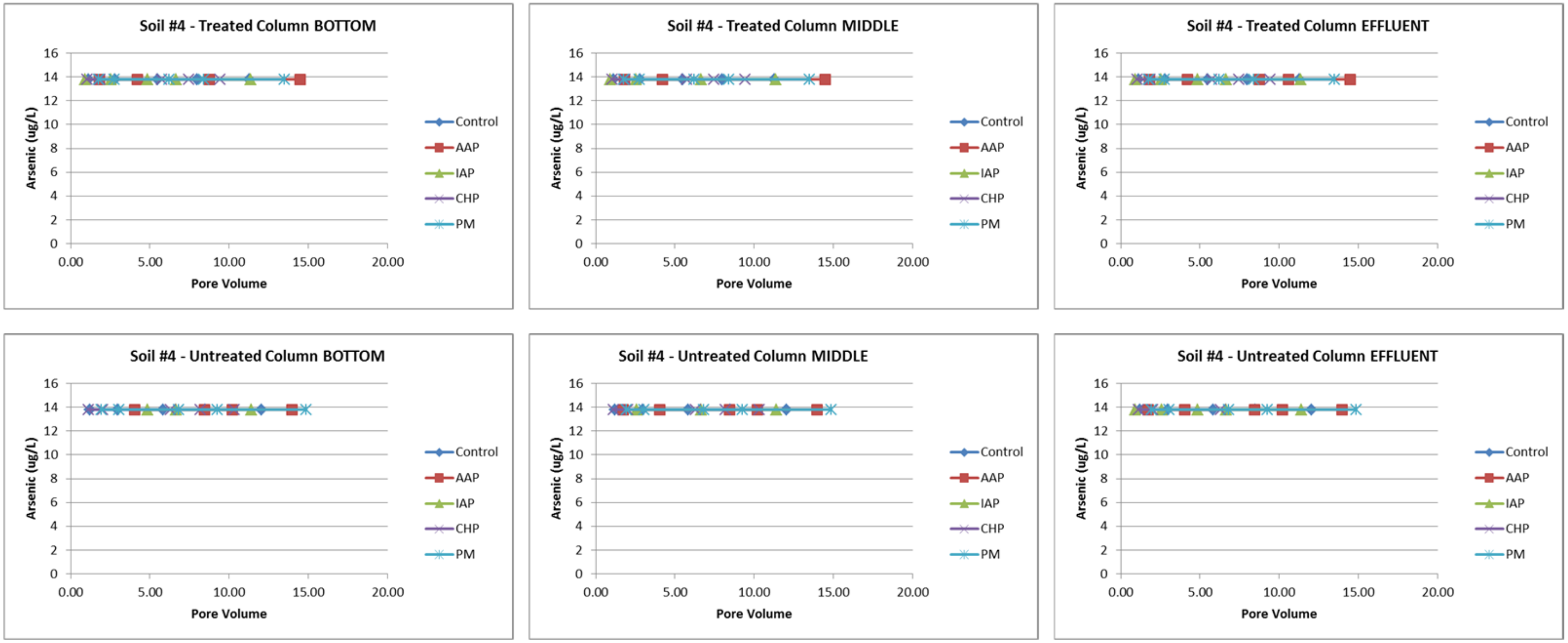


Figure 4.3.23 Column Experiment: Soil #4 – Arsenic mobilization

Note: Upper three panels are *up-gradient* column, lower three panels are *down-gradient* column. Left panels are bottom ports. Center panels are middle ports. Right panels are effluent ports. Columns were operated in upflow direction.

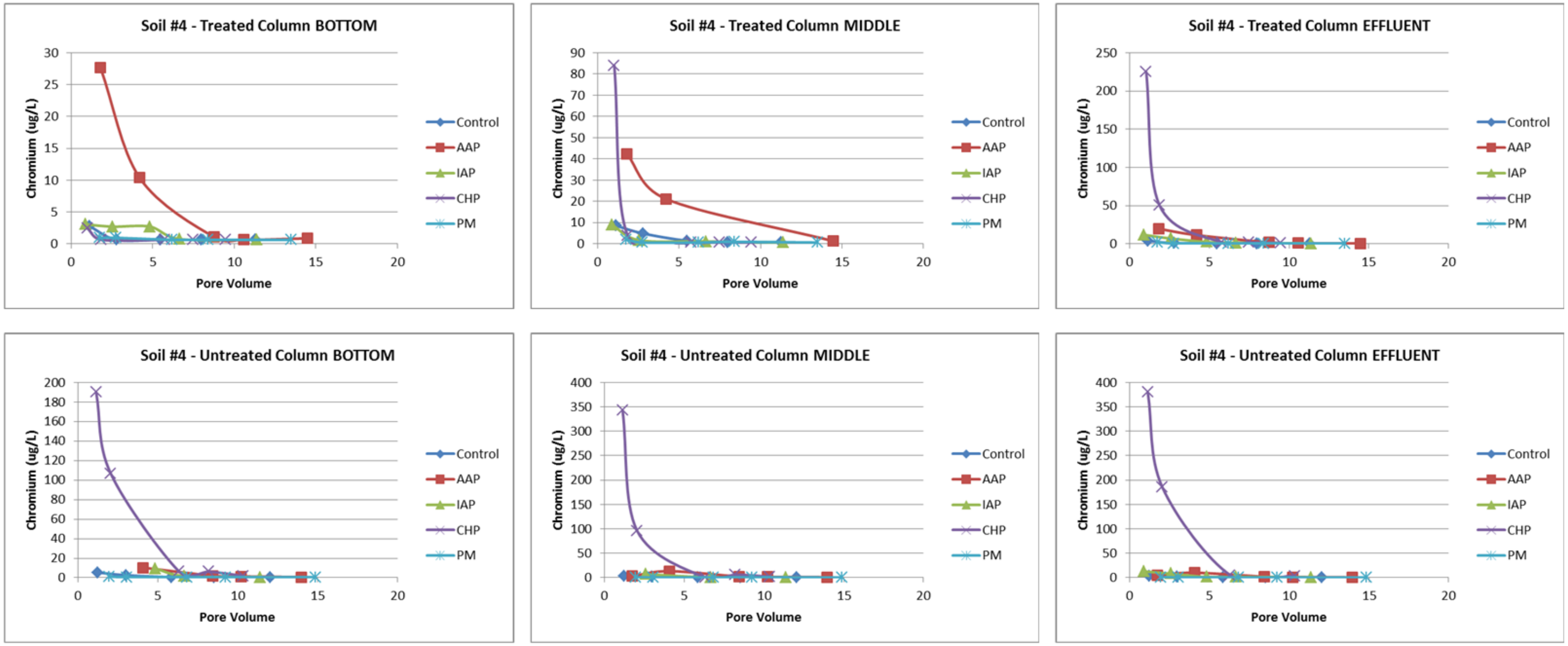


Figure 4.3.24 Column Experiment: Soil #4 – Chromium mobilization

Note: Upper three panels are *up-gradient* column, lower three panels are *down-gradient* column. Left panels are bottom ports. Center panels are middle ports. Right panels are effluent ports. Columns were operated in upflow direction.

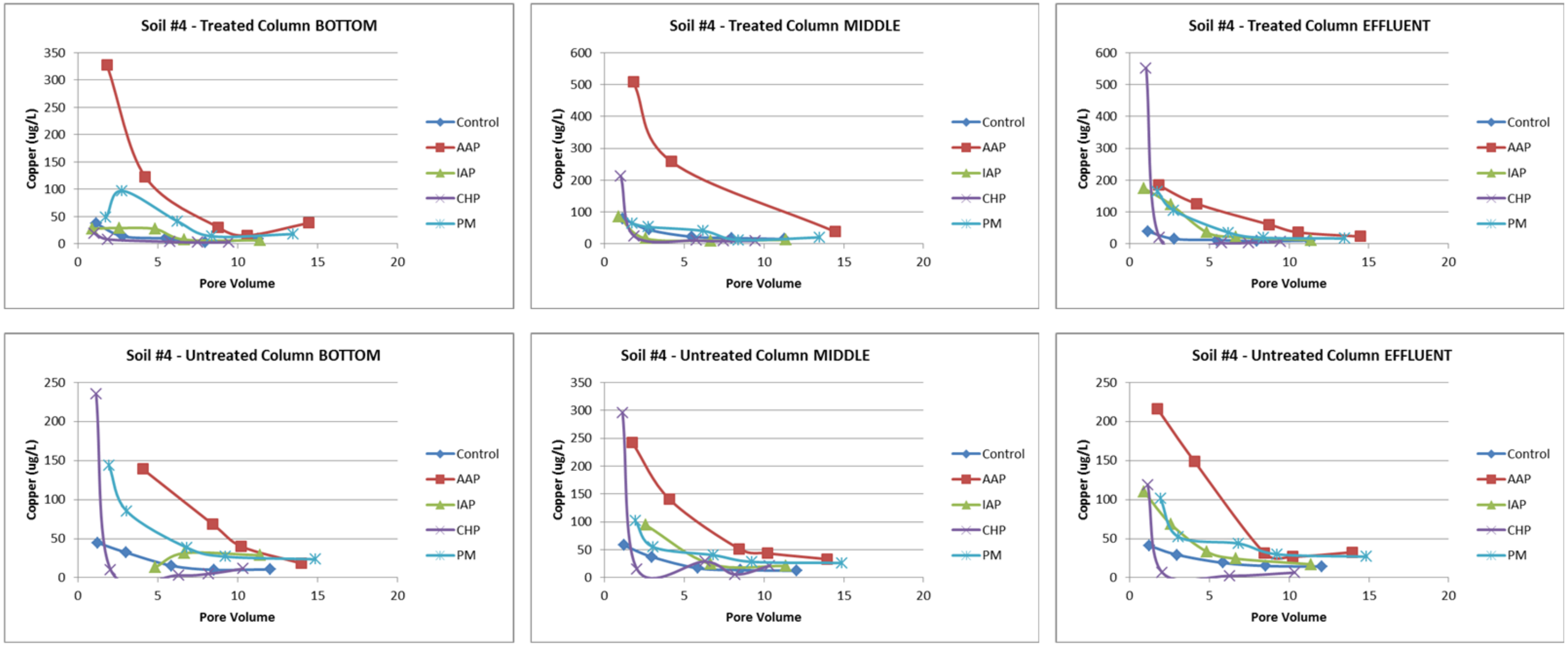


Figure 4.3.25 Column Experiment: Soil #4 – Copper mobilization

Note: Upper three panels are *up-gradient* column, lower three panels are *down-gradient* column. Left panels are bottom ports. Center panels are middle ports. Right panels are effluent ports. Columns were operated in upflow direction.

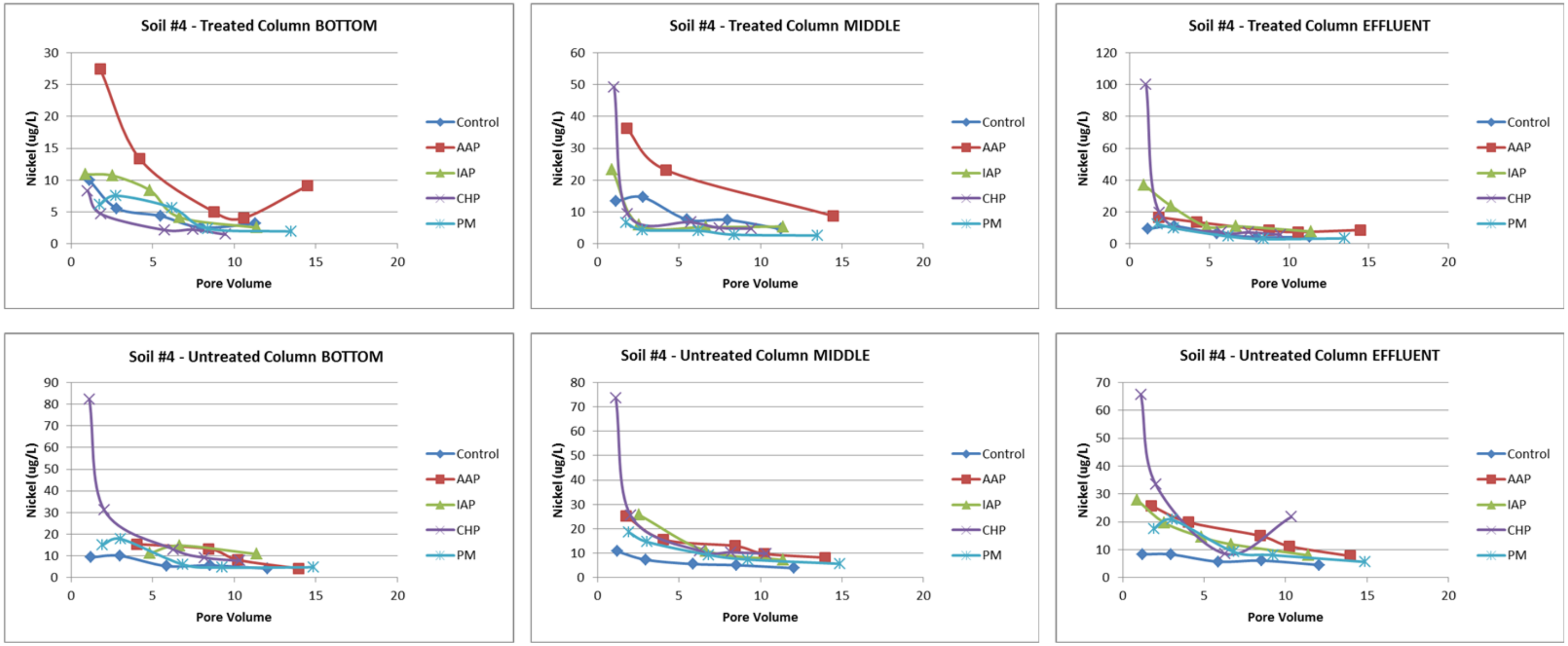


Figure 4.3.26 Column Experiment: Soil #4 – Nickel mobilization

Note: Upper three panels are *up-gradient* column, lower three panels are *down-gradient* column. Left panels are bottom ports. Center panels are middle ports. Right panels are effluent ports. Columns were operated in upflow direction.

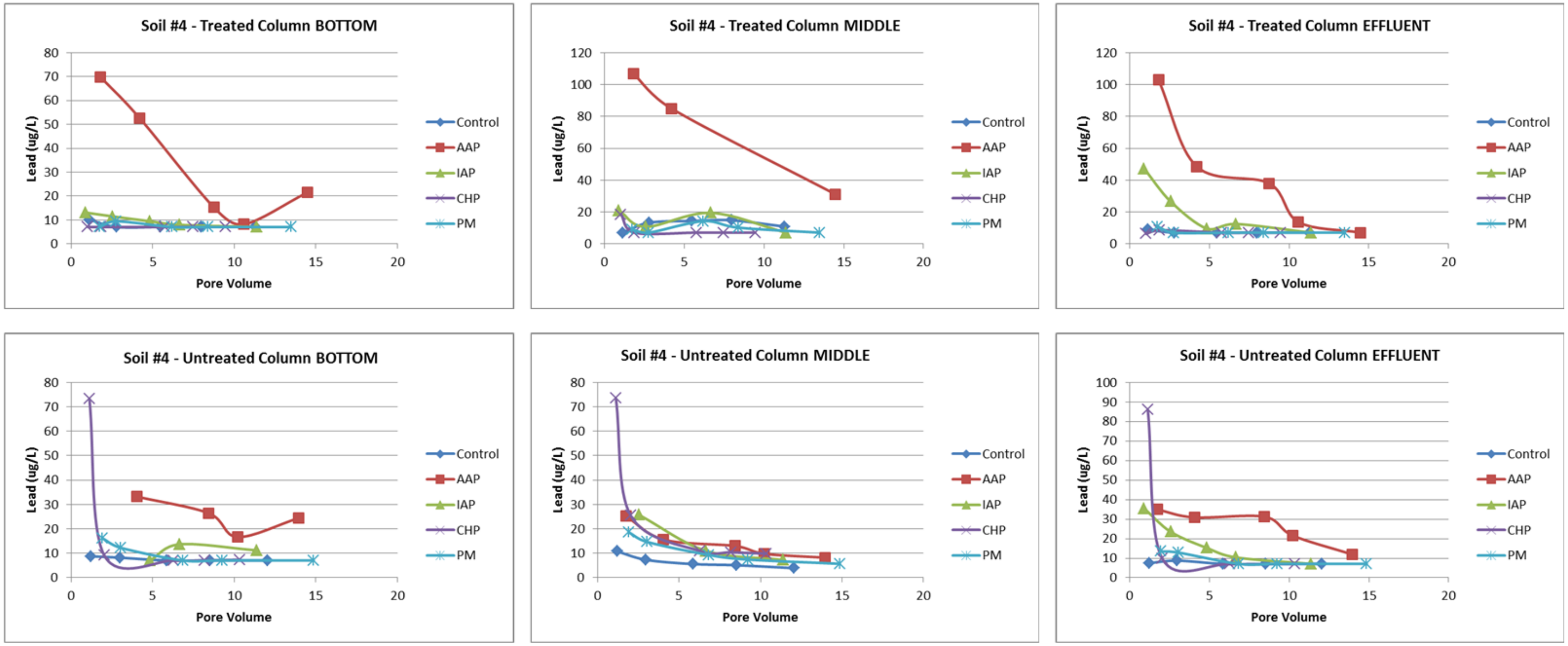


Figure 4.3.27 Column Experiment: Soil #4 – Lead mobilization

Note: Upper three panels are *up-gradient* column, lower three panels are *down-gradient* column. Left panels are bottom ports. Center panels are middle ports. Right panels are effluent ports. Columns were operated in upflow direction.

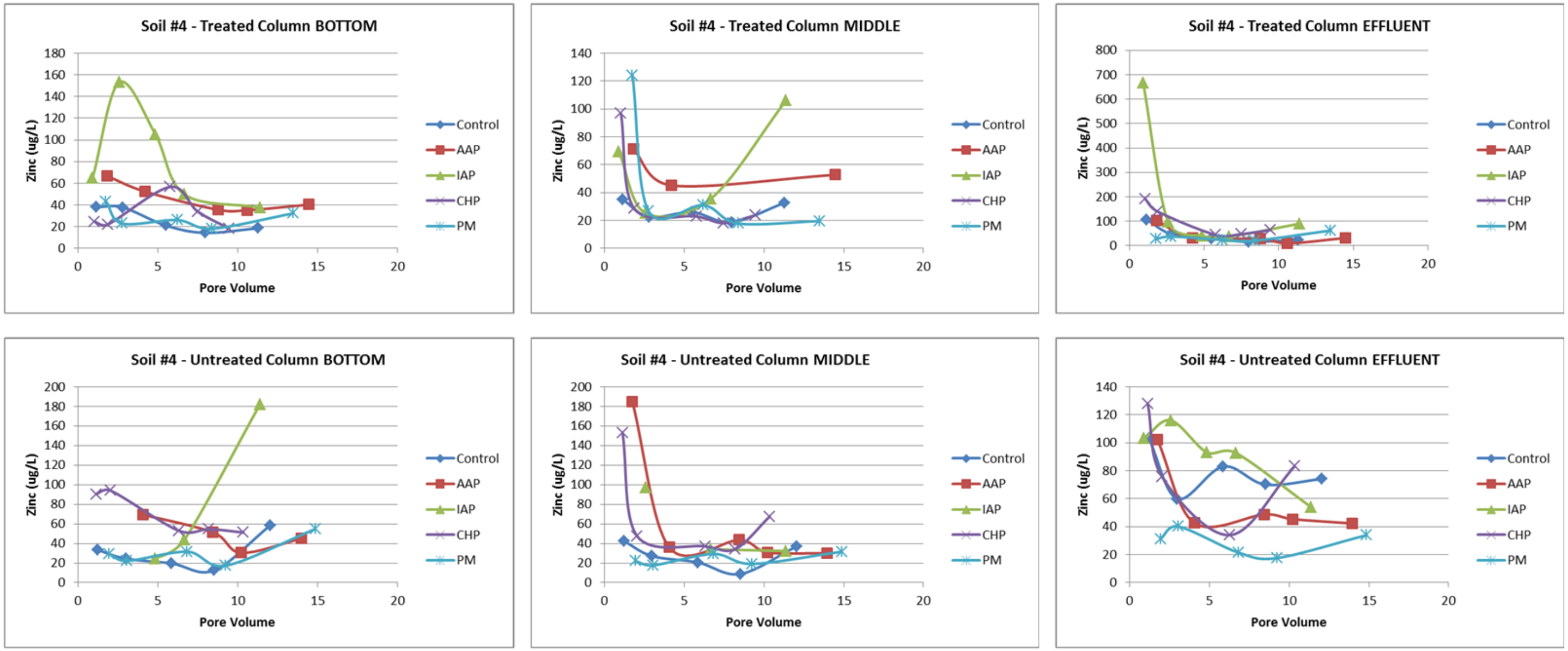


Figure 4.3.28 Column Experiment: Soil #4 – Zinc mobilization

Note: Upper three panels are *up-gradient* column, lower three panels are *down-gradient* column. Left panels are bottom ports. Center panels are middle ports. Right panels are effluent ports. Columns were operated in upflow direction.

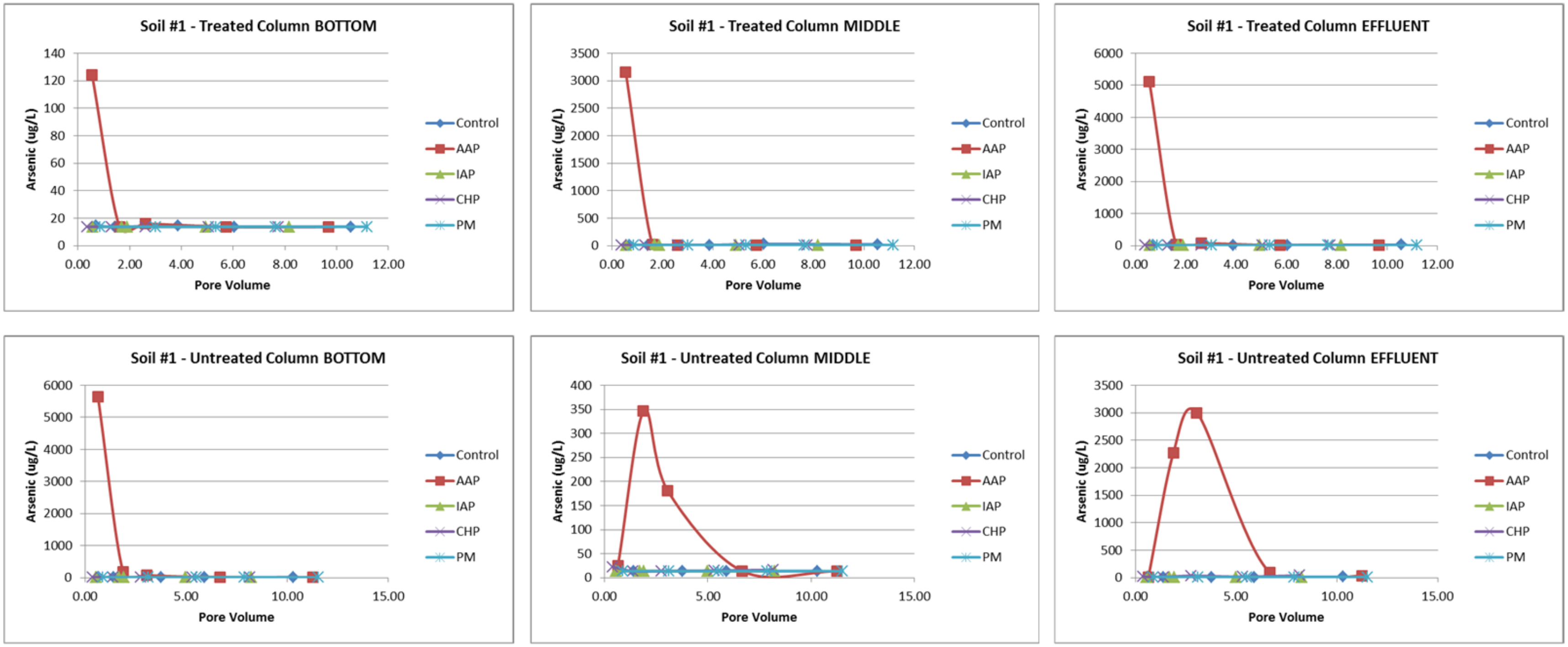


Figure 4.3.29 Column Experiment: Soil #1 – Arsenic mobilization

Note: Upper three panels are *up-gradient* column, lower three panels are *down-gradient* column. Left panels are bottom ports. Center panels are middle ports. Right panels are effluent ports. Columns were operated in upflow direction.

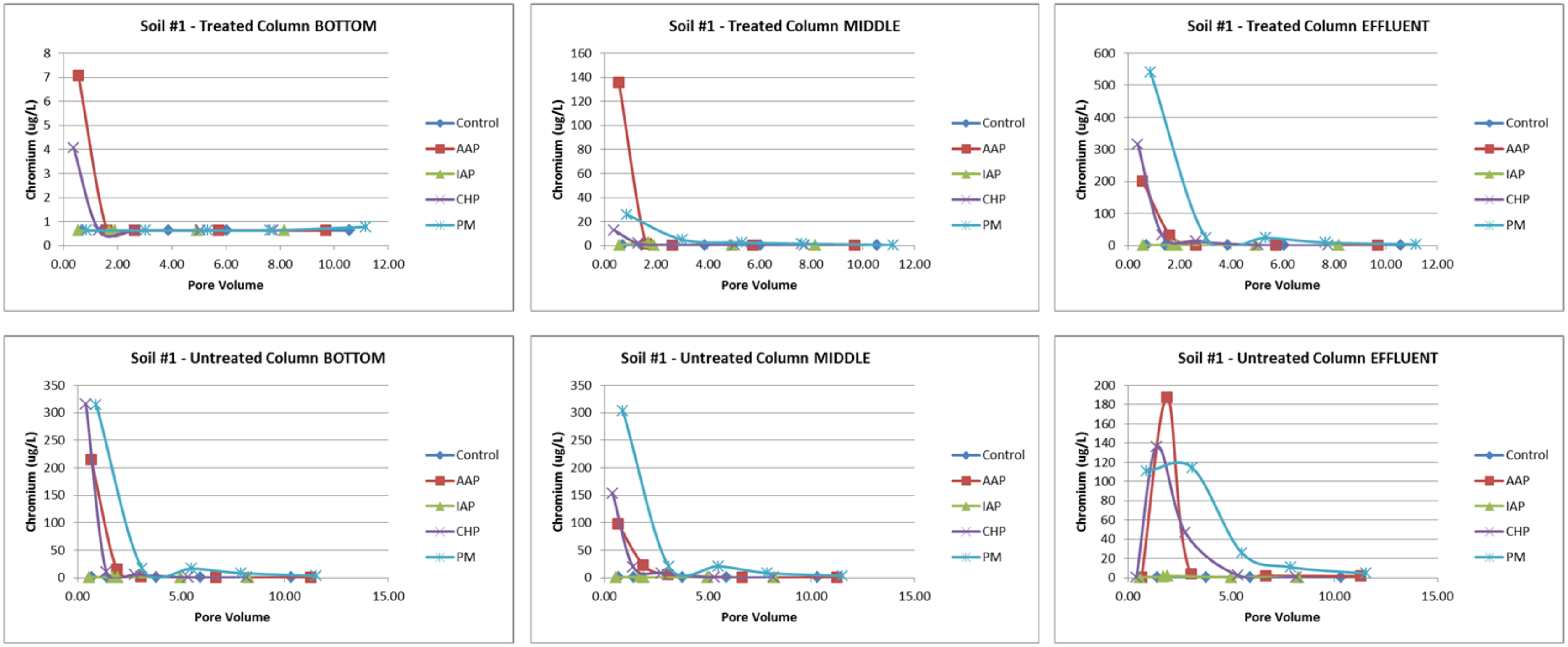


Figure 4.3.30 Column Experiment: Soil #1 –Chromium mobilization

Note: Upper three panels are *up-gradient* column, lower three panels are *down-gradient* column. Left panels are bottom ports. Center panels are middle ports. Right panels are effluent ports. Columns were operated in upflow direction.

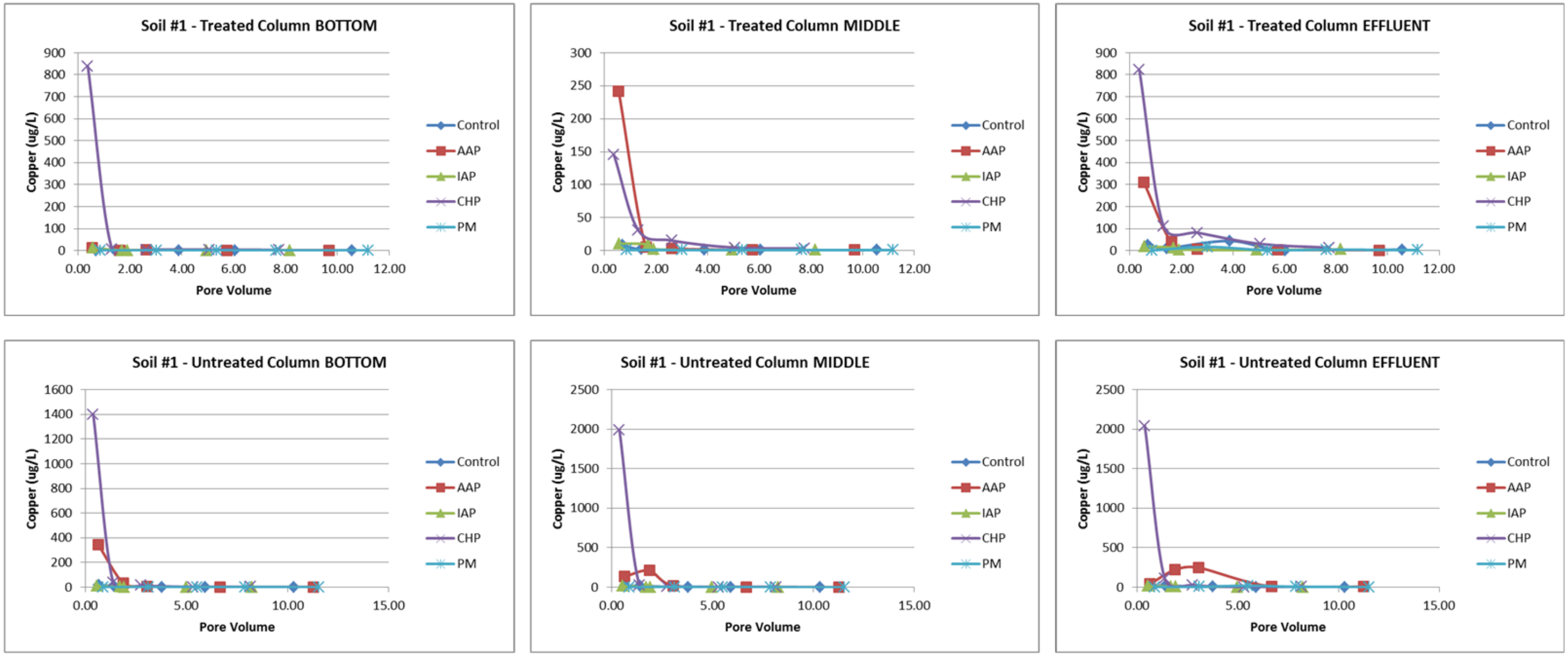
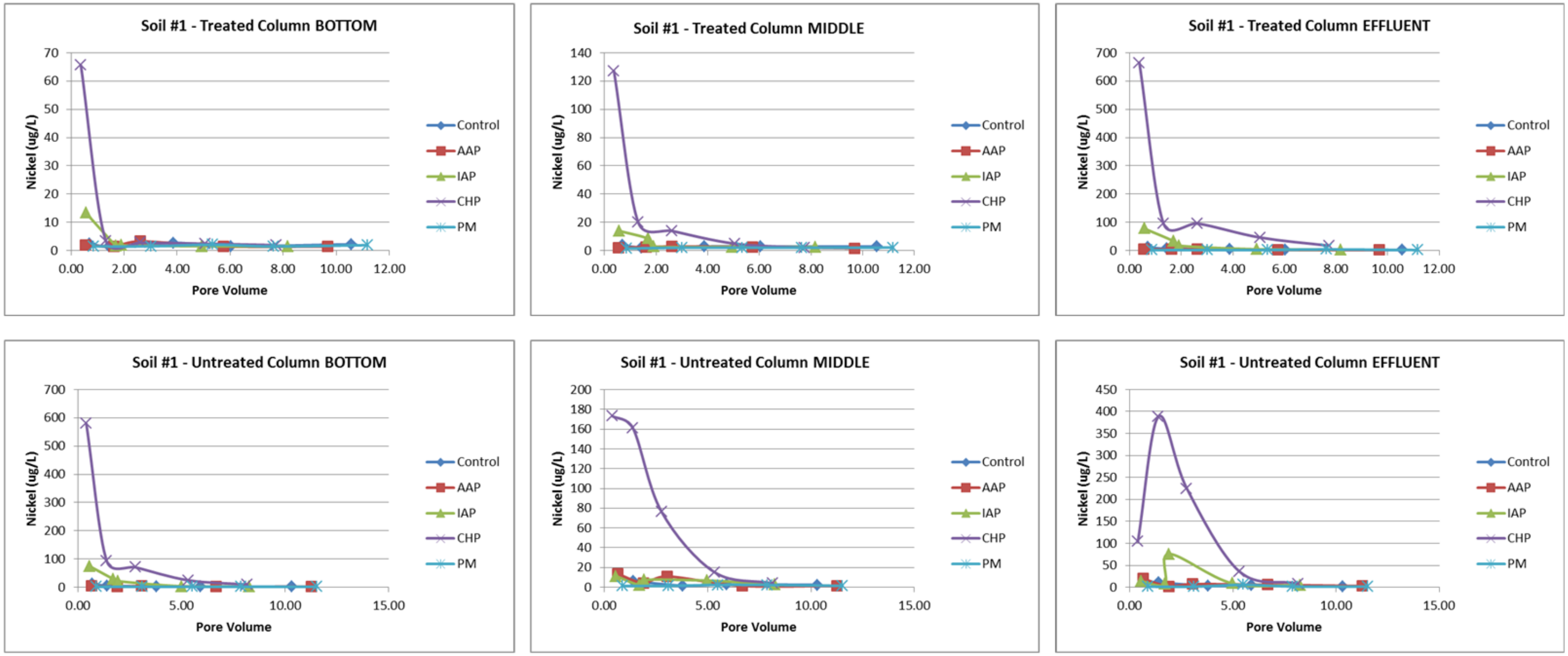


Figure 4.3.31 Column Experiment: Soil #1 –Copper mobilization

Note: Upper three panels are *up-gradient* column, lower three panels are *down-gradient* column. Left panels are bottom ports. Center panels are middle ports. Right panels are effluent ports. Columns were operated in upflow direction.


Soil #1 - Treated Column BOTTOM

Soil #1 - Treated Column MIDDLE

Soil #1 - Treated Column EFFLUENT

Soil #1 - Untreated Column BOTTOM

Soil #1 - Untreated Column MIDDLE

Soil #1 - Untreated Column EFFLUENT

Figure 4.3.32 Column Experiment: Soil #1 –Nickel mobilization

Note: Upper three panels are *up-gradient* column, lower three panels are *down-gradient* column. Left panels are bottom ports. Center panels are middle ports. Right panels are effluent ports. Columns were operated in upflow direction.

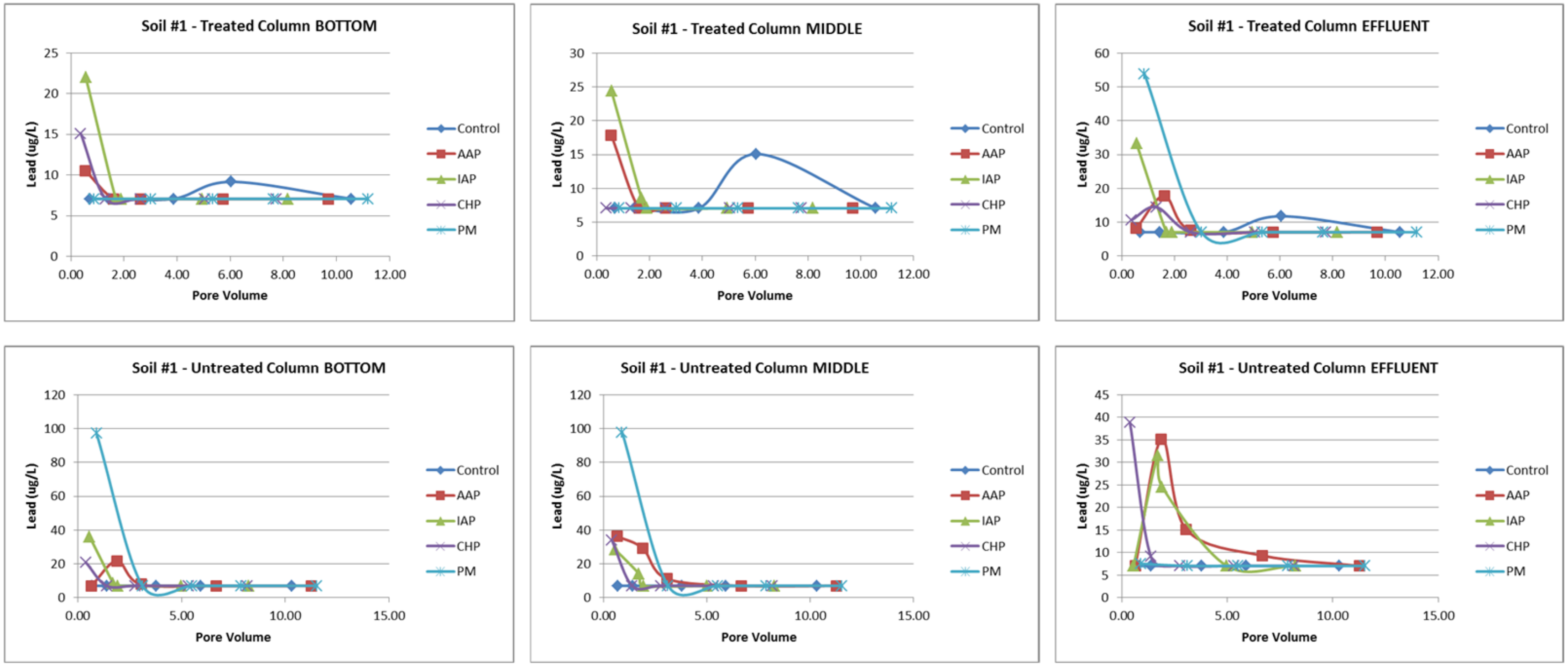


Figure 4.3.33 Column Experiment: Soil #1 –Lead mobilization

Note: Upper three panels are *up-gradient* column, lower three panels are *down-gradient* column. Left panels are bottom ports. Center panels are middle ports. Right panels are effluent ports. Columns were operated in upflow direction.

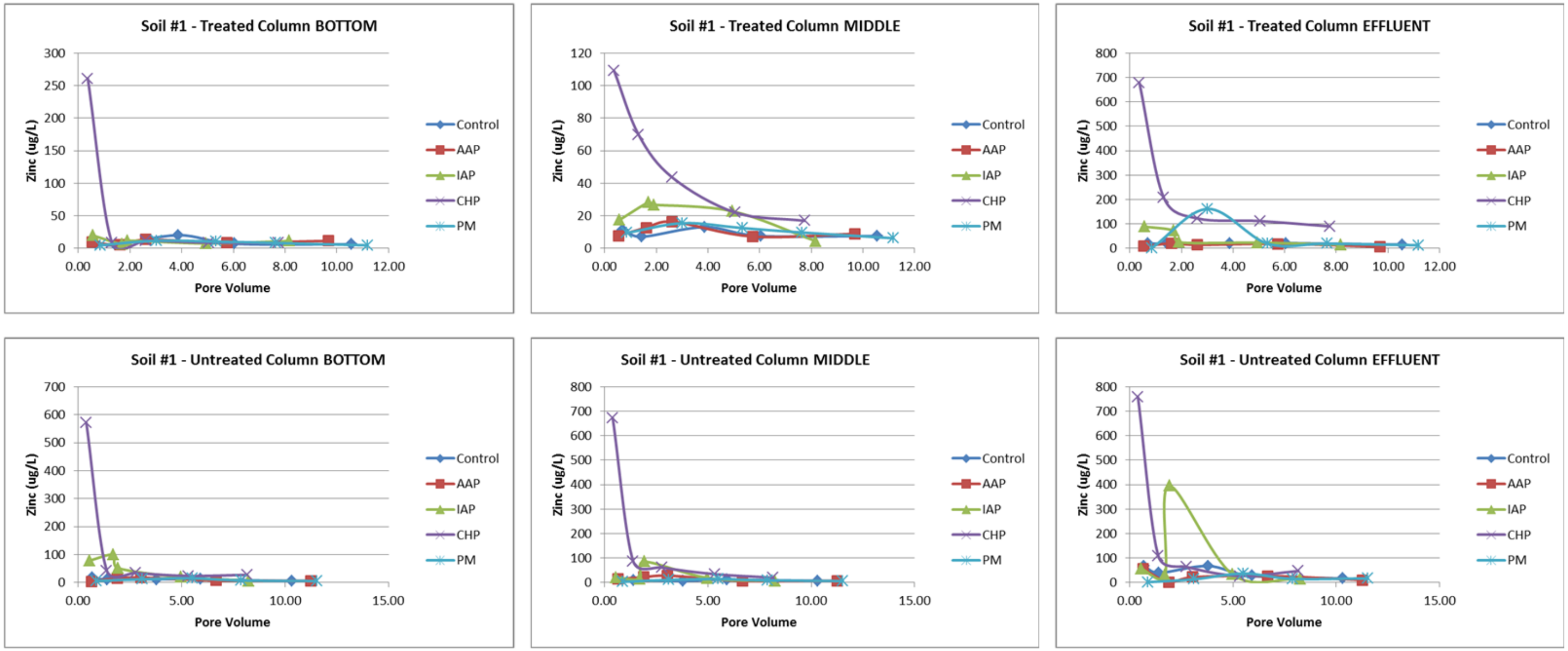


Figure 4.3.34 Column Experiment: Soil #1 –Zinc mobilization

Note: Upper three panels are *up-gradient* column, lower three panels are *down-gradient* column. Left panels are bottom ports. Center panels are middle ports. Right panels are effluent ports. Columns were operated in upflow direction.

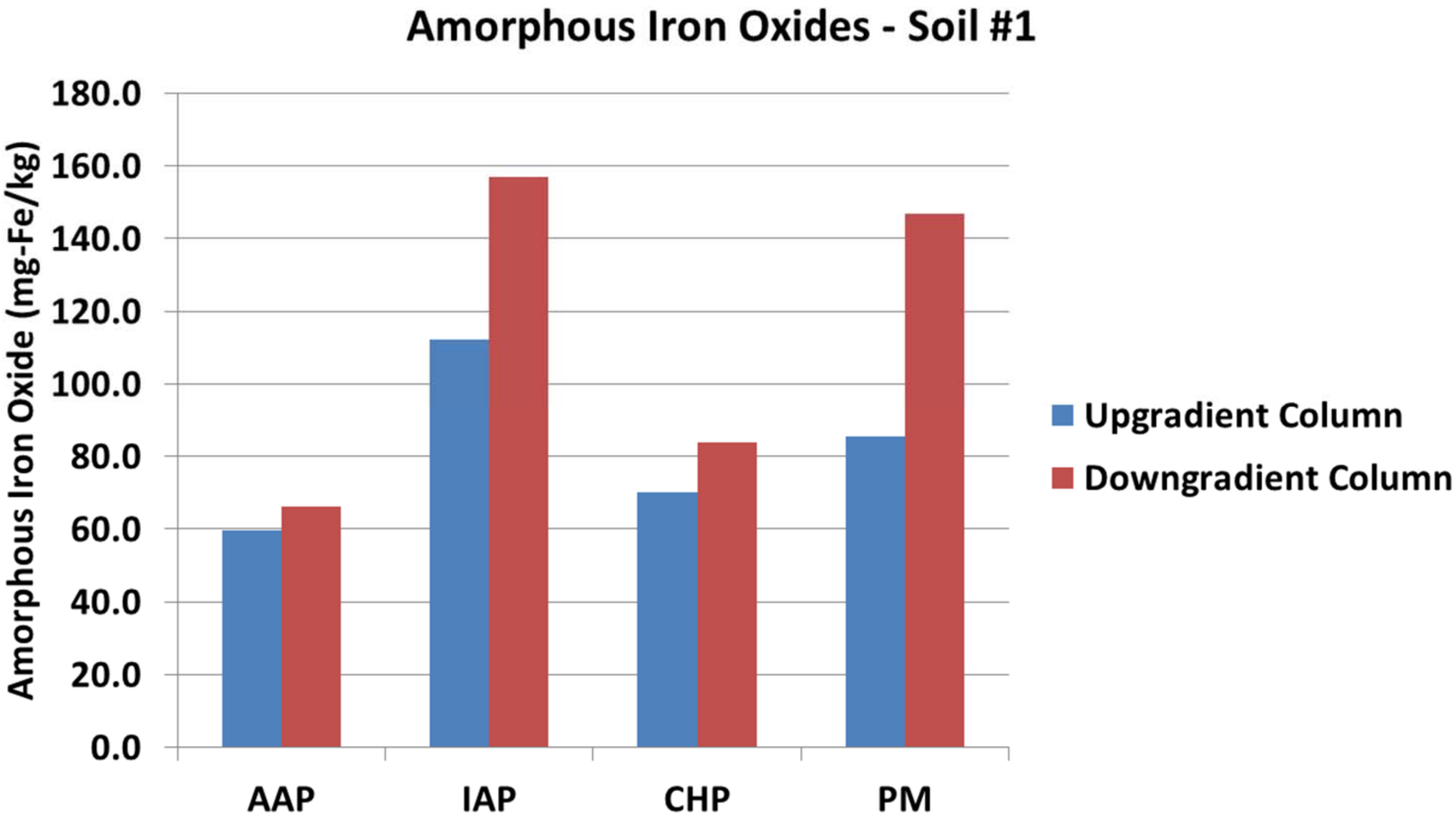


Figure 4.3.35 Amorphous iron oxides extracted from soils sampled from *up-gradient* (ISCO-treated) and *down-gradient* (untreated) columns.

Note: The original soil material was found to contain 69.6 mg-Fe/kg.

Summary of Column Study Results

Table 4.3.2 shows the propensity of the different ISCO reagents to mobilize metals from the different soils. Metal concentrations which exceed the MCL for the treatment are described as mobile. Simularly, metals that remained below the MCL for each soil are described as "Non Mobile" for the ISO treatment. As demonstrated, each soil responded differently to the different ISCO reagents. However, a few trends can be useful for selection of ISCO regent based upon considerations of metals mobilization. First AAP mobilized arsenic, where the other treatments did not. This trend is consistent across other aspects of this project where consistently elevated concentrations of arsenic were observed after contact with alkaline activated persulfate. PM was found to mobilize chromium in soils 1 and 2 to much higher levels than the other reagents. For the divalent metals Cu, Ni and Pb, CHP was found to mobilize metals for all three soils. As such, it is important to recognize that this table can be used as a general guide for technology selection, however bench scale evaluation with site-specific materials is highly recommended.

Table 4.3.2 Metals mobilized from three different aquifer materials upon treatment with 4 different ISCO technologies.

Metal	**Soil 1**		**Soil 2**		**Soil 4**	
	Mobile	*Not Mobile*	*Mobile*	*Not Mobile*	*Mobile*	*Not Mobile*
Arsenic	AAP	IAP CHP PM	AAP	IAP CHP PM	*None*	AAP IAP CHP PM
Chromium	AAP PM	IAP CHP	AAP CHP PM	IAP	AAP CHP	IAP PM
Copper	IAP CHP	AAP PM	AAP CHP	IAP PM	AAP CHP	IAP PM
Nickel	IAP CHP	AAP PM	CHP	AAP IAP PM	AAP CHP	IAP PM
Lead	AAP CHP PM	IAP	AAP IAP CHP PM	*None*	AAP CHP	IAP PM
Zinc	AAP IAP CHP	PM	AAP IAP CHP	PM	AAP IAP CHP PM	*None*

TASK 4: MITIGATING METALS MOBILIZATION AS A RESULT OF THE APPLICATION OF ISCO

The metals mobilization mitigation study investigated if the addition of a chemical amendment would reduce the mobilization of metals in the subsurface. The effect of the amendment on the overall efficacy of the ISCO treatment to reduce COCs was also evaluated at the same time. Evaluations investigated the application of amendment prior to ISCO treatment; concurrent with treatment; and following the treatment application. Results of the study are presented in that same order in the following 4 sections.

4.4.1 Pretreatment Stabilization Evaluation

The pretreatment evaluation investigated the addition of reagents intended to help mitigate the mobilization of metals before the addition of the ISCO reagents. This type of approach would be planned prior to the implementation of ISCO reagents or could exist in treating a mixed metal and organic contamination plume where the metals were stabilized prior to the treatment of the organic contamination. While 22 metals were monitored, the Priority Pollutant metals as defined in the Clean Water Act, with the exception of mercury, are discussed below. These metals include antimony (Sb), arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), selenium (Se), silver (Ag), thallium (Tl), and zinc (Zn).

The various test conditions evaluated were intended to form precipitates with certain metals or help buffer geochemical conditions near baseline either by modifying pH or ORP. The ISCO technologies evaluated include:

- Alkaline activated persulfate (AAP)
- Iron-chelate activated persulfate (IAP)
- Catalyzed hydrogen peroxide (CHP)
- Potassium permanganate ($KMnO_4$)

Alkaline-Activated Persulfate. Figure 4.4.1 presents the concentration of measured priority pollutant metals in reactors treated with AAP normalized to the control reactors (water only) for Soils 1, 2, and 6. The data show that As, and Cr increased for all three soil types containing AAP over up to a 90 day period compared to the control reactors. Other metals were also found to increase in threat least one of the soil types included Be, Cu, Ni, and Zn for Soil 1 (2 day time point only due to soil limitations), and Pb Soils 2 and 6. Conversely, the concentration of Ni appeared to decrease in the presence of AAP with Soil 6.

The screening results, collected after 2 days of contact between the ISCO reagents and the pretreated soils are presented in Figure 4.4.2. The data shows the priority pollutant metal concentration in the reactors with pretreated soils and AAP, normalized to the respective metal concentration in reactors treated with only AAP. The data show that the concentration of As decreased for Soils 2 and 6 when pretreated with sodium phosphate, sodium sulfide or a combination of the two. Ferric sulfate, sodium phosphate, sodium sulfide, and a combination of sodium sulfide and sodium phosphate were observed to have significant impacts on several metals for Soil 1, but not Soil 2 and 6, after the 2 day screening period.

Based upon the screening test results, pretreatment of soils with ferric sulfate, sodium phosphate, and sodium sulfide were evaluated over additional time points to evaluate the longer term impacts of soil pretreatment on metals mobilization with AAP. Figure 4.4.3 shows the pH and ORP of the various reactors including the control, AAP only, and the test conditions that contained AAP and ferric sulfate, sodium phosphate, and sodium sulfide, respectively, for Soils 2 and 6. Additional time points were not evaluated for Soil 1 as Soil 1 was consumed in the screening tests. The data show that the addition of AAP increased the pH of the system to greater than pH 12. The addition of ferric sulfate resulted in the pH decreasing with time in both soil types, but more significantly in Soil 6, where the pH was below the control by Day 56. Reactors containing sodium phosphate remained above the pH in the AAP only reactors and above pH 12 for the duration of the tests. The addition of sodium sulfate resulted in a pH similar to the sodium phosphate reactors in the presence of Soil 2, but in the presence of Soil 6, the pH was above the control but below the AAP only reactors. This may be the result of oxidation of the sulfides by persulfate.

The ORP for both soil types varied significantly. Pretreatment with sodium phosphate resulted in a lower ORP than both the control and AAP only reactors for both soil types. The addition of ferric sulfate resulted in ORP values greater than the AAP only reactors. The addition of sodium sulfide resulted in ORP values below the AAP only reactor for Soil 2 but intermixed with the AAP only reactors for Soil 6.

As shown in Figure 4.4.1, As and Cr were the priority pollutant metals most consistently mobilized in the presence of AAP. Figure 4.4.4 shows the concentrations of priority pollutant metals in soil pretreated with selected test conditions (at 4 time points) and the control (at Day 90), normalized to the respective metals concentrations observed in soils treated with AAP only.

The data presented in Figures 4.4.4A and B show that Soil 2 pretreated with sodium phosphate had minimal impact on most metals with a moderate reduction in concentration of Cu and Pb. Most other metals were similar to the results observed in the AAP only reactors. More significant reductions of metal concentrations were observed in Soil 6 pretreated with sodium phosphate where Be, Cd, Cr, Cu, Ni, and Zn were observed to have respective metals concentrations one to three orders of magnitude below those observed in the AAP only reactors. In the same data set, As was observed to have increased as a result of the sodium phosphate, and over the duration of the period monitored, was slowly returning to a concentration near the AAP only reactors.

Figures 4.4.4C and D present the results of soils pretreated with sodium sulfide prior to the addition of AAP. The data show that pretreatment with sodium sulfide resulted in reduced concentrations of As and Cr, the two priority pollutant metals consistently observed to be mobilized by AAP. The extent of mitigation with Soil 2 was less compared with Soil 6, where the concentrations after 90 days were more than 90 percent less than the AAP only reactors. Other metals, such as Pb, showed some indication of also being mitigated by the treatment with sodium sulfide.

Figures 4.4.4E and F present the results from soils pretreated with ferric sulfate. The data from Soil 6 show that As and Cr were reduced to concentrations similar to the control reactors by Day 90. The data from Soil 2 show that As was similarly reduced to concentrations near the control by day 90 and Cr was only moderately reduced. Other metals were similar to the Day 90 controls and AAP only reactors except for Be, Ni, and Zn in Soil 6 reactors, with concentrations showing an increasing trend with time.

To assess if the pretreatment of soils had an impact on the efficacy of AAP, the degradation of three common contaminants (carbon tetrachloride, benzene, and trichloroethene) was evaluated with the results presented in Figure 4.4.5. The data is presented as the respective concentrations normalized to the control reactors. The data show that the addition of ferric sulfate had a negative effect on the treatment of all three probe compounds for Soil 2, and only carbon tetrachloride for Soil 6. However, the addition of ferric sulfate resulted in a more significant reduction of benzene and trichloroethene compared to the AAP only reactors for Soil 6. The results from soils pretreated with sodium phosphate were similar to the AAP only reactors for all three probe compounds for both soil types indicating minimal, if any, interference or benefit. The pretreatment of soils with sodium sulfide also resulted in similar results as the AAP only reactors for both soil types and carbon tetrachloride and benzene and trichloroethene and Soil 2. However, it resulted in more significant reductions in concentration when compared to the control for benzene and trichloroethene in the presence of Soil 6.

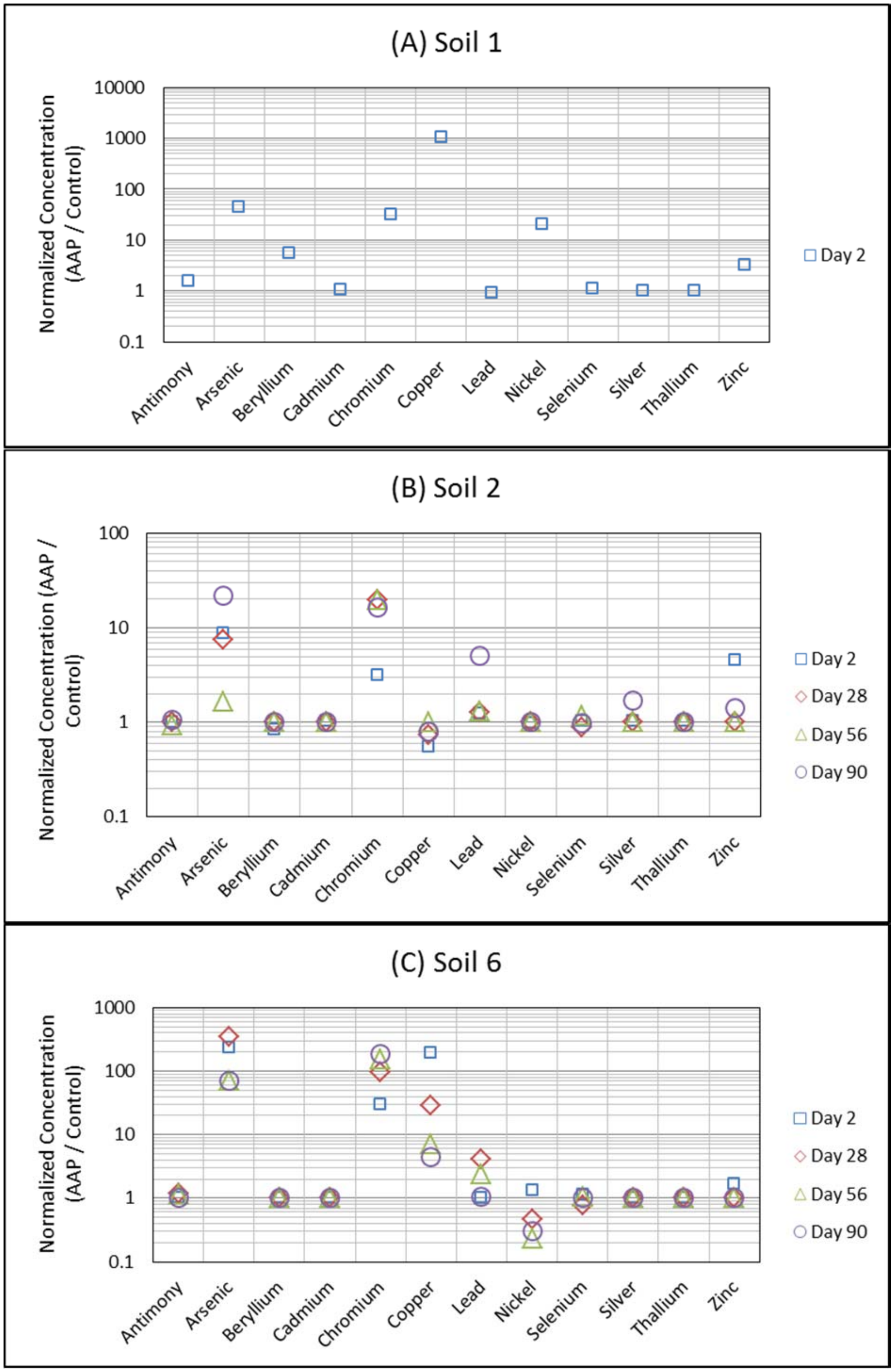


Figure 4.4.1 Pretreatment Stabilization: Normalized concentration of metals for reactors with AAP applied versus control conditions (no AAP treatment).

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C).

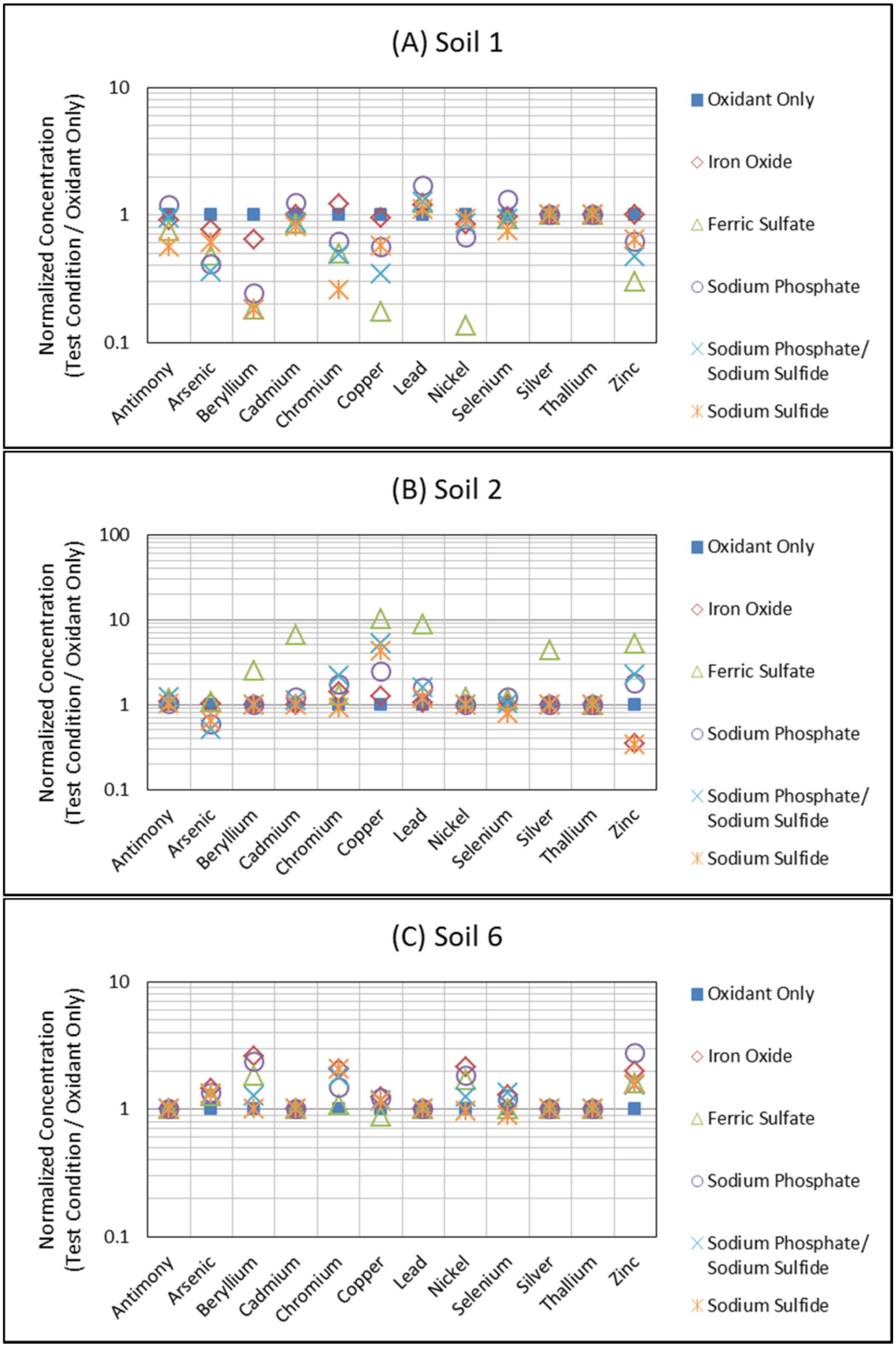


Figure 4.4.2 Pretreatment Stabilization of AAP System: Select normalized metal concentrations for 5 Pretreatment options.

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C).

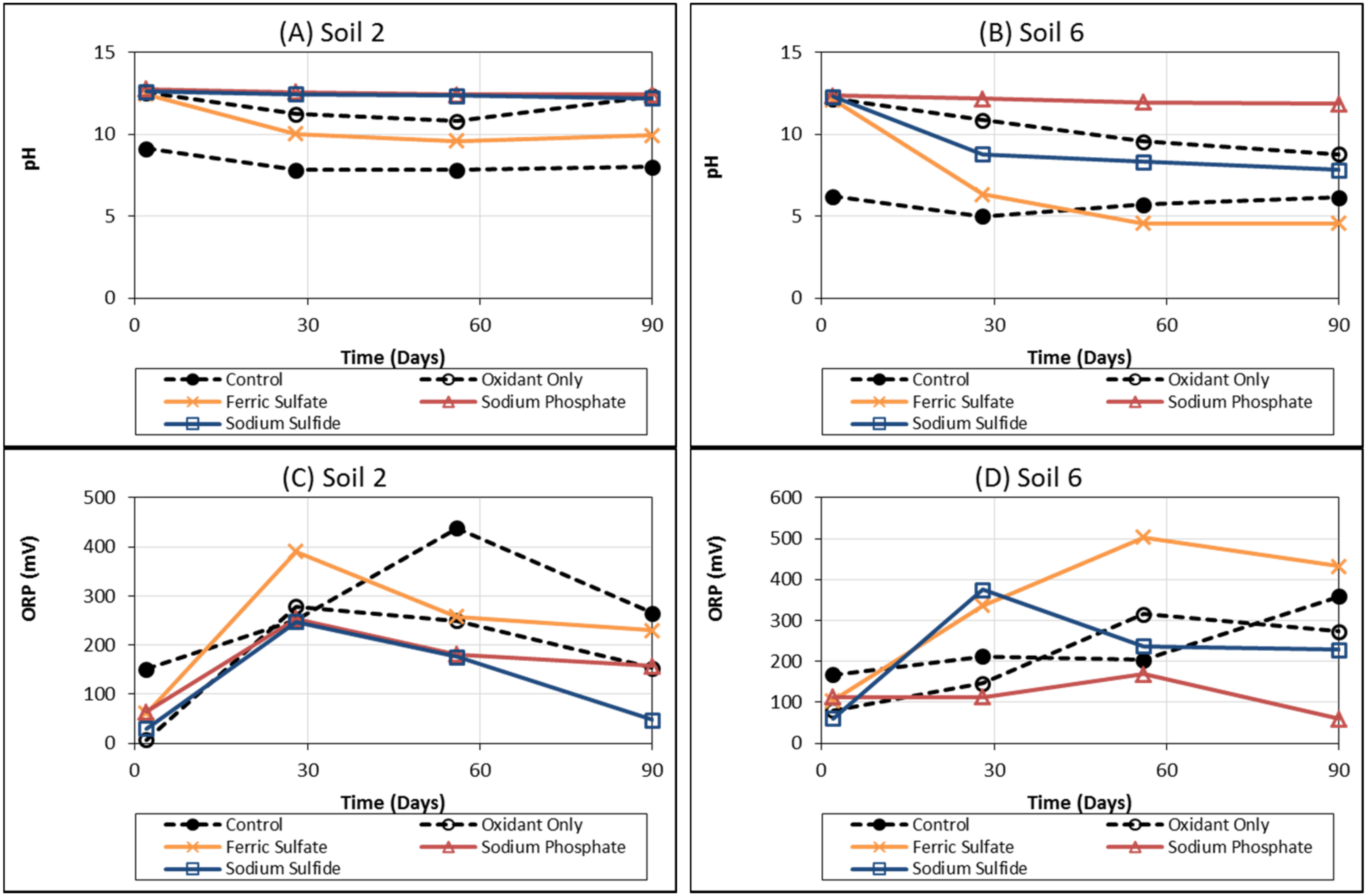


Figure 4.4.3 Pretreatment Stabilization of AAP System: Geochemical parameters at 2, 28, 56, and 90 days

Note: Soil 2 (A, pH, C, ORP) and Soil 6 (B, pH, D, ORP)

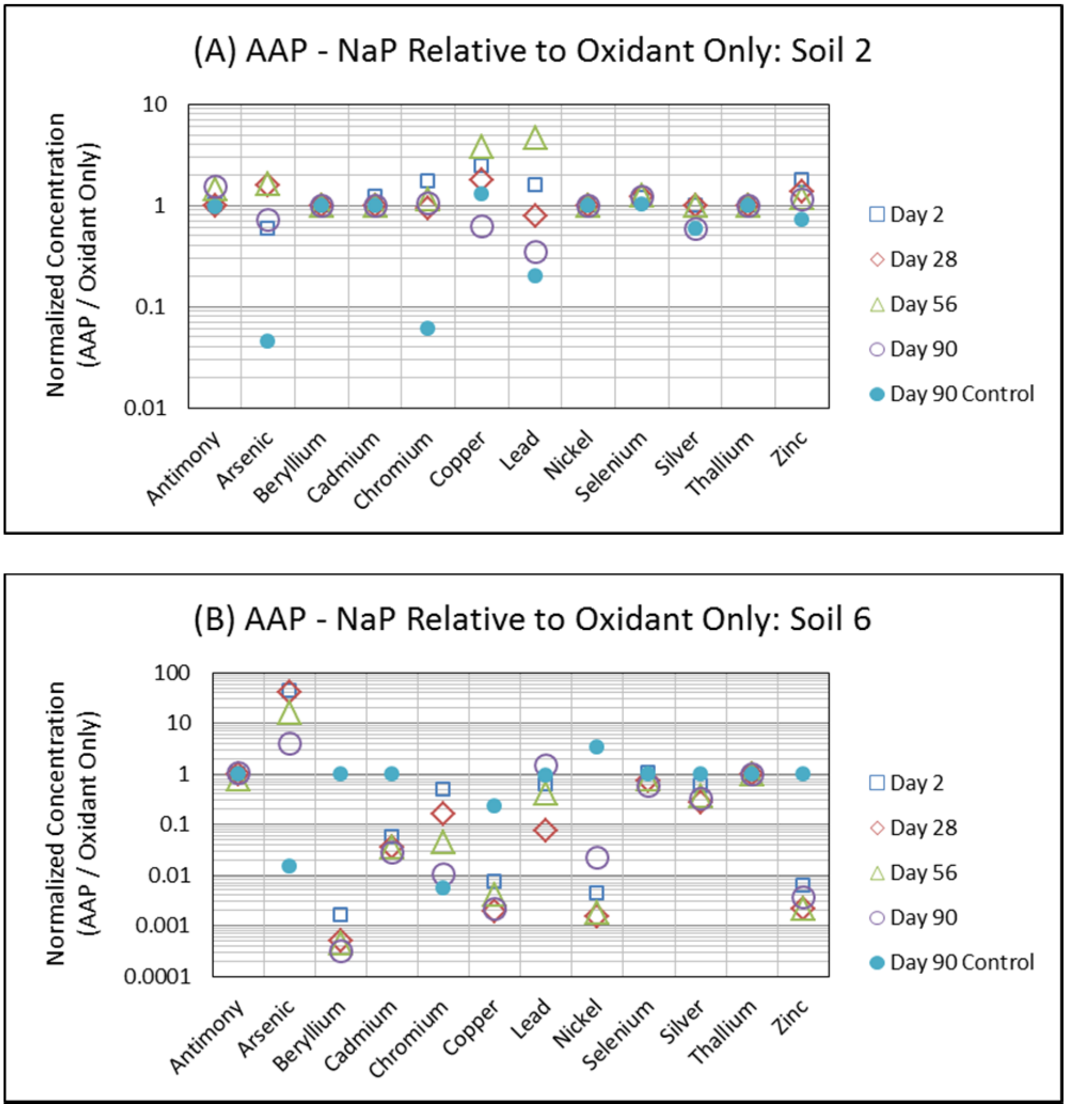
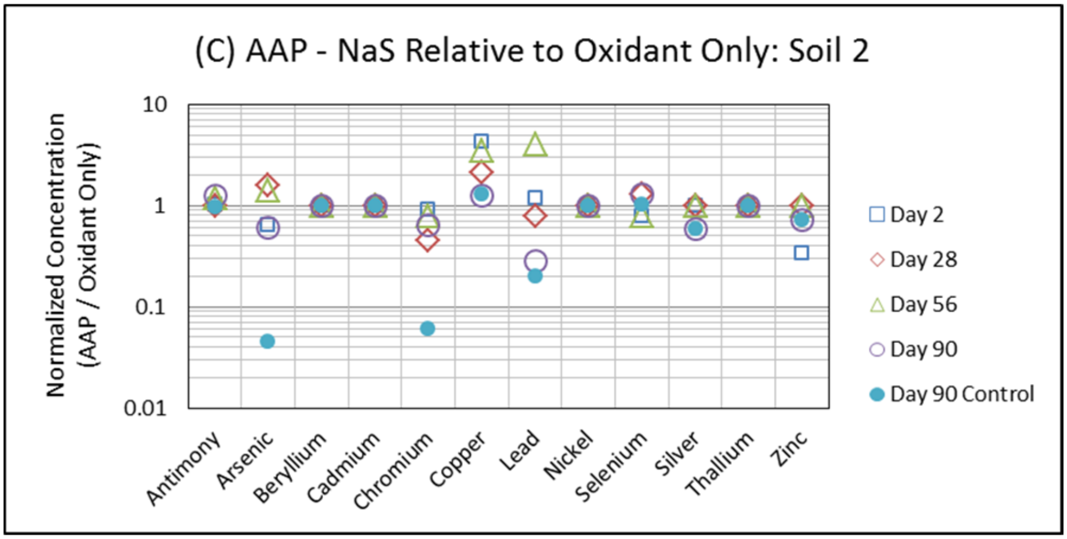


Figure 4.4.4 Pretreatment Stabilization of AAP System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Pretreatment with sodium phosphate (A,B), and sodium sulfide (C,D) and ferric oxide (E,F) for both Soil 2 and 6.



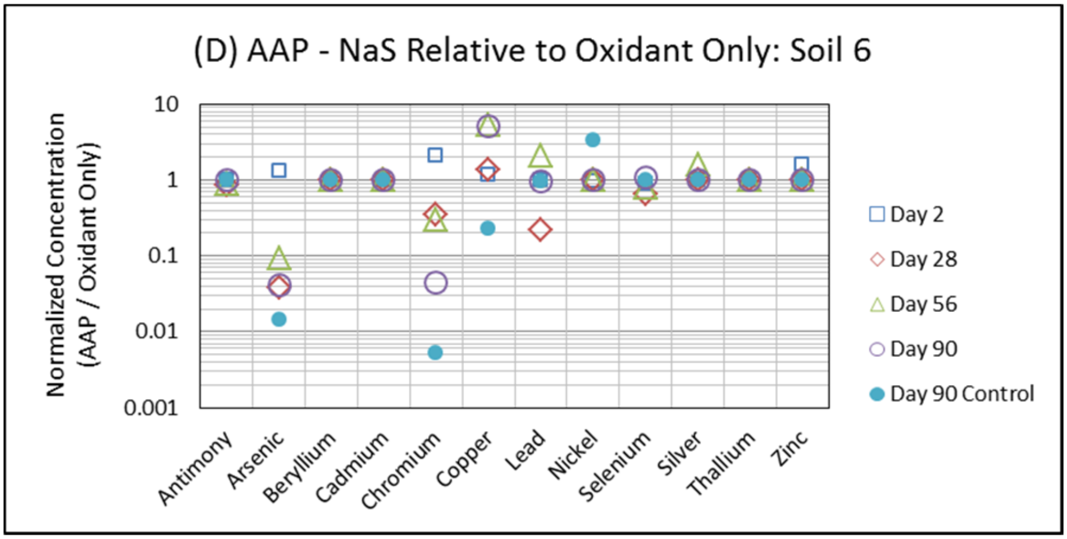
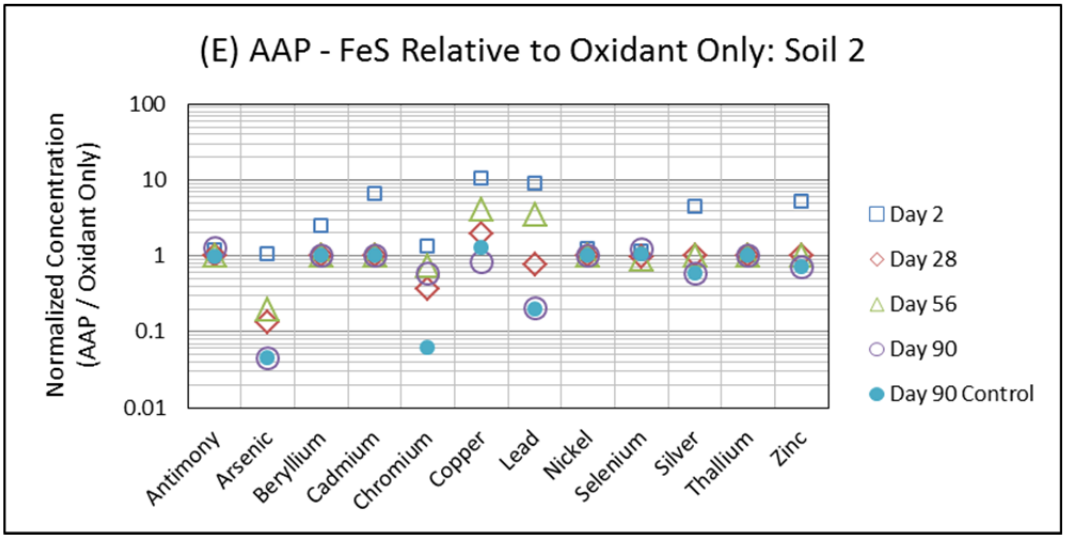


Figure 4.4.4 (cont.) Pretreatment Stabilization of AAP System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Pretreatment with sodium phosphate (A,B), and sodium sulfide (C,D) and ferric oxide (E,F) for both Soil 2 and 6



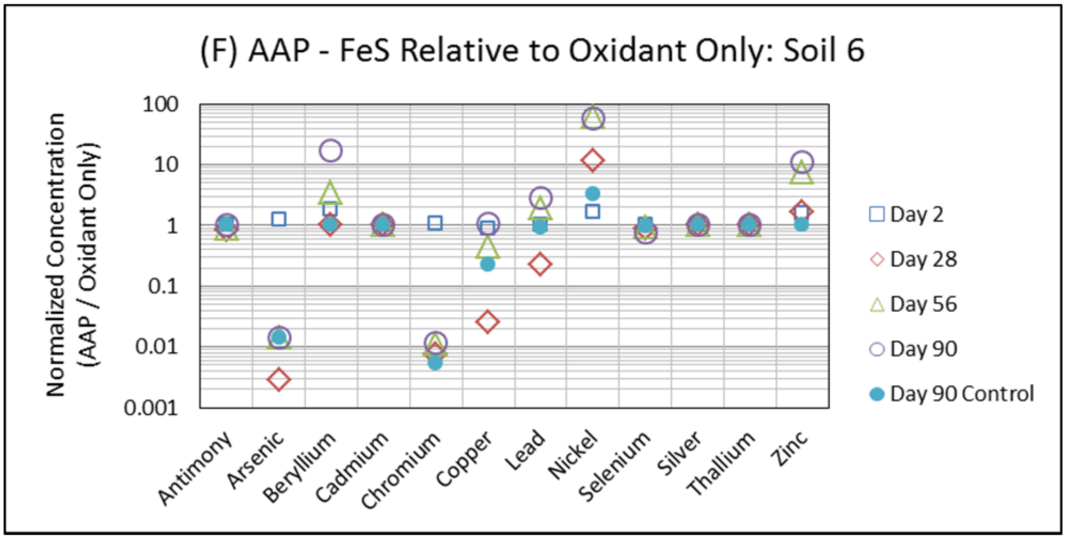


Figure 4.4.4 (cont.) Pretreatment Stabilization of AAP System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Pretreatment with sodium phosphate (A,B), and sodium sulfide (C,D) and ferric oxide (E,F) for both Soil 2 and 6

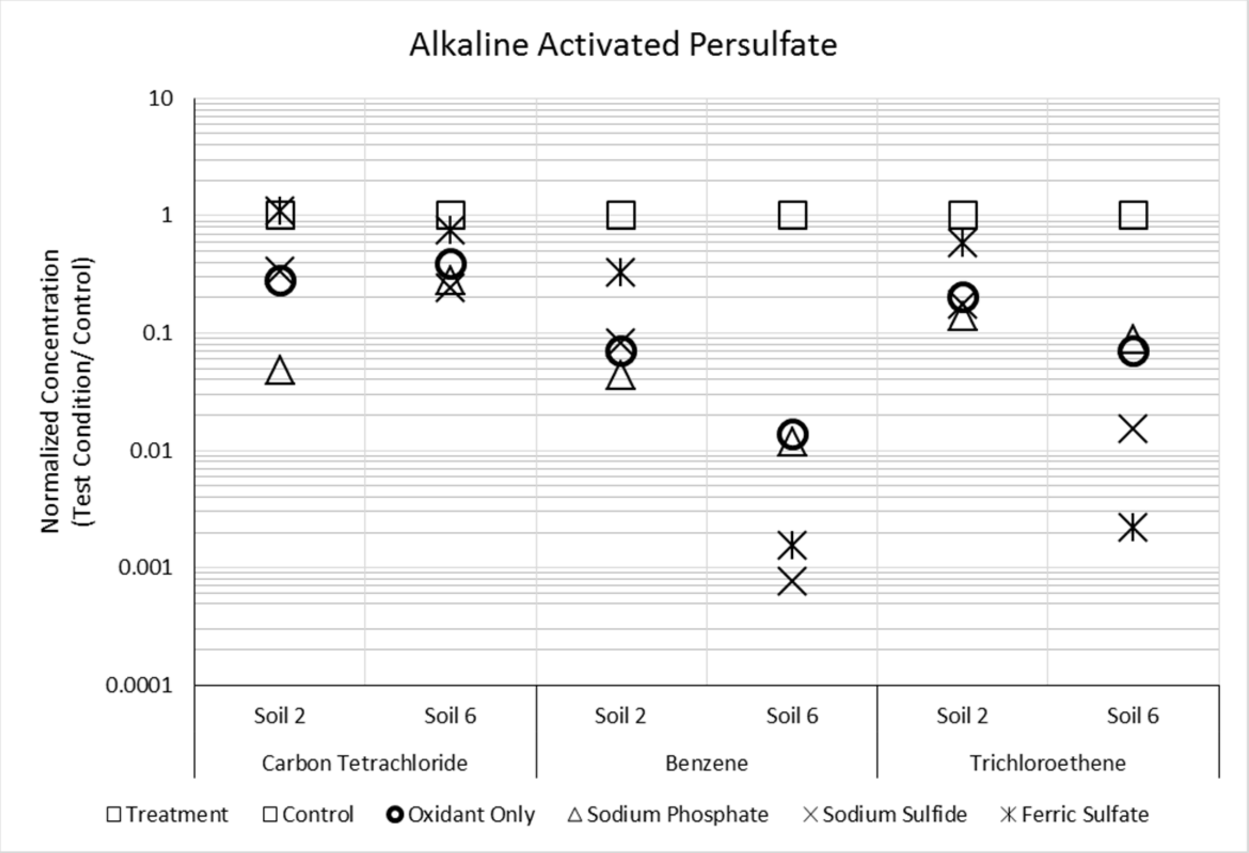


Figure 4.4.5 Pretreatment Stabilization of AAP System: Treatment Efficacy- Normalized Concentrations of probe compounds carbon tetrachloride, benzene, and trichloroethene.

Iron Activated Persulfate. Figure 4.4.6 shows the concentration of priority pollutant metals in reactors treated with IAP normalized to the metals concentration in the control reactors for each respective time point for Soils 1, 2, and 6. The data indicated that the addition of IAP to the soils resulted in increased concentrations relative to the control of Be, Cd, Cr, Pb, Ni, and Zn for each of the three soil types tested. Other metals, such as Cu, increased in two of the three soil types. Several metals were initially elevated above the control reactor but were observed to be returning to concentrations similar to the control reactors after 90 days of contact. These include Be, Cd, and Ni for Soil 2.

The concentration of aqueous phase metals, collected after 2 days of contact between IAP reagents and the pretreated soils, normalized to concentrations in soils treated with IAP only, are presented in Figure 4.4.7. The pretreatment of soils with sodium phosphate, sodium sulfide or a combination of the two reagents resulted in a decreased concentration of Be, Cd, Cr, Cu, Ni, and Zn in multiple soil types after two days of contact. Of those metals, Be, Cu, Ni, and Zn were reduced by greater than 90 percent by sodium phosphate and sodium sulfide pretreatment.

Based upon the results, the pretreatment of soils with sodium sulfide and sodium phosphate were evaluated over additional time points to evaluate the longer term impacts of soil pretreatment on metals mobilization with IAP. Figure 4.4.8 shows the pH and ORP over time during the experiment. Reactors containing IAP were observed to have pH values 2 to 4 pH units below the control for both Soil 2 and 6. Pretreatment of soils with sodium phosphate resulted in pH values that were several pH units higher than the IAP only reactors. Pretreatment of soils with sodium sulfide resulted in a pH very similar to the control reactors for Soil 2, and values that were very similar to the IAP only reactors after Day 28 for Soil 6. The addition of IAP resulted ORP values that were elevated compared to those observed in the control reactors. The pretreatment of soils with sodium phosphate resulted in ORP values that were consistently below those observed in the IAP only reactors. The pretreatment of soils with sodium sulfide resulted in ORP values lower than the IAP only reactors for Soil 2, but, as with pH, similar ORP values after Day 28. The data indicate that the pretreatment of soils with sodium phosphate and sodium sulfide altered the geochemical conditions of the IAP treatment with the exception of Soil 6 after Day 28.

Figure 4.4.9 presents the concentrations of metals for soils pretreated with sodium sulfide and sodium phosphate (at 4 time points) and the control (at Day 90),normalized to concentrations in soils treated with IAP only. All reactors contained IAP except for the Day 90 Control. Figures 4.4.9A and B indicate that the pretreatment of soils with sodium phosphate resulted in metals concentrations approaching or similar to the control reactors after 90 days of contact with the exception of As for both soil types and Cr in Soil 2. The data indicate that the pretreatment of soils with sodium phosphate significantly minimized the mobilization of most metals, with the exception of As, with concentrations in the pretreated reactors observed to be above both the IAP only reactors and controls for both soil types.

The pretreatment of soils with sodium sulfide resulted in metals concentrations similar to, or lower than, the control by Day 90 for Soil 2 for each of the priority pollutant metals evaluated. This includes concentrations that were below the IAP only reactors for Cr, Pb, Ni, Ag, and Zn. However, similar to the results observed for pH and ORP, where by Day 28 the geochemical conditions were similar to those observed in the IAP only reactors, the metals concentrations after Day 28 for Soil 6 were also very similar to the IAP only reactors. After 2days of treatment, Be, Cd, Cr, Cu, Ni, and Zn were below the IAP only reactors. However, the data would indicate that any benefit by the addition of sodium sulfide for Soil 6 was eliminated by Day 28 whereas continued benefit was observed up to Day 90 for Soil 2.

The pretreatment of soils with sodium phosphate or sodium sulfide was intended to bind metals into insoluble minerals that would be resistant to mobilization during the application of ISCO. To assess if this pretreatment also had an impact on the efficacy of IAP, the degradation of carbon tetrachloride, benzene, and trichloroethene was evaluated (Figure 4.4.10). Carbon tetrachloride was not degraded when compared to the concentration in the control reactor for any of the pretreatment conditions with both soil types. Both benzene and trichloroethene treatment was limited in the presence of Soil 2. The residual contaminant concentrations on soils pretreated with sodium sulfide were nearly identical to the untreated soils while the respective concentrations of each contaminant was less in the presence of soils treated with sodium phosphate. The treatment of benzene and trichloroethene in the presence of untreated soils was 95 percent and 83 percent lower than the control reactors, respectively, for Soil 6. Whereas the residual concentration of benzene and trichloroethene were approximately 44 percent and 24 percent lower than the controls, respectively, for Soil 2. The data indicate that the efficacy of IAP was inhibited by Soil 2 and by the pretreatment of soils with sodium sulfide and sodium phosphate for Soil 6.

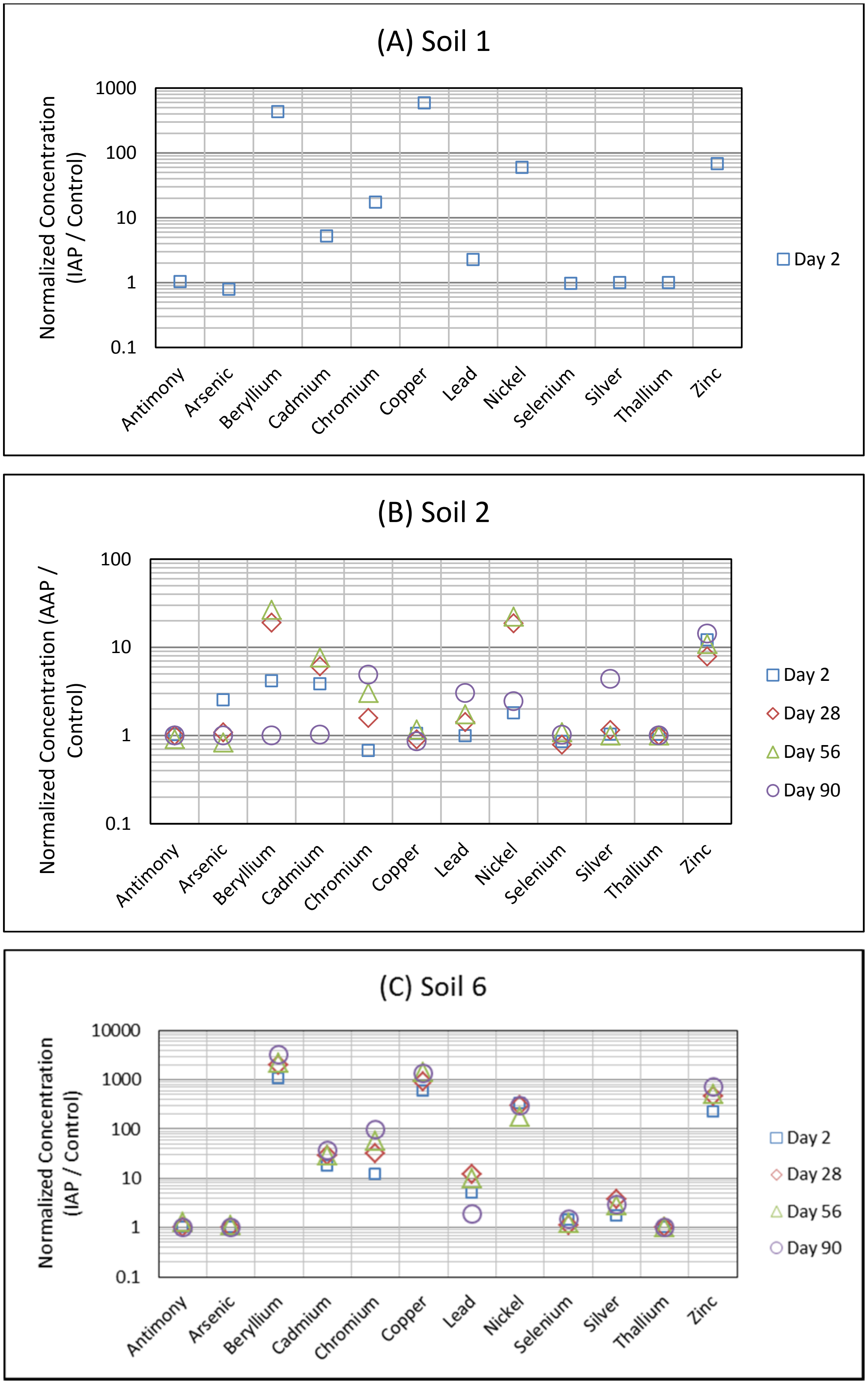


Figure 4.4.6 Pretreatment Stabilization: Normalized concentration of metals for reactors with IAP applied versus control conditions (no IAP treatment).

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C).

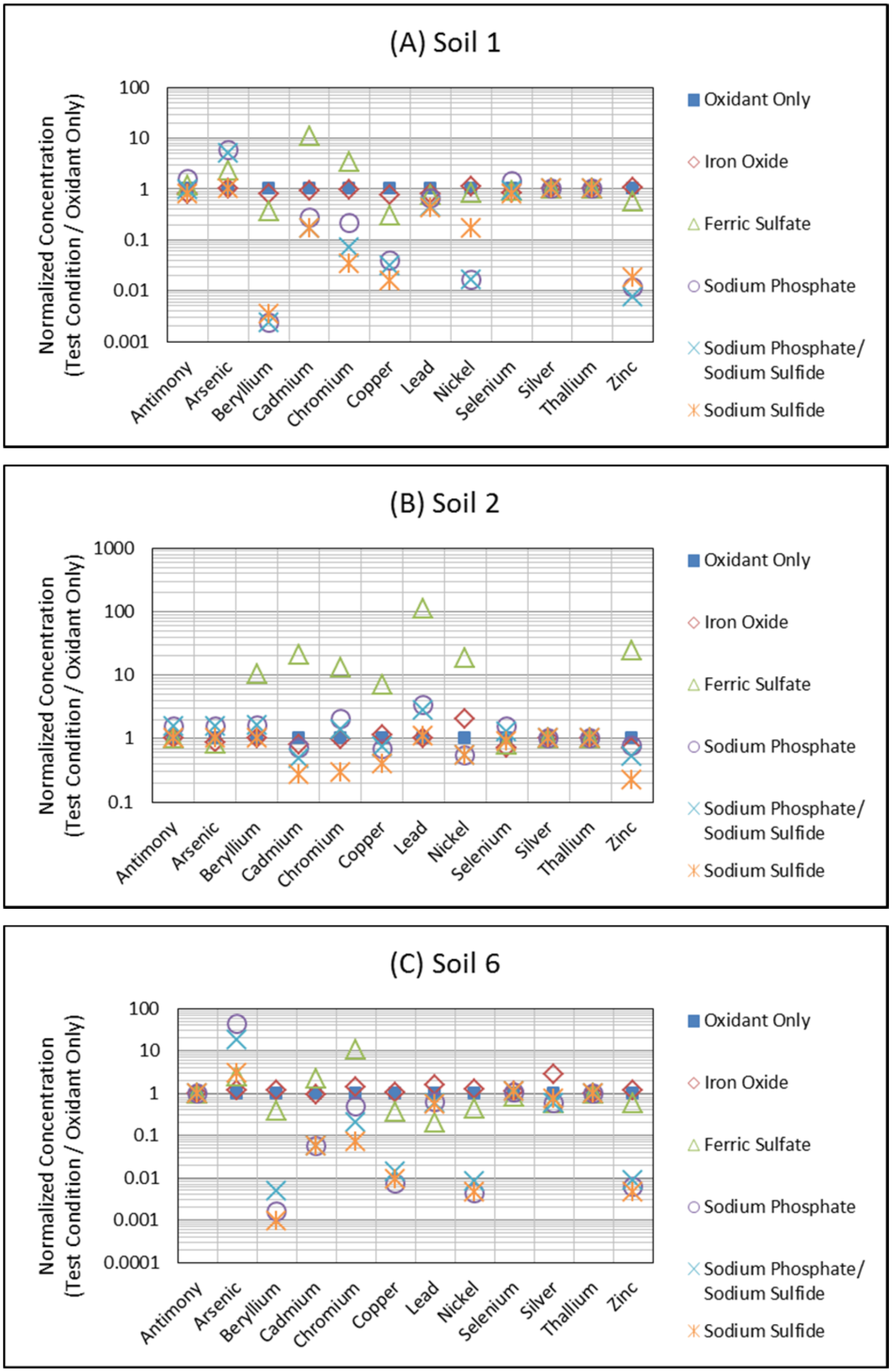


Figure 4.4.7 Pretreatment Stabilization of IAP System: Select normalized metal concentrations for 5 Pretreatment options.

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C).

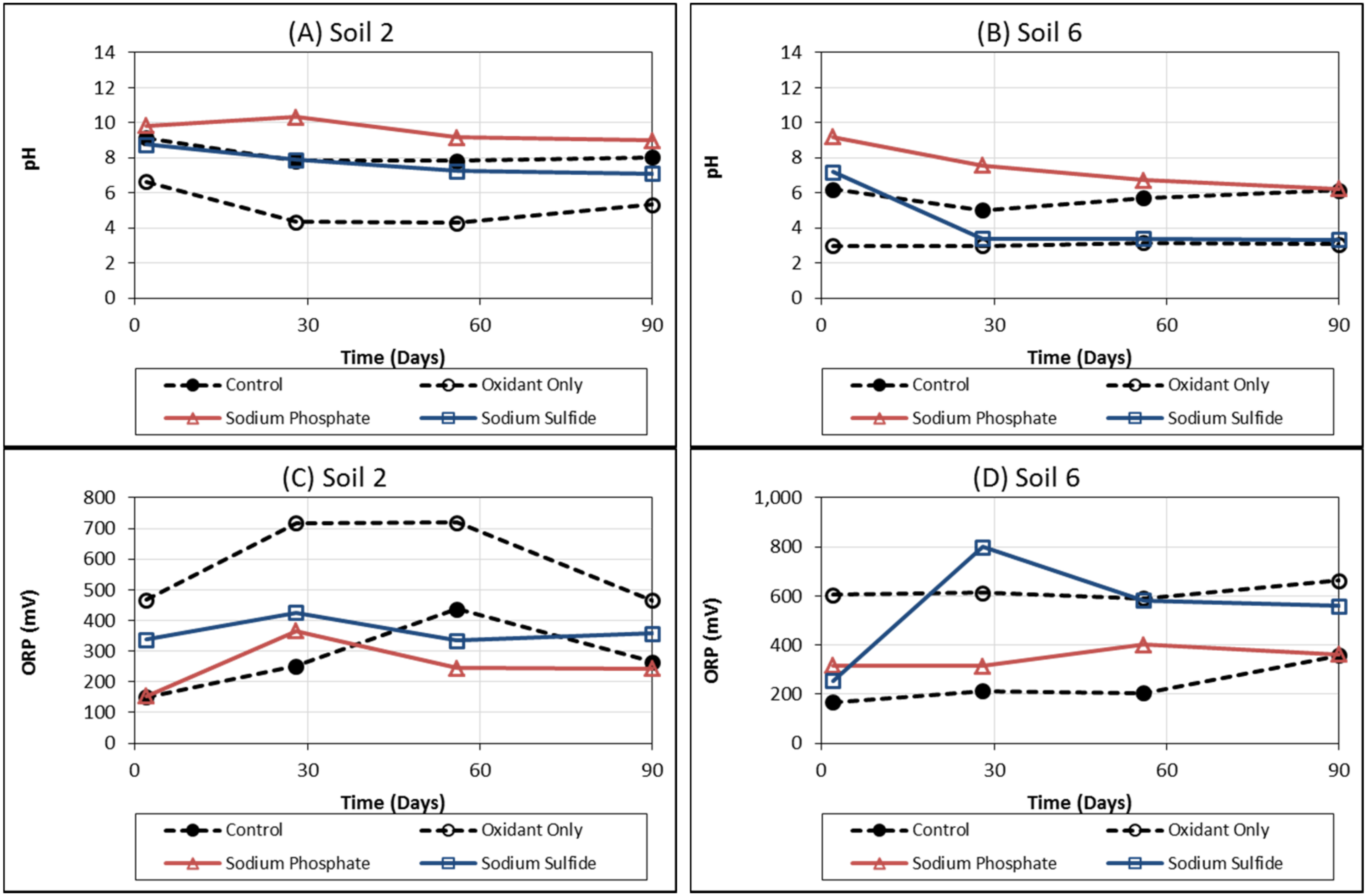


Figure 4.4.8 Pretreatment Stabilization of IAP System: Geochemical parameters at 2, 28, 56, and 90 days

Note: Soil 2 (A, pH, C, ORP) and Soil 6 (B, pH, D, ORP).

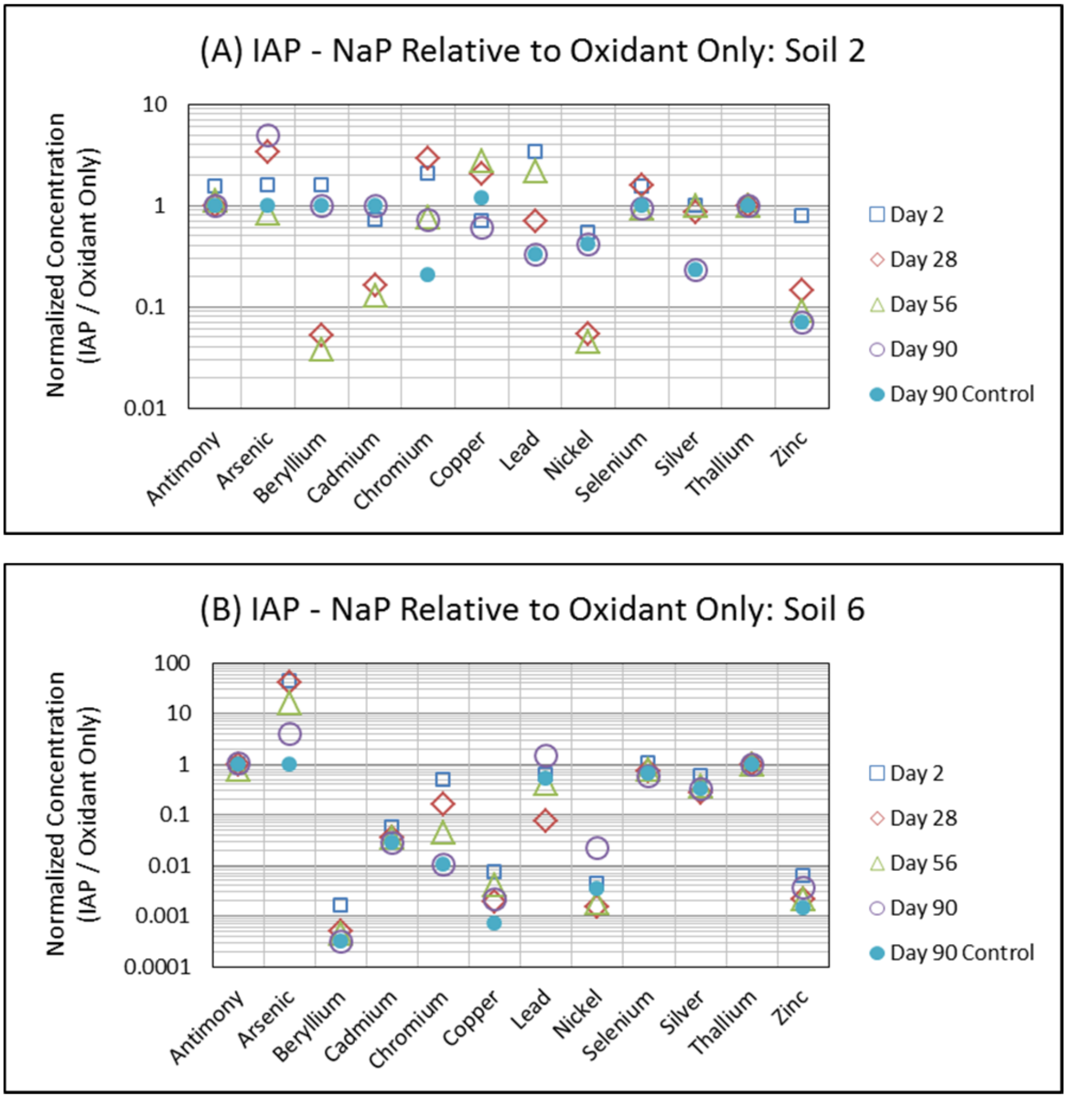
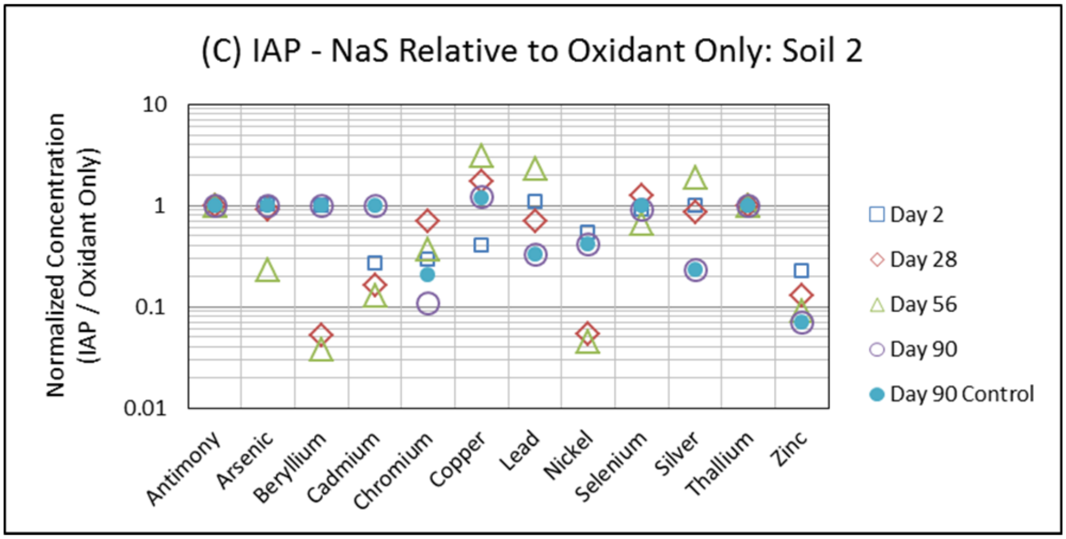


Figure 4.4.9 Pretreatment Stabilization of IAP System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Pretreatment with sodium phosphate (A,B), and sodium sulfide (C,D) for both Soil 2 and 6.



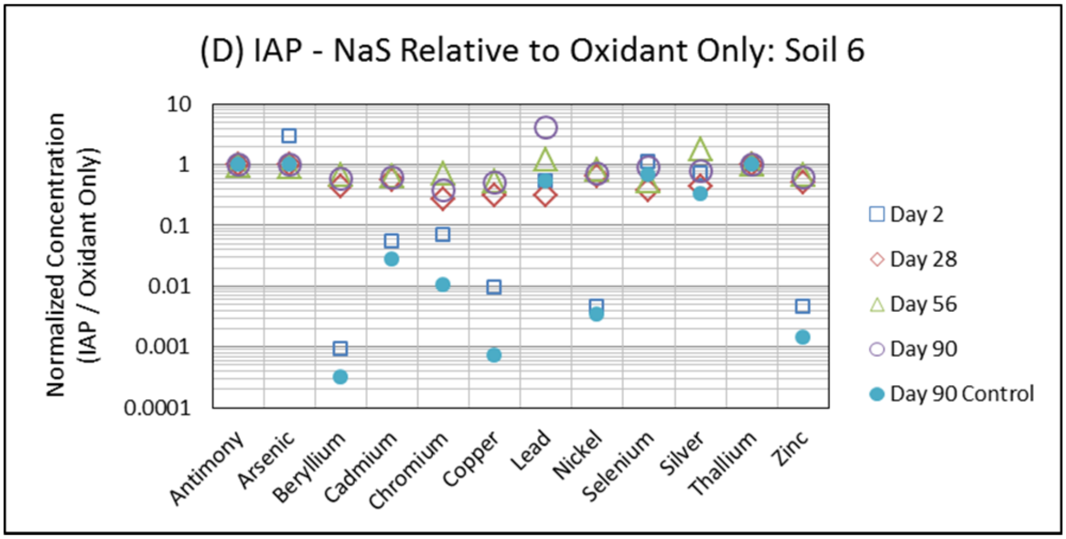


Figure 4.4.9 (cont.) Pretreatment Stabilization of IAP System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Pretreatment with sodium phosphate (A,B), and sodium sulfide (C,D) for both Soil 2 and 6.

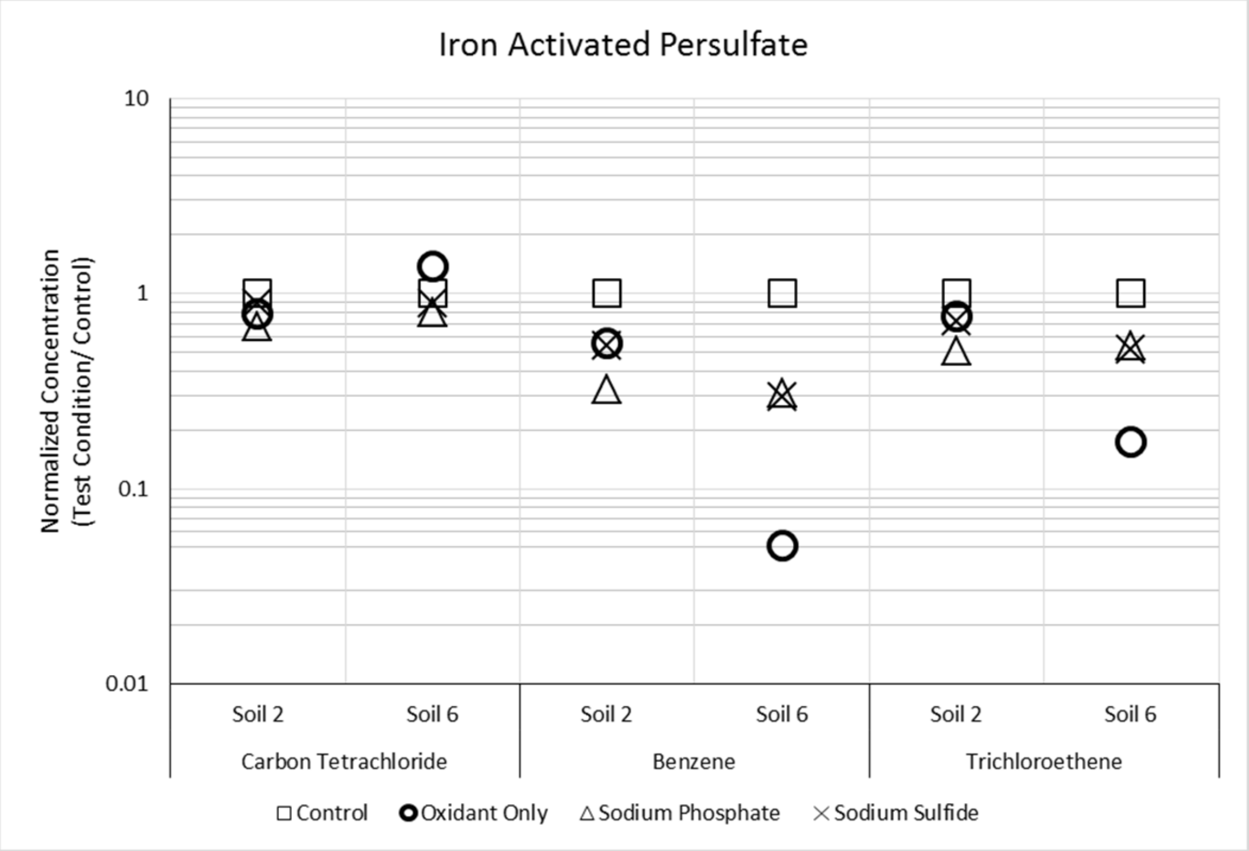


Figure 4.4.10 Pretreatment Stabilization of IAP System: Treatment Efficacy- Normalized Concentrations of probe compounds carbon tetrachloride, benzene, and trichloroethene.

Catalyzed Hydrogen Peroxide. Figure 4.4.11 shows the concentration of priority pollutant metals in reactors treated with CHP normalized to the metals concentration in the control reactors for each respective time point for Soils 1, 2, and 6. Concentrations of priority pollutant metals including Be, Cd, Cr, Cu, Ni, and Zn were greater in reactors treated with CHP compared to the control reactors for Soil types 1, 2, and 6.

The concentration of aqueous phase metals, collected after 2 days of contact between CHP reagents and the pretreated soils, normalized to concentrations in soils treated with CHP only, are presented in Figure 4.4.12. The pretreatment of soils with sodium phosphate, sodium sulfide or a combination of the two reagents resulted in a decreased concentration of Be, Cd, Cu, Ni, and Zn in multiple soil types after 2 days of contact. The most significant treatment within 2 days was observed in Soil 1 where Be, Cd, Cu, and Zn were reduced by greater than 90 percent in the two pretreatment conditions containing sodium phosphate. Based upon the data presented in Figure 4.4.12, pretreatment of soils with sodium phosphate and sodium sulfide were evaluated over additional time points to evaluate the longer term impacts of soil pretreatment on metals mobilization with CHP. .

The pH and ORP for each treatment condition measured at 2, 28, 56, and 90 days after the addition of CHP are presented in Figure 4.4.13. The data show that the addition of the CHP reagent solution typically decreased the system pH relative to the control reactor for the duration of the 90 day period. This is likely the result of acid formation during the reaction and the use of citric acid to chelate the iron added with the CHP. The pretreatment of soils with sodium phosphate and sodium sulfide resulted in pH values closer to the control reactor and higher than the CHP only reactors.

The ORP data, presented in Figures 4.4.13C and D, show that the addition of CHP resulted in elevated ORP values, compared to the control reactor, for the duration of the test. The ORP values in the pretreated soils were less than the CHP only reactors for the Day 2 time point, but alternated above and below the CHP only reactors thereafter.

Figure 4.4.14 presents the concentrations of metals for soils pretreated with sodium phosphate and sodium sulfide (at 4 time points) and the control (at Day 90), normalized to concentrations in soils treated with CHP only. The data for Soil 2 and Soil 6 pretreated with sodium phosphate are presented in Figures 4.4.14A and B, respectively, and show that the pretreated soils resulted in lower aqueous metals concentrations for Be, Cd, Cr, Cu, Ni, Ag, and Zn when compared to the soils treated with CHP only. The pretreatment of Soil 2 with sodium phosphate resulted in metals concentrations similar to, or approaching, the control by Day 90 for each of the priority pollutant metals evaluated, with the exception of As, which was observed to have increased. Pretreatment of Soil 6 with sodium phosphate also resulted in metals concentrations below untreated soils. Be, Cd, Cr, Cu, Ni, and Zn had decreasing concentration trends, but where greater than the control reactors.

Pretreatment of Soils 2 and 6 with sodium sulfide (Figures 4.4.14C and D), resulted in concentrations of Be, Cd, Cr, Cu, Ni, Ag, and Zn lower than the soils treated with CHP only, for one or both soil types. The addition of sodium sulfide appeared to have little impact on metals that were not typically impacted by the addition of CHP, including Ag, As, Pb, Se, Sb, and Tl for either soil type.

The pretreatment of soils with sodium phosphate or sodium sulfide was intended to bind metals into insoluble minerals that would be resistant to mobilization during the application of ISCO. To assess if this pretreatment also had an impact on the efficacy of CHP, the degradation of carbon tetrachloride, benzene, and trichloroethene were evaluated (Figure 4.4.15). The data indicate that the addition of CHP resulted in residual concentrations from 94 percent to greater than 99.9 percent lower than the control reactors. Pretreatment with sodium sulfide had little impact on the treatment efficacy for all three probe contaminants. The pretreatment of soils with sodium phosphate had little impact on the treatment efficacy of carbon tetrachloride, but appeared to decrease the treatment efficacy of benzene and trichloroethene. This may be the result of phosphate scavenging the hydroxyl radical. Treatment of benzene and trichloroethene, while impacted, was still greater than 98 percent reduction in concentration when compared to the control reactors.

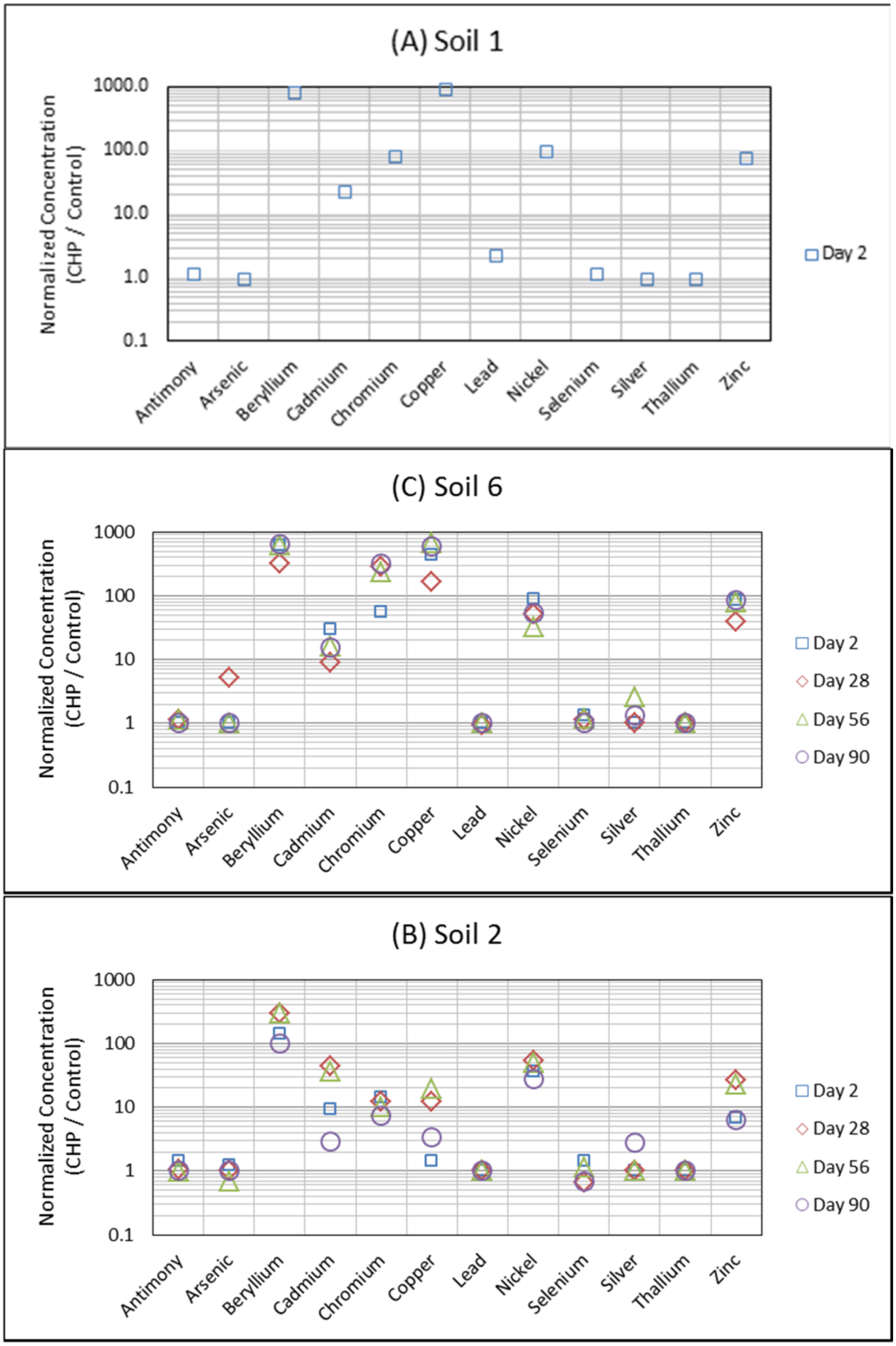


Figure 4.4.11 Pretreatment Stabilization: Normalized concentration of metals for reactors with CHP applied versus control conditions (no CHP treatment).

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C).

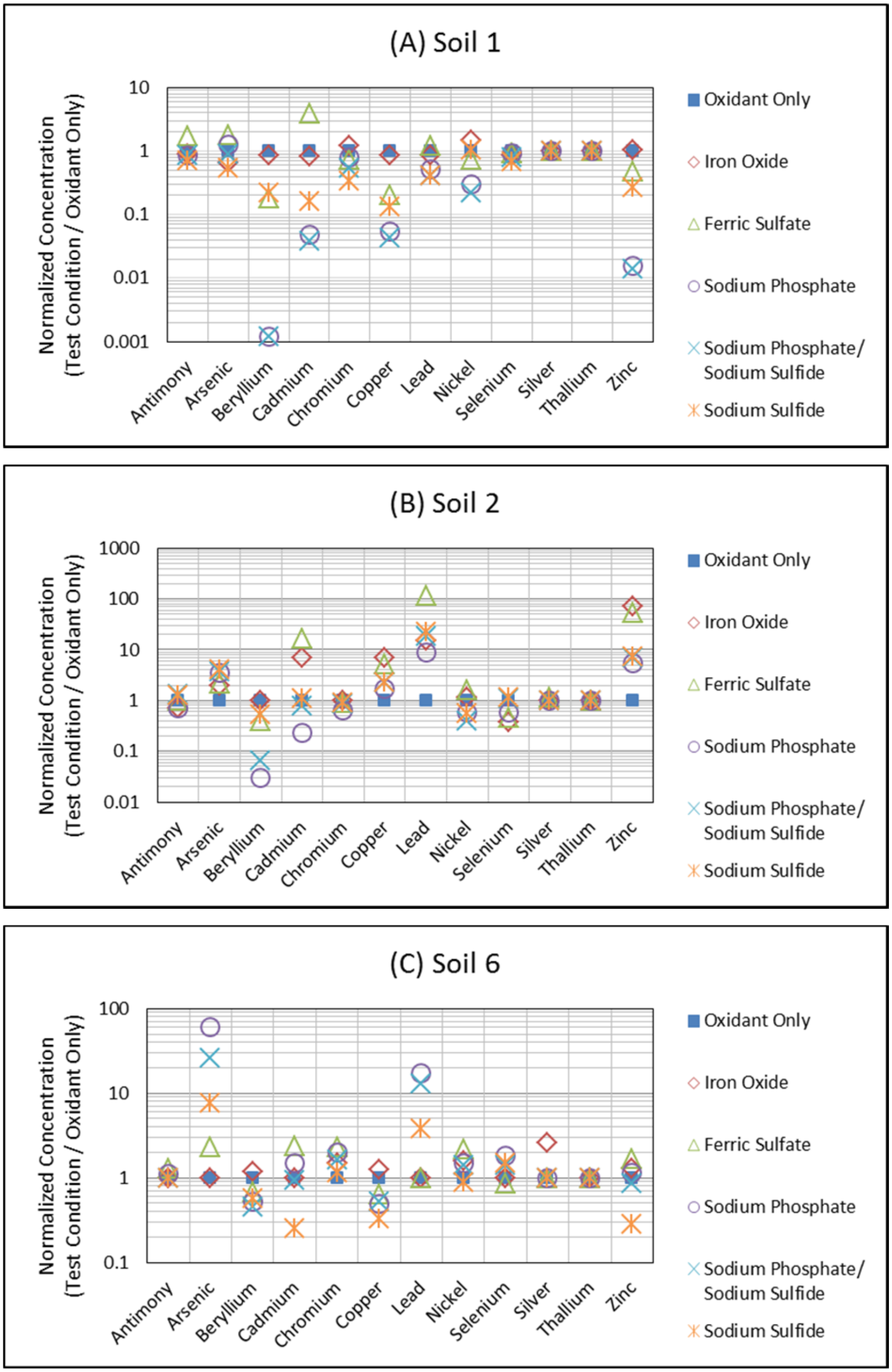


Figure 4.4.12 Pretreatment Stabilization of CHP System: Select normalized metal concentrations for 5 Pretreatment options.

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C).

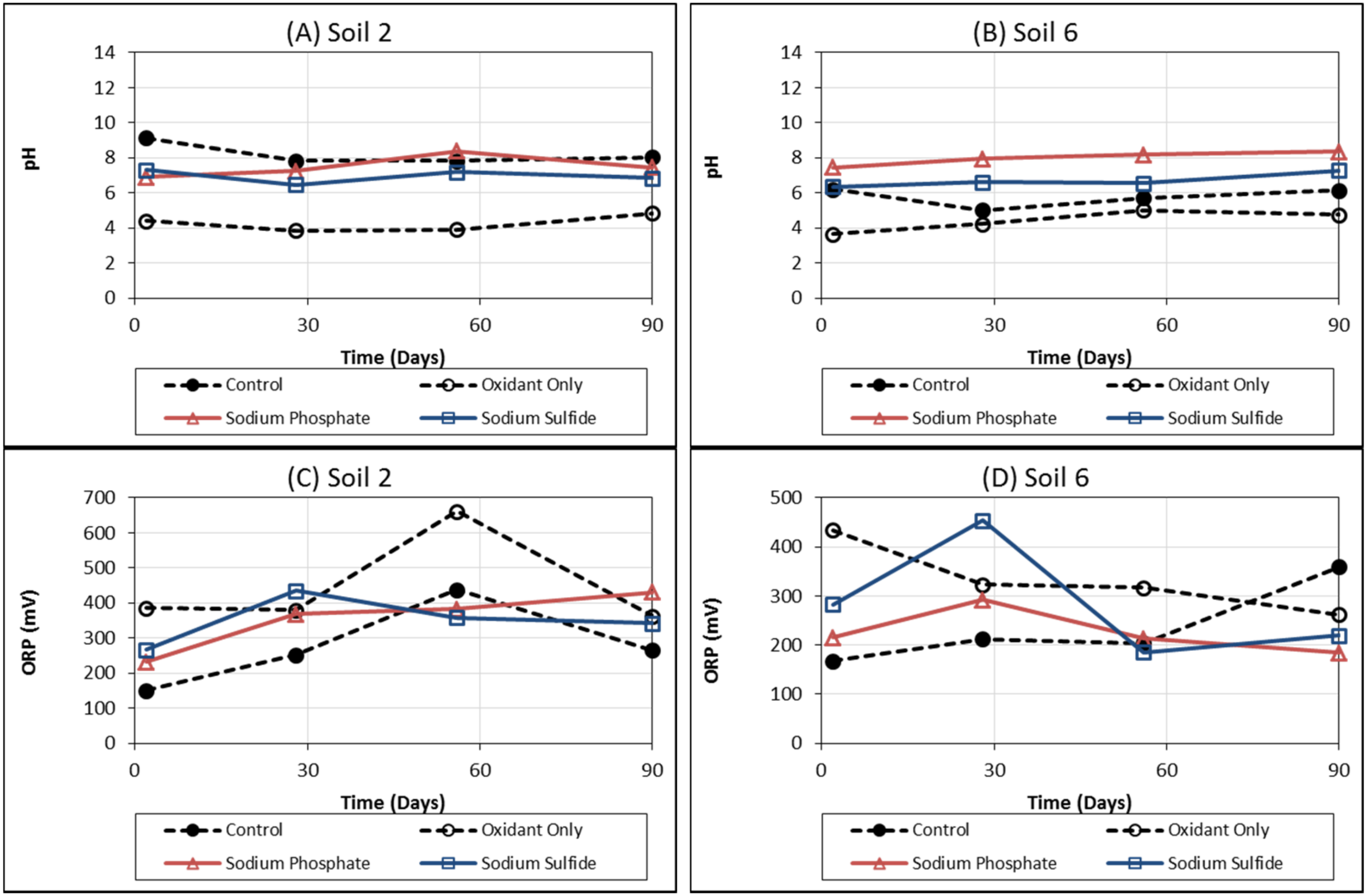


Figure 4.4.13 Pretreatment Stabilization of CHP System: Geochemical parameters at 2, 28, 56, and 90 days

Note: Soil 2 (A, pH, C, ORP) and Soil 6 (B, pH, D, ORP)

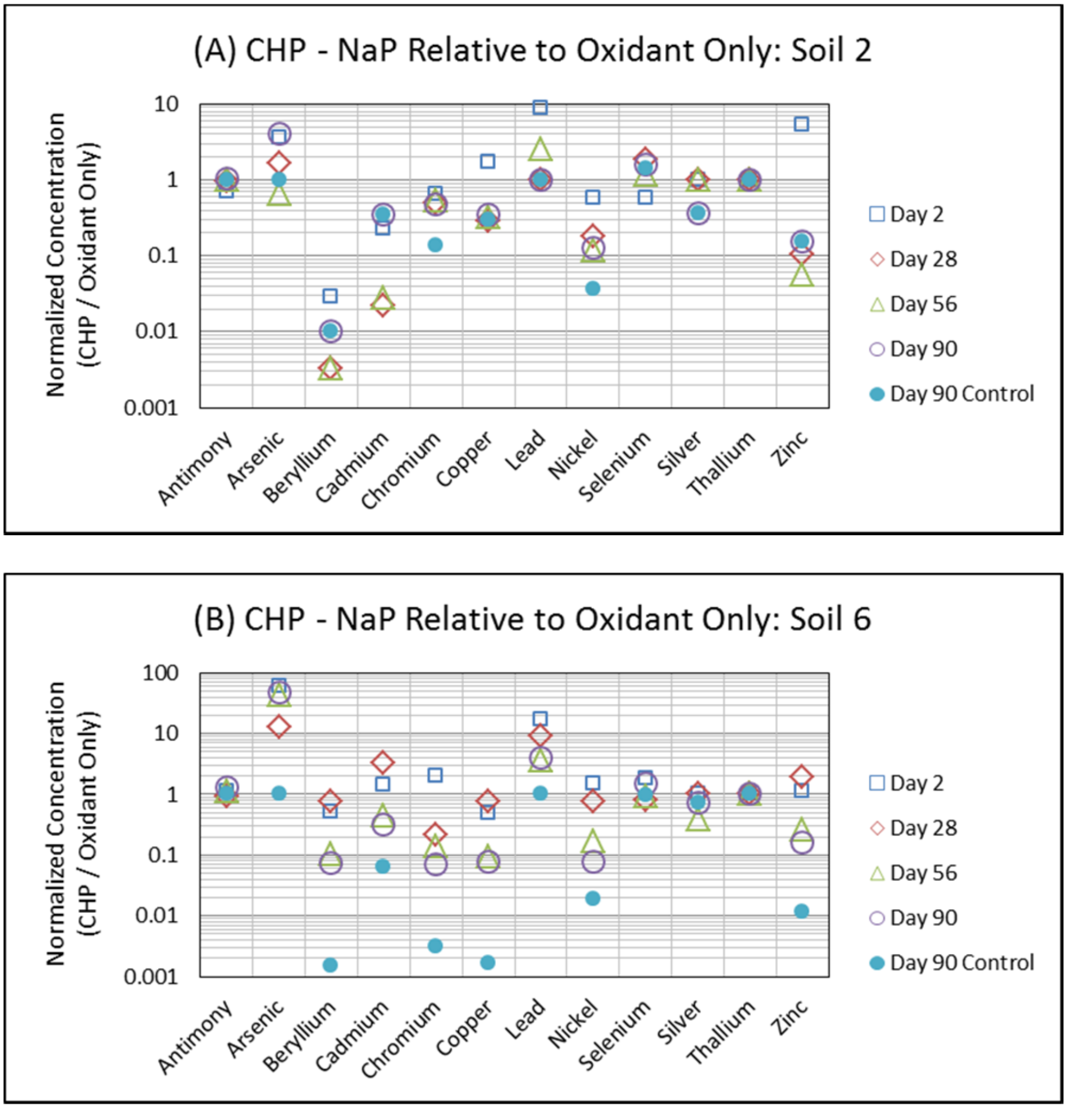
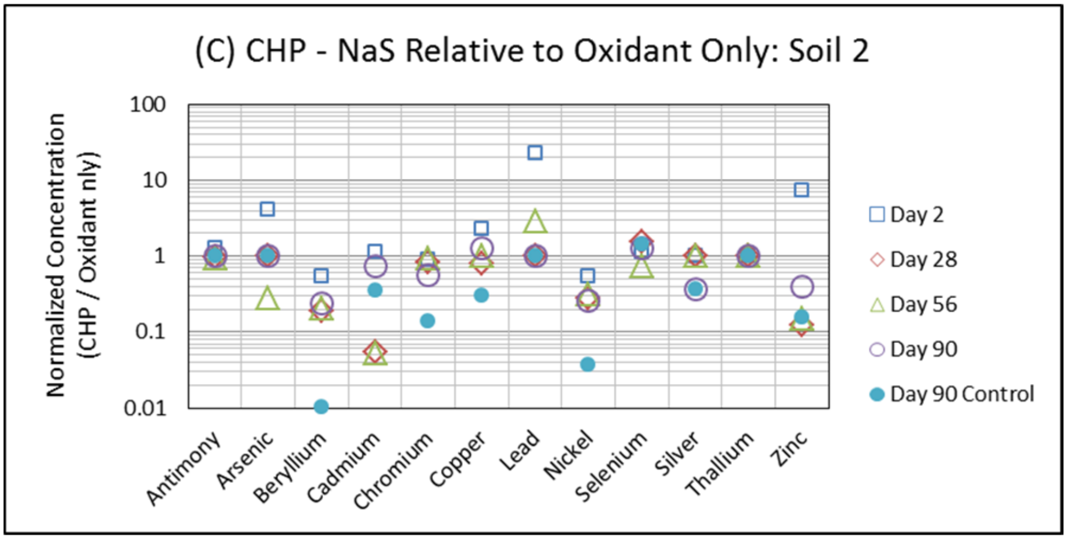


Figure 4.4.14 Pretreatment Stabilization of CHP System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Pretreatment with sodium phosphate (A,B), and sodium sulfide (C,D) for both Soil 2 and 6.



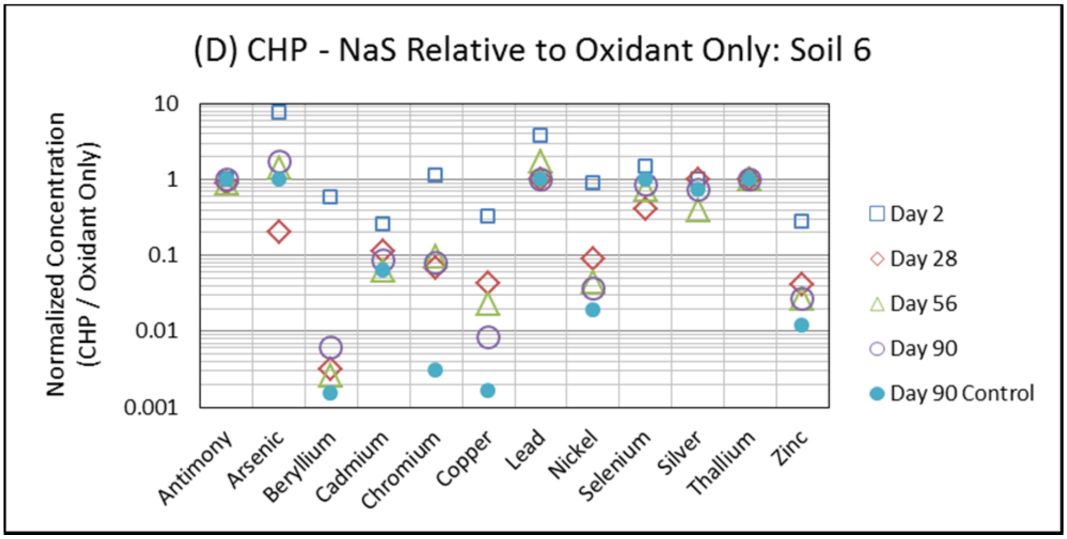


Figure 4.4.13 (cont.) Pretreatment Stabilization of CHP System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Pretreatment with sodium phosphate (A,B), and sodium sulfide (C,D) for both Soil 2 and 6

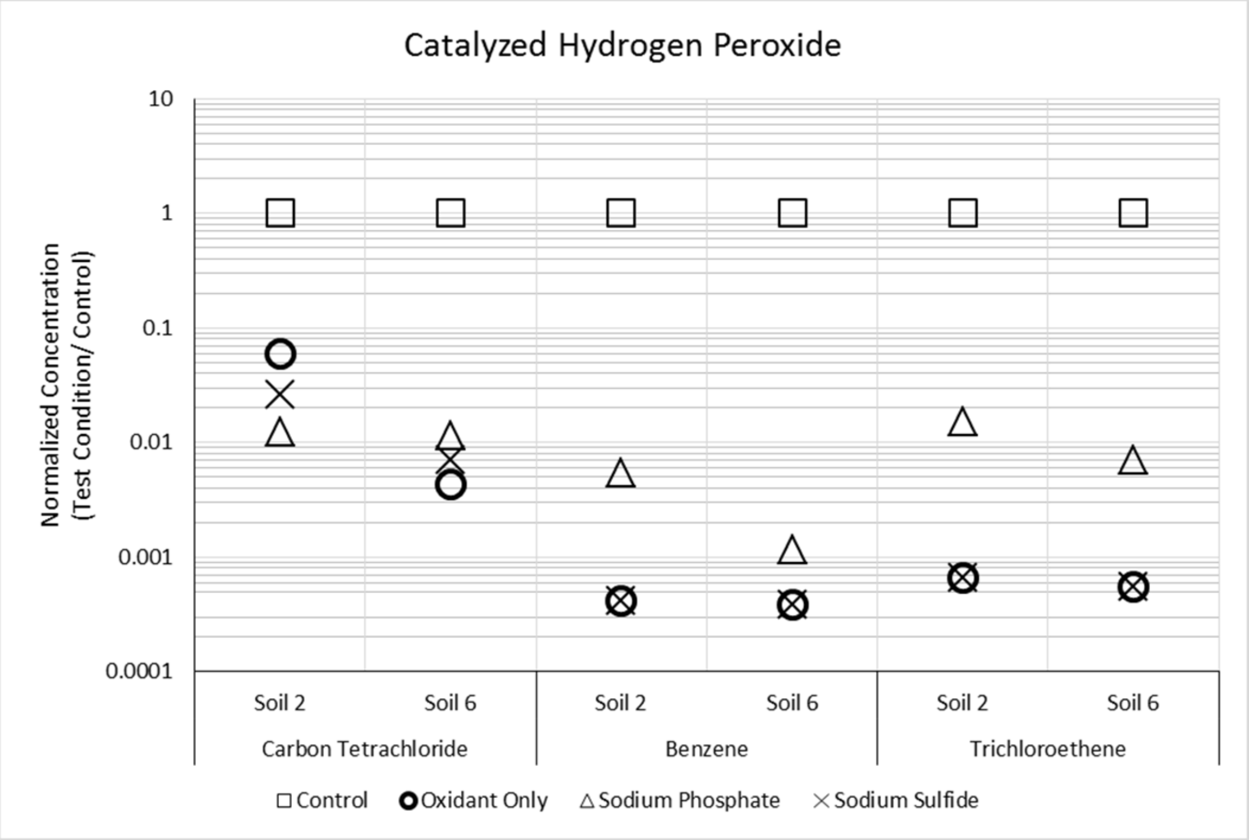


Figure 4.4.15 Pretreatment Stabilization of CHP System: Treatment Efficacy- Normalized Concentrations of probe compounds carbon tetrachloride, benzene, and trichloroethene.

Potassium Permanganate. Figure 4.4.16 shows the concentration of priority pollutant metals in soils treated with potassium permanganate, normalized to the metals concentration in the control reactors for each respective time point for Soils 1, 2, and 6. Priority pollutant metals that evolved from two or more of the soil types evaluated include Be, Cr, Pb, Ag, and Tl. Chromium and Ag were found to be in the highest ratio of concentration in soils treated with potassium permanganate to the control reactors. For Soil 6, concentrations of several metals showed downward trends with time including Ag, Be, Pb, Ni, Se, and Tl. Similar downward trends were not observed with Soil 2.

The concentration of aqueous phase metals, collected after 2 days of contact between potassium permanganate and the pretreated soils normalized to concentrations in soils treated with potassium permanganate only, are presented in Figure 4.4.17. The results varied between the soil types. For Soil 1, the pretreatment with ferric sulfate and sodium sulfide appeared to decrease the ratio of respective concentration of several metals to the soils treated with potassium permanganate only. However, no pretreatment of Soil 2 resulted in lower metal concentrations relative to the potassium permanganate only system, and pretreatment with ferric sulfate resulted in elevated concentrations for several metals. Pretreatment of Soil 6 resulted in a reduction in concentration for several metals and an increase in concentration for other conditions. Again, ferric sulfate resulted in the most consistent increases and decreases in metals concentrations. Based on these results, soils pretreated with ferric sulfate were evaluated over additional time points to evaluate the longer term impacts of soil pretreatment on metals mobilization with potassium permanganate.

The observed pH in the control and permanganate only reactors were similar and typically in the neutral pH range over the course of treatment (Figure 4.4.18). The data also show that the pretreatment of soils with ferric sulfate consistently resulted pH 2 to pH 4 for both soil types throughout the period evaluated. The addition of permanganate resulted in elevated ORP values compared to the control. The pretreatment of soils with ferric sulfate subsequently treated with permanganate resulted in an ORP above the permanganate only system for the entire test period for Soil 2, and for the Day 2 time point for Soil 6. By Day 28, the ORP in the Soil 6 system had decreased to less than the permanganate only system but remained above the ORP observed in the control.

The extended evaluation of ferric sulfate demonstrated that several metals, including Be, Cu, Ni, and Zn, increased in both soil types, and several of those had continual increasing trends. For Soil 6, the addition of ferric sulfate showed modest treatment of Cr, Pb, Ag, and Tl. However, with the exception of the Cr, the other metals returned to concentrations similar to the permanganate only reactor by Day 90.

To assess if this pretreatment also had an impact on the efficacy of permanganate, the degradation of the three probe compounds was evaluated (Figure 4.4.20). The data indicate that soils treated with potassium permanganate only resulted in little to no treatment of carbon tetrachloride or benzene in both soil types after 28 days. Reactors with soils pretreated with ferric sulfate and then contacted with permanganate for 28 days had similar results. Trichloroethene decreased by greater than 99 percent in in systems with soils pretreated with ferric sulfate and in soils treated with permanganate only. . The data indicate that pretreatment with ferric sulfate had little to no effect on the treatment efficacy of potassium permanganate.

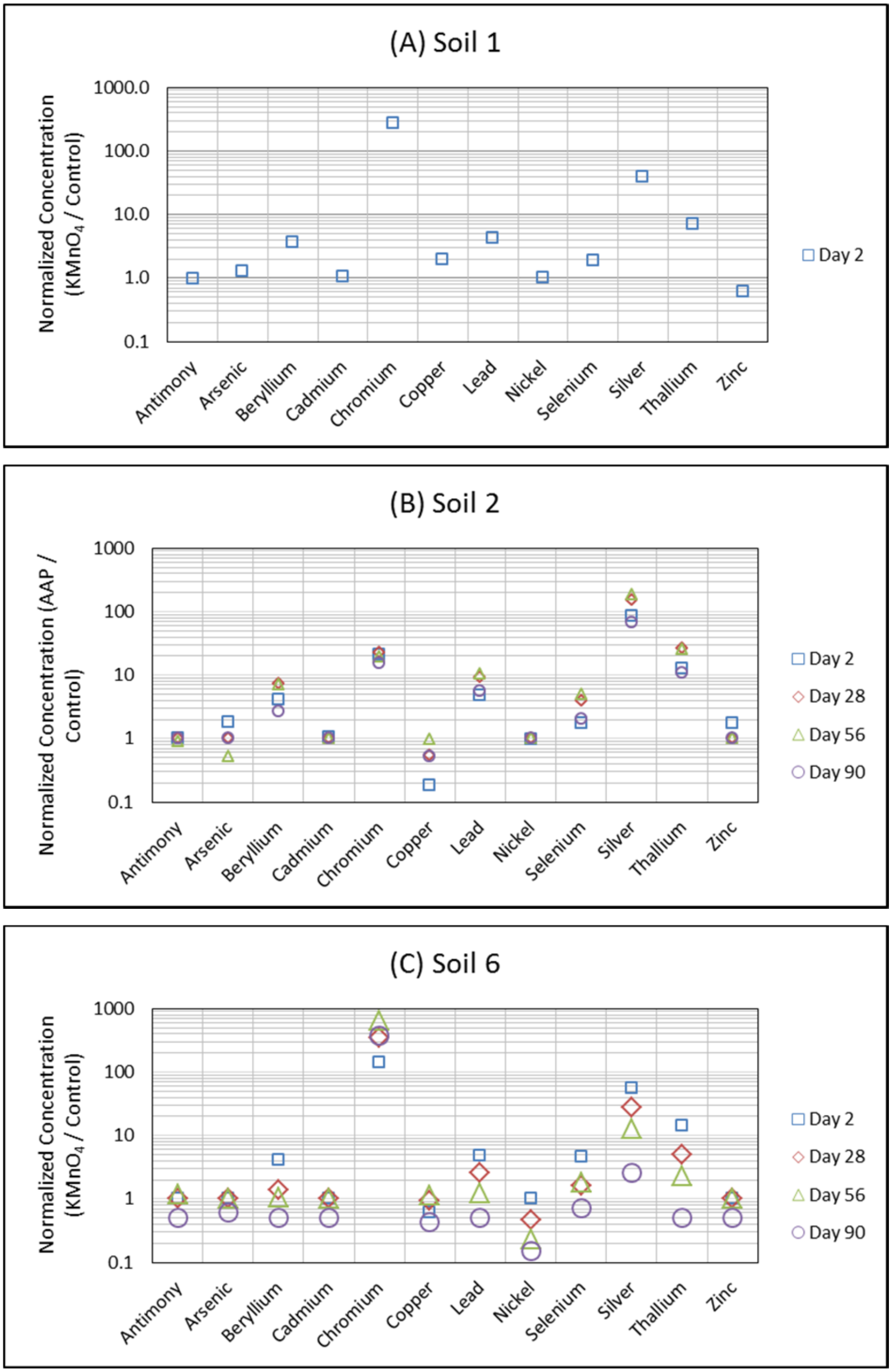


Figure 4.4.16 Pretreatment Stabilization: Normalized concentration of metals for reactors with PM applied versus control conditions (no PM treatment).

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C).

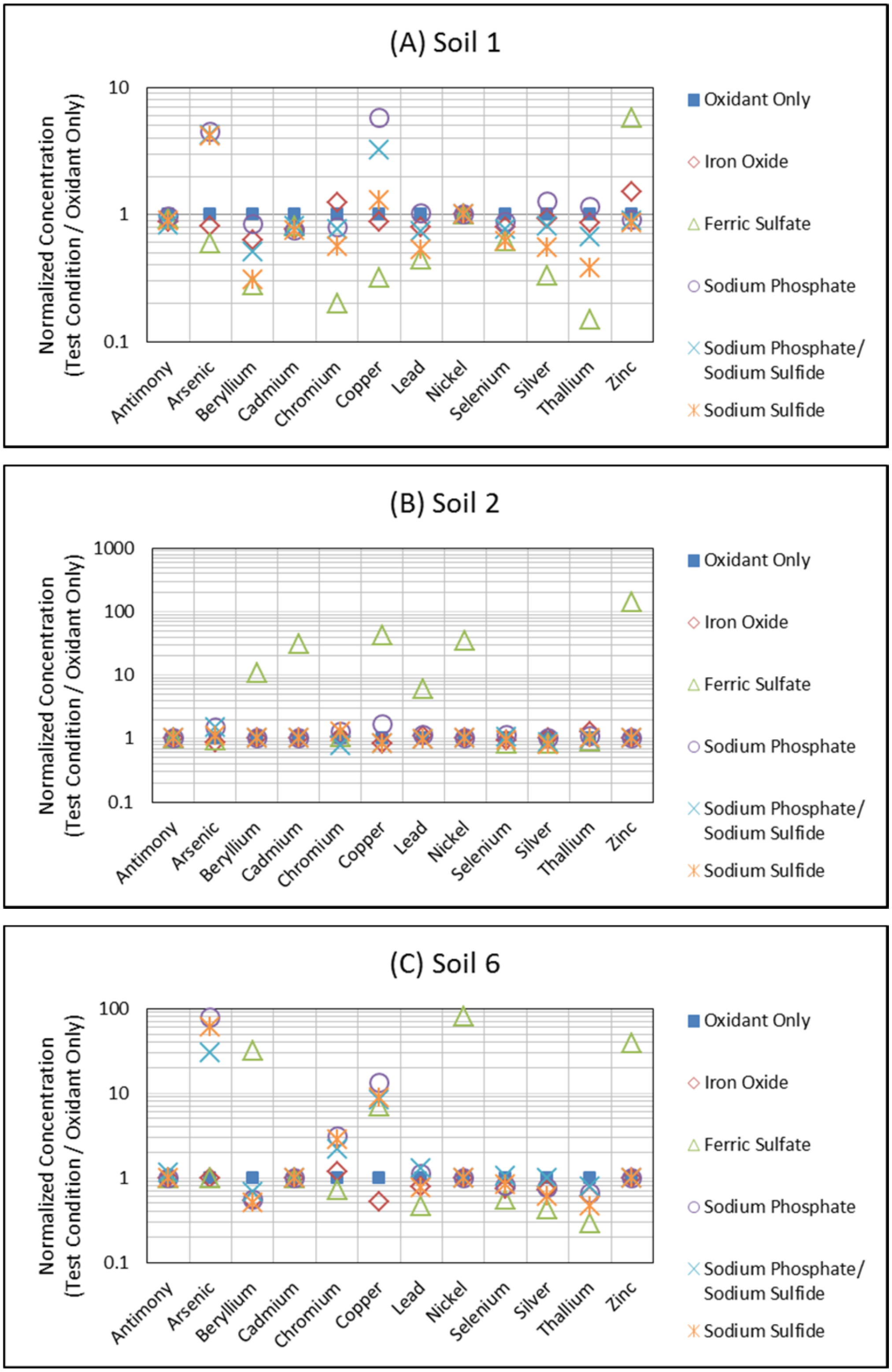


Figure 4.4.17 Pretreatment Stabilization of PM System: Select normalized metal concentrations for 5 Pretreatment options.

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C).

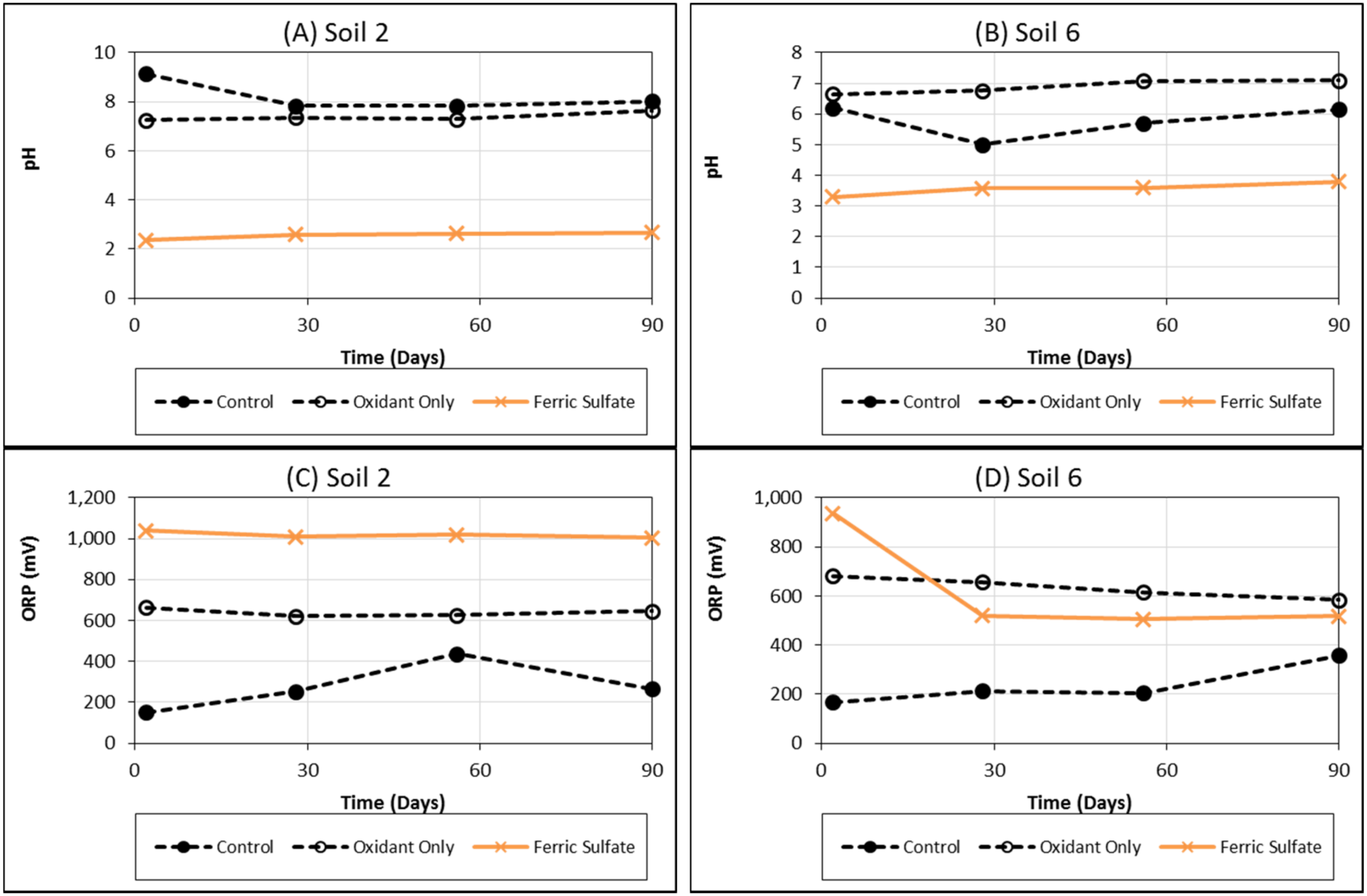
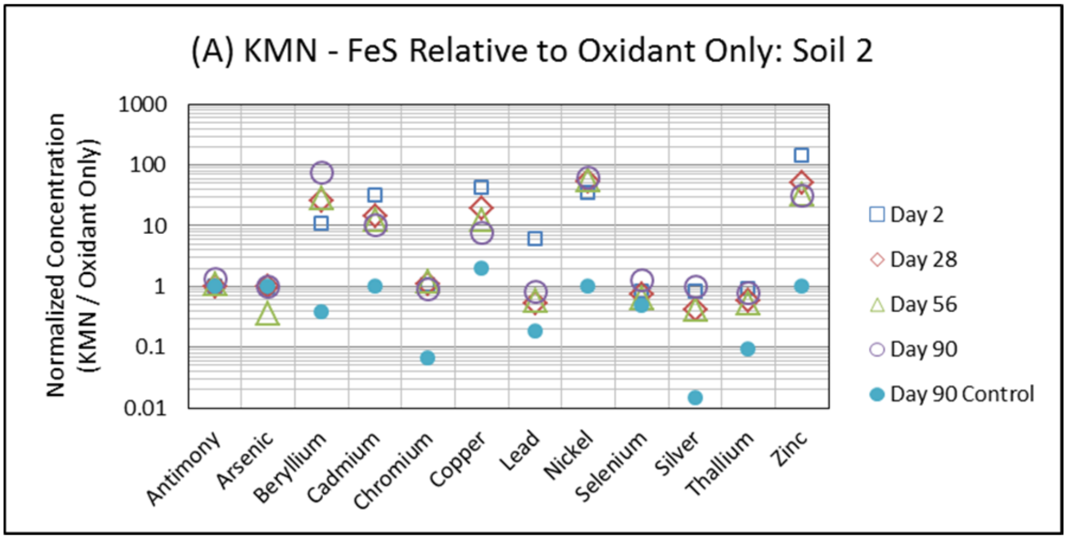


Figure 4.4.18 Pretreatment Stabilization of PM System: Geochemical parameters at 2, 28, 56, and 90 days

Note: Soil 2 (A, pH, C, ORP) and Soil 6 (B, pH, D, ORP)



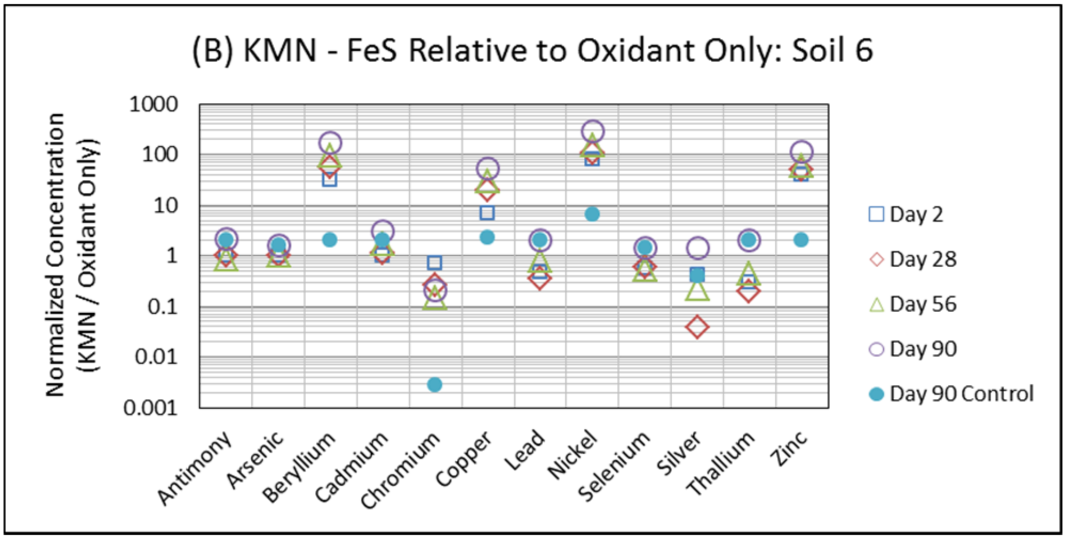


Figure 4.4.19 Pretreatment Stabilization of PM System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Pretreatment with ferric sulfate (A,B) for both Soil 2 and 6.

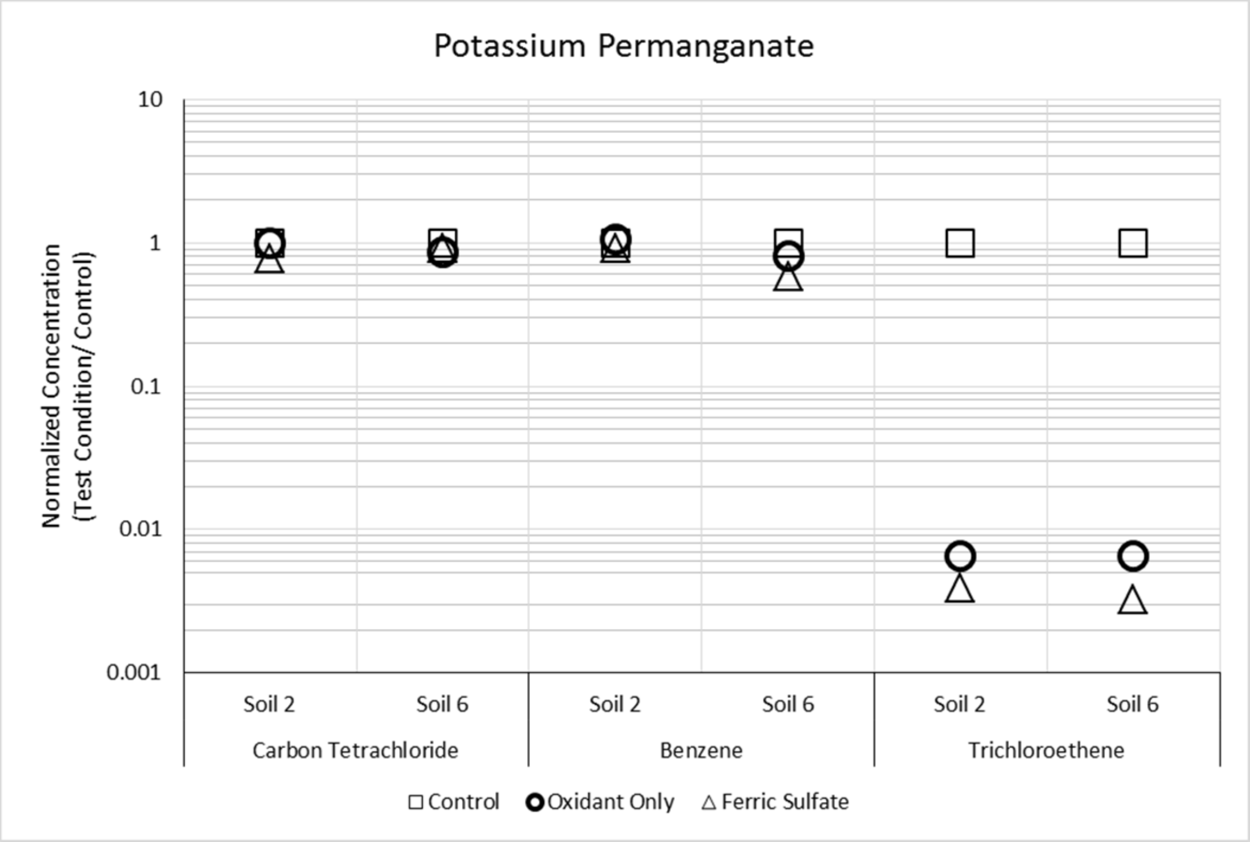


Figure 4.4.20 Pretreatment Stabilization of PM System: Treatment Efficacy- Normalized Concentrations of probe compounds carbon tetrachloride, benzene, and trichloroethene.

4.4.2 Concurrent Biological Stabilization Evaluation

The concurrent biological evaluation was intended to assess the addition of potential biological stimulants to stimulate biotic activity during and following the application of ISCO reagents from a single solution containing both the biological stimulants and ISCO reagents. The premise being tested was if stimulated biotic activity would aid a site in returning to its original baseline geochemical conditions at which time mobilized metals would also return to their original conditions.

The ISCO technologies tested include:

- Alkaline Activated Persulfate (AAP)
- Iron Activated Persulfate (IAP)
- Catalyzed Hydrogen Peroxide (CHP)
- Potassium Permanganate ($KMnO_4$)

Data was gathered for 22 metals during these experiments. The discussion of the data presented in this section will focus on metals that are listed as priority pollutants under the Safe Drinking Water Act as Task 4 is intended to help identify methods to mitigate the mobilization of metals of environmental concern. These metals include silver (Ag), arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), thallium (Tl), and zinc (Zn). Mercury (Hg) is also listed as a priority pollutant but was not analyzed for during these experiments.

Alkaline-Activated Persulfate. Figure 4.4.21 presents the concentrations of the selected priority pollutant metals in reactors treated with AAP only normalized to the metal concentrations found in the control reactor (water only) for each respective time point for Soils 1, 2, and 6. The data show that the concentration of several metals in the presence of the AAP solution was greater the concentration of the same metals in the control reactors. Concentrations of As and Cr were higher in reactors containing AAP compared to the control reactors for each soil type. The degree of the increase varied with the impacts observed in Soil 6 greater than those observed in Soil 1 or 2. Concentrations of Cu, Ni, and Pb were observed to be higher in reactors containing AAP compared to the controls for at least one soil type. The concentration of Ni in the AAP reactors was less than that of the controls for Soil 6. Time trends could also be observed in Figure 4.4.21. The ratio of Cr in the AAP reactors compared to the control tended to increase over time; whereas the concentration of Cu and Ni tended to decrease over time.

Figure 4.4.22 presents concentrations of selected priority pollutant metals in reactors with biological stimulants added to the AAP solution normalized to the metals concentration in the reactors treated with AAP only, for each soil type after 90 days of contact. These data show that the concentrations of most of the priority pollutant metals were unchanged or increased as a result of treatment with the biological stimulants. The concentration of As in the Soil 6 reactors decreased for each treatment condition with the exception of citrate and concentrations of Cr decreased in the Soil 2 reactors. These decreases were not consistent with the observed results with the other soil types.

Table 4.4.1 presents the results of the heterotrophic plate counts collected after 90 days of contact. With the exception of the whey protein treatment condition, plate counts were below the detection limit of 100,000 CFUs in all test reactors with AAP. The presence of whey resulted in plate counts greater than the control for each soil type. However, this is thought to be the result of whey rapidly reacting with the persulfate solution and potentially impacting the efficacy of the ISCO treatment. One of the duplicate reactors treated with citrate in the presence of Soil 2 had detectable plate counts, although lower when compared to the control. The below detection limit of 100,000 CFUs may be a function of the controlled system with complete contact for an extended period of time that was achieved in the batch reactors. This is not likely to occur in field events.

Based on the screening level results for the AAP system, none of the biological stimulants tested were selected for further evaluation with AAP. This conclusion was due to the lack of significant reductions in metals concentrations after treatment, coupled with frequent increases in metals concentration after biological stimulant treatment.

Table 4.4.1 Biological activity represented by colony forming units (CFU/100mL) determined by heterotrophic plate counts in an AAP system treated with biological stimulants.

Test Condition	**Microbial Population after 90 Days (log CFUs)**		
	SOIL 1	**SOIL 2**	**SOIL 6**
Control	8.84	6.35	6.81
AAP with Amendments			
AAP Only	< 5.00	< 5.00	< 5.00
Acetate, Phosphate, Nitrate	< 5.00	< 5.00	< 5.00
Citrate, Phosphate, Nitrate	< 5.00	< 5.00	< 5.00
Lactate, Phosphate, Nitrate	< 5.00	< 5.00	< 5.00
Phosphate, Nitrate	< 5.00	< 5.00	< 5.00
Soybean Oil, Phosphate, Nitrate	< 5.00	< 5.00	< 5.00
Whey Protein, Phosphate, Nitrate	9.77	9.39	9.11

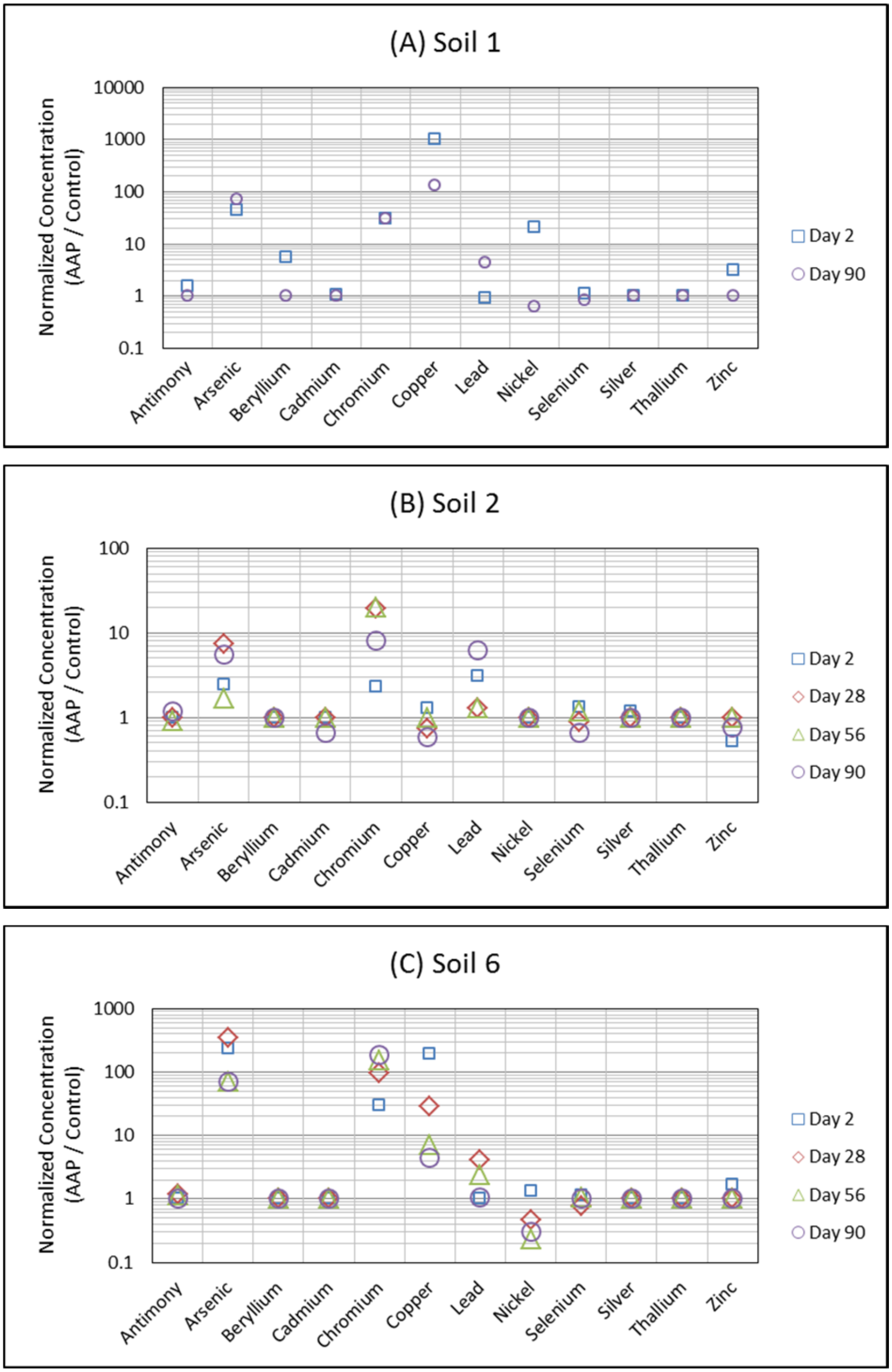


Figure 4.4.21 Co-Treatment Biological Stabilization: Normalized concentration of metals for reactors with AAP applied versus control conditions (no AAP treatment).

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C).

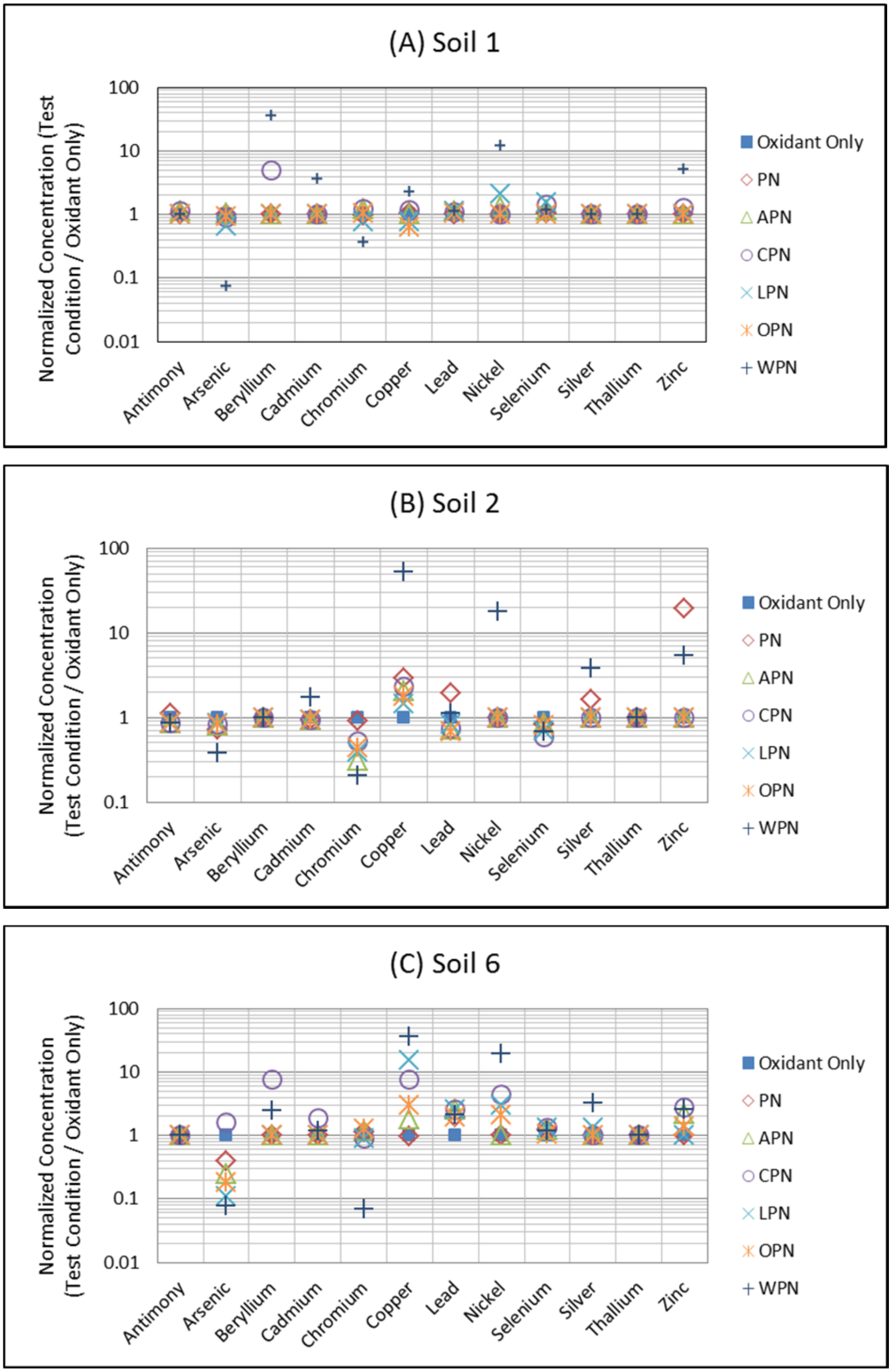


Figure 4.4.22 Co-Treatment Biological Stabilization of AAP System: Select normalized metal concentrations for 6 biological treatment options.

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C).

Iron-Activated Persulfate. Figure 4.4.23 shows the concentrations of the selected priority pollutant metals in reactors treated with IAP only normalized to the metal concentrations in the control reactors (water only) for each respective time point for Soils 1, 2, and 6. Figure 4.4.23A shows that Be, Cd, Cr, Cu, Pb, Ni, and Zn were all mobilized with the addition of IAP to Soil 1. Figure 4.4.23B shows significant metals mobilization of Sb, As, Cr, Pb, Ni, Se Tl and Zn with the addition of IAP to Soil 2. Figure 4.4.23C shows that Be, Cd, Cr, Cu, Ni, and Zn were mobilized with IAP addition to Soil 6 reactors. The data shows that Cr, Ni, and Zn were mobilized for each soil type and Be, Cd, Cu, Pb, Se, and Tl increased in concentration after treatment with IAP in the presence of at least one soil type.

Figure 4.4.24 shows the concentrations of metals after 90 days in reactors with IAP amended with biological stimulants normalized to the metal concentrations in the reactors treated with IAP only, for Soils 1, 2, and 6. IAP systems with acetate and citrate resulted in lower concentrations of several metals compared to reactors with IAP only for all three soil types. Conversely, the data also indicate that the concentration of several metals increased with the addition of the organic substrates, most notably soybean oil and whey.

The final screening test involved the assessment of the impact of each treatment condition on the biological activity as measured by colony forming units (CFUs) after 90 days of contact. As shown in Table 3.15, systems treated with IAP only decreased biological activity to below the method detection limit. The data indicate that the addition of several of the biological stimulants increased the number of CFUs observed in those systems. In Soil 1, the CFUs in the presence IAP amended with acetate, citrate and whey were greater than the IAP only system. In Soil 2, IAP amended with citrate/phosphate/nitrate, lactate/phosphate/nitrate), and whey/phosphate/nitrate treatment conditions resulted in more CFUs than the IAP only system. For Soil 6, only IAP amended with whey/phosphate/nitrate showed any recovery of biological activity.

Based on the screening data, acetate and citrate were chosen for further evaluation over additionnal time points to evaluate the longer term impacts of biological stimulants on metals mobilization with IAP. The additional evaluation involved collecting data from time points at 2, 28, 56 and 90 days of contact with IAP amended with the biological stimulants in the presence of Soil 2 and Soil 6. Additional evaluation was not conducted on Soil 1 as it was depleted during the screening tests.

The observed pH and ORP for both soil types is presented in Figure 4.4.25. For both Soil 2 (Figure 4.4.25A) and Soil 6 (Figure 4.4.25B), addition of the unamended IAP reagents resulted in a lower pH compared to the control by Day 28 and Day 2, respectively. The presence of acetate and citrate with the IAP reagents helped maintain pH similar to the control reactor. For both soil types, the IAP only resulted in an ORP of up to 600 to 700 mV. The presence of the citrate and acetate with the IAP resulted in a diminished ORP.

Figure 4.4.26 shows the change in concentration for the priority pollutants over time in the IAP system with each of the selected biological treatments. As shown in Figure 4.4.26A and 4.4.26B, the addition of acetate to IAP with Soils 2 and 6 resulted in lower concentrations of Be, Cd, Cr, Cu (Soil 6), Ni and Zn as compared to IAP only reactors for the respective metals. In several of the instances, the concentration of these metals was close to or below the observed concentration in the control reactor (no oxidant) at Day 90. In reactors with the citrate amended

IAP, concentrations of Be and Zn in the Soil 2 system (Figure 4.4.26C) and concentrations of Be, Cu, Pb, Ni and Zn in the Soil 6 system (Figure 4.4.26D) were lower compared to the observed concentrations in the reactors with IAP only.

To evaluate the potential impact of the biological stimulants on the efficacy of the IAP, the degradation of three common contaminants (carbon tetrachloride, benzene, and trichloroethene) were evaluated (Figure 4.4.27). As IAP is not known to treat carbon tetrachloride, the data shows little treatment, as expected. In systems containing IAP only, benzene was reduced by 44 percent (Soil 2) and 95 percent (Soil 6). The addition of citrate into the IAP system decreased the percent reduction of benzene to 15 percent (Soil 2) and 56 percent (Soil 6). The addition of acetate into the IAP system resulted in a similar level of treatment as IAP only (46 percent reduction) for Soil 2, but decreased the treatment of benzene in Soil 6 from 95 percent reduction in reactors with IAP only to 54 percent reduction in the acetate amended IAP system. The concentration of TCE in the systems treated with IAP was reduced by 24 percent (Soil 2) and 83 percent (Soil 6) compared to the controls. The addition of citrate into the IAP system reduced the treatment of TCE to 5 percent (Soil 2) and 51 percent (Soil 6), and the addition of acetate to the IAP system increased the treatment of TCE in Soil 2 (38 percent) and decreased treatment of TCE in Soil 6 (53 percent).

Table 4.4.2 presents the impact of each treatment condition on the biological activity as measured by CFUs after 90 days of contact with amended and unamended IAP. The addition of IAP resulted in a measured microbial population lower than the control for all soil types. Only Soil 2 reactors amended with citrate, lactate and whey resulted in plate counts greater than the control. Soil 1 reactors amended with acetate, citrate and whey, Soil 2 reactors amended with acetate, and Soil 6 reactors amended with whey all had detectable microbial populations; however, they were lower than the control. With the exception of the whey protein treatment condition, plate counts were below the detection limit of 100,000 CFUs in all Soil 6 test reactors with IAP.

Table 4.4.2 Biological activity represented by colony forming units (CFU/100mL) determined by heterotrophic plate counts in an IAP system treated with biological stimulants.

Test Condition	**Microbial Population after 90 Days (log CFUs)**		
	SOIL 1	**SOIL 2**	**SOIL 6**
Control	8.84	6.35	6.81
IAP with Amendments			
IAP Only	< 5.00	< 6.00	< 5.00
Acetate, Phosphate, Nitrate	8.35	5.40	< 5.00
Citrate, Phosphate, Nitrate	8.45	8.59	< 5.00
Lactate, Phosphate, Nitrate	< 5.00	8.10	< 5.00
Phosphate, Nitrate	< 5.00	< 6.74	< 5.00
Soybean Oil, Phosphate, Nitrate	< 5.18	< 5.00	< 5.00
Whey Protein, Phosphate, Nitrate	6.62	6.41	6.41

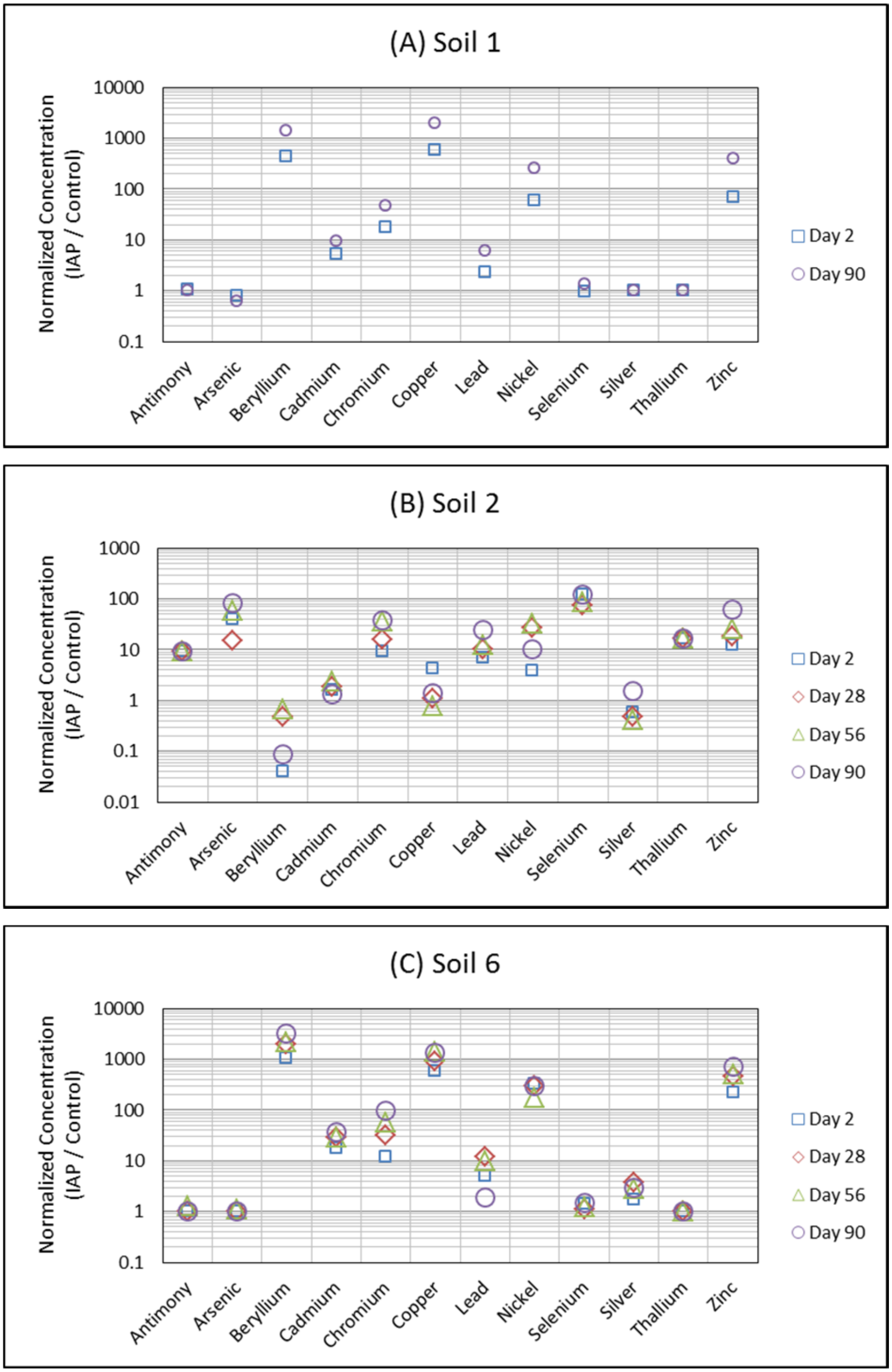


Figure 4.4.23 Co-Treatment Biological Stabilization: Normalized concentration of metals for reactors with IAP applied versus control conditions (no IAP treatment).

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C).

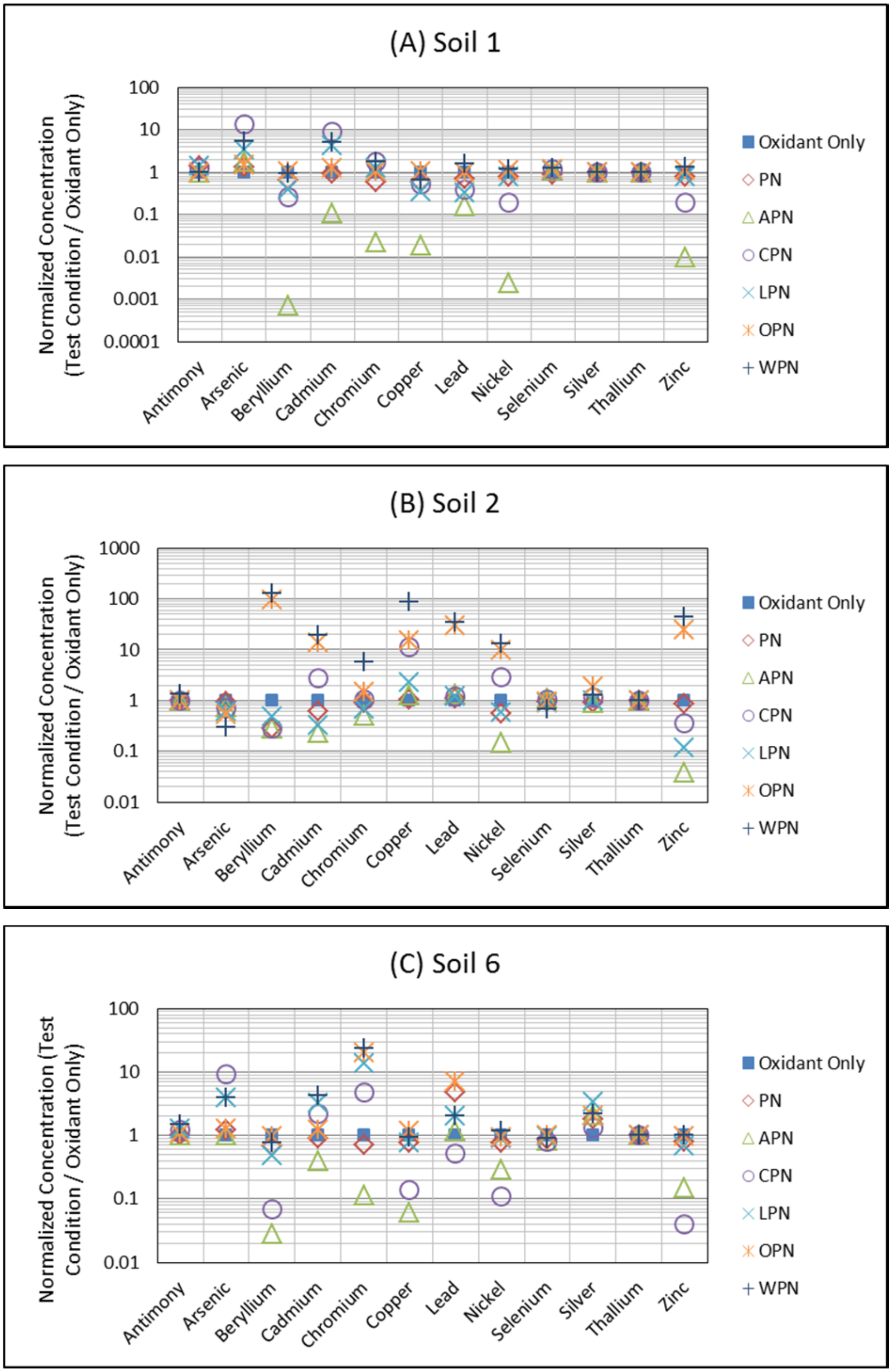


Figure 4.4.24 Co-Treatment Biological Stabilization: Select normalized metal concentrations for 6 biological treatment options

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C).

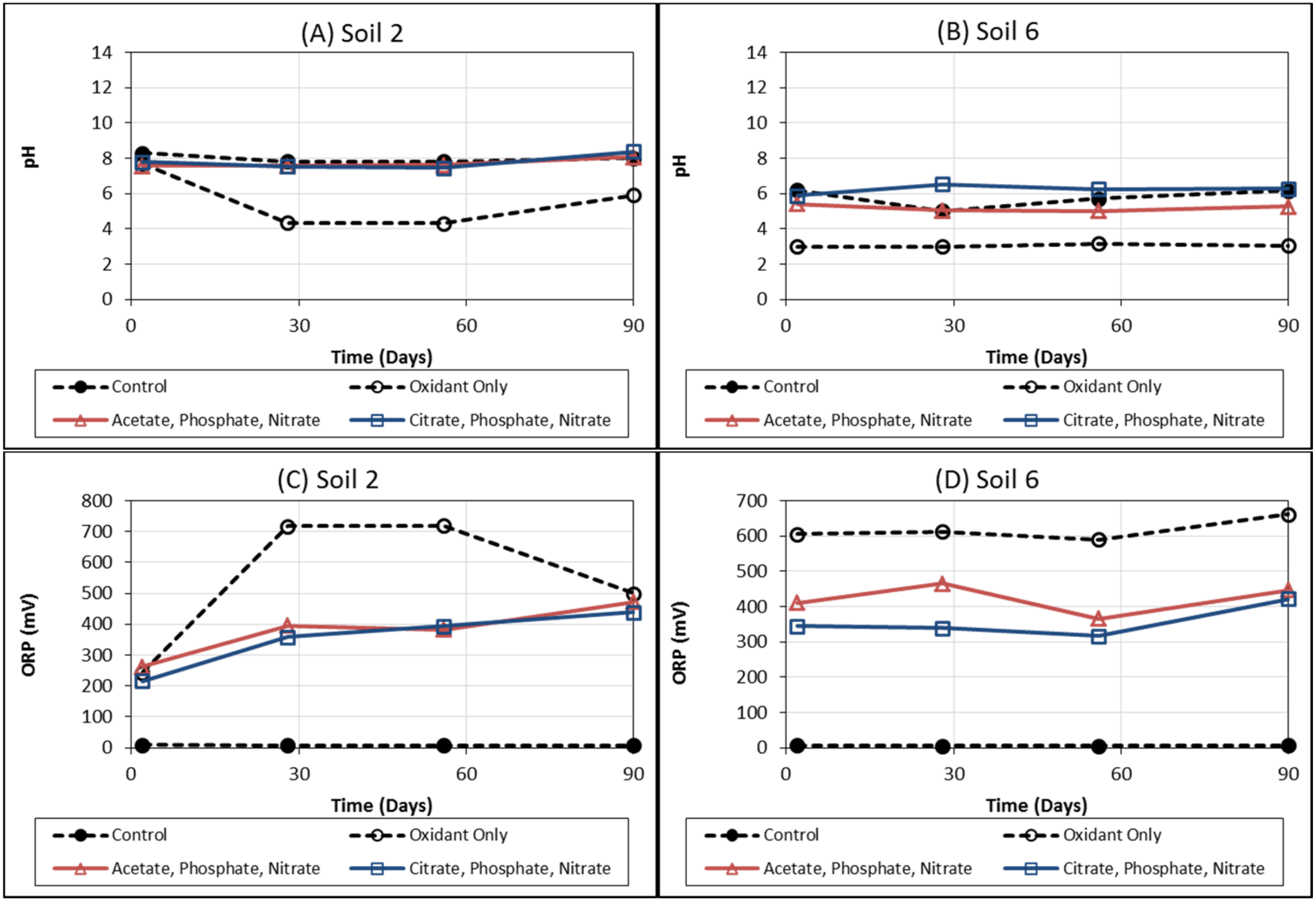


Figure 4.4.25 Co-Treatment Biological Stabilization of IAP System: Geochemical parameters at 2, 28, 56, and 90 days

Note: Soil 2 (A, pH, C, ORP) and Soil 6 (B, pH, D, ORP)

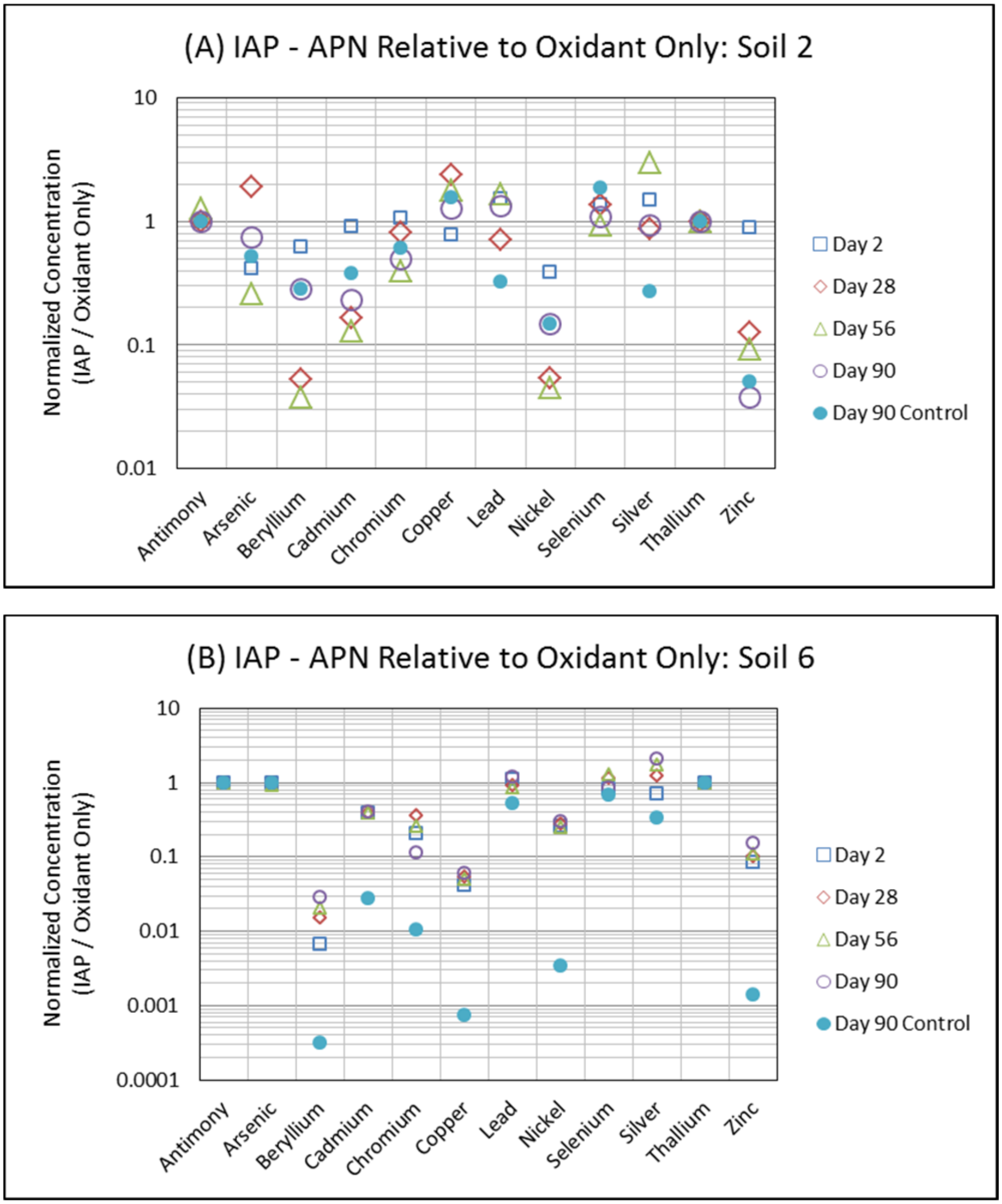


Figure 4.4.26 Co-Treatment Biological Stabilization of IAP System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Biological Co-treatment with APN (A,B), and CPN (C,D) for both Soil 2 and 6

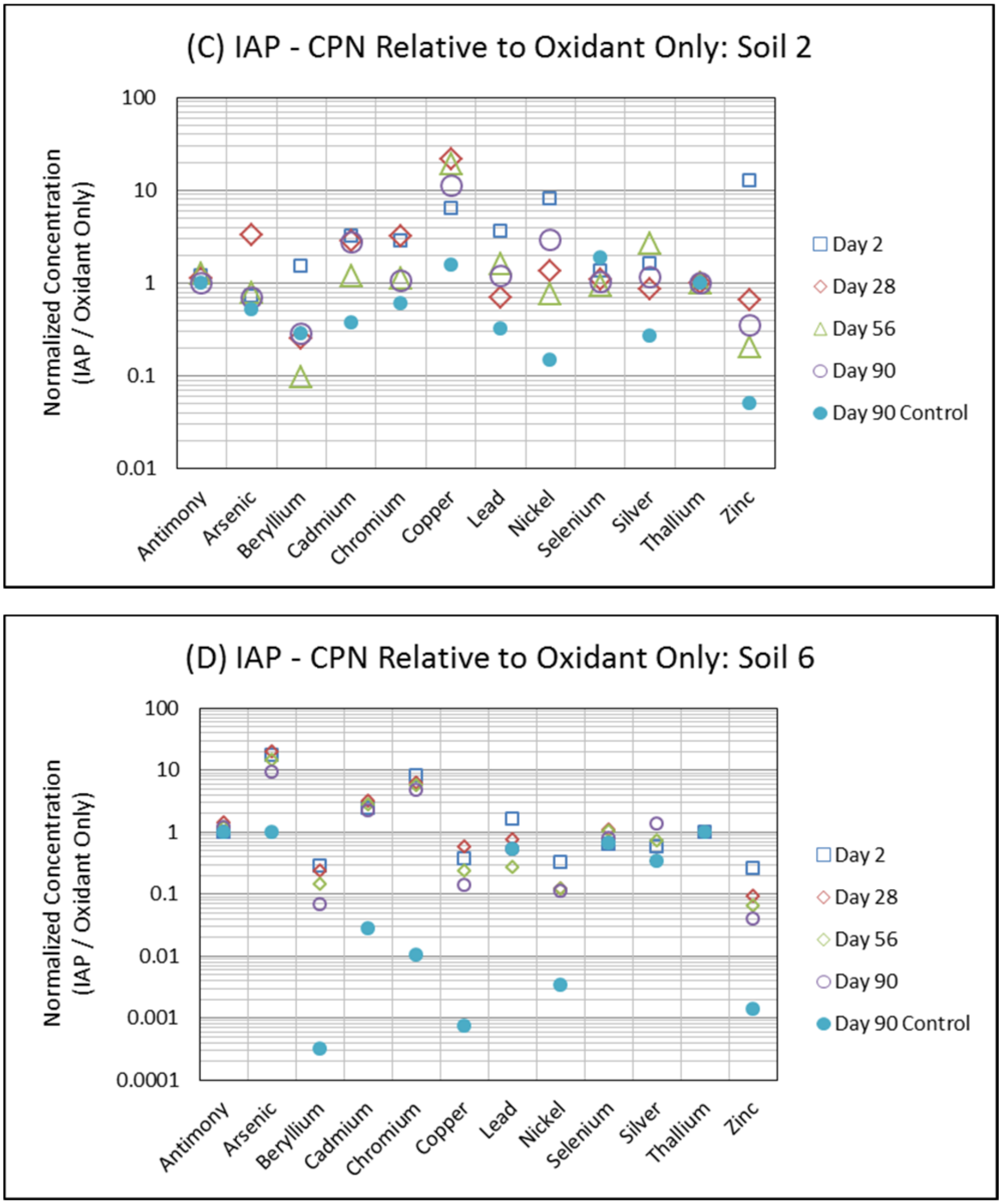


Figure 4.4.26 (cont.) Co-Treatment Biological Stabilization of IAP System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Biological Co-treatment with APN (A,B), and CPN (C,D) for both Soil 2 and 6

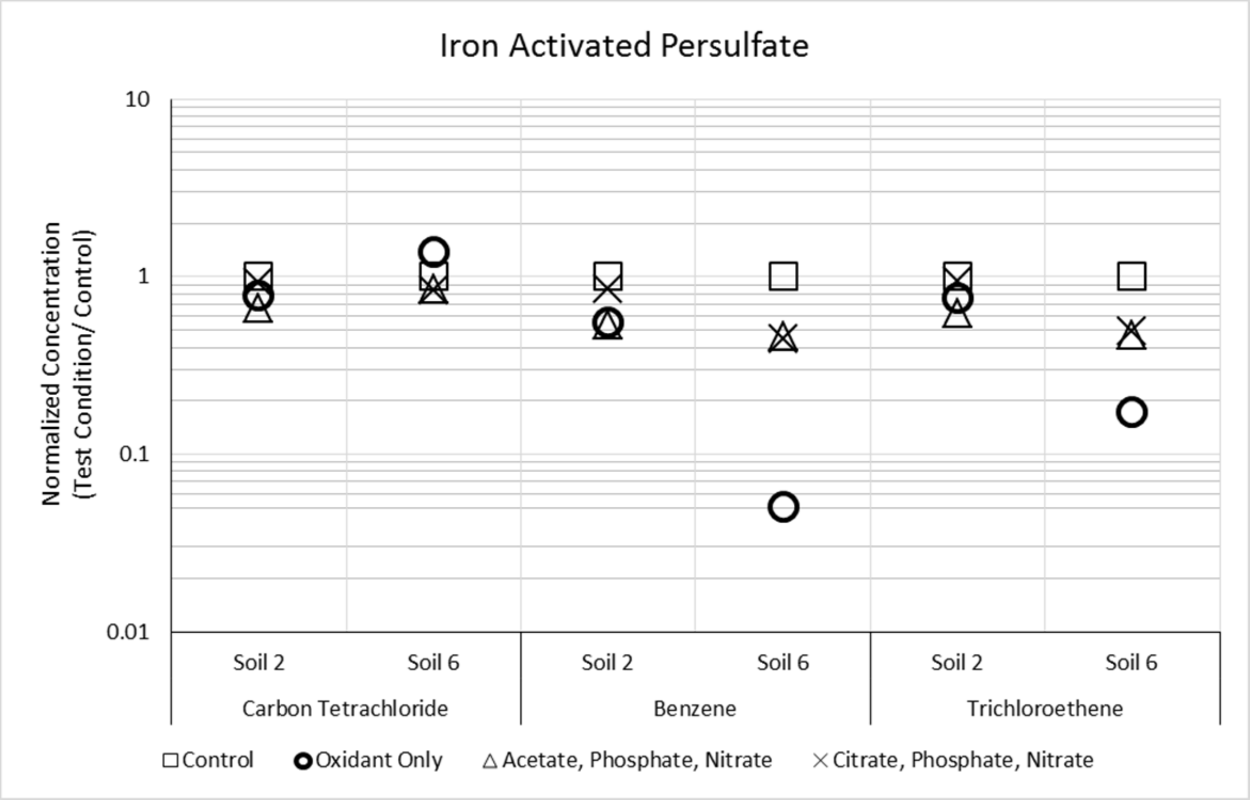


Figure 4.4.27 Co-Treatment Biological Stabilization of IAP System: Treatment Efficacy-Normalized Concentrations of probe compounds carbon tetrachloride, benzene, and trichloroethene.

Catalyzed Hydrogen Peroxide. Figure 4.4.28 shows the concentrations of the selected priority pollutant metals in reactors treated with CHP only, normalized to the metal concentrations in the control reactors (water only) for each respective time point for Soils 1, 2, and 6. The data show that the concentration of Be, Cd, Cr, Cu, Ni, and Zn in reactors treated with CHP were higher than the control reactors for Soils 1, 2 and 6. The data also show significant reducing trends with time for Soils 1 and 2. After 90 days of contact with CHP, each metal in Soil 1 (Figure 4.4.28A) had decreased closer to the control, except for Ni and Cr which decreased to a lower concentration than the control. After 90 days of contact, concentrations of each metal in Soil 2 (Figure 4.4.28B) had decreased to near the control. However, as presented in Figure 4.4.28C, each of the metals concentrations remained elevated compared to the control in the presence of Soil 6.

Figure 4.4.29 shows the concentrations of metals after 90 days in reactors with CHP amended with biological stimulants normalized to the metal concentrations in the reactors treated with CHP only for Soils 1, 2, and 6. The normalized data show that for Soil 1 and Soil 2, the addition of the biological stimulants resulted in an increase in metals concentration compared to the reactors with CHP only, with few exceptions. The data for Soil 6 (Figure 4.4.29C) show that for each of the metals shown to be mobilized in Figure 4.4.28, the addition of several biological stimulants resulted in lower metal concentrations compared to the CHP only reactors. In particular, the addition of acetate, citrate, phosphate and nitrate, and lactate (for some metals) all appeared to have a beneficial effect for Soil 6.

Based on the screening data, acetate and citrate were chosen for further evaluation over additional time points to evaluate the longer term impacts of biological stimulants on metals mobilization with CHP. The additional evaluation involved collecting data from time points after at 2, 28, 56 and 90 days of contact with CHP amended with the biological stimulants in the presence of Soil 2 and Soil 6. Additional evaluation was not conducted on Soil 1 as Soil 1 was depleted during the screening tests.

Figure 4.4.30 presents the geochemical parameters measured for each treatment condition at each time point. The data show that the addition of acetate and citrate to the CHP systems resulted in pH values closer to neutral than the reactors with CHP only. The modification to the pH was observed within 2 days of contact, which could be attributed to pH buffering; however, the pH in the CHP reactors amended with acetate and citrate increased with time indicating the potential for a second mechanism.

The addition of citrate and acetate to the CHP system also resulted in more reducing conditions compared to the CHP only reactors over the 90 day period evaluated (Figure 4.4.30C and D). For both soil types, an ORP between 200 mV and 400 mV was observed for the control and the CHP only reactors after 90 days of contact. Comparatively, the ORP in the reactors amended with citrate and acetate ranged between 0 mV and -200 mV after 90 days of contact. The ORP in the acetate and citrate amended systems for both soil types decreased throughout the experiment.

The moderated pH, steady reduction in ORP and increase in microbial population do indicate that the addition of selected electron donors with CHP can stimulate microbial activity and help return soils to neutral pH and reducing conditions.

Figure 4.4.31 shows the concentration of priority pollutant metals in CHP reactors amended with acetate and lactate normalized to the concentrations in CHP only reactors at Days 2, 28, 56, and 90. For Soil 2, the data show that most priority pollutant metal concentrations in the CHP only reactors were close to the control reactors by 90 days. The return to control conditions over time corresponds with the CHP only system returning to near-baseline pH conditions (see Figure 4.4.31A). The addition of acetate resulted in concentrations of Be, Cd, Cu, Ni, and Zn decreasing in the presence of CHP sooner than 90 days. In Soil 6, the addition of acetate to CHP resulted in concentrations of Cd, Cu, Ni, and Zn lower than CHP only. The amendment of CHP with acetate and citrate typically resulted in concentrations lower than the CHP only reactors in Days 28, 56 and 90. The data for each presented metal for CHP reactors amended with acetate and citrate show decreasing trends over the period evaluated, and a return to near control level concentrations by Day 90, with the exception of Ni in the acetate amended system, which was below the CHP only concentration.

To evaluate the potential impact of the biological stimulants on the efficacy of the CHP, the degradation of carbon tetrachloride, benzene, and trichloroethene were evaluated. Figure 4.4.32 shows the concentrations of probe compounds in systems treated with CHP, both with and without the addition of biological stimulants after 28 days of contact. With both soil types, concentrations of the probe compounds were reduced by greater than 90 percent for carbon tetrachloride and greater than 99 percent for benzene and trichloroethene in systems with CHP only. The impact of treatment efficacy by the addiction of the biological amendments varied with each soil type. For Soil 6, the addition of citrate and acetate to the CHP reactors had minimal impact on the treatment efficacy of carbon tetrachloride and trichloroethene and no observable impact on the treatment efficacy of benzene. For Soil 2, the addition of citrate and acetate with CHP also had little impact on the treatment of carbon tetrachloride. While treatment of benzene and trichloroethene in CHP reactors amended with acetate and citrate was still greater than 85 percent compared to the control reactors, the treatment efficacy was less than compared to the CHP only reactors. The addition of citrate resulted in approximately two orders of magnitude less treatment compared to the CHP only reactors for benzene and trichloroethene, and the addition of acetate resulted in approximately one order of magnitude less treatment in the presence of Soil 2.

Table 4.4.3 presents the impact of each treatment condition on the biological activity as measured by CFUs after 90 days of contact with amended and unamended CHP. The addition of CHP resulted in a measured microbial population greater than the control for Soil 1 and Soil 6, while Soil 2 reactors had detectable plate count, although lower than the control. The data indicates little detrimental effect on biological activity by the addition of CHP in all three soil systems. For all three soil types, the addition of lactate, soybean oil, and whey protein decreased biological activity in each system compared to the control and CHP only reactors. The presence of acetate, citrate, and phosphate and nitrate only resulted in microbial populations greater than the control for all soil types (with the exception of acetate in Soil 6 reactors).

Table 4.4.3 Biological activity represented by colony forming units (CFU/100mL) determined by heterotrophic plate counts in a CHP system treated with biological stimulants.

Test Condition	**Microbial Population after 90 Days (log CFUs)**		
	SOIL 1	**SOIL 2**	**SOIL 6**
Control	8.84	6.35	6.81
CHP with Amendments			
CHP Only	9.72	5.78	8.56
Acetate, Phosphate, Nitrate	9.48	9.19	< 5.00
Citrate, Phosphate, Nitrate	9.69	9.24	9.95
Lactate, Phosphate, Nitrate	< 5.00	< 5.00	< 5.00
Phosphate, Nitrate	9.83	9.43	9.16
Soybean Oil, Phosphate, Nitrate	< 5.00	< 5.00	< 5.00
Whey Protein, Phosphate, Nitrate	< 5.85	< 5.00	< 5.00

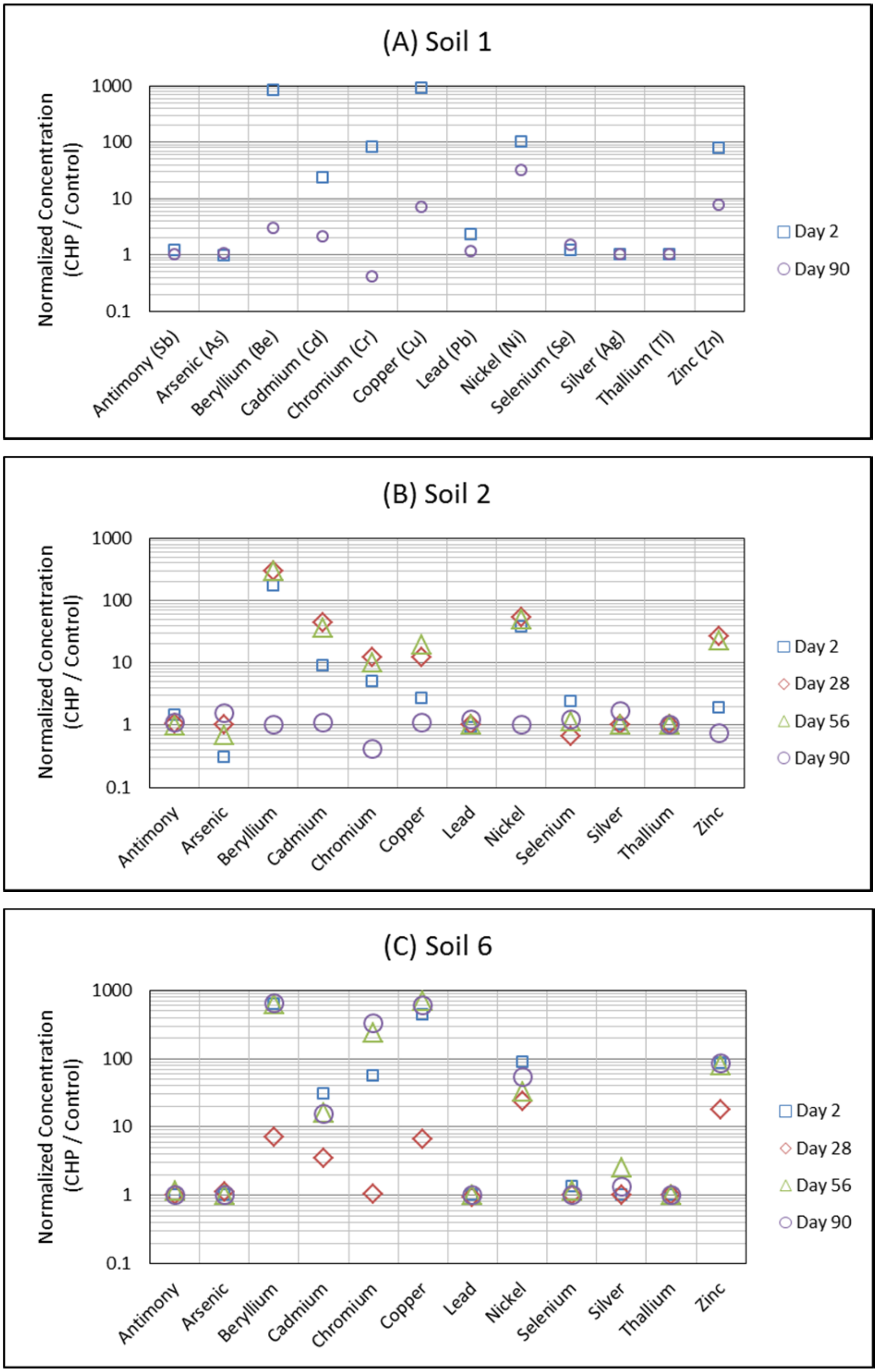


Figure 4.4.28 Co-Treatment Biological Stabilization: Normalized concentration of metals for reactors with CHP applied versus control conditions (no CHP treatment).

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C)

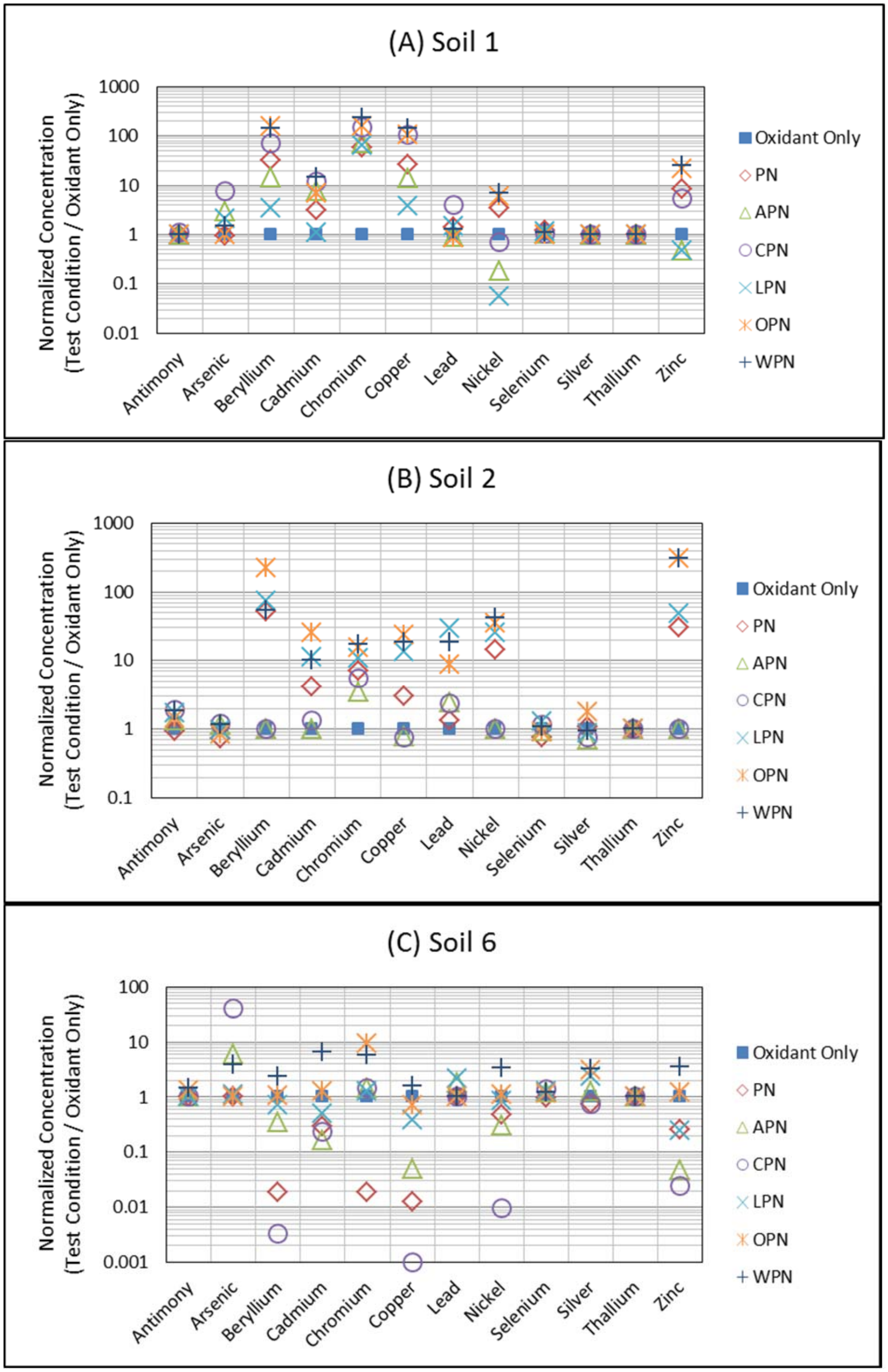


Figure 4.4.29 Co-Treatment Biological Stabilization of CHP System: Select normalized metal concentrations for 6 biological treatment options

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C).

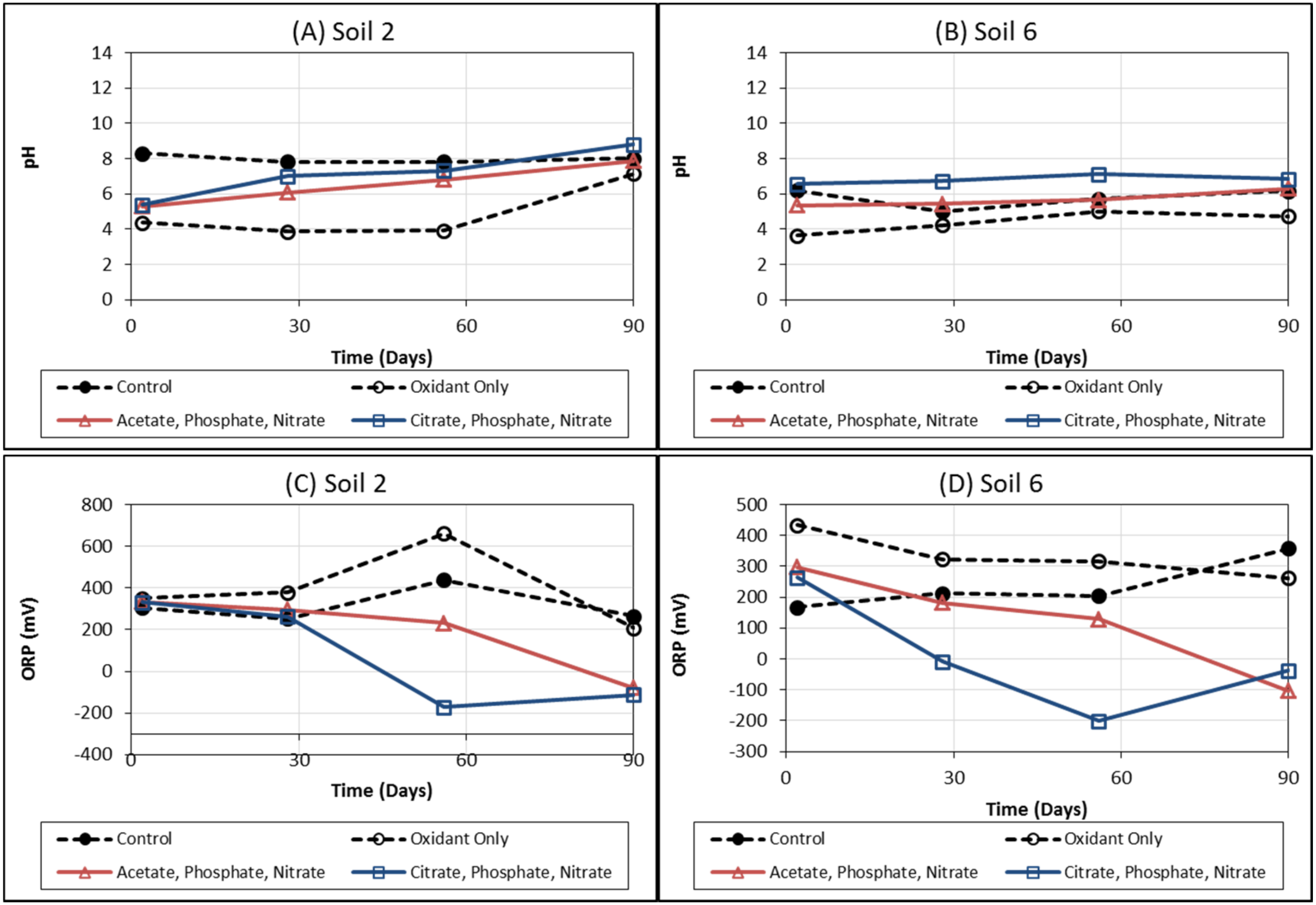


Figure 4.4.30 Co-Treatment Biological Stabilization of CHP System: Geochemical parameters at 2, 28, 56, and 90 days

Note: Soil 2 (A, pH, C, ORP) and Soil 6 (B, pH, D, ORP)

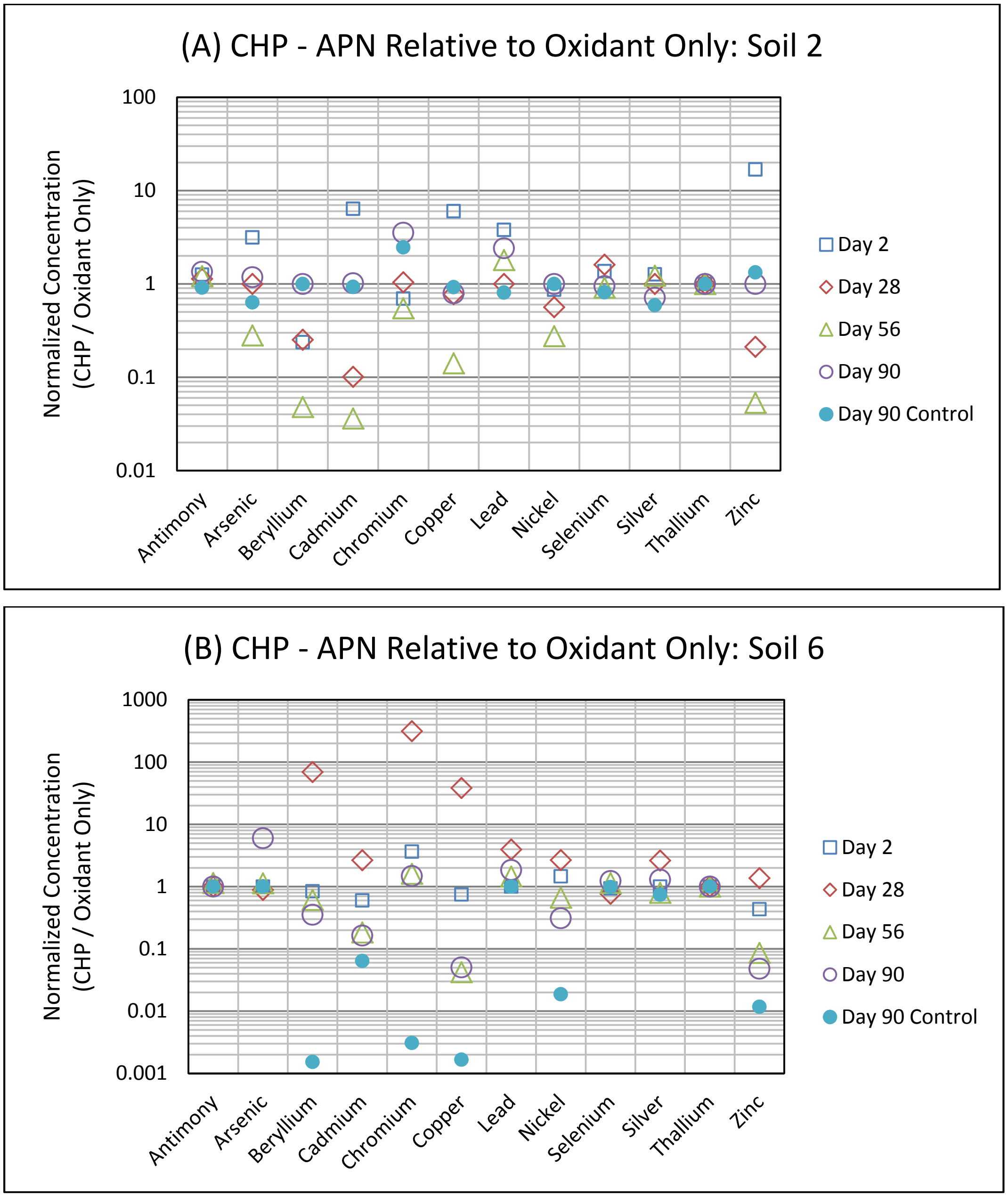
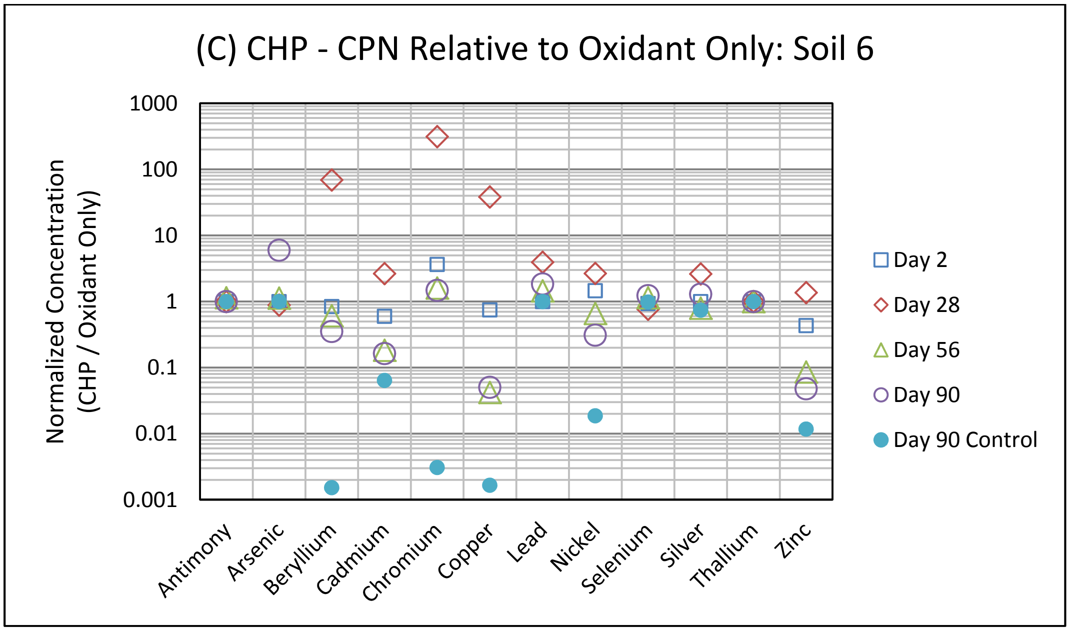


Figure 4.4.31 Co-Treatment Biological Stabilization of CHP System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Co-treatment with APN (A,B), and CPN (C,D) for both Soil 2 and 6.



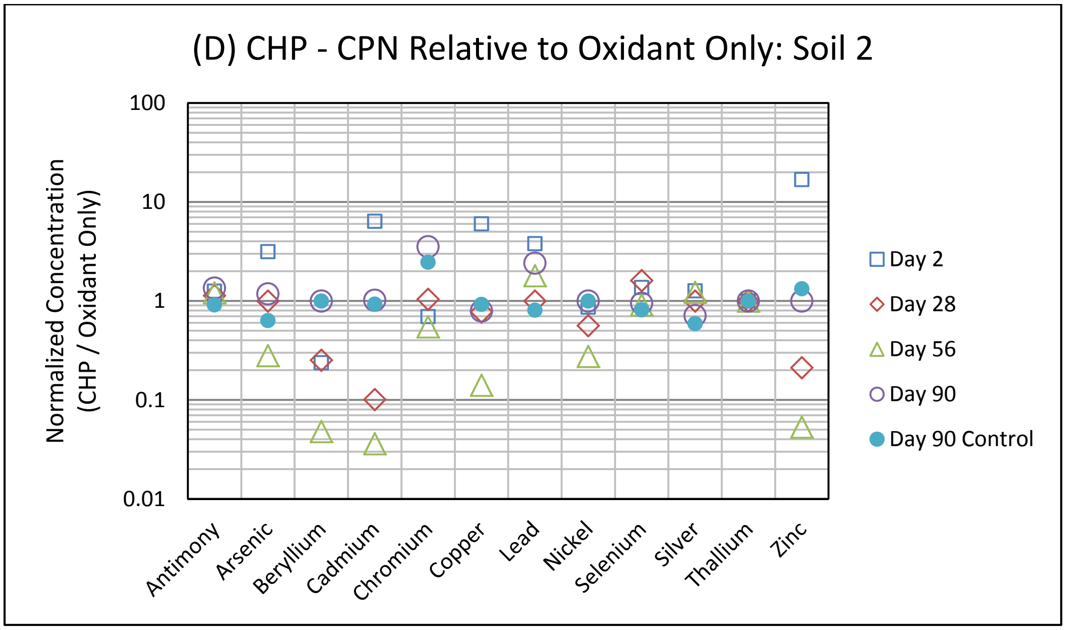


Figure 4.4.31 (cont) Co-Treatment Biological Stabilization of CHP System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Co-treatment with APN (A,B), and CPN (C,D) for both Soil 2 and 6.

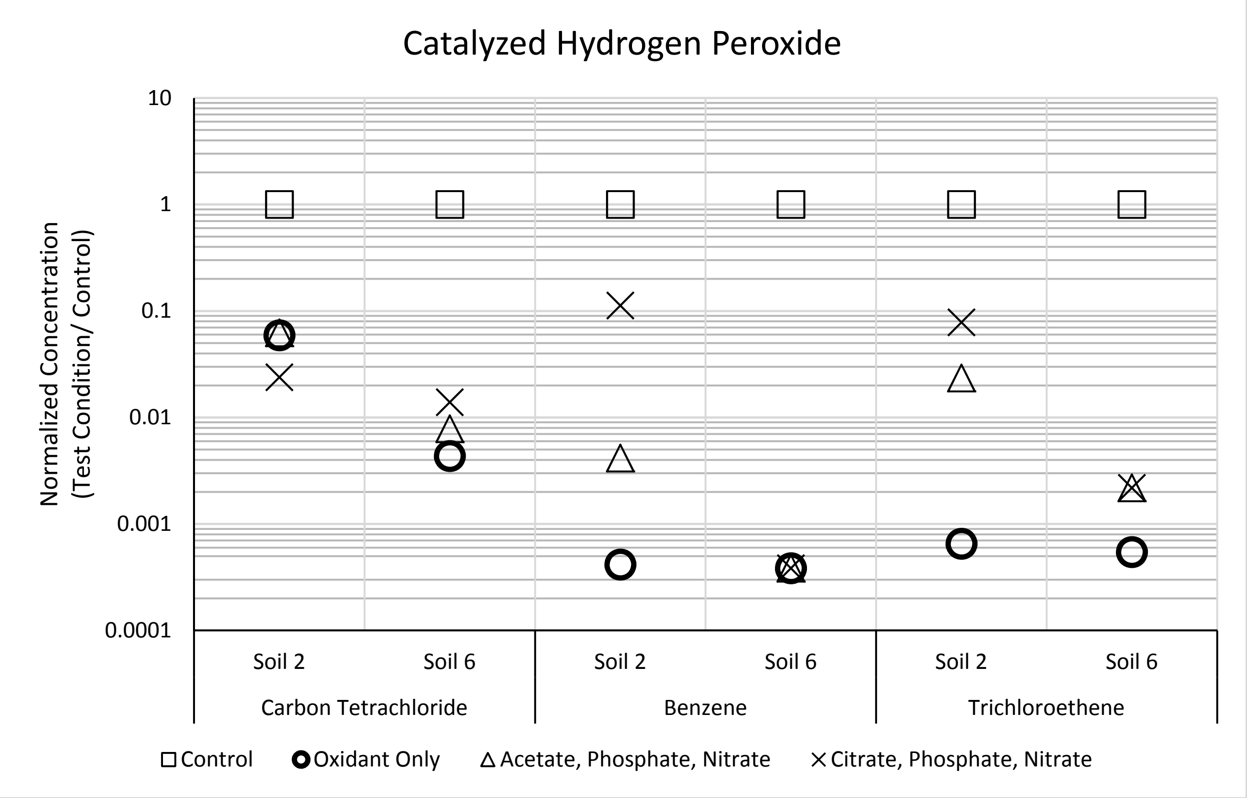


Figure 4.4.32 Co-Treatment Biological Stabilization of CHP System: Treatment Efficacy-Normalized Concentrations of probe compounds carbon tetrachloride, benzene, and trichloroethene.

Potassium Permanganate. Figure 4.4.33 shows the concentrations of the selected priority pollutant metals in reactors treated with $KMnO_4$ only normalized to the metal concentrations in the control reactors (water only) for each respective time point for Soils 1, 2, and 6. For Soil 1, the addition of potassium permanganate yielded an increase in Be, Cr, Cu Pb, Ag and Tl after 2 days of exposure. By Day 90, only Cu remained elevated in relation to the concentration of metals in the control reactors. Figure 4.4.33B indicates that concentrations of Be, Cr, Pb, Ag, and Tl were elevated in the reactors containing $KMnO_4$ compared to the control. Selenium concentrations in the $KMnO_4$ reactors returned to near the control by Day 90. For Soil 6, reactors containing $KMnO_4$ resulted in elevated concentrations of Cr, Pb, Se, Ag, and Tl compared to the control reactor, with Pb, Se, and Tl returning to concentrations close to the control by Day 90.

Figure 4.4.34 shows the concentrations of metals after 90 days in reactors with $KMnO_4$ amended with biological stimulants normalized to the metal concentrations in the reactors treated with $KMnO_4$ only for Soils 1, 2, and 6. For Soils 2 and 6, addition of lactate, soybean oil, and citrate with the $KMnO_4$ resulted in lower concentrations of Cr, Ag, and Tl compared to the $KMnO_4$ only reactors. For Soil 2, the addition of citrate to the $KMnO_4$ system also yielded reductions in Tl concentrations. Several metals increased with the addition of the electron donors. Most notably, As increased with all five biological amendments Soil 1 and in four of the five in the presence of Soil 6, but did not increase under any condition for Soil 2.

Based on the screening data, lactate was chosen for further evaluation over additional time points to evaluate the longer term impacts of biological stimulants on metals mobilization with $KMnO_4$. The additional evaluation involved collecting data from time points after at 2, 28, 56 and 90 days of contact with $KMnO_4$ amended with the biological stimulants in the presence of Soil 2 and Soil 6. Additional evaluation was not conducted on Soil 1 as it was depleted during the screening tests.

Figure 4.4.35 shows the pH and ORP for the $KMnO_4$ system for both Soil 2 and Soil 6. For both soil types, there was little change in pH with the addition of $KMnO_4$ with or without sodium lactate, when compared to the $KMnO_4$ only system. The addition of $KMnO_4$ alone changed the ORP from a slightly oxidative system to a strongly oxidative system with a measured ORP at each time step of above 600 mV in both soil systems. The addition of lactate amended $KMnO_4$ reduced the ORP to near-control levels initially, and on Day 56 for Soil 2 and Days 56 and 90 for Soil 6, reduced the ORP to reductive conditions.

Figure 4.4.36 shows the concentration of priority pollutant metals in $KMnO_4$ reactors amended with lactate, normalized to the concentrations in $KMnO_4$ only reactors at Days 2, 28, 56, and 90. The data indicate that the addition of lactate with $KMnO_4$ resulted in lower concentrations of Cr, Ag, and Th in Soil 2 and lower concentrations of Be, Cr, Pb, Se, Ag, and Th in Soil 6. For several of the priority pollutant metals, the addition of lactate resulted in concentrations similar to or approaching the concentrations observed in the control reactor after 90 days. Chromium was observed to steadily increase over the 90 day timeframe evaluated in the $KMnO_4$only system. Comparatively, Cr concentrations in the reactors with $KMnO_4$ amended with lactate were consistently similar to the control reactors and did not exhibit an increasing trend.

Figure 4.4.37 shows concentrations of carbon tetrachloride, benzene, and trichloroethene after 28 days in contact with unamended and lactate amended $KMnO_4$ with Soil 2 and 6. As would be expected based on known relativities, permanganate had little to no effect on the concentrations of carbon tetrachloride or benzene. With both soil types, $KMnO_4$ reduced concentrations of trichloroethene by greater than 99 percent. The addition of lactate to the permanganate solution resulted in trichloroethene concentrations of 82 and 84 percent lower than the control for Soil 2 and Soil 6, respectively.

Table 4.4.4 shows the impact of each treatment condition on the biological activity as measured by CFUs after 90 days of contact with amended and unamended $KMnO_4$. For Soil 1, the microbial population in the $KMnO_4$ only reactors was greater than the control reactors For Soil 2 and Soil 6, the data show that treatment with $KMnO_4$ only resulted in microbial populations below the detection limit of 100,000 CFUs. With the exception of acetate and phosphate in Soil 2 reactors, all treatment conditions resulted in microbial populations higher than the control.

Table 4.4.4 Biological activity represented by colony forming units (CFU/100mL) determined by heterotrophic plate counts in an KMnO4 system treated with biological stimulants.

Test Condition	Microbial Population after 90 Days (log CFUs)		
	SOIL 1	SOIL 2	SOIL 6
Control	8.84	6.35	6.81
$KMnO_4$ with Amendments			
KMn Only	9.33	< 5.00	< 5.00
Acetate, Phosphate, Nitrate	9.42	< 5.00	9.49
Citrate, Phosphate, Nitrate	9.33	9.19	8.44
Lactate, Phosphate, Nitrate	9.42	9.26	9.88
Phosphate, Nitrate	9.37	< 5.00	9.00
Soybean Oil, Phosphate, Nitrate	9.64	8.30	9.67
Whey Protein, Phosphate, Nitrate	9.49	8.79	10.01

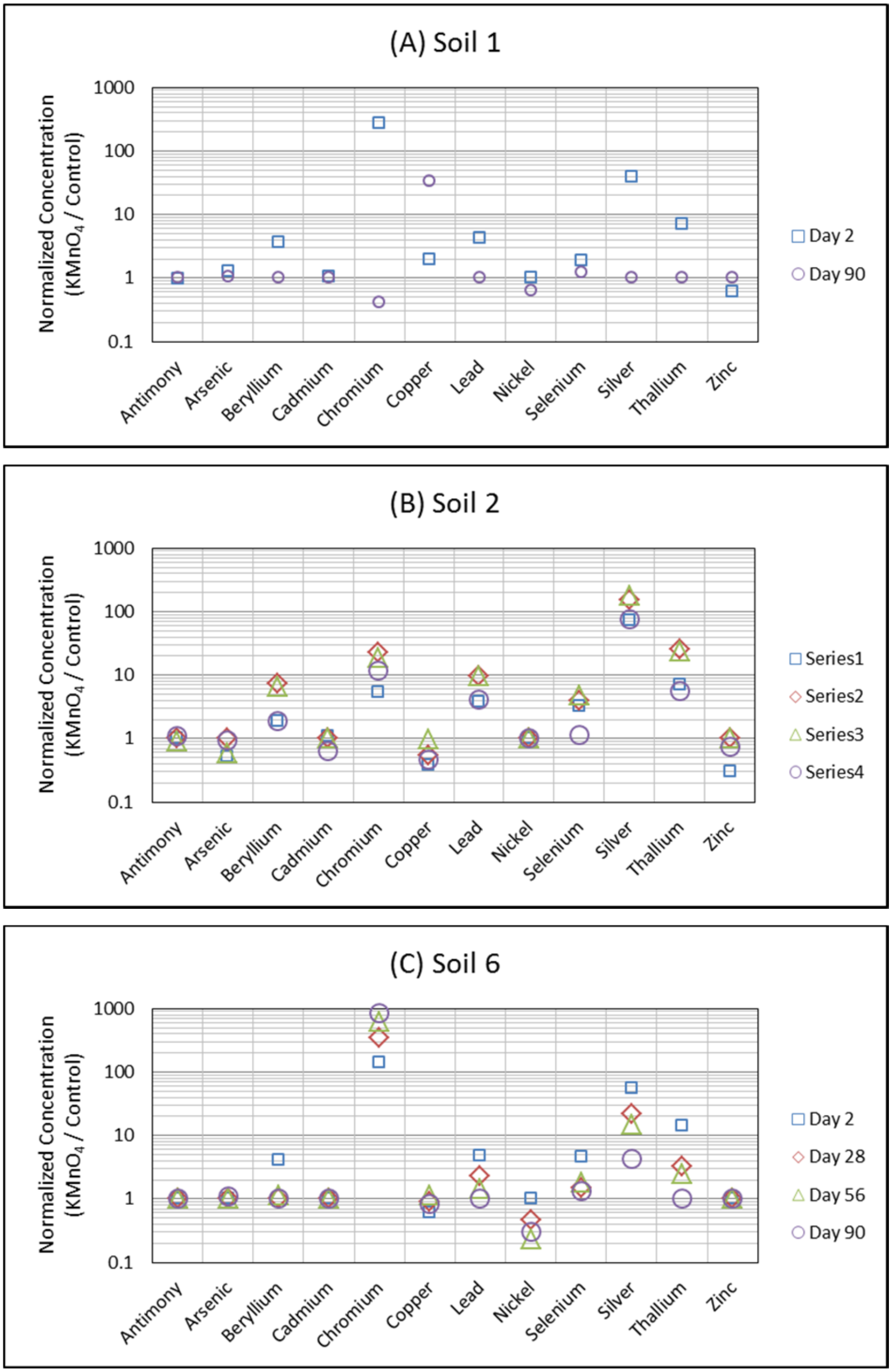
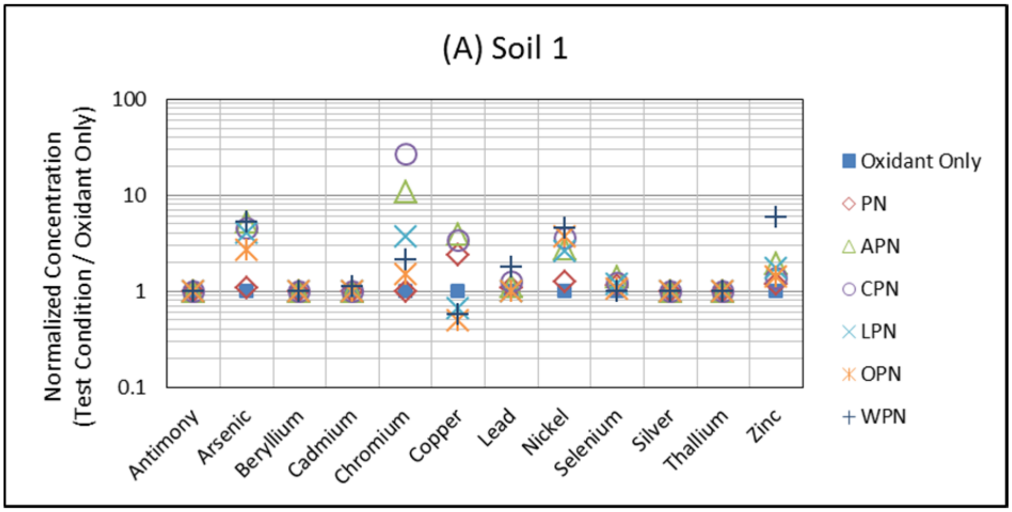
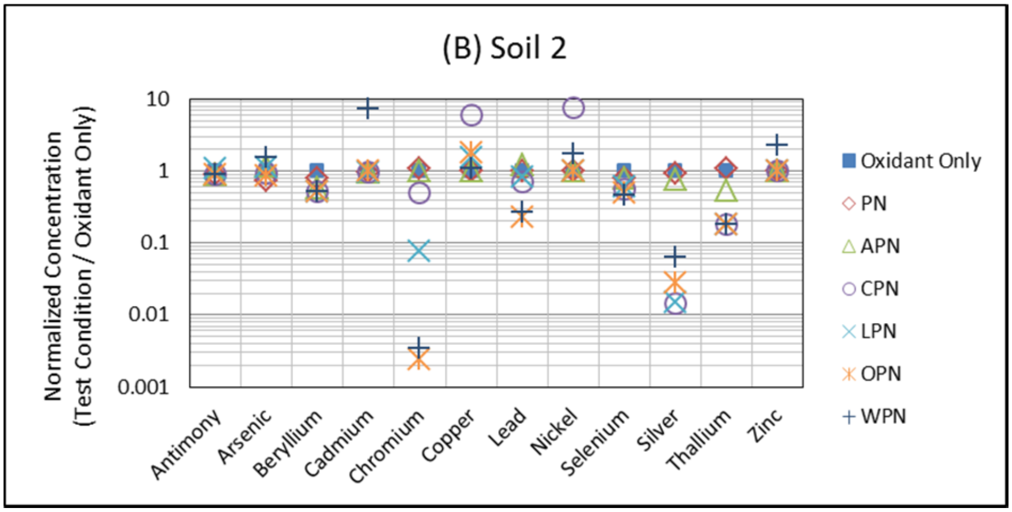


Figure 4.4.33 Co-Treatment Biological Stabilization: Normalized concentration of metals for reactors with PM applied versus control conditions (no PM treatment).

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C).





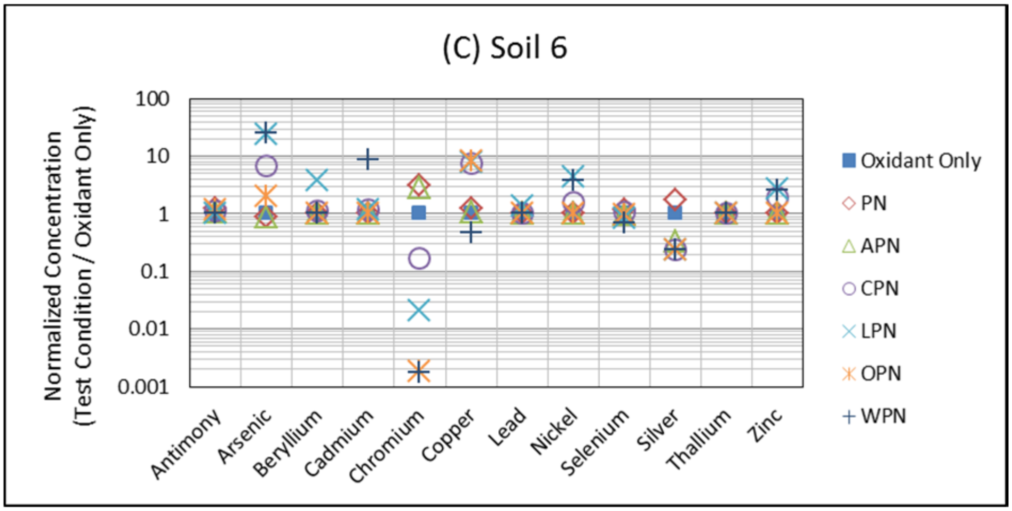


Figure 4.4.34 Co-Treatment Biological Stabilization of PM System: Select normalized metal concentrations for 6 biological treatment options

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C).

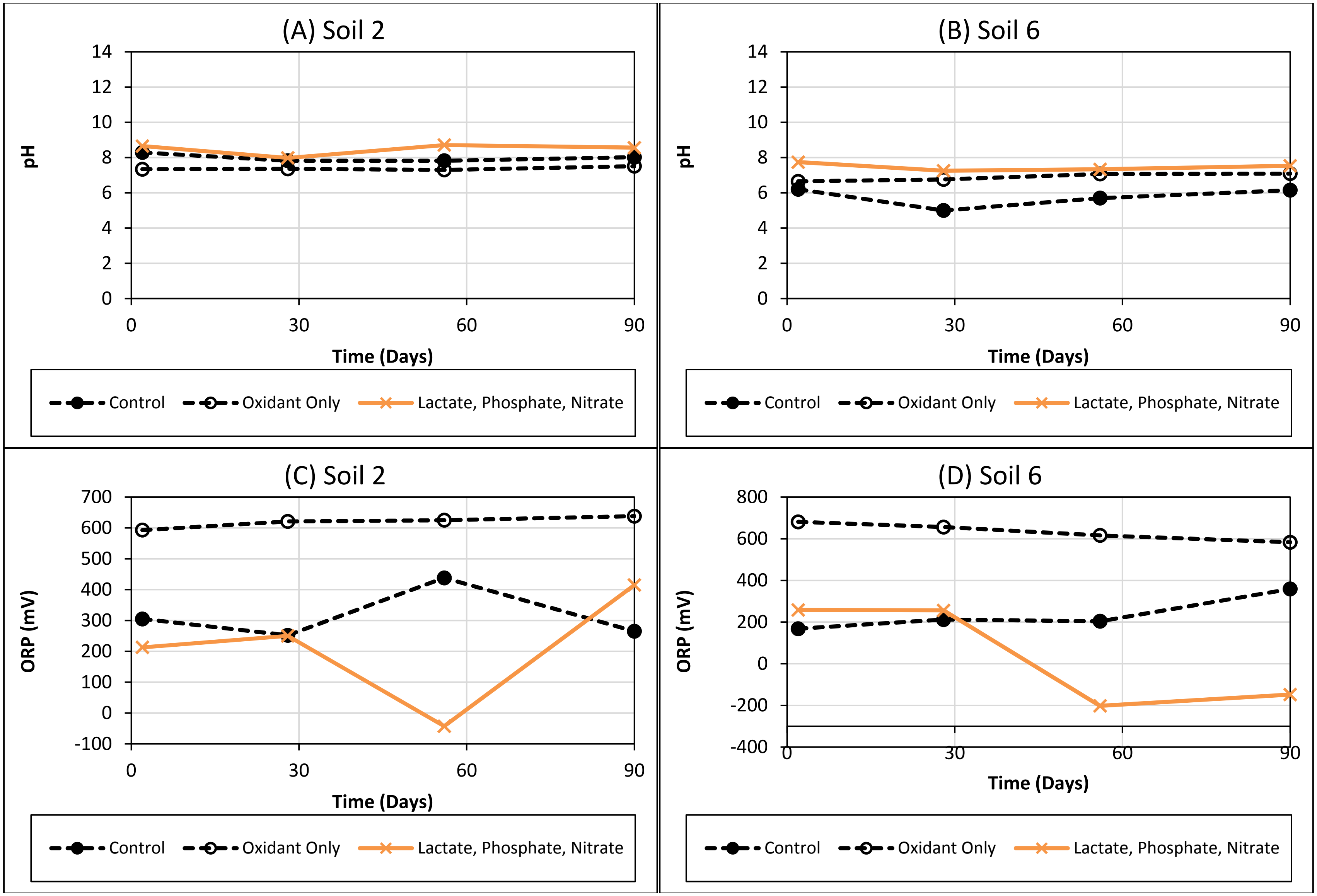


Figure 4.4.35 Co-Treatment Biological Stabilization of PM System: Geochemical parameters at 2, 28, 56, and 90 days

Note: Soil 2 (A, pH, C, ORP) and Soil 6 (B, pH, D, ORP)

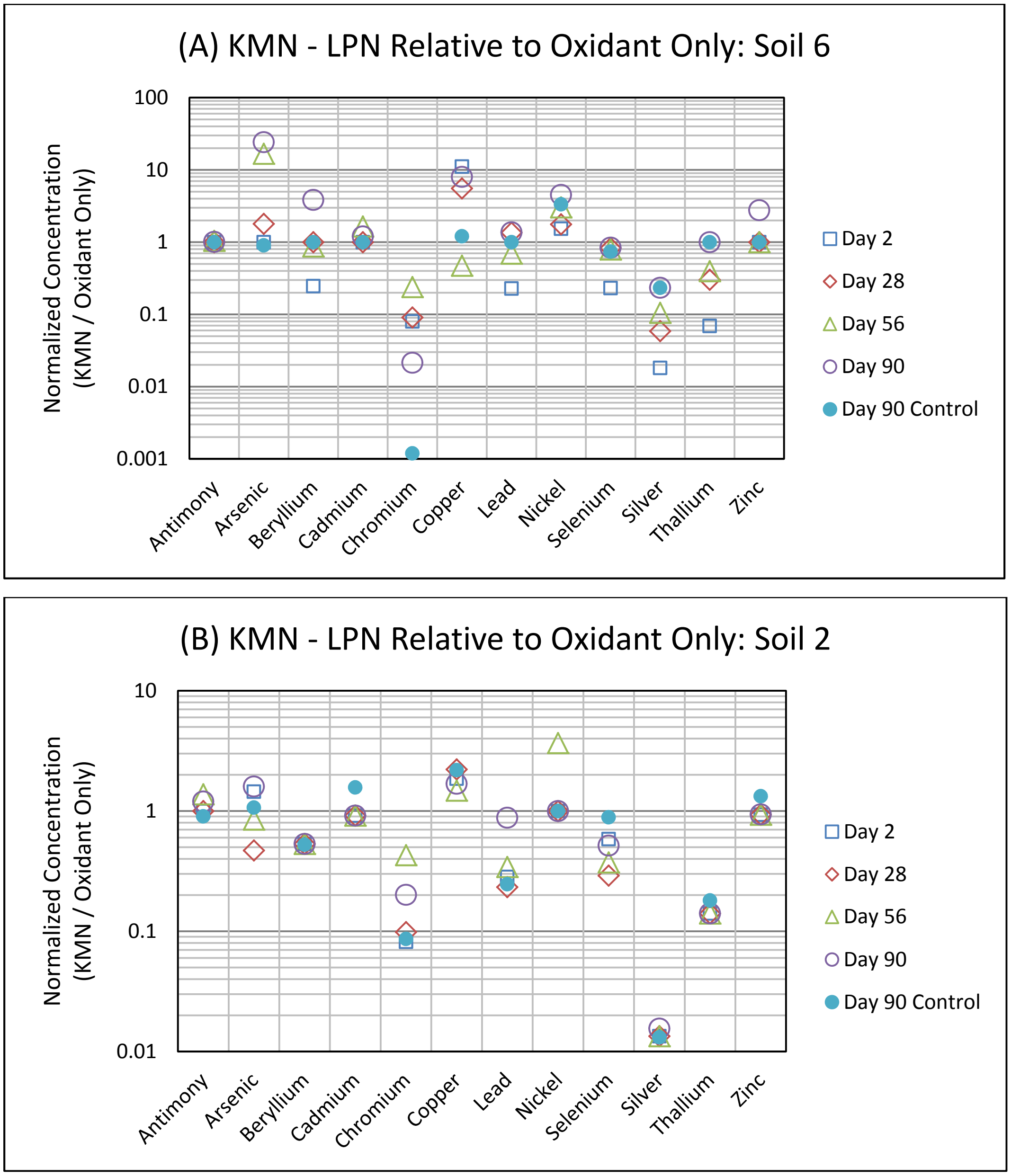


Figure 4.4.36 Co-Treatment Biological Stabilization of PM System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Co-treatment with LPN (A,B) for both Soil 2 and 6.

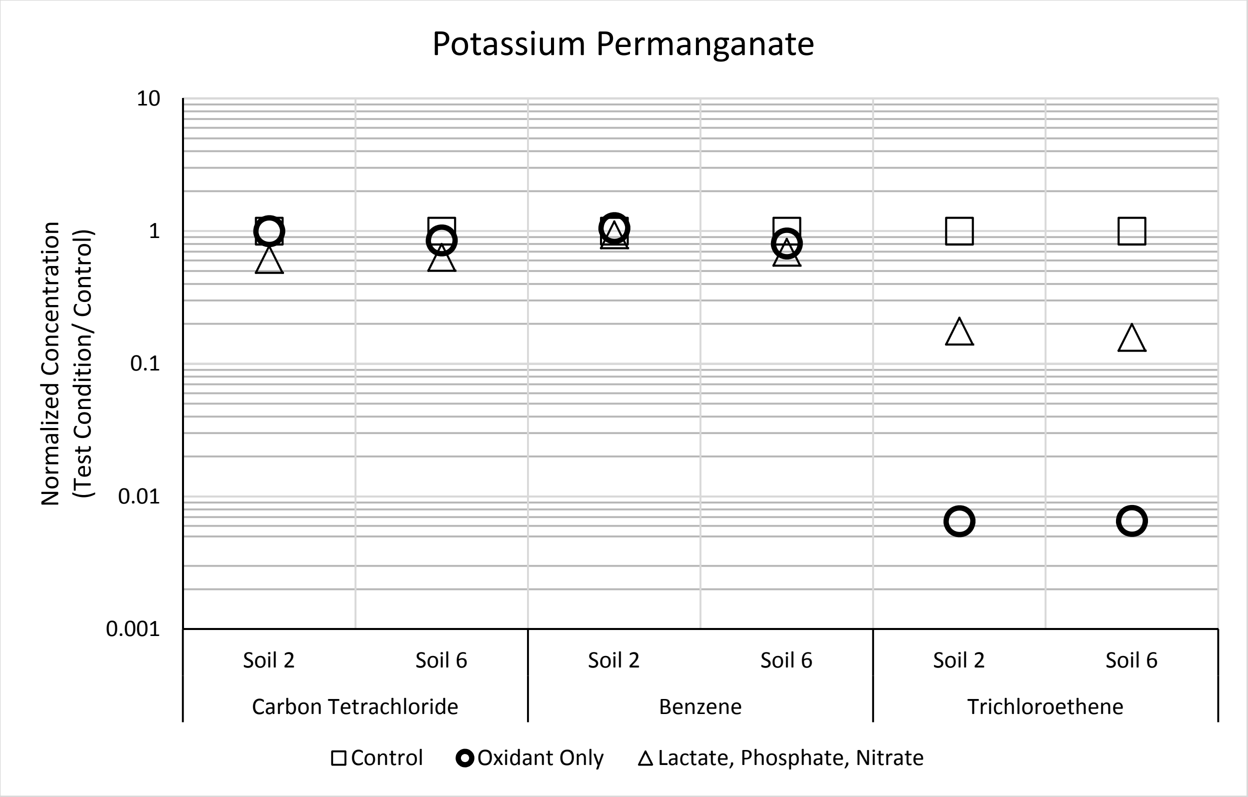


Figure 4.4.37 Co-Treatment Biological Stabilization of PM System: Treatment Efficacy-Normalized Concentrations of probe compounds carbon tetrachloride, benzene, and trichloroethene.

4.4.3 Concurrent Chemical Stabilization Evaluation

The chemical additives tested in the concurrent chemical evaluation were intended to limit or reduce the concentrations of metals formed during ISCO by either buffering the pH or precipitating metals from the solution. This task evaluated both the ability of the chemical additive in minimizing metals mobilization as well as each additive's impact on the treatment efficacy of each ISCO technology.

The ISCO technologies tested include:

- Alkaline Activated Persulfate (AAP)
- Iron Activated Persulfate (IAP)
- Catalyzed Hydrogen Peroxide (CHP)
- Potassium Permanganate ($KMnO_4$)

Data was gathered for 22 metals during these experiments. The discussion of the data presented in this section will focus on metals that are listed as priority pollutants under the Safe Drinking Water Act as Task 4 is intended to help identify methods to mitigate the mobilization of metals of environmental concern. These metals include silver (Ag), arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), thallium (Tl), and zinc (Zn). Mercury (Hg) is also listed as a priority pollutant but was not analyzed for during these experiments. The test result for each ISCO technology are discussed in the following sections.

Alkaline-Activated Persulfate. Figure 4.4.38 presents the concentrations of the selected priority pollutant metals in reactors treated with AAP only normalized to the metal concentrations found in the control reactor (water only) for each respective time point for Soils 1, 2, and 6. The data show that the concentration of several metals in the presence of the AAP solution was greater the concentration of the same metals in the control reactors. Concentrations of As and Cr were higher in reactors containing AAP compared to the control reactors for each soil type. The impacts in Soil 6 were observed to be greater than those observed in Soil 1 or Soil 2. For Soil 1 (Figure 4.4.38A), the results show higher concentrations of As, Cr, Cu, and, to a lesser extent, Pb. Lower concentrations of Cd, Ni, and Zn were also observed after 90 days in the reactors with AAP compared to the control at Day 90. For Soil 2 (Figure 4.4.38B), the results show concentrations of As, Cr, and Pb in the AAP only systems were more than double the concentrations found in the control reactors after 90 days. For Soil 6 (Figure 4.4.38C), the results show significantly higher concentrations of As, Cr, and Cu compared to the controls after 90 days. The concentration of Cu, Pb, and Ni relative to the control reactors decreased with time whereas the concentration of Cr increased.

Figure 4.4.39 presents the screening test results adding the chemical additives in the same solution with AAP normalized to each respective metals concentration in reactors containing AAP only and contacting Soils 1, 2, and 6 for 2 days. The previous data indicated that As, Cr, Cu, and Pb were the metals with concentrations greater than the control in the AAP system after 90 days. The data presented in Figure 4.4.39 indicate that the bicarbonate buffer treatment condition was the only chemical additive to result in a lower concentration of these metals in Soil 1 and Soil 2 after 2 days of contact compared to the AAP only reactors. However, the bicarbonate buffer system achieved pH 10.3, which is less than the desired pH 10.5 to pH 11 required for the activation system. The phosphate buffer system did result in a lower concentration of Cu in the Soil 6 reactors.

Based on the screening level results for the AAP system, no chemical additives were selected for further evaluation due to the lack of significant reductions in metals concentrations after treatment where a viable pH was obtained.

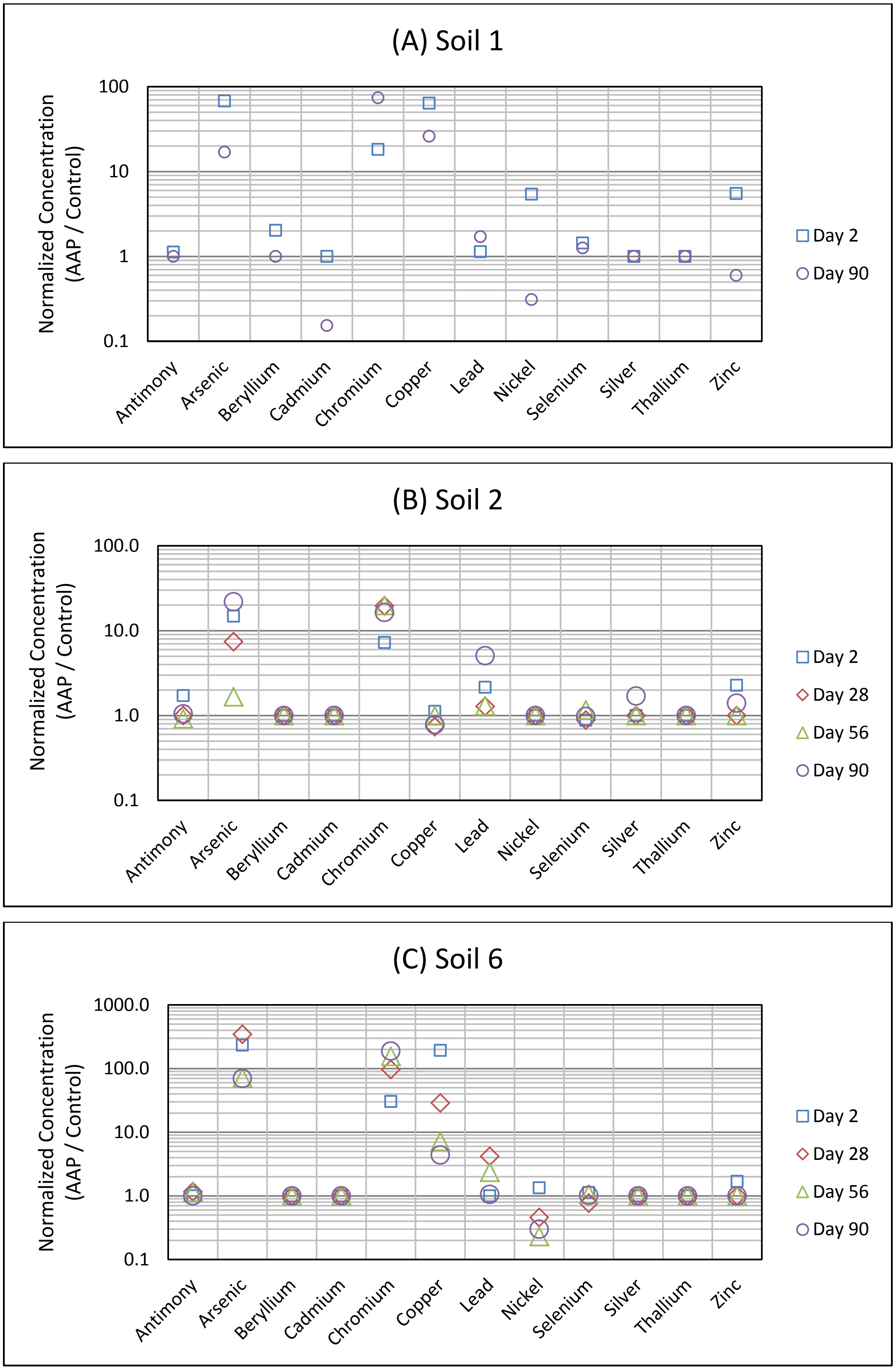


Figure 4.4.38 Co-Treatment Chemical Stabilization: Normalized concentration of metals for reactors with AAP applied versus control conditions (no AAP treatment).

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C).

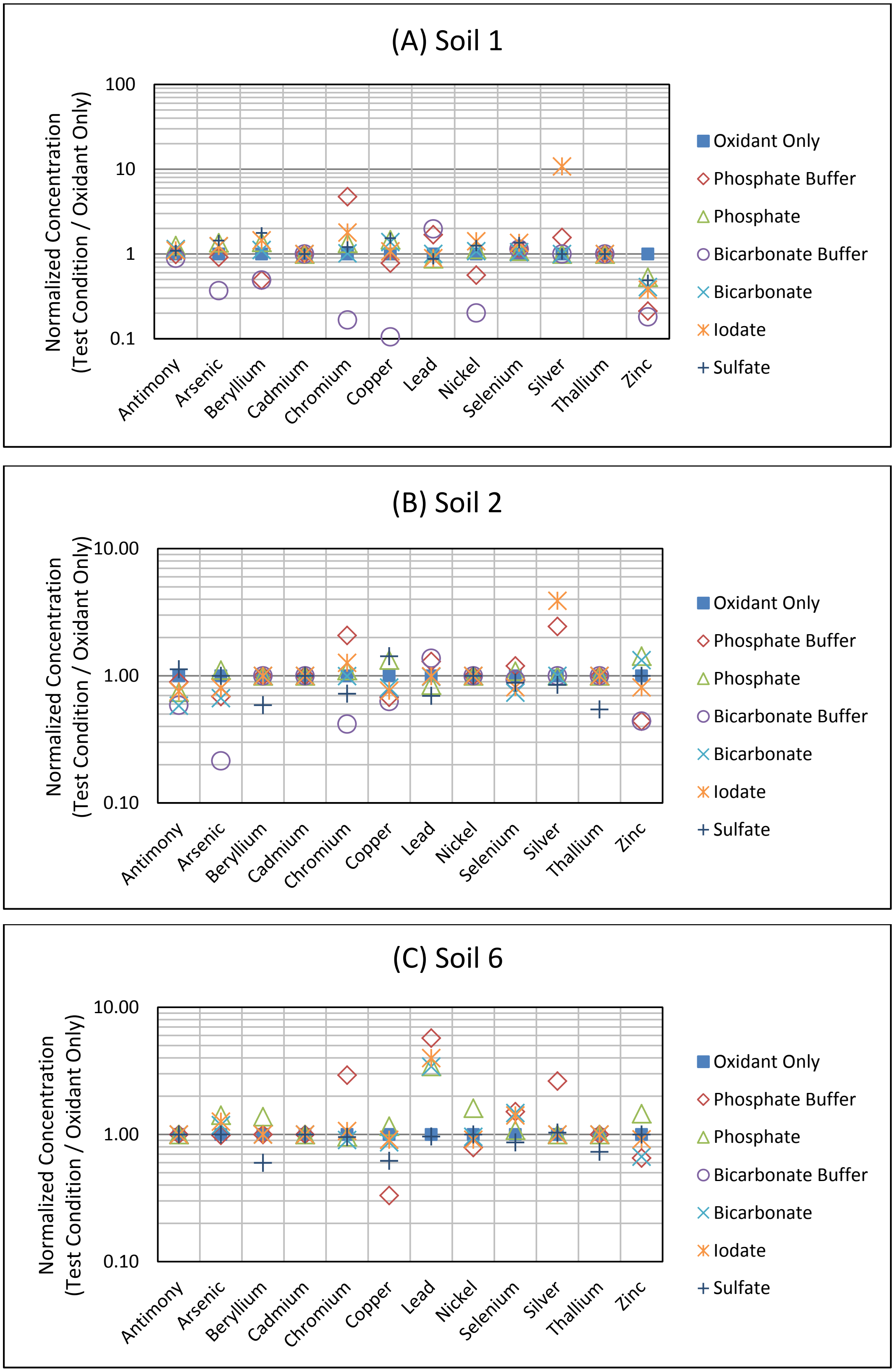


Figure 4.4.39 Co-Treatment Chemical Stabilization of AAP System: Select normalized metal concentrations for 6 chemical treatment options.

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C).

Iron-Activated Persulfate. Figure 4.4.40 presents the concentrations of the selected metals in reactors treated with IAP only, normalized to the metal concentrations in the control reactors (water only) for each respective time point for Soils 1, 2, and 6. The data shows that CR, Ni, and Zn increased on concentration after treatment of all three soil types with IAP. Other metals, such as Be, Cd, Cu, increased in two of the three soil types after treatment with IAP compared to the control reactors.

Figure 4.4.41 presents concentrations of selected metals in reactors with chemical additives added to the IAP solution, normalized to the metals concentration in the reactors treated with IAP only, for Soils 1, 2, and 6 after 2 days of contact. The previous data indicated that Be, Cr, Cu, Pb, Ni, and Zn were most typically mobilized with IAP after 90 days of contact with the various soils and the IAP system. Figure 4.4.41 also shows, phosphate, phosphate buffer, bicarbonate, and bicarbonate buffer each resulted in decreases in several of these targeted priority pollutant metals. The addition of iodate also resulted in lower concentrations of metals in Soil 1, but had limited to no effect in Soil 2 and Soil 6. Several of the additives resulted in increased concentrations of As in the Soil 6 reactors. The addition of sulfate had little or no effect in any of the soil types.

Based upon the screening results, phosphate, phosphate buffer, bicarbonate and bicarbonate buffer treatment conditions were selected for further evaluation over a 90 day period to evaluate the longer term impacts of chemical additives on metals mobilization with IAP, and to evaluate the impact of these additives on the treatment efficacy of IAP on probe compounds. The additional experiments were conducted on Soils 2 and Soil 6 as Soil 1 was depleted during the screening tests.

Figure 4.4.42 presents the pH and ORP at each time point for the selected test conditions. For Soil 2, the data show that the pH in the IAP only reactors decreased to between pH 4 and pH 6, which is below the control reactors which were approximately pH 8. For Soil 6, the pH in the IAP only reactors decreased to between pH 3 and pH 3.2, which is below the control reactors which were typically near pH 6. For Soil 2, the addition of phosphate and bicarbonate amendment at both the low and high concentrations resulted in a higher pH than the IAP only reactors. For Soil 6, only the high concentration of the phosphate buffer and bicarbonate buffer amendments successfully maintained the pH near neutral. In the presence of Soil 6, the pH in the reactors amended with the low concentration of phosphate and bicarbonate resulted in pH values similar to the IAP only reactors.

For Soil 2, the ORP in all treatment conditions were significantly lower compared to the reactors with IAP only. For Soil 6, the ORP in the phosphate buffer and carbonate buffer systems were significantly lower than the IAP only systems throughout the test, while the ORP in the phosphate and carbonate systems were similar to the IAP only system.

Figure 4.4.43 shows the change in concentration of priority pollutant metals over time, normalized to the respective metal concentrations in the reactors containing IAP only for the selected treatment conditions. The data show for Soil 2 that the concentrations of Sb, As, Be, Cd, Cu, Se, and Th in the IAP only reactors were similar to the control reactors by Day 90, while the concentrations of Cr, Pb, Ni, Ag, and Zn were lower in the control reactors compared to the IAP only reactors at Day 90. For Soil 6, the concentrations of Sb, As, Se, Pb and Tl were similar to the control by Day 90, while concentrations of Be, Cd, Cr, Cu, Ni, and Zn in the control were greater than 90 percent lower than the IAP only reactors.

The following effects of the treatment conditions were observed:

- Phosphate Buffer (4.4.43A and B): The data indicate that the addition of phosphate buffer (100 mM phosphate per Kg soil) could result in lower concentrations of Be, Cd, Cu, Ni, and Zn compared to IAP only reactors. Not all metals in the treatment reactors were comparatively lower than the IAP only reactors. For example, concentrations of Cu were approximately 99 percent lower in the reactors with phosphate buffer compared to the IAP only reactors for Soil 6 but were similar in concentration for Soil 2, while concentrations of As increased in the treatment reactors for both Soil 2 and Soil 6.

- Phosphate (4.4.43C and D): The addition of the lower concentration of phosphate (5 mM phosphate per Kg soil) with IAP resulted in lower concentrations of Ni, Ag, and Zn for Soil 2 and lower concentrations of Be, Cd, and Cr for Soil 6 compared to the IAP only reactor by Day 90. The addition of phosphate also resulted in lower relative concentrations of Be, Cd, and Cr for Soil 2, but returned close to the concentrations in the IAP only reactor by Day 90. This lower dose of phosphate resulted in a higher concentration of As in Soil 2 but not Soil 6 after 90 Days.

- Bicarbonate Buffer (4.4.43E and F): For Soil 6, the impacts of the bicarbonate buffer (100 mM bicarbonate per Kg soil) were generally limited to the Day 2 time-point. Following that time point, most metals concentrations moderated to be close to those found in the IAP only reactors. At Day 90, slightly lower concentrations of Be, Cd, Cr, Ni, and Zn were observed and higher concentrations of Pb were observed, compared to the IAP only reactors. By Day 90, most IAP only concentrations were similar to the control reactors. However, the addition of the bicarbonate buffer resulted in lower concentrations of As, Be, Cd, Ni, and Zn for one or more of the intermediate time points for Soil 2.

- Bicarbonate: The data show that the addition of bicarbonate (5 mM bicarbonate per Kg soil) to IAP resulted in a minimal (less than 50 percent) reduction in Be, Cd, Cr, Cu, Ag and Zn relative to IAP only test condition for Soil 6. For Soil 2, the concentrations Ni, and Zn in the bicarbonate reactors were both less than the IAP only and similar to the control by Day 90. Concentrations of As, Be, Cd, and Ni were less than the IAP only reactor for intermediate time points.

Figure 4.4.44 shows the concentrations of probe compounds (carbon tetrachloride, benzene, and trichloroethene) in systems treated with IAP, both with and without chemical additives. The data show that carbon tetrachloride concentrations in all IAP treatment conditions were similar to the control, indicating a lack of treatment. The treatment of benzene and trichloroethene appear to have been inhibited by the presence of Soil 2. However, for Soil 6 IAP only reactors, benzene and trichloroethene concentrations were 95 percent and 83 percent lower than the control reactors, respectively. The reduction in concentration of benzene and trichloroethene were moderated for Soil 6 reactors containing phosphate buffer and carbonate buffer treatment conditions. The concentrations in the reactors with the phosphate and carbonate treatment condition were very similar to the IAP only reactors, indicating that the lessor concentrations of phosphate and bicarbonate had little to no effect on treatment efficacy.

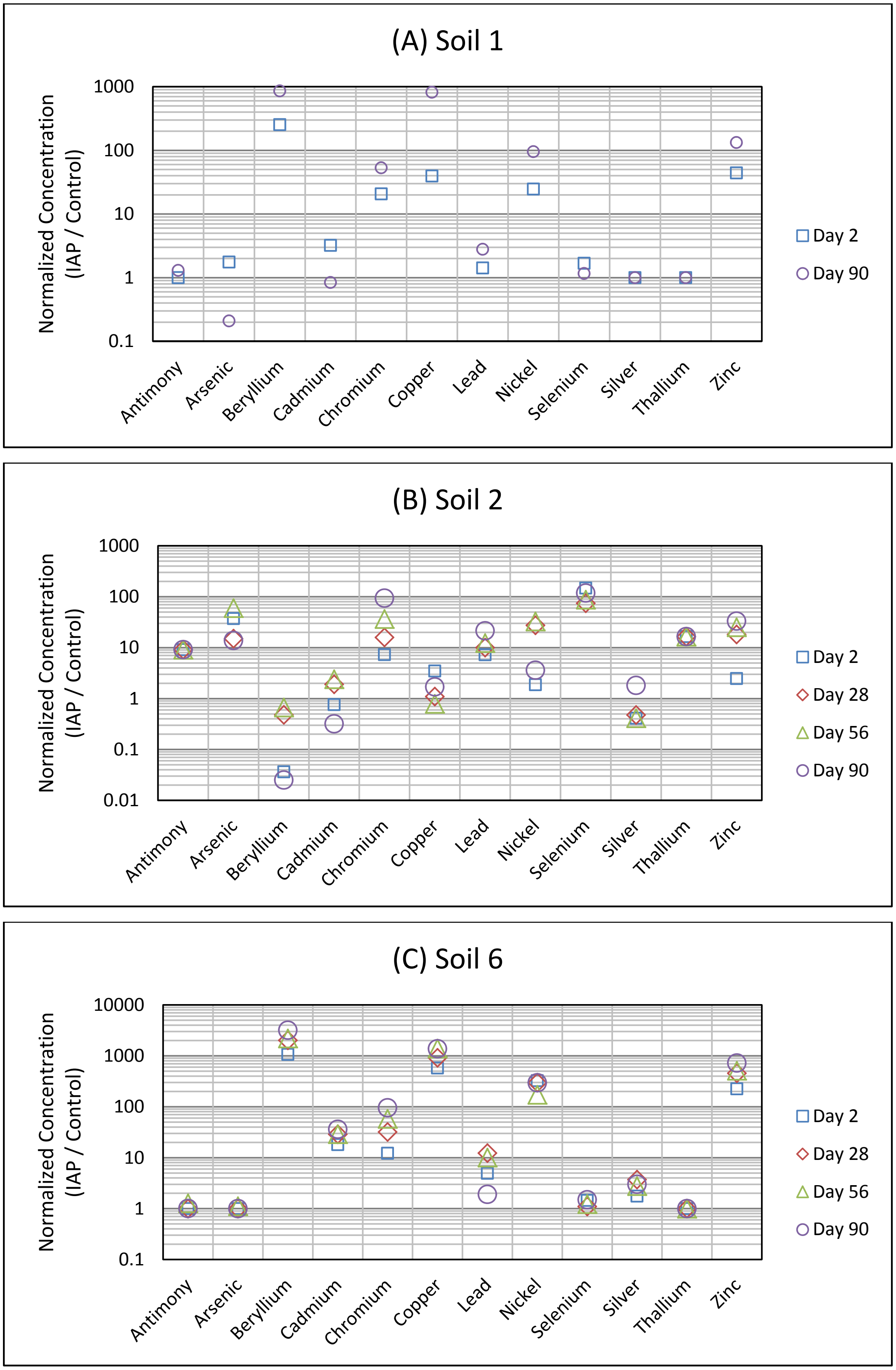


Figure 4.4.40 Co-Treatment Chemical Stabilization: Normalized concentration of metals for reactors with IAP applied versus control conditions (no IAP treatment).

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C).

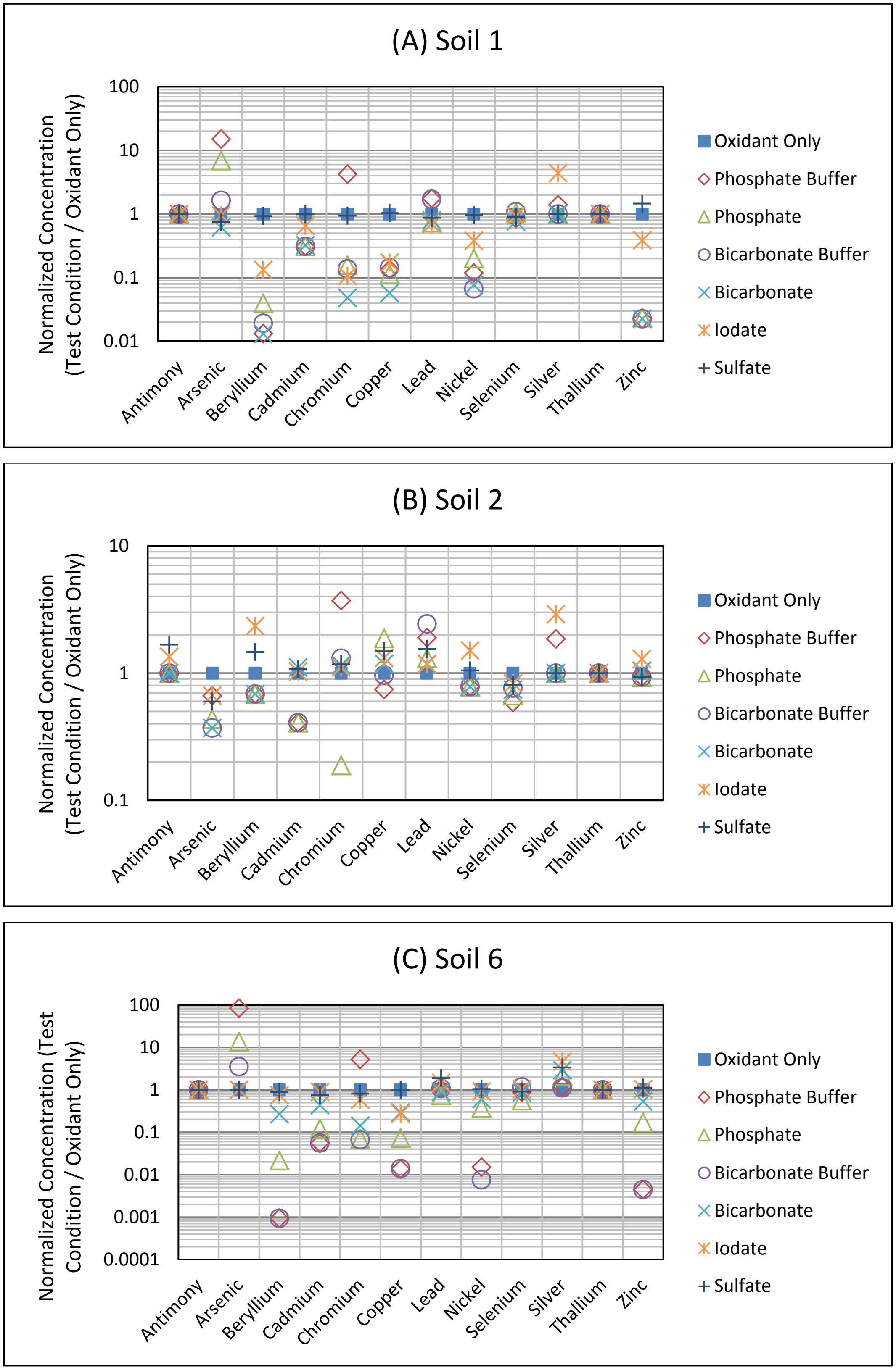


Figure 4.4.41 Co-Treatment Chemical Stabilization: Select normalized metal concentrations for 6 chemical treatment options.

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C).

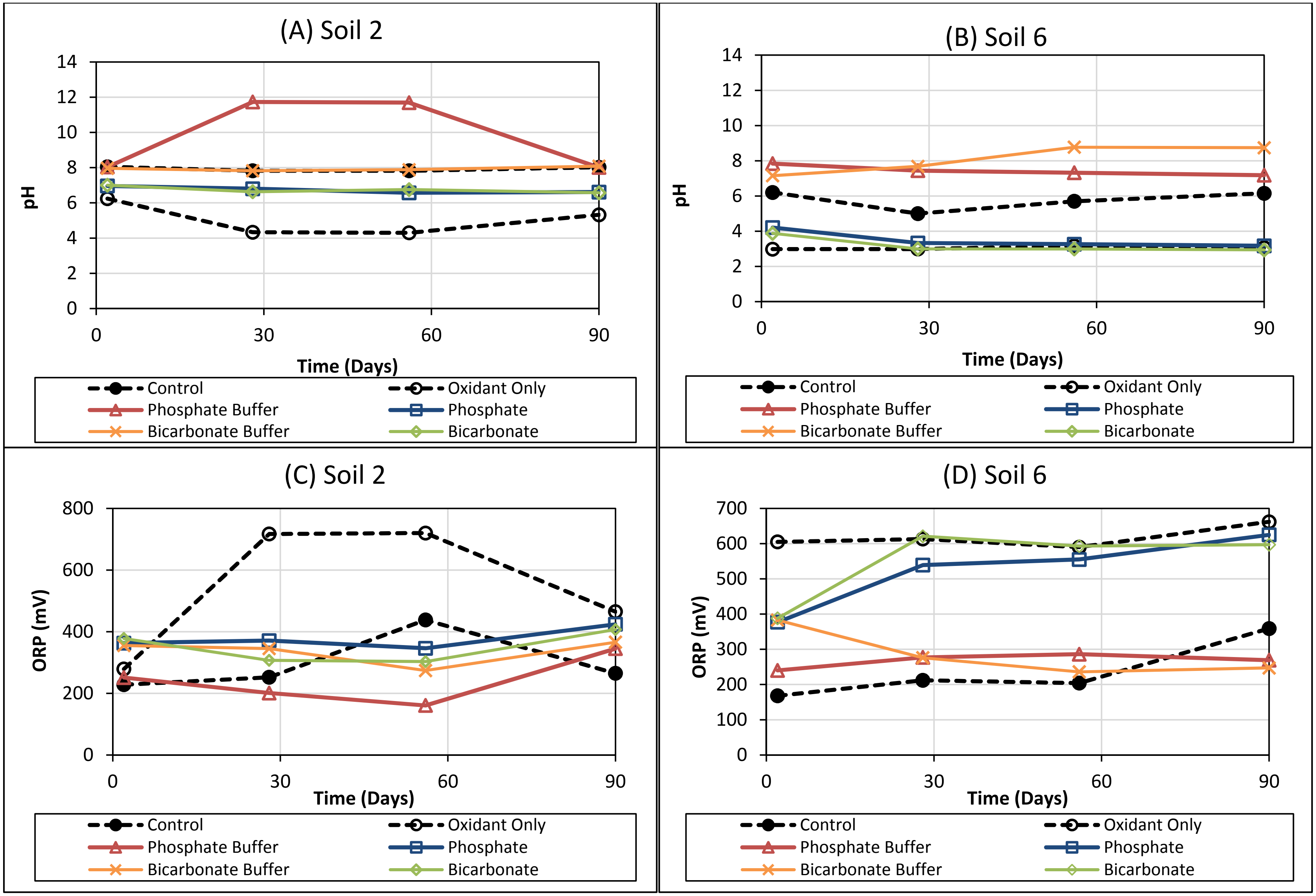


Figure 4.4.42 Co-Treatment Chemical Stabilization of IAP System: Geochemical parameters at 2, 28, 56, and 90 days

Note: Soil 2 (A, pH, C, ORP) and Soil 6 (B, pH, D, ORP)

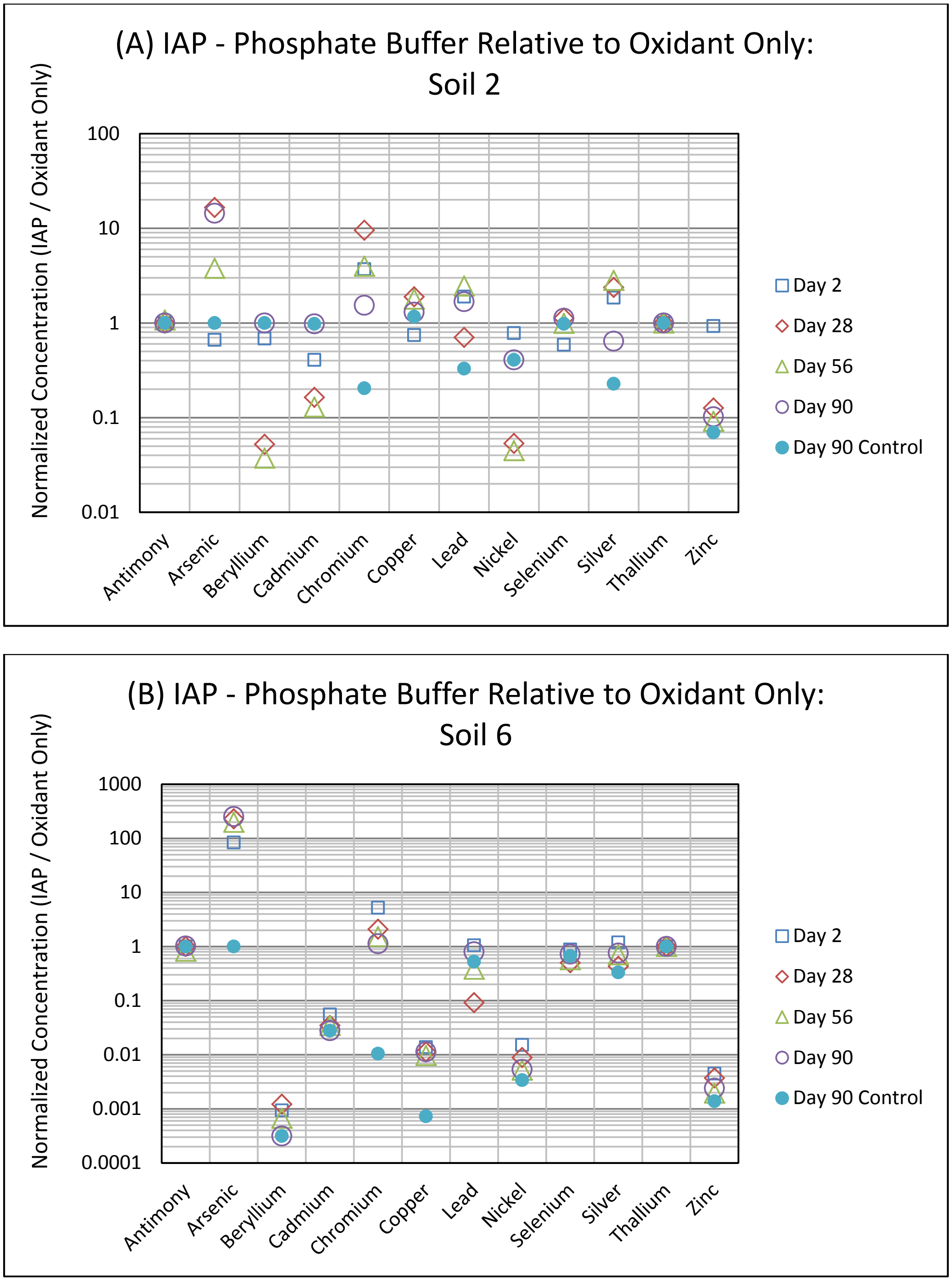


Figure 4.4.43 Co-Treatment Chemical Stabilization of IAP System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Chemical Co-treatment with Phosphate Buffer (A,B), Phosphate(C,D), Carbonate Buffer(E,F) and Carbonate (G,H) for both Soil 2 and 6

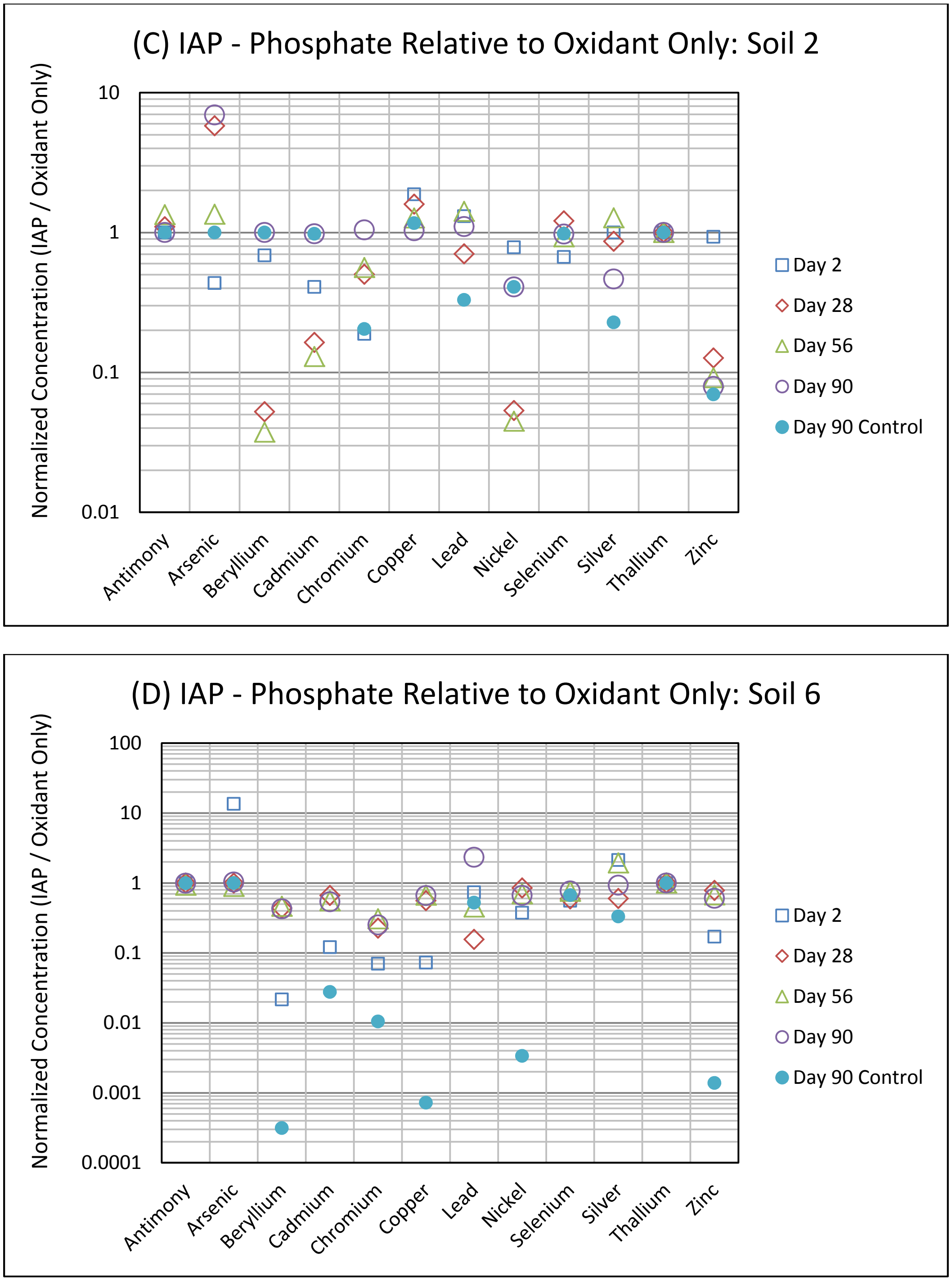
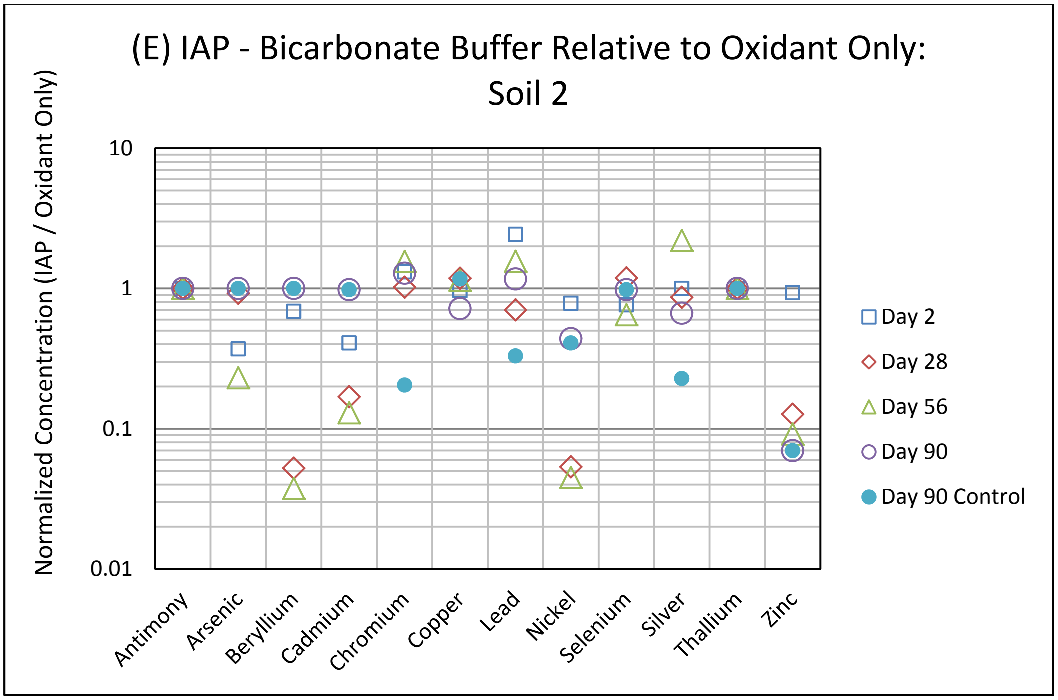


Figure 4.4.43 (cont.) Co-Treatment Chemical Stabilization of IAP System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Chemical Co-treatment with Phosphate Buffer (A,B), Phosphate(C,D), Carbonate Buffer(E,F) and Carbonate (G,H) for both Soil 2 and 6



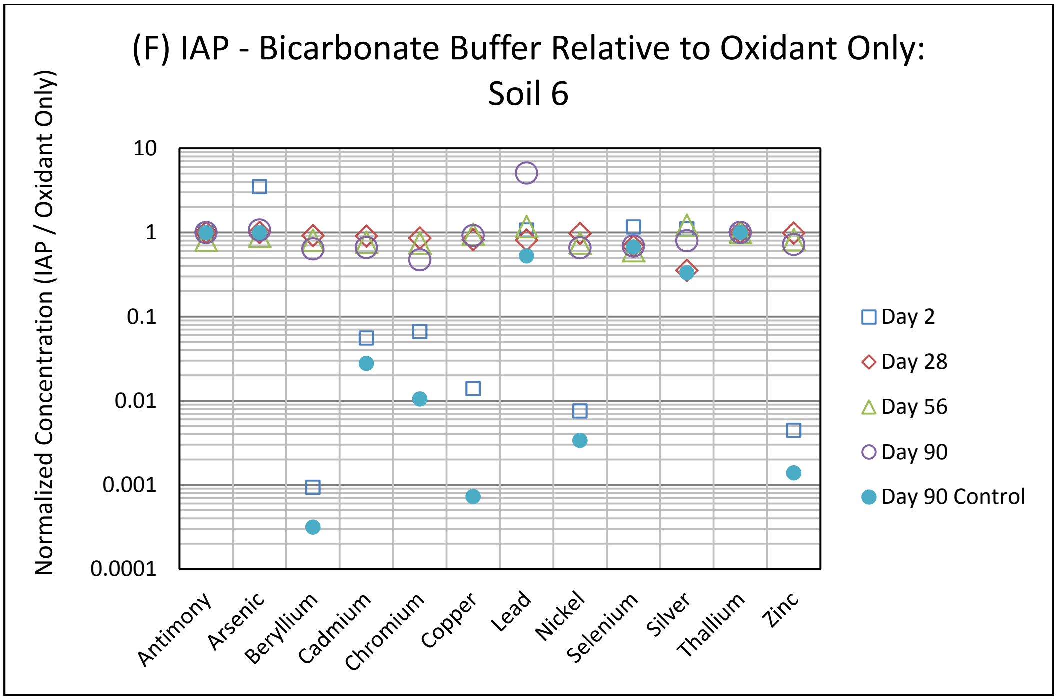
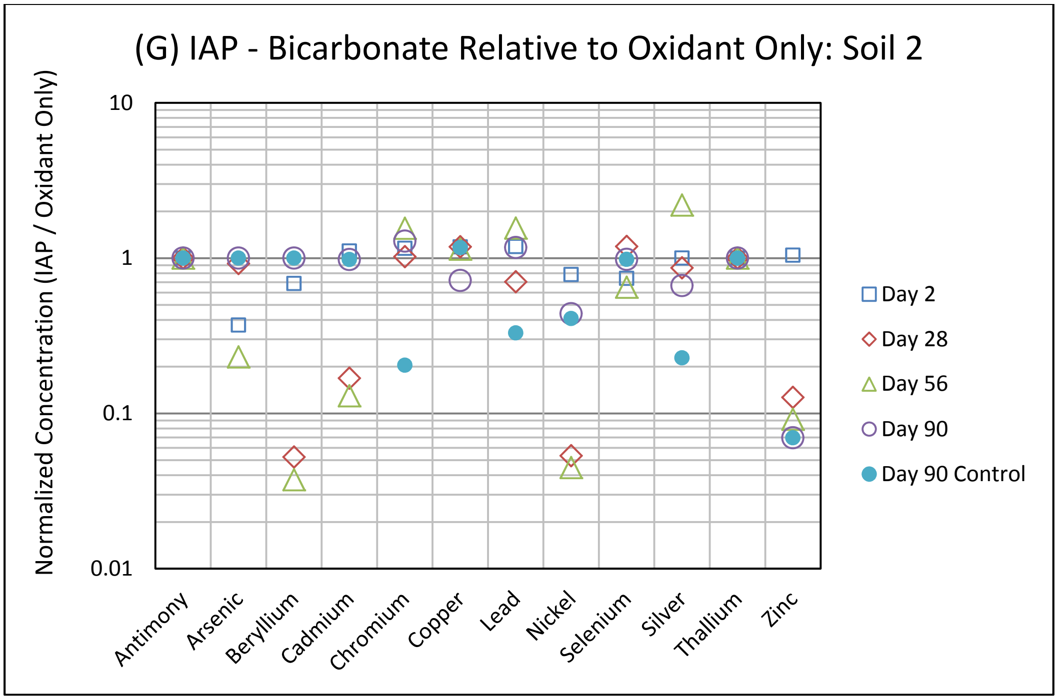


Figure 4.4.43 (cont.) Co-Treatment Chemical Stabilization of IAP System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Chemical Co-treatment with Phosphate Buffer (A,B), Phosphate(C,D), Carbonate Buffer(E,F) and Carbonate (G,H) for both Soil 2 and 6



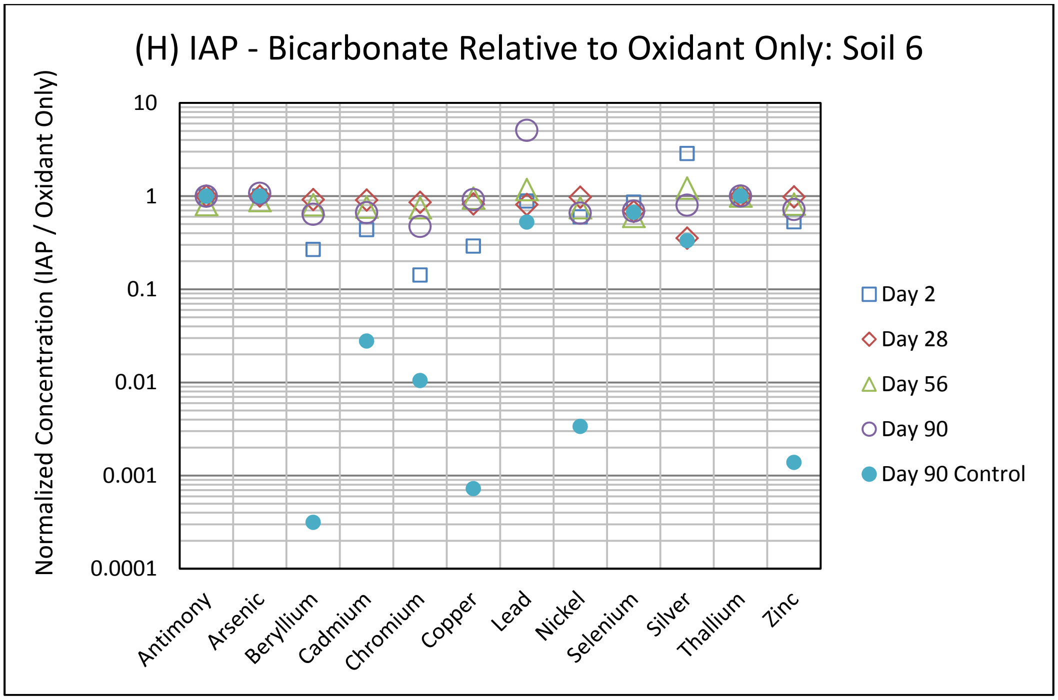


Figure 4.4.43 (cont.) Co-Treatment Chemical Stabilization of IAP System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Chemical Co-treatment with Phosphate Buffer (A,B), Phosphate(C,D), Carbonate Buffer(E,F) and Carbonate (G,H) for both Soil 2 and 6

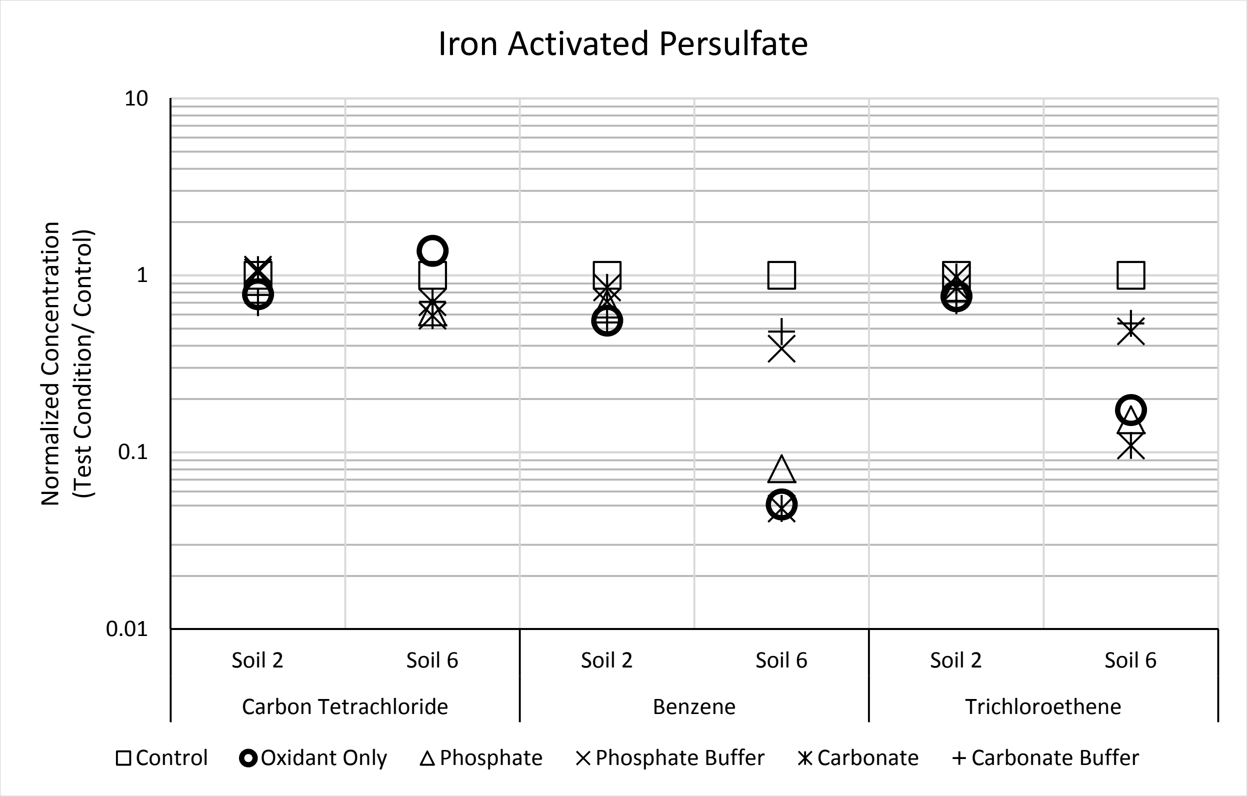


Figure 4.4.44 Co-Treatment Chemical Stabilization of IAP System: Treatment Efficacy-Normalized Concentrations of probe compounds carbon tetrachloride, benzene, and trichloroethene.

Catalyzed Hydrogen Peroxide. Figure 4.4.45 presents the concentrations of the selected metals in reactors treated with CHP normalized to the metal concentrations in the control reactors for each respective time point for Soils 1, 2, and 6. The data show that concentrations of Be, Cd, Cr, Cu, Ni, and Zn were higher than the control reactors for Soils 1, 2 and 6. Most other priority pollutants in the reactors containing CHP were similar in concentration to the control reactors. The similar data between the three soil types indicates that the priority pollutants most likely to be mobilized after contact with CHP include Be, Cd, Cr, Cu, Ni, and Zn.

Figure 4.4.46 presents concentrations after 2 days of contact of selected metals in reactors with chemical additives added to CHP, normalized to the metals concentration in the reactors treated with CHP only, for Soils 1, 2, and 6. Each of the metals found to increase in concentration in Figure 4.4.46 was observed to decrease in concentration in the presence of several of the treatment conditions.

The screening data show that both the phosphate buffer and bicarbonate buffer consistently resulted in lower concentrations of three to five of the six metals that were observed to be potentially impacted by CHP. The metals that were reduced varied with each soil type, but included Be and Zn for all three soil types, and included Cd, Cr, Cu, and Ni for certain treatment condition and soil combinations. However, because carbonates are considered a scavenger of the hydroxyl radical, a critical oxidant formed in CHP, the bicarbonate buffer system was not selected for further evaluation.

The phosphate treatment condition resulted decreases in concentration of two to three of the priority pollutant metals that had been observed to increase in concentration compared to the control reactors in the presence of CHP. The bicarbonate and iodate treatment conditions both resulted in a reduction of zero to three of the metals, depending upon soil. The addition of sulfate had no effect on the six metals of concern with CHP.

Based upon these results and the concern that bicarbonate could interfere with the CHP treatment process, the phosphate and phosphate buffer treatment conditions were selected for further evaluation over a 90 day period to evaluate the longer term impacts of chemical additives on metals mobilization with CHP, and to evaluate the impact of these additives on the treatment efficacy of CHP on probe compounds. It should be noted that the screening level data did indicate that several metals increased as a result of the treatment conditions. This was further evaluated with additional time points up to 90 days.

Figure 4.4.47 shows the pH and ORP during the experiment for the test conditions selected for additional evaluation. For both Soil 2 and Soil 6, the pH of the phosphate buffer system remained near neutral and higher than the pH of the CHP only systems throughout the 90 days evaluated. In the Soil 2 phosphate systems, the pH was higher than the oxidant only systems, and in the Soil 6 phosphate systems, the pH was similar to the oxidant only systems.

The ORP in the phosphate buffer systems was generally lower than the CHP only system for both soil types evaluated. For Soil 6, both the phosphate and CHP only systems started near 400 mV and showed a decreasing trend over the duration evaluated with the phosphate system generally lower than the CHP only system. The ORP in the phosphate buffer systems and the CHP only systems fluctuated throughout the test, both returning to near baseline conditions by Day 90. For Soil 2, the ORP in the phosphate systems remained relatively stable and lower than the CHP only systems throughout the test. The data indicate that both dosage levels of phosphate had an impact on both pH and ORP of the systems.

Figure 4.4.48 shows the change in concentration of priority pollutant metals over time, normalized to the respective metal concentrations in the reactors containing CHP only for the selected treatment conditions. The data show that by Day 90 the concentrations of Be, Cd, Cr, Cu, Ni, Ag, and Zn were lower in the control reactors compared to CHP only for both soil types.

For Soil 6 only, the phosphate buffer system (100 mM phosphate per kg soil; Figure 4.4.48B) resulted in concentrations of Be, Cd and Zn close to the control reactors after 90 days. An effect was also observed for Cr, Cu, and Ni which had concentrations less than the CHP only reactor during the test. The phosphate buffer system was observed to increase the concentrations of As which persisted throughout the time evaluated.

The phosphate system (5 mM phosphate per Kg soil) has a similar but more muted effect as the phosphate buffer system. Concentrations of Be, Cd, Cu, Ni, Ag, and Zn were less in the systems treated with the lower dose of phosphate than the CHP only reactors. At Day 90, concentrations of Cd were near those in the control reactors, while the concentration of As was observed to increase in Soil 2, but was near the control and CHP only reactor for Soil 6.

Figure 4.4.49 shows the concentrations of probe compounds (carbon tetrachloride, benzene, and trichloroethene) in systems treated with CHP, both with and without the addition of phosphate and phosphate buffer, normalized to the contaminant concentrations in the control reactors. With both Soil 2 and Soil 6, CHP alone reduced probe compound concentrations by greater than 90 percent for carbon tetrachloride and greater than 99.9 percent for benzene and trichlorobenzene. In Soil 2, the addition of phosphate buffer reduced the treatment efficacy of benzene and trichloroethene, with reductions near 90 percent. Both dosage levels of phosphate had a minor effect on the CHP treatment efficacy of carbon tetrachloride for Soil 6, but concentrations were similar to the CHP only reactors for Soil 2. In the phosphate systems, treatment results were very similar to the CHP only system for benzene and trichloroethene for both soil types.

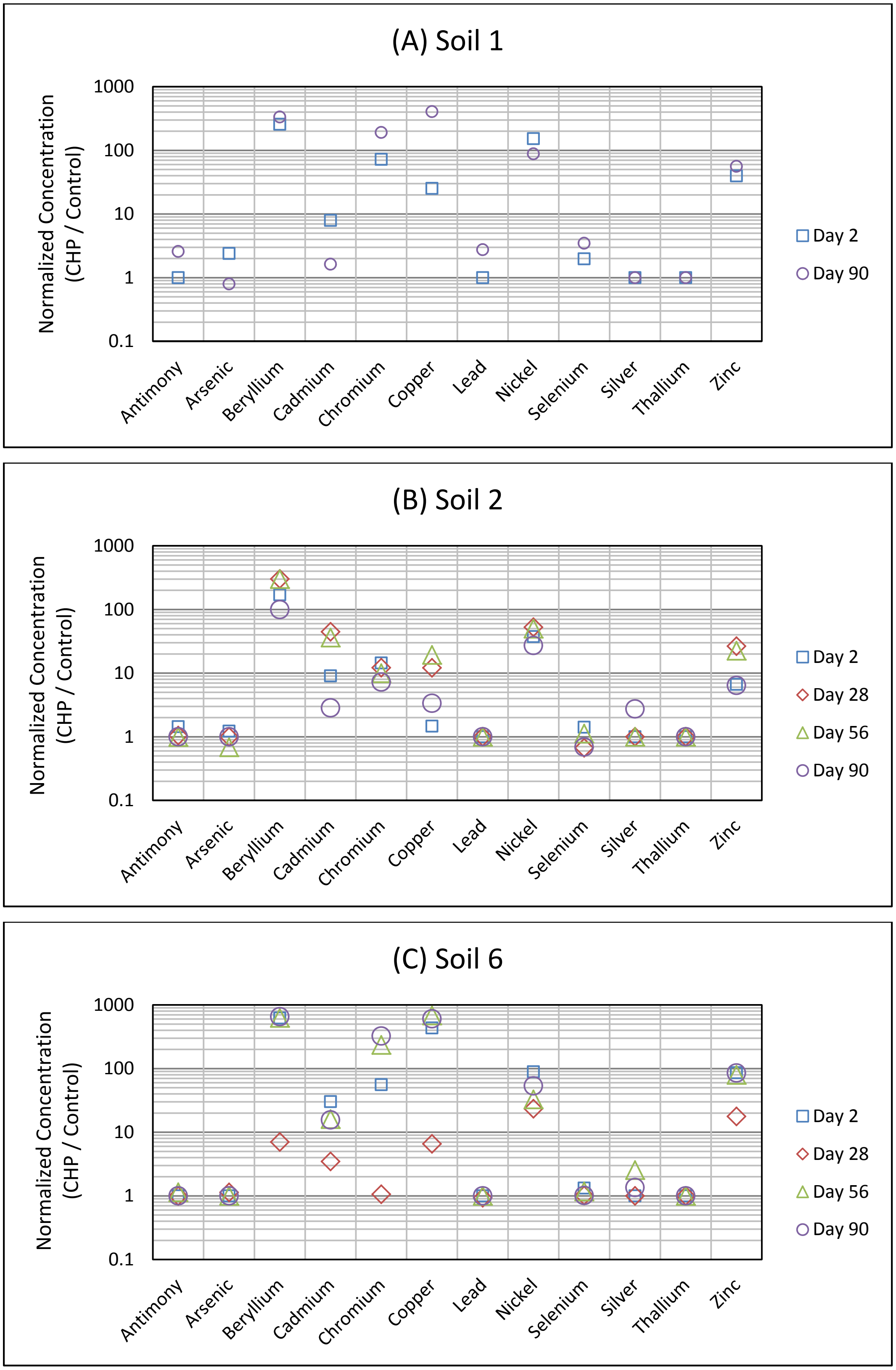


Figure 4.4.45 Co-Treatment Chemical Stabilization: Normalized concentration of metals for reactors with CHP applied versus control conditions (no CHP treatment).

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C)

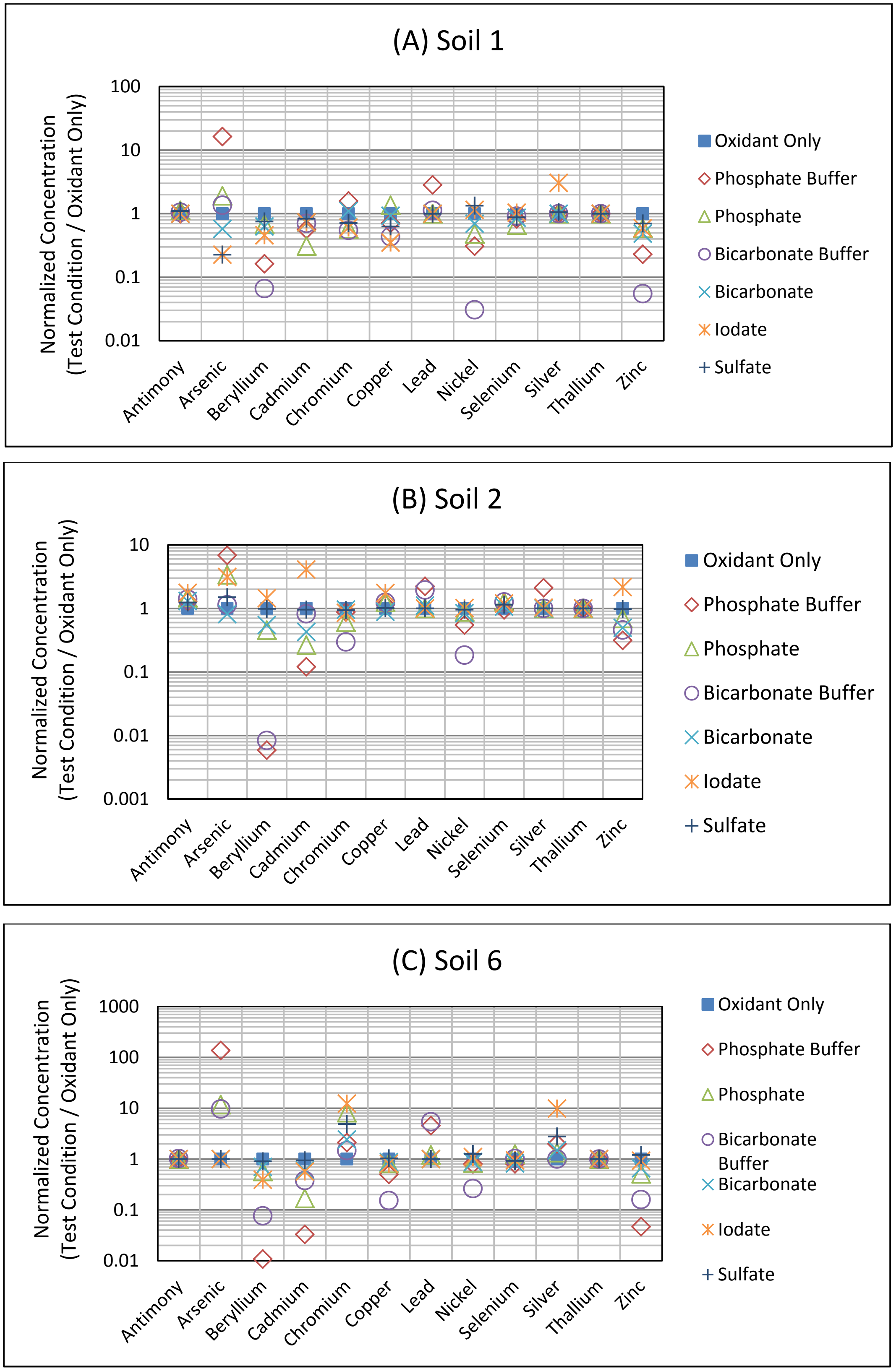


Figure 4.4.46 Co-Treatment Chemical Stabilization of CHP System: Select normalized metal concentrations for 6 chemical treatment options.

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C).

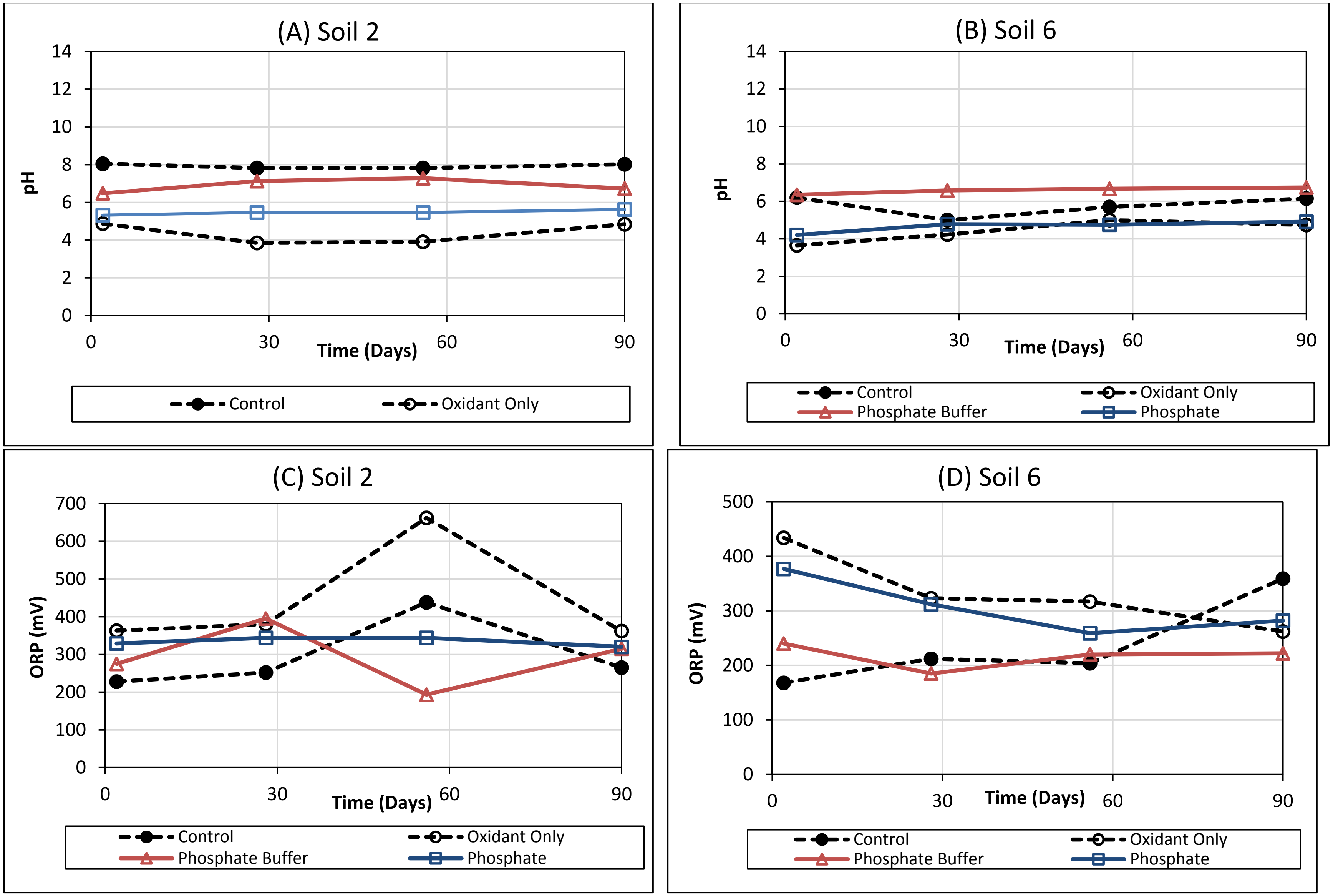


Figure 4.4.47 Co-Treatment Biological Stabilization of CHP System: Geochemical parameters at 2, 28, 56, and 90 days

Note: Soil 2 (A, pH, C, ORP) and Soil 6 (B, pH, D, ORP)

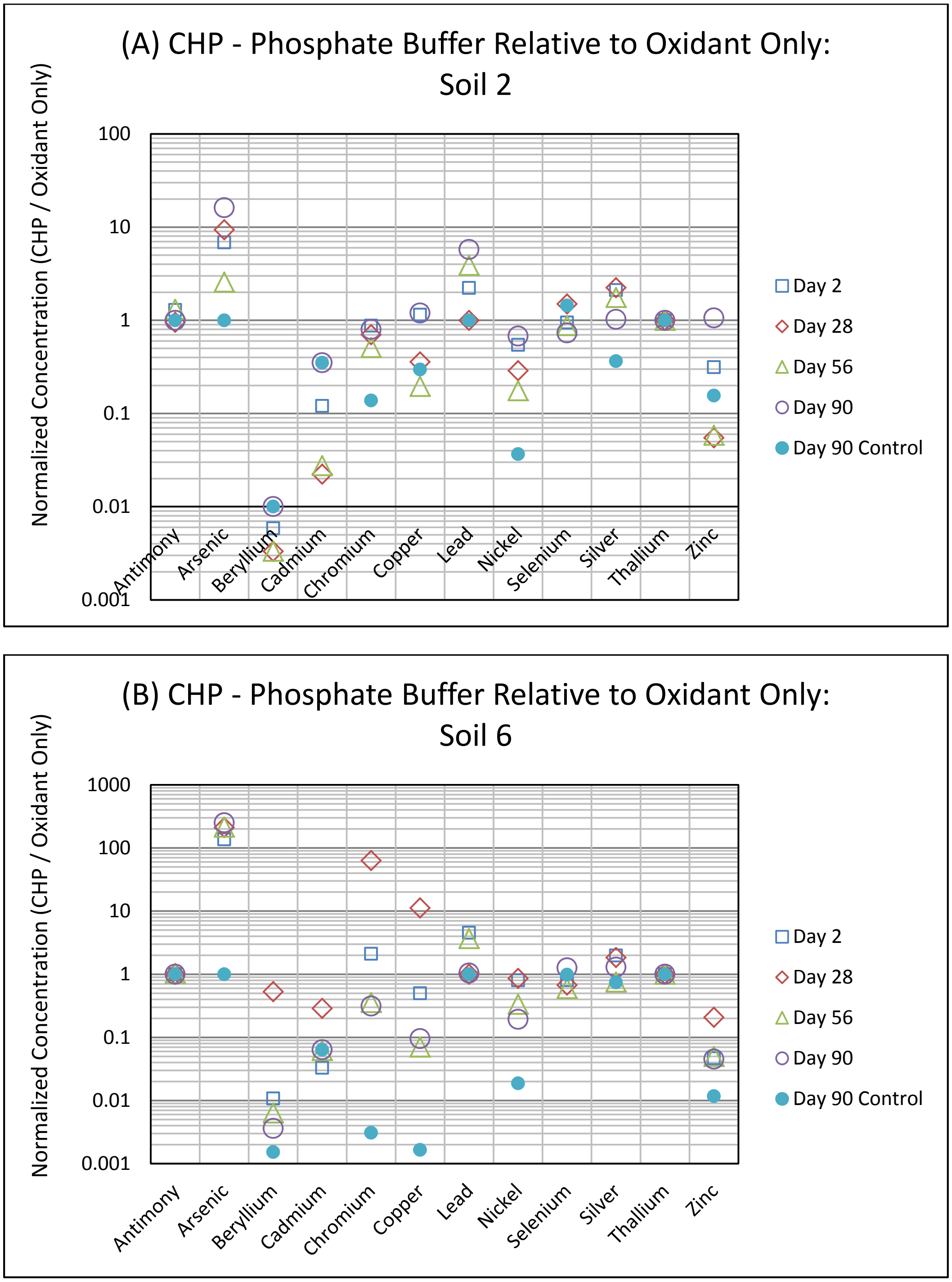
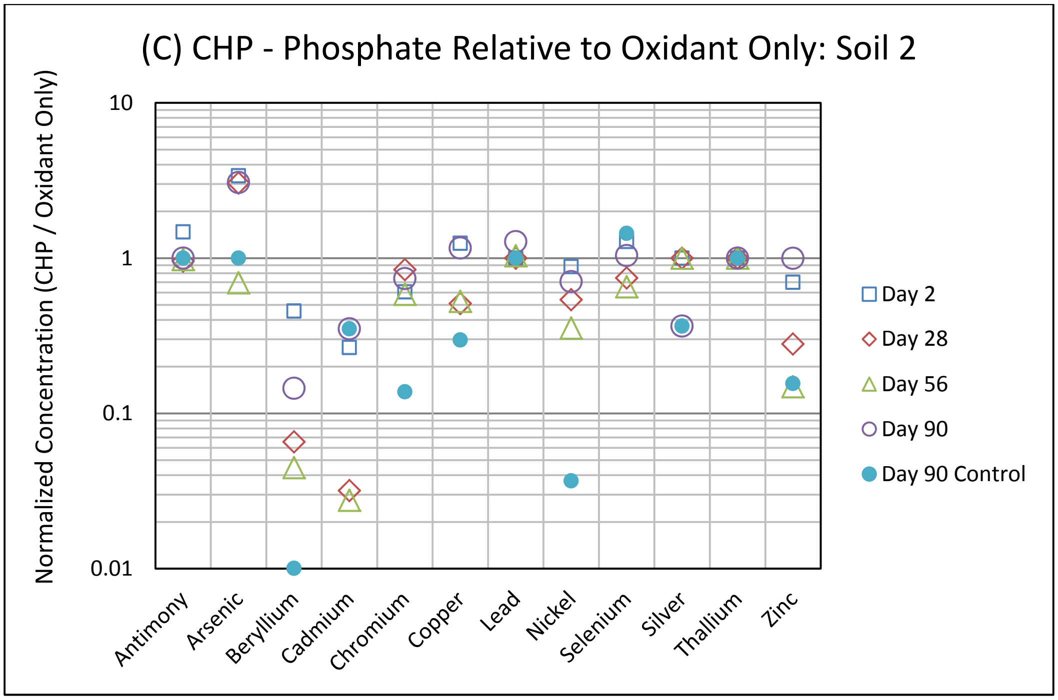


Figure 4.4.48 Co-Treatment Chemical Stabilization of CHP System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Co-treatment with Phosphate Buffer (A,B), and Phosphate (C,D) for both Soil 2 and 6.



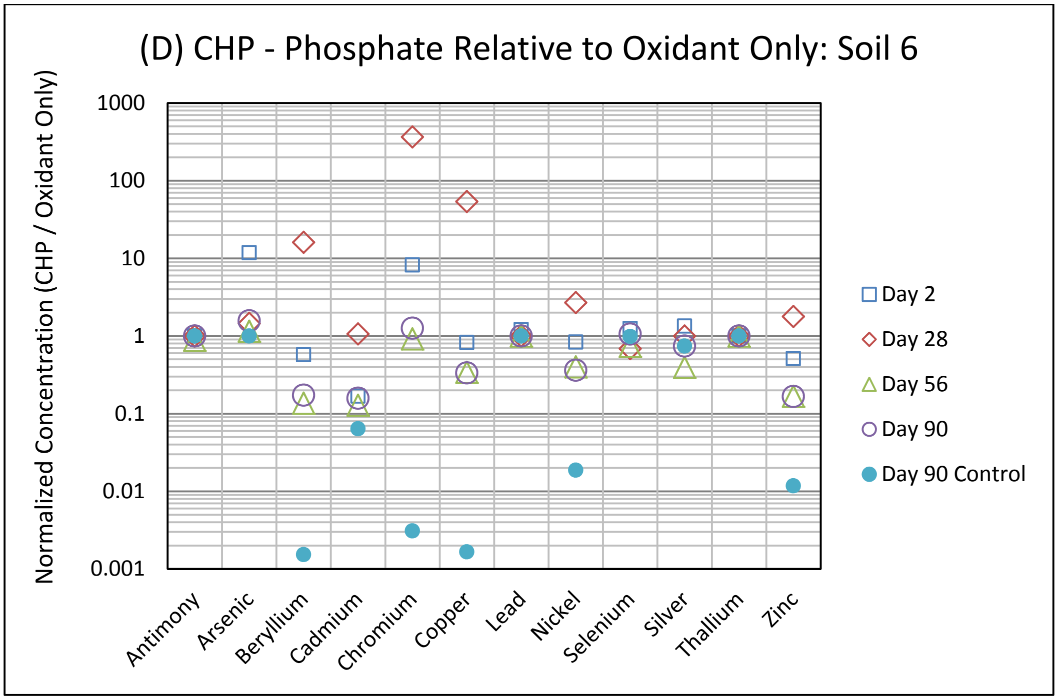


Figure 4.4.48 (cont.) Co-Treatment Chemical Stabilization of CHP System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Co-treatment with Phosphate Buffer (A,B), and Phosphate (C,D) for both Soil 2 and 6..

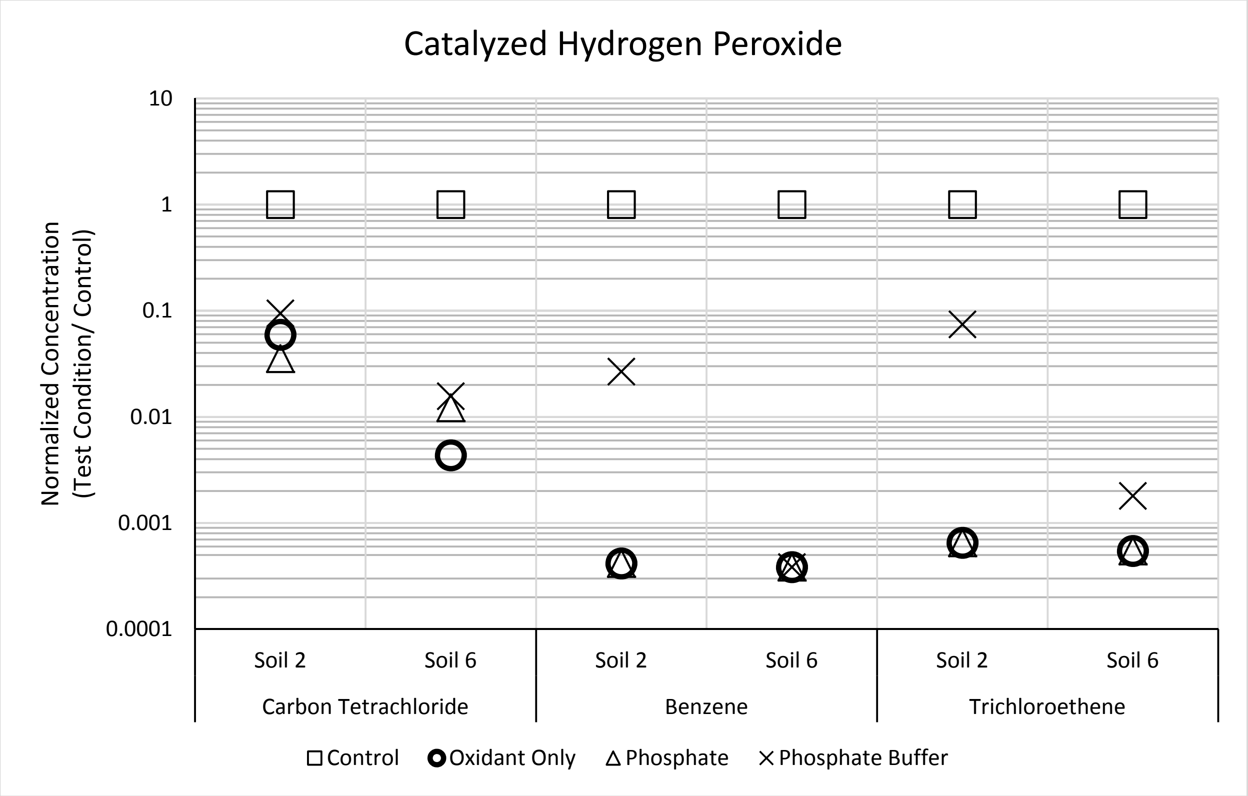


Figure 4.4.49 Co-Treatment Chemical Stabilization of CHP System: Treatment Efficacy-Normalized Concentrations of probe compounds carbon tetrachloride, benzene, and trichloroethene.

Potassium Permanganate. Figure 4.4.50 presents the concentrations of the selected priority pollutant metals in reactors treated with $KMnO_4$ only, normalized to the metal concentrations in the control reactors (water only) for each respective time point for Soils 1, 2, and 6. . The data show that Be, Cr, Pb, Se, Ag, and Tl concentrations increased with the addition of $KMnO_4$ when compared to the concentration observed in the control reactors. Several metals, including Be, Pb, Se and Th, showed a decreasing trend, and in several instances, returned to near the control concentrations over the 90 day period evaluated. However, concentrations of Cr remained elevated relative to the control, and in Soil 6, the difference between the control and reactors treated with $KMnO_4$ increased over time. The concentrations of Sb, As, Cd, Ni, and Zn in the reactors treated with $KMnO_4$ remained very similar to, or were slightly less than, the control reactors throughout the experiment. Concentrations of Cu were similar for Soil 2 and Soil 6, but varied in the presence of Soil 1.

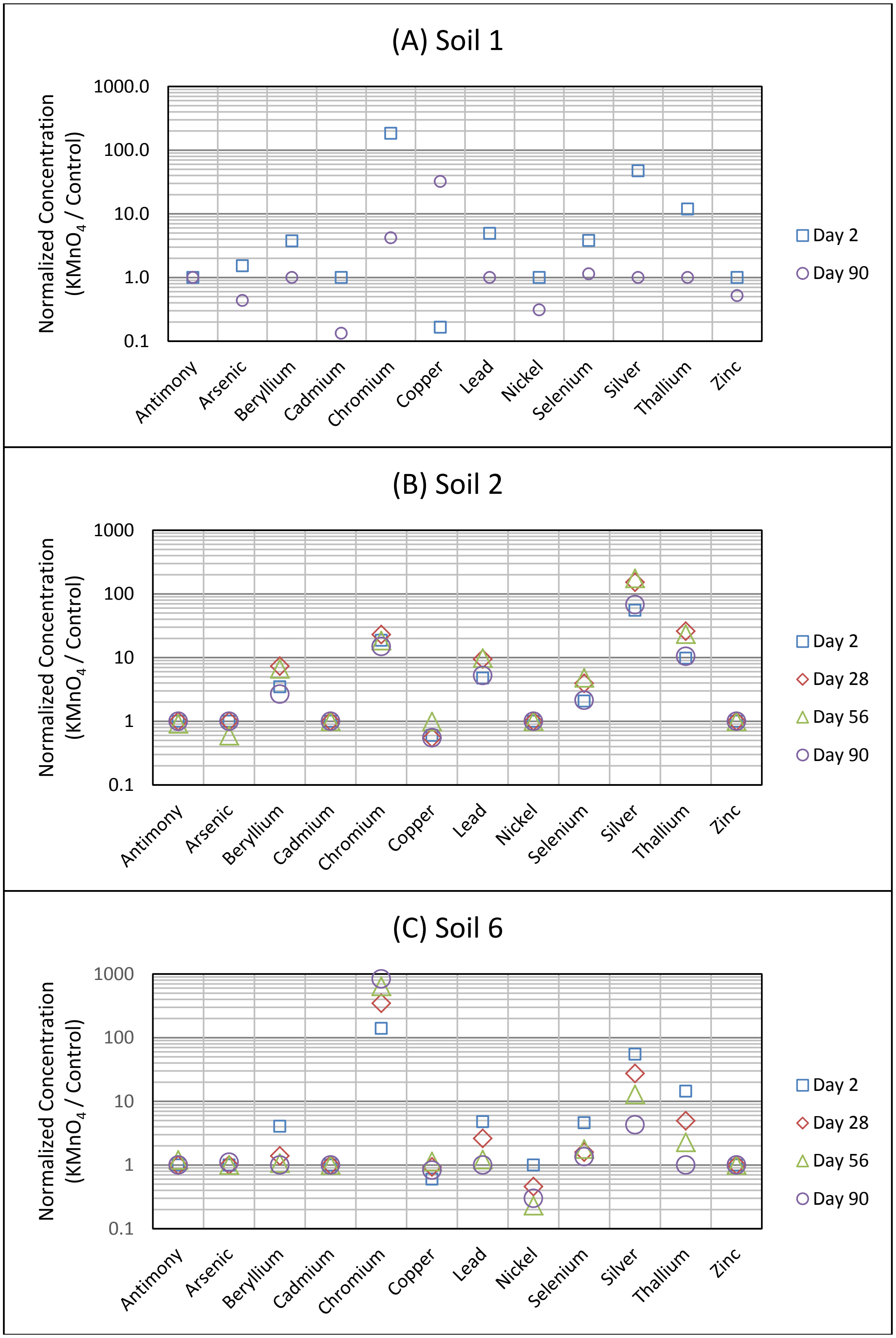
Figure 4.4.51 presents concentrations of selected metals in reactors with selected chemical additives added to $KMnO_4$, normalized to the metals concentration in the reactors treated with $KMnO_4$ only, for Soils 1, 2, and 6 after 2 days of contact. The data show that after 2 days, bicarbonate generally resulted in lower concentrations of most metals for Soil 1, an effect that was not observed in the presence of Soil 2 or Soil 6. The presence of bicarbonate buffer and sulfate resulted in slightly lower concentrations of Be and Tl. Concentrations of As increased with the addition of phosphate, phosphate buffer, and bicarbonate buffer.

Based results from the screening test demonstrating its effectiveness with several metals in Soil 1, the carbonate test condition was selected for further evaluation over a 90 day period to evaluate its longer term impacts of on metals mobilization with $KMnO_4$, and to evaluate its impact on the treatment efficacy of $KMnO_4$ on probe compounds.

Figure 4.4.52 shows the pH and OPR measured at each of the four time points of the experiment (2, 28, 56 and 90 days). The addition of $KMnO_4$ amended with sodium bicarbonate had a minimal effect on system pH compared to the control, with all three test conditions having relatively stable pH throughout the experimental period. However, addition of $KMnO_4$ to both Soil 2 and Soil 6 increased system ORP to 600 mV. The addition of bicarbonate to $KMnO_4$ resulted in less than 80 mV decrease in system ORP compared to the $KMnO_4$ only system.

As shown in Figure 4.4.53, the addition of bicarbonate (5 mM/Kg) to $KMnO_4$ reactors resulted in minimal changes in the presence of Soil 2 and Soil 6. In Soil 2, the concentration of several metals initially decreased, including As, Be, Cr, Pb, Ag, and Th. By the end of the study, the difference in metal concentration between the $KMnO_4$ reactors with carbonate and without was less than 10 percent. The data also show that the concentrations of several metals in the control reactors were significantly less than in reactors containing $KMnO_4$. For Soil 2, concentrations of Be, Cr, PB, Ag, and Th in the control reactor were less than 20 percent of concentrations observed in the reactors with $KMnO_4$. For Soil 6, a concentration of Cr in the control reactor was less than 0.1 percent of that observed in reactors containing $KMnO_4$.

Figure 4.4.54 shows the concentrations of probe compounds (carbon tetrachloride, benzene, and trichloroethene) in systems treated with $KMnO_4$, both with and without the addition of carbonate, normalized to the contaminant concentrations in the control reactors. Treatment with $KMnO_4$ did not show reduction in carbon tetrachloride or benzene, but showed greater than 99 percent removal of trichloroethene. The addition of bicarbonate had little to no effect on the efficacy of $KMnO_4$ on trichloroethene destruction for either Soil 2 or Soil 6.



(A) Soil 1

(B) Soil 2

(C) Soil 6

Figure 4.4.50 Co-Treatment Chemical Stabilization: Normalized concentration of metals for reactors with PM applied versus control conditions (no PM treatment).

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C).

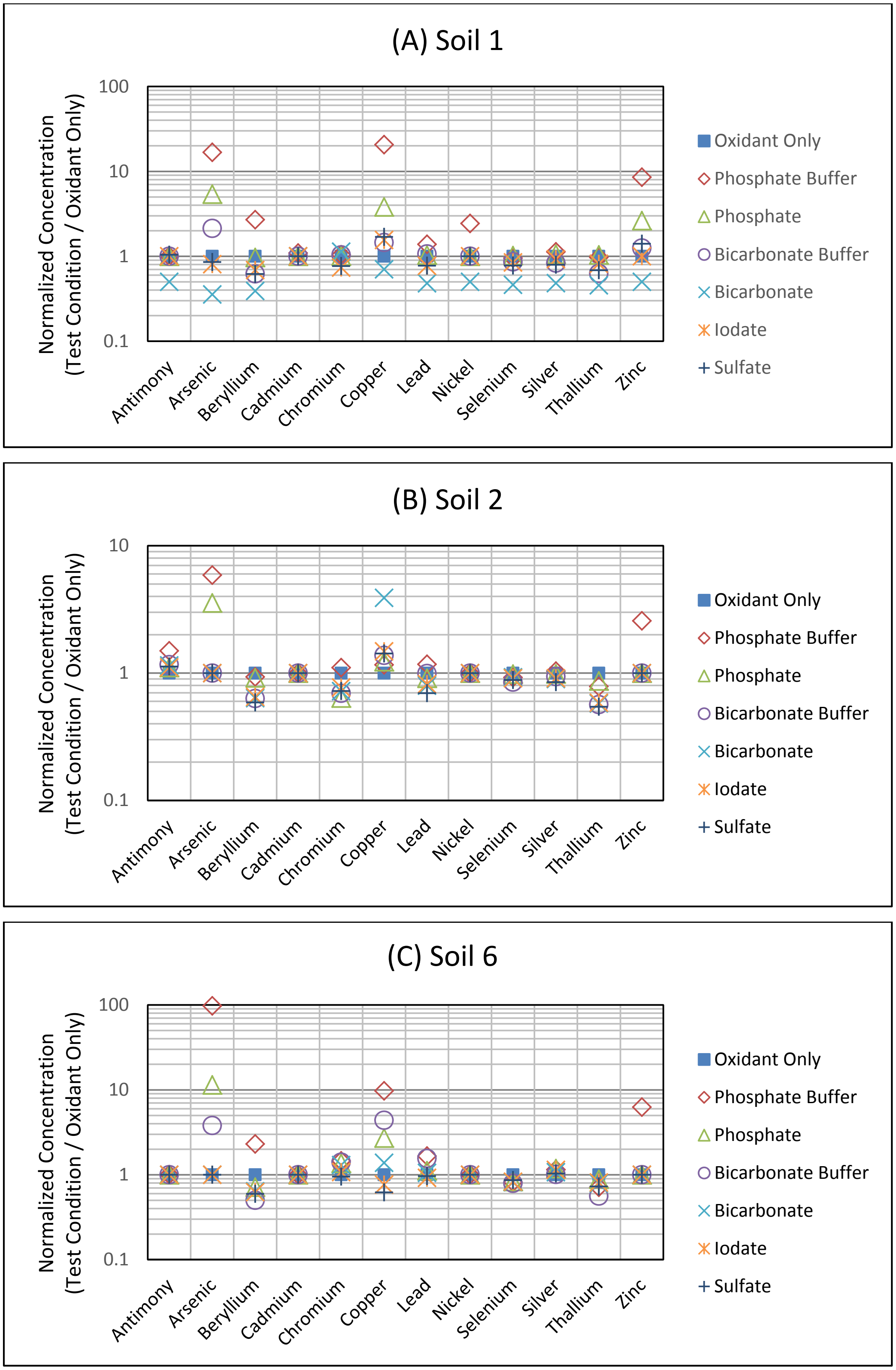


Figure 4.4.51 Co-Treatment Chemical Stabilization of PM System: Select normalized metal concentrations for 6 chemical treatment options.

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C).

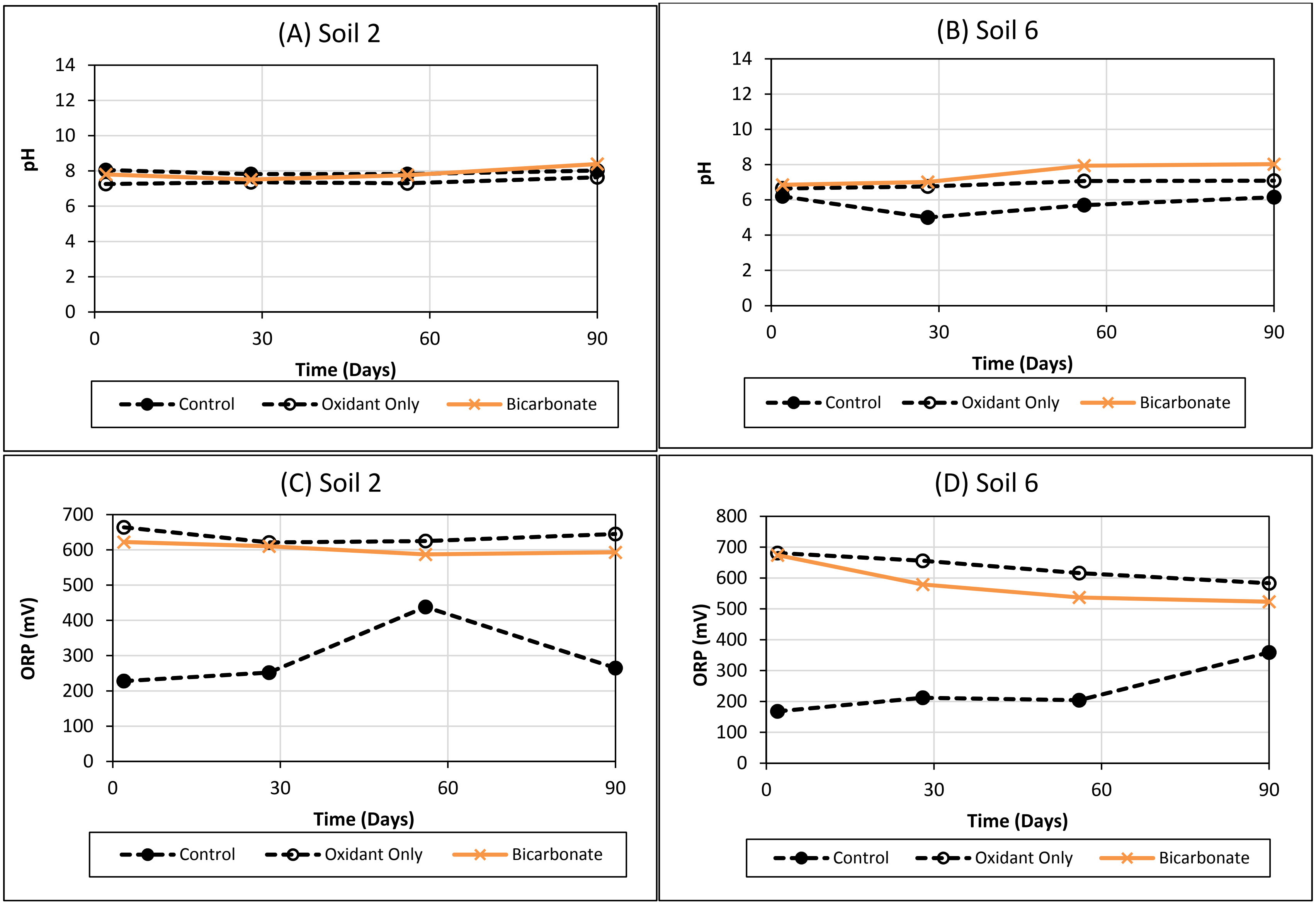
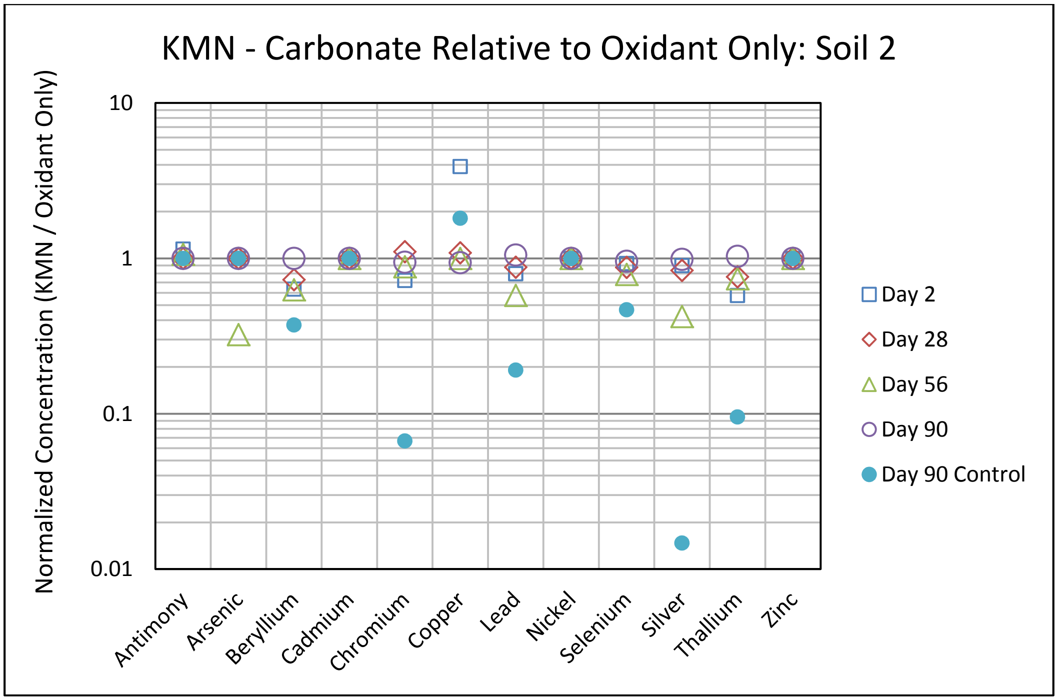


Figure 4.4.52 Co-Treatment Chemical Stabilization of PM System: Geochemical parameters at 2, 28, 56, and 90 days

Note: Soil 2 (A, pH, C, ORP) and Soil 6 (B, pH, D, ORP).



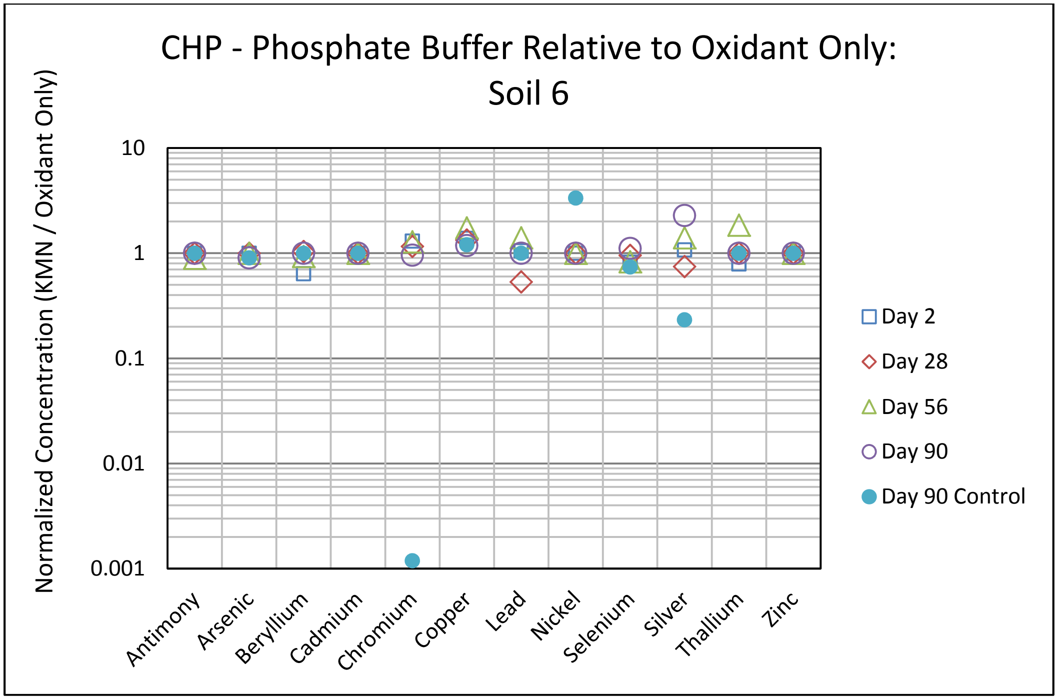


Figure 4.4.53 Co-Treatment Chemical Stabilization of PM System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Co-treatment with Phosphate Buffer (A,B) for both Soil 2 and 6.

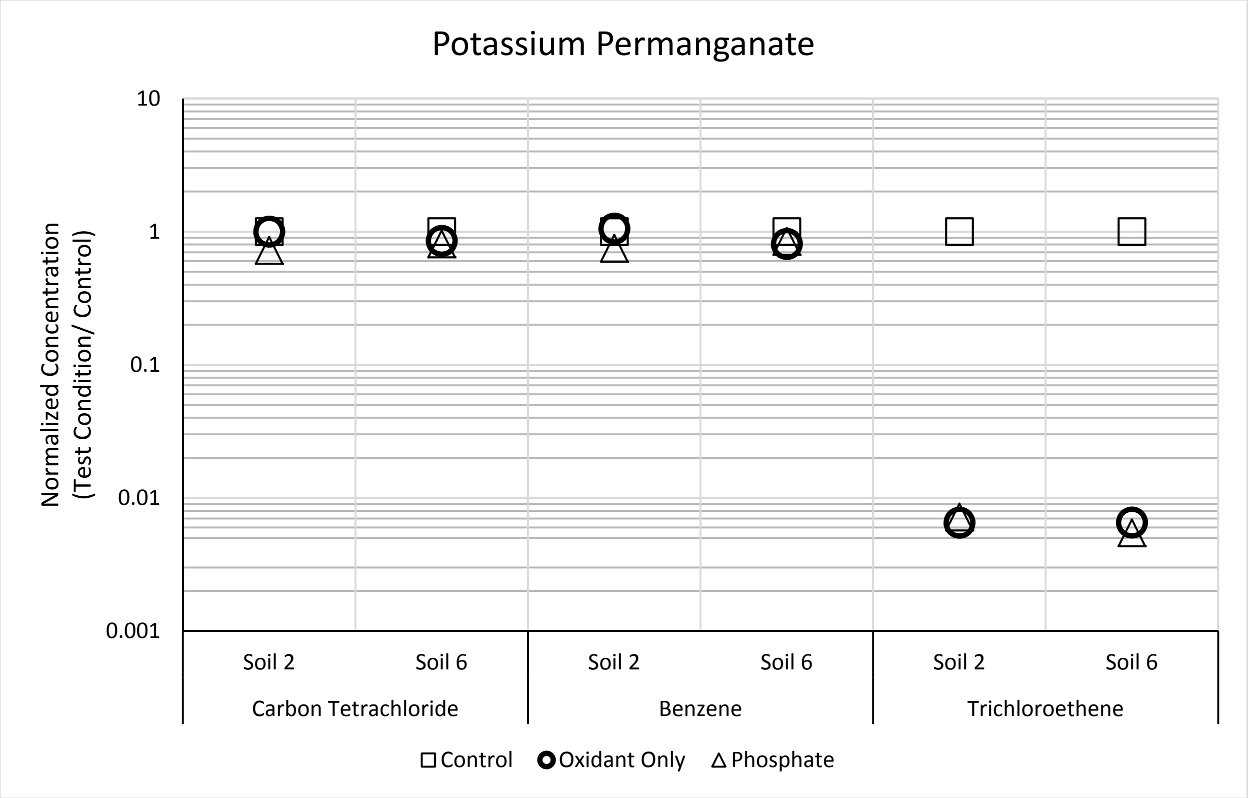


Figure 4.4.54 Co-Treatment Chemical Stabilization of PM System: Treatment Efficacy-Normalized Concentrations of probe compounds carbon tetrachloride, benzene, and trichloroethene.

4.4.4 Post-Treatment Stabilization Evaluation

Sections 4.1 to 4.3 evaluated the addition of reagent before and with the ISCO reagents, respectively. The post-treatment evaluation, involves the addition of reagents after the completion of an ISCO application. This type of approach could be both reactionary to field observations or as a planned strategy to help mitigate the mobilization of metals. As the reagents are theoretically to be added after the ISCO reagents have had sufficient time to react with the site soils, there is less concern regarding the compatibility and interaction of the metals stabilization reagents and oxidants from ISCO allowing the use of compounds known to react quickly with ISCO reagents, such as the sulfide anion.

The various test conditions evaluated were intended to form precipitates with certain metals or help revert the system geochemical conditions back to baseline, either by modifying pH or ORP. The ISCO technologies evaluated include:

- Alkaline activated persulfate (AAP)
- Iron-chelate activated persulfate (IAP)
- Catalyzed hydrogen peroxide (CHP)
- Potassium permanganate ($KMnO_4$)

Data was gathered for 22 metals during these experiments. The discussion of the data presented in this section will focus on metals that are listed as priority pollutants under the Safe Drinking Water Act as Task 4 is intended to help identify methods to mitigate the mobilization of metals of environmental concern. These metals include silver (Ag), arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), thallium (Tl), and zinc (Zn). Mercury (Hg) is also listed as a priority pollutant but was not analyzed for during these experiments due to limitations in the analytical equipment.

Alkaline-Activated Persulfate. Figure 4.4.55 presents the concentrations of the selected priority pollutant metals in reactors treated with AAP only, normalized to the metal concentrations found in the control reactor (water only) for each respective time point for Soils 1, 2, and 6. The data show that As, Cr, and Cu increased in reactors containing AAP over a 118 day period compared to the control reactors. Other metals were also found to increase in less than all three of the soil types, including Pb in Soils 1 and 2 and Zn in Soil 2. Conversely, with Soils 1 and 6, the concentration of Ni decreased in reactors treated with AAP.

Various amendments were added to reactors after 28 days of contact with AAP. These amendments were allowed 2 days of contact with the ISCO reagents and soils, and on Day 30, the concentrations of metals were assessed. Figure 4.4.56 shows the concentration of priority pollutant metals in the amended AAP reactors, normalized to the concentrations in AAP only reactors. The data presented in Figure 4.4.56 indicate that the addition of sulfide (intended to both create reducing conditions and precipitate the mobilized metals) reduced the concentrations of As, Cr, and Cu in the presence of all three soil types, while resulting in increased concentrations of Cd, Ni, and Zn for Soil 1 and Ni for Soil 6. The pH neutralization treatment condition resulted in lower concentrations of As for all three soil types and lower concentrations of Cu in the presence of Soil 1. However, pH neutralization appears to increase the concentration of several metals in the presence of Soil 2 (Figure 4.4.56B). As shown in Figure 4.4.56, other treatment conditions had limited and somewhat inconsistent effects for different metals for each soil type.

Based on the screening results, the test conditions of pH neutralization and sulfide addition were selected for further evaluation over additional time points to evaluate their longer term impacts of on metals mobilization with AAP. The additional evaluation involved collecting data from time points after 30, 56, 84 and 118 days of contact with AAP in the presence of Soil 2 and Soil 6. Additional evaluation was not conducted on Soil 1 it was depleted during the screening tests

Figure 4.4.57 shows the pH and ORP over the 4 time points for each test condition for Soil 2 and Soil 6. The pH of the AAP only reactor for Soil 2 was above pH 12 and remained above pH 10.5 for the duration of the experiment while the pH in Soil 6 was above pH 10.5 at the Day 30 time point, but had dropped below pH 10.5 by Day 56. For both Soil 2 and Soil 6, the addition of sulfide to AAP resulted in a very similar pH to AAP only while resulting in a significantly lower ORP for both Soil 2 and 6, with the exception of Day 118 for Soil 2. The pH neutralization test condition maintained near pH 8 for both Soil 2 and 6 for the time period evaluated. The ORP for both soil types was similar to the control and AAP only reactors, varying between 200 and 400 mV.

Figure 4.4.58 shows the concentration of priority pollutant metals in AAP reactors for each of the selected test conditions, normalized to the respective concentrations in AAP only reactors at Days 30, 56, 84, and 118. The data presented in Figures 4.4.58A and B show the impact of the pH neutralization test condition for Soil 2 and Soil 6, respectively. The concentrations of several metals at the Day 30 and, to a lesser extent, Day 56, time points are greater than those observed in the AAP only reactor, indicating that pH neutralization initially resulted in an increase in the concentration of several metals. By Day 118, 90 days after the addition of HCl to neutralize the pH, concentrations of all metals, with the exception of Ag, were at or below concentrations observed in the AAP only reactors. For both Soil 2 and Soil 6, the pH neutralization test condition resulted in As and Cr concentrations lower than AAP only reactors, with the concentrations of As after pH neutralization lower than the pH of the Day 118 control reactor. The concentrations of Cu were lower than the AAP only reactor for Soil 6 but similar to the AAP only reactor for Soil 2. At 118 days, concentrations of Pb were similar to the control for Soil 6 and lower than AAP only for Soil 2.

In both Soil 2 and Soil 6 systems, As and Cr concentrations increased significantly with the addition of AAP. The data presented in Figure 4.4.58C and D show that the addition of sulfide decreased the concentration of both As and Cr to concentrations similar to, or lower than, the control at Day 118. This is a critical result for the two primary metals of concern with AAP. The addition of sulfide resulted in concentrations higher than the AAP only reactor for several metals, including Ag. This is considered less critical as many of these concentrations for both the sulfide and AAP only test conditions were similar to the control reactors.

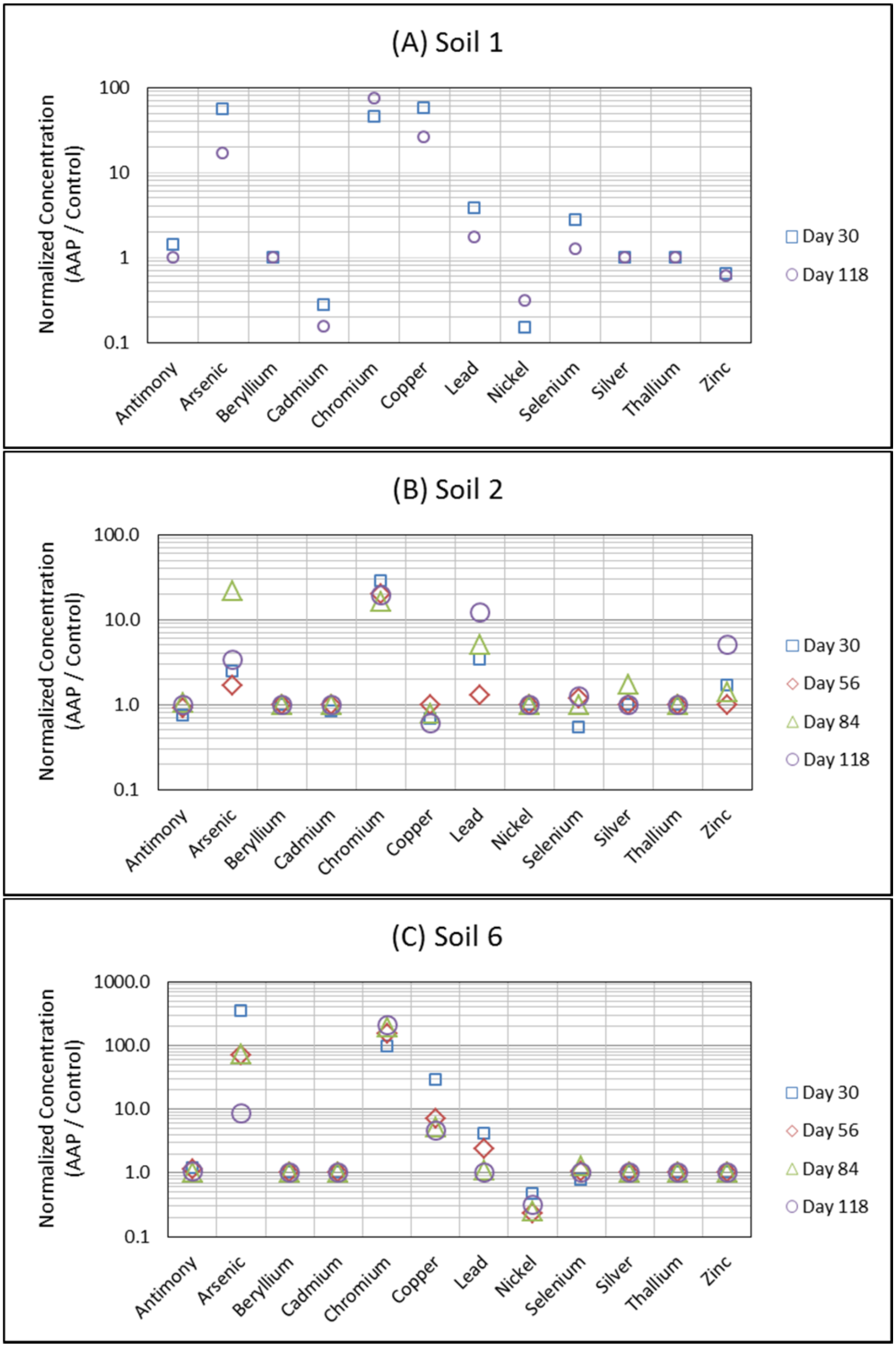


Figure 4.4.55 Post-Treatment Chemical Stabilization: Normalized concentration of metals for reactors with AAP applied versus control conditions (no AAP treatment).

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C).

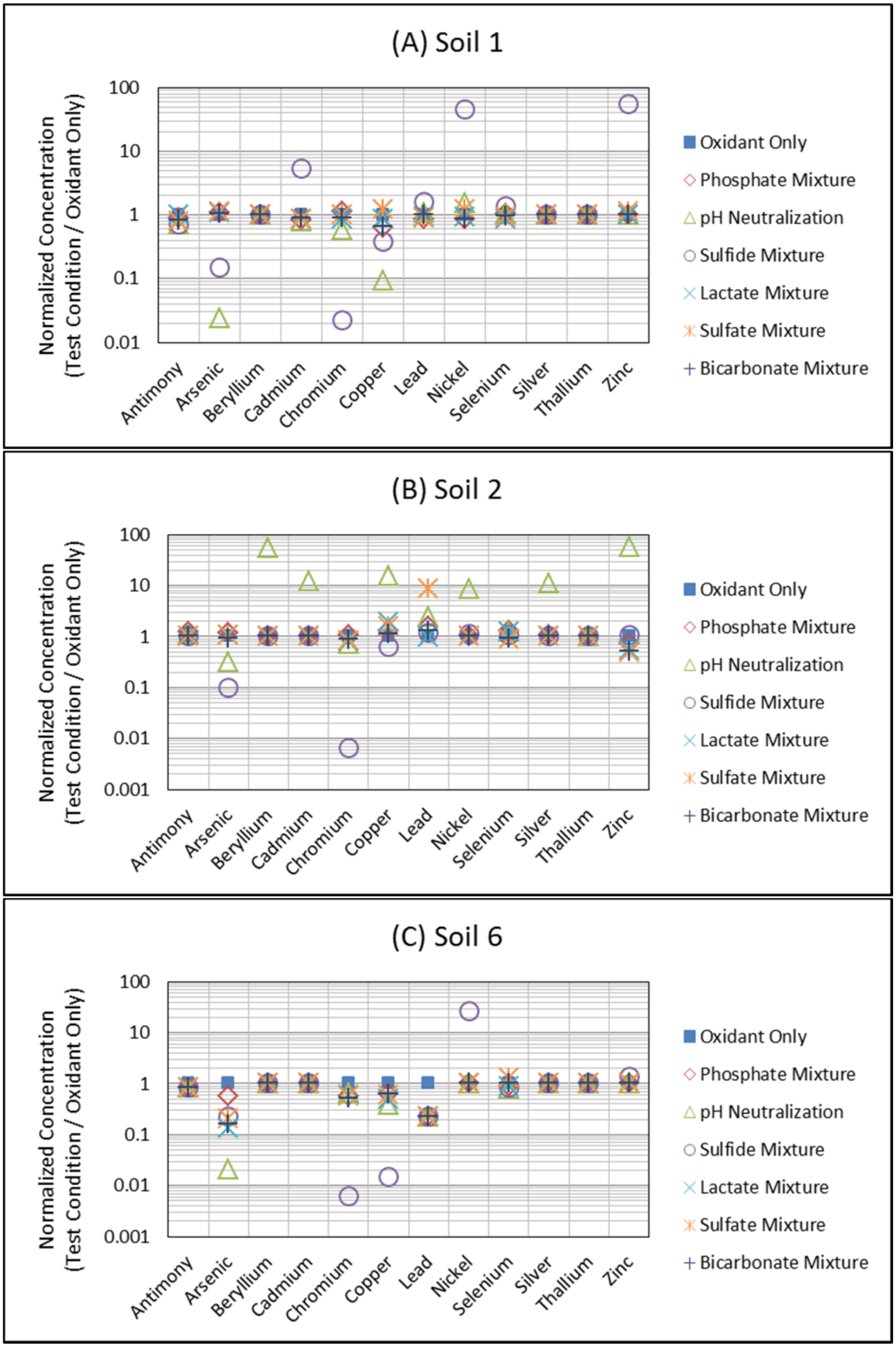


Figure 4.4.56 Post-Treatment Chemical Stabilization of AAP System: Select normalized metal concentrations for 6 chemical treatment options.

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C).

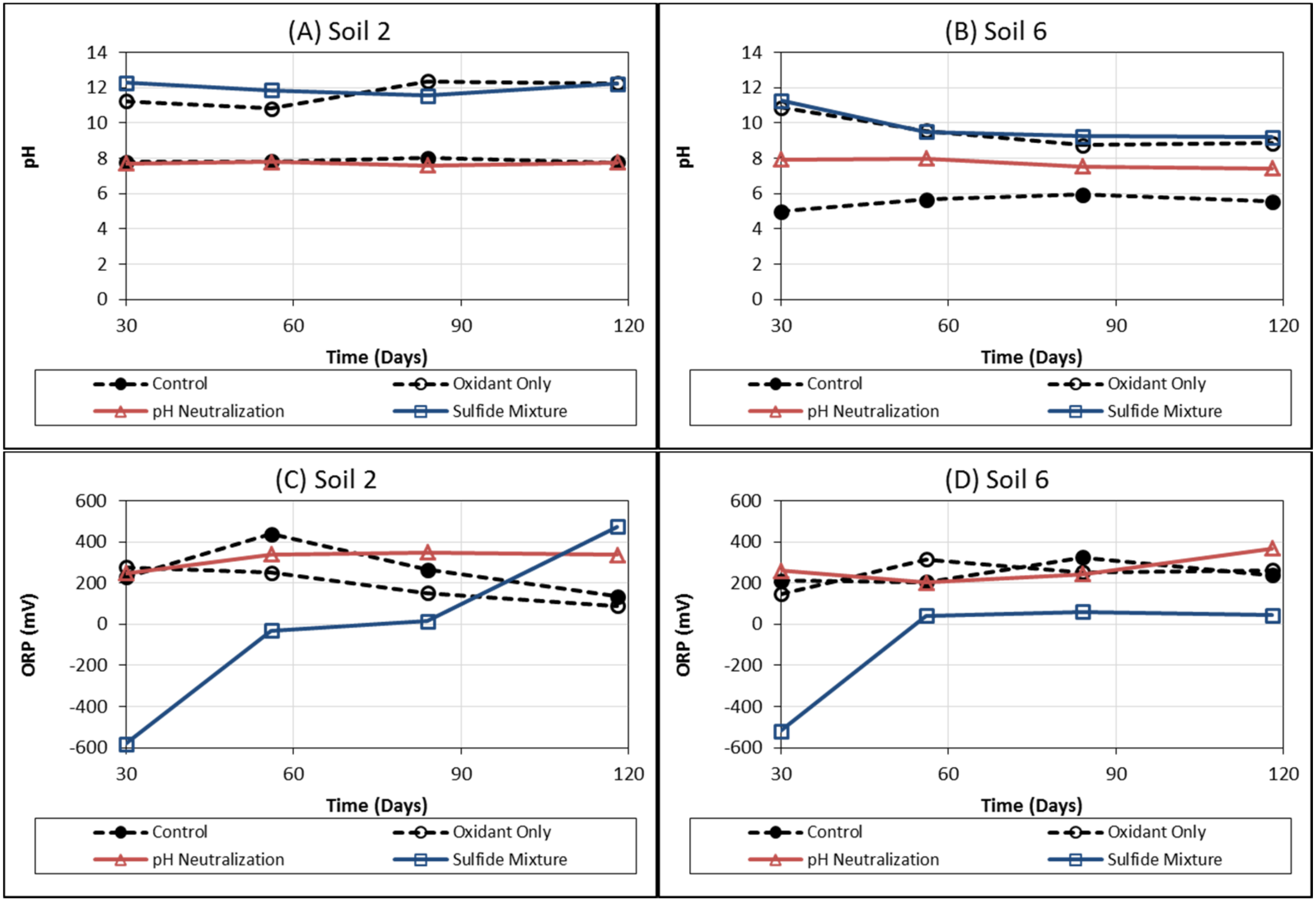


Figure 4.4.57 Post-Treatment Chemical Stabilization of AAP System: Geochemical parameters at 2, 28, 56, and 90 days

Note: Soil 2 (A, pH, C, ORP) and Soil 6 (B, pH, D, ORP)

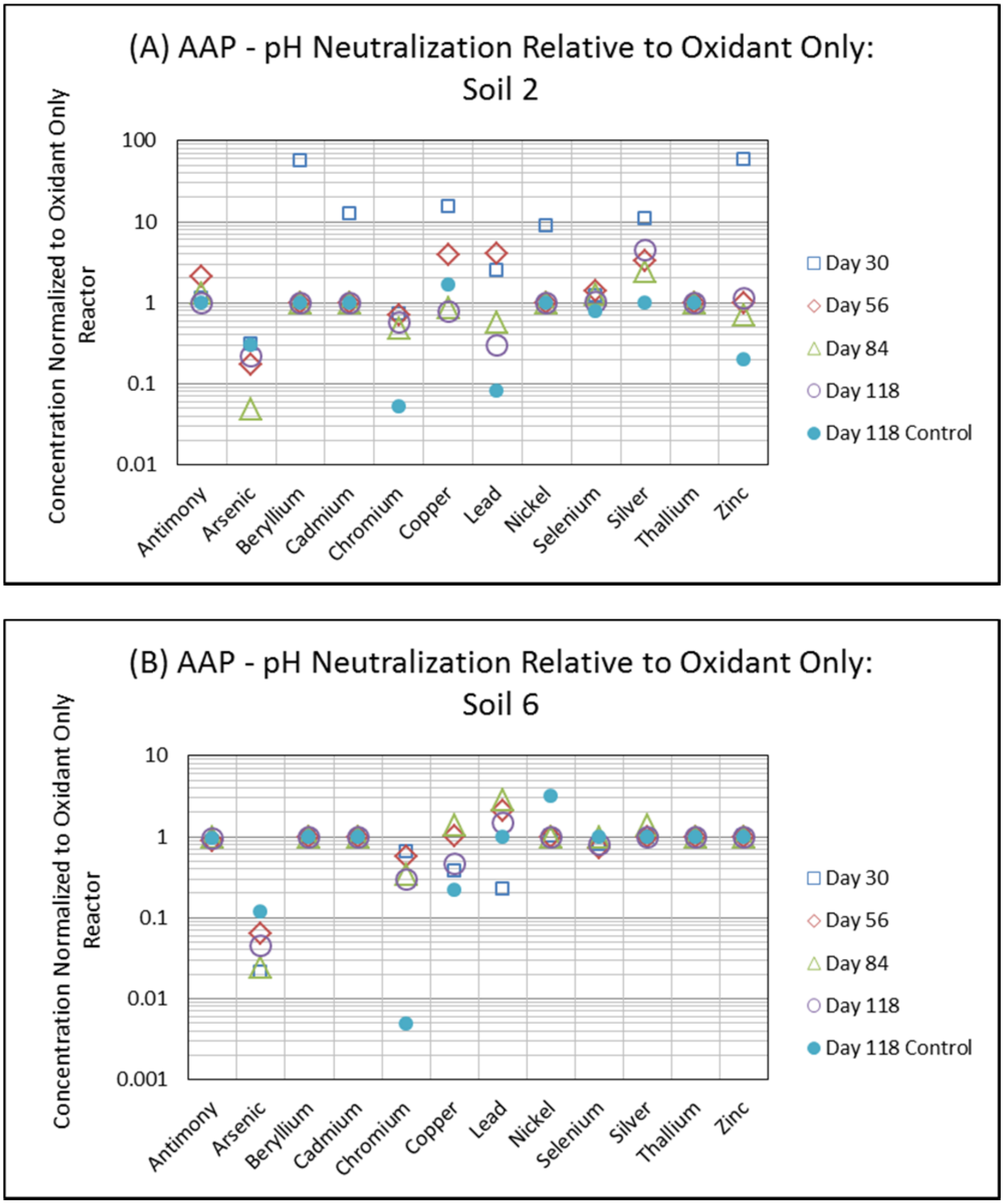


Figure 4.4.58 Post-Treatment Chemical Stabilization of AAP System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Chemical Post-treatment with pH Neutralization (A,B), sulfide mixture(C,D) for both Soil 2 and 6

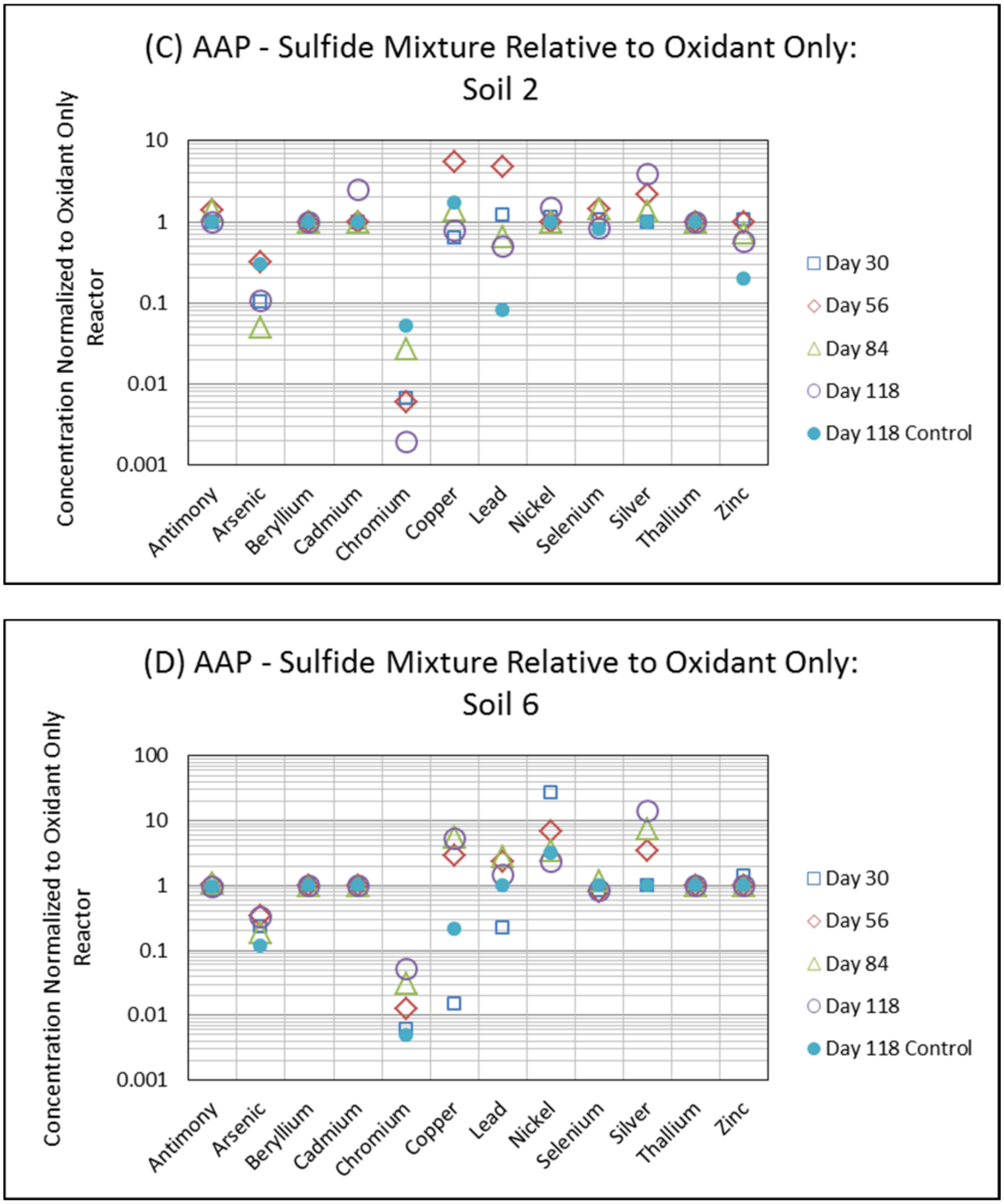


Figure 4.4.58 (cont.) Post-Treatment Chemical Stabilization of AAP System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Chemical Post-treatment with pH Neutralization (A,B), sulfide mixture(C,D) for both Soil 2 and 6

Iron-Activated Persulfate. Figure 4.4.59 presents the concentrations of the selected priority pollutant metals in reactors treated with IAP only normalized to the metal concentrations found in the control reactor (water only) for each respective time point for Soils 1, 2, and 6. The data indicate that the addition of IAP resulted in increased concentrations of Cr, Pb, Ni, and Zn, relative to the control of for each of the three soil types tested. Other metals, including as Sb, Be Cu, increased in two of the three soil types, and As and Cd increased in at least one of the soil types.

Figure 4.4.60 presents the amendment screening data which shows the concentration of priority pollutant metals in reactors with amendments added after 28 days of contact with IAP normalized to the concentrations in IAP only reactors. These amendments were allowed 2 days of contact with the ISCO reagents and soils, and on Day 30, the concentrations of metals were assessed. With Soil 1, addition of sulfide reduced Be, Cd, Cr, Cu, Ni, and Zn concentrations, while neutralization of system pH reduced Be, Cd, Cr, Cu and Zn concentrations greater than 50 percent as compared to IAP only conditions. For the Soil 2 system, addition of sulfide decreased As, Cr, and Cu concentrations, while increasing Cd and Zn concentrations. Neutralizing the Soil 2 system pH decreased Ni concentrations while increasing Cu concentrations. Addition of phosphate increased Be, Cd, and Zn concentrations. For Soil 6, addition of sulfide and neutralization of pH decreased Be, Cd, Cr, Cu, Pb, Ni, Ag, and Zn concentrations. Addition of sulfide increased As concentrations.

Based on the screening results, the test conditions of pH neutralization and sulfide addition were selected for further evaluation over additional time points to evaluate their longer term impacts of on metals mobilization with IAP. The additional evaluation involved collecting data from time points after 30, 56, 84 and 118 days of contact with IAP in the presence of Soil 2 and Soil 6. Additional evaluation was not conducted on Soil 1 it was depleted during the screening tests

Figure 4.4.61 shows the pH and ORP over time during the experiment. Reactors containing IAP were observed to have pH values 2 to 4 pH units below the control for both Soil 2 and Soil 6. The addition of sulfide with IAP resulted in conditions between pH 7.7 and pH 9.3, above both the control and IAP only reactors. pH neutralization returned the reactors to near-control conditions, but for both soil types, system pH became more acidic as the experiment progressed. Adding IAP to both soil types increased the ORP above 600 mV, while neutralizing the pH reduced the ORP for both Soil 2 and Soil 6, but the ORP returned to near 600 mV by the end of the experiment for both systems. Adding sulfide to reactors treated with IAP created a reducing condition on Day 30 in both soils, but the ORP increased in Soil 6 moving to a slightly oxidized condition by the end of the experiment.

Figure 4.4.62 presents the concentration of priority pollutant metals in IAP reactors for each of the selected test conditions, normalized to the respective concentrations in IAP only reactors at Days 30, 56, 84, and 118. The data indicate that neutralizing the pH after 28 days of contact resulted in a decrease in concentration of As and Cr for both soil types. Concentrations of Pb decreased initially for Soil 6 and by Day 118 for Soil 2. Several metals saw little change to modest increases for Soil 2 after pH neutralization. In the presence of Soil 6 neutralizing the pH with sodium hydroxide resulted in elevated pH by the end of the period evaluated for Be, Cu, Ni, and Zn. This may be due to the fact that while the pH was raised in the reactor to between pH 7 - 8, within 2 days after adding sodium hydroxide, the pH had returned to pH 4.8 and decreased to pH 4.2 by the end of the period evaluated. This is likely the result of acid formed from the decomposition of persulfate.

The addition of sulfide was intended to quench the residual persulfate, decrease the oxidative potential of the system and potentially form precipitates with the mobilized metals. As shown in Figure 4.4.62C and D, the addition of sulfide resulted in metals concentrations below the IAP only reactors for most metals in Soil 2, and very similar to the control reactors for Soil 6. Results of treatment of Soil 2 showed the concentrations of metals below the IAP only reactors for As, Be, Cd, Cr, and Cu. Variability in the Soil 2 dataset was observed, but this was often attributable to the comparison of low metal concentrations.

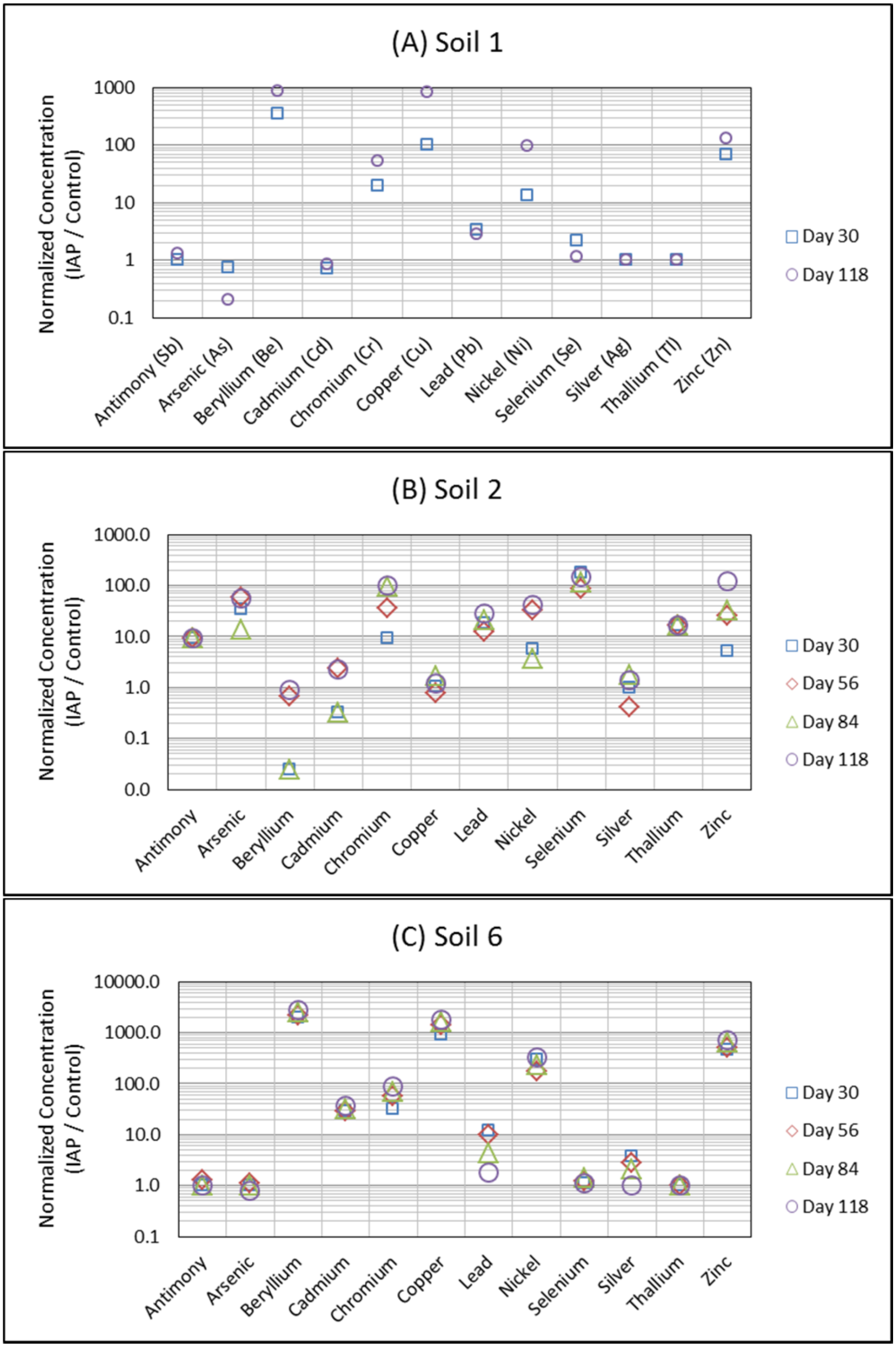
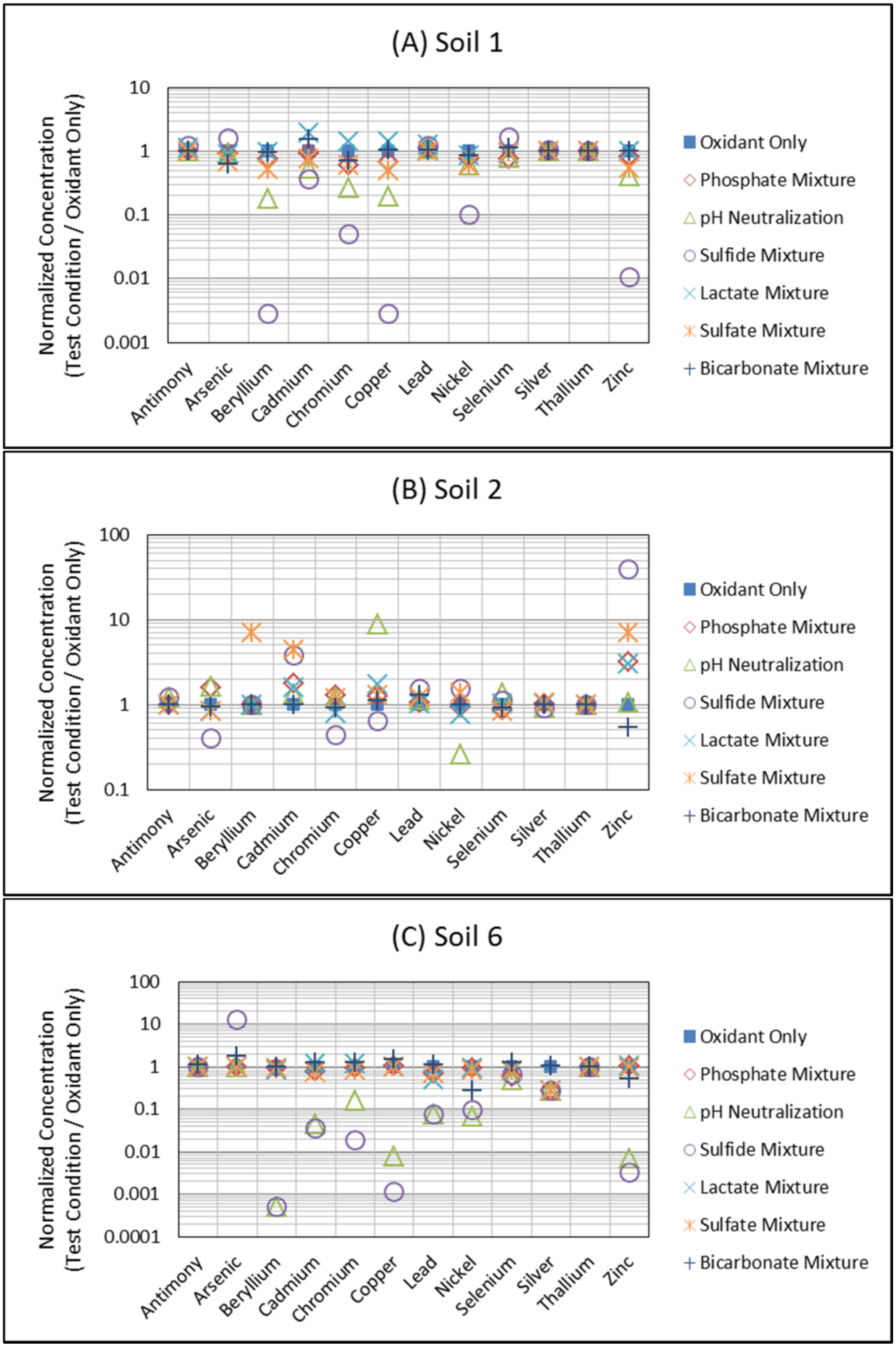


Figure 4.4.59 40 Post-Treatment Chemical Stabilization: Normalized concentration of metals for reactors with IAP applied versus control conditions (no IAP treatment).

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C).


(A) Soil 1

(B) Soil 2

(C) Soil 6

Figure 4.4.60 Post-Treatment Chemical Stabilization: Select normalized metal concentrations for 6 chemical treatment options.

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C)

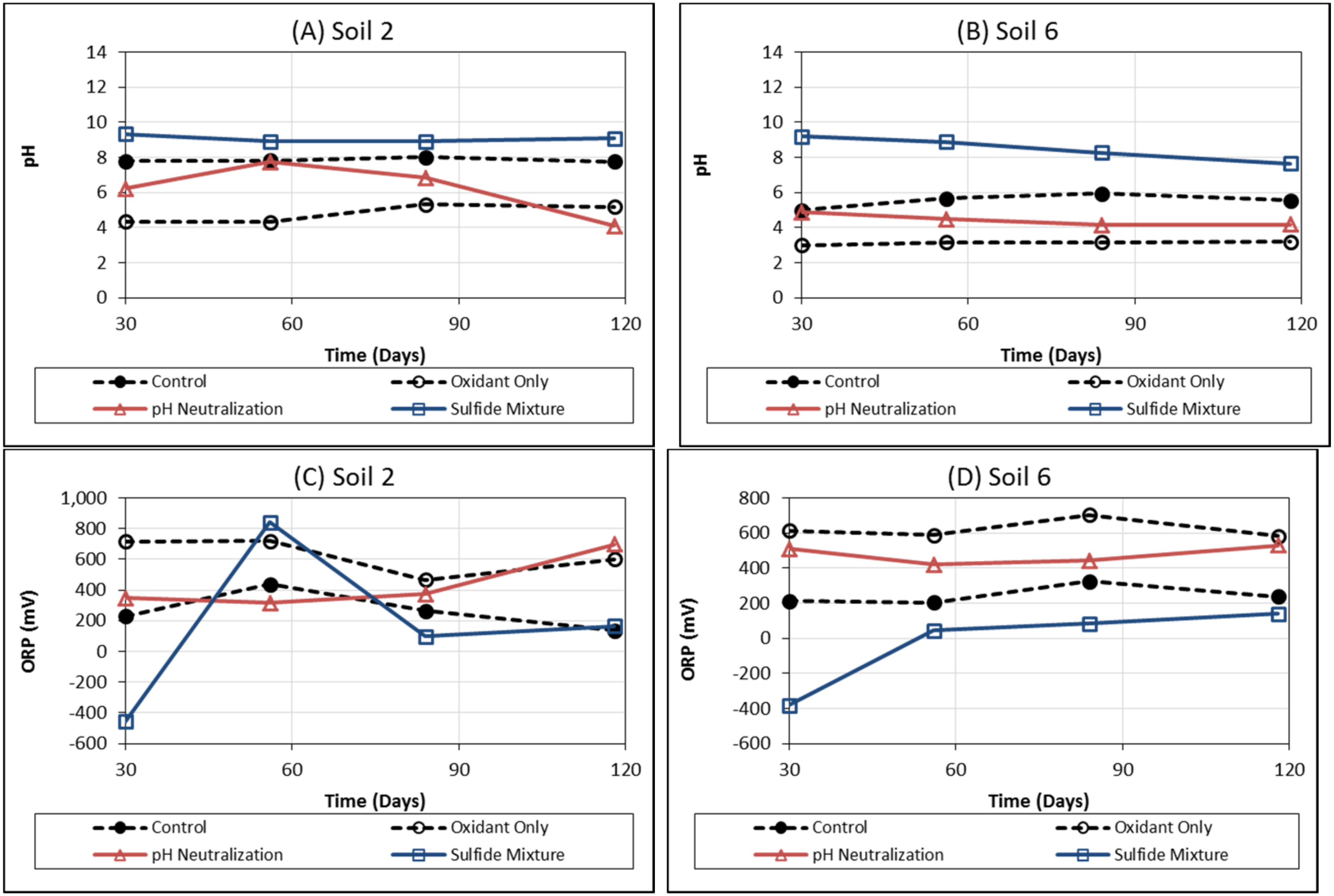


Figure 4.4.61 Post-Treatment Chemical Stabilization of IAP System: Geochemical parameters at 2, 28, 56, and 90 days

Note: Soil 2 (A, pH, C, ORP) and Soil 6 (B, pH, D, ORP)

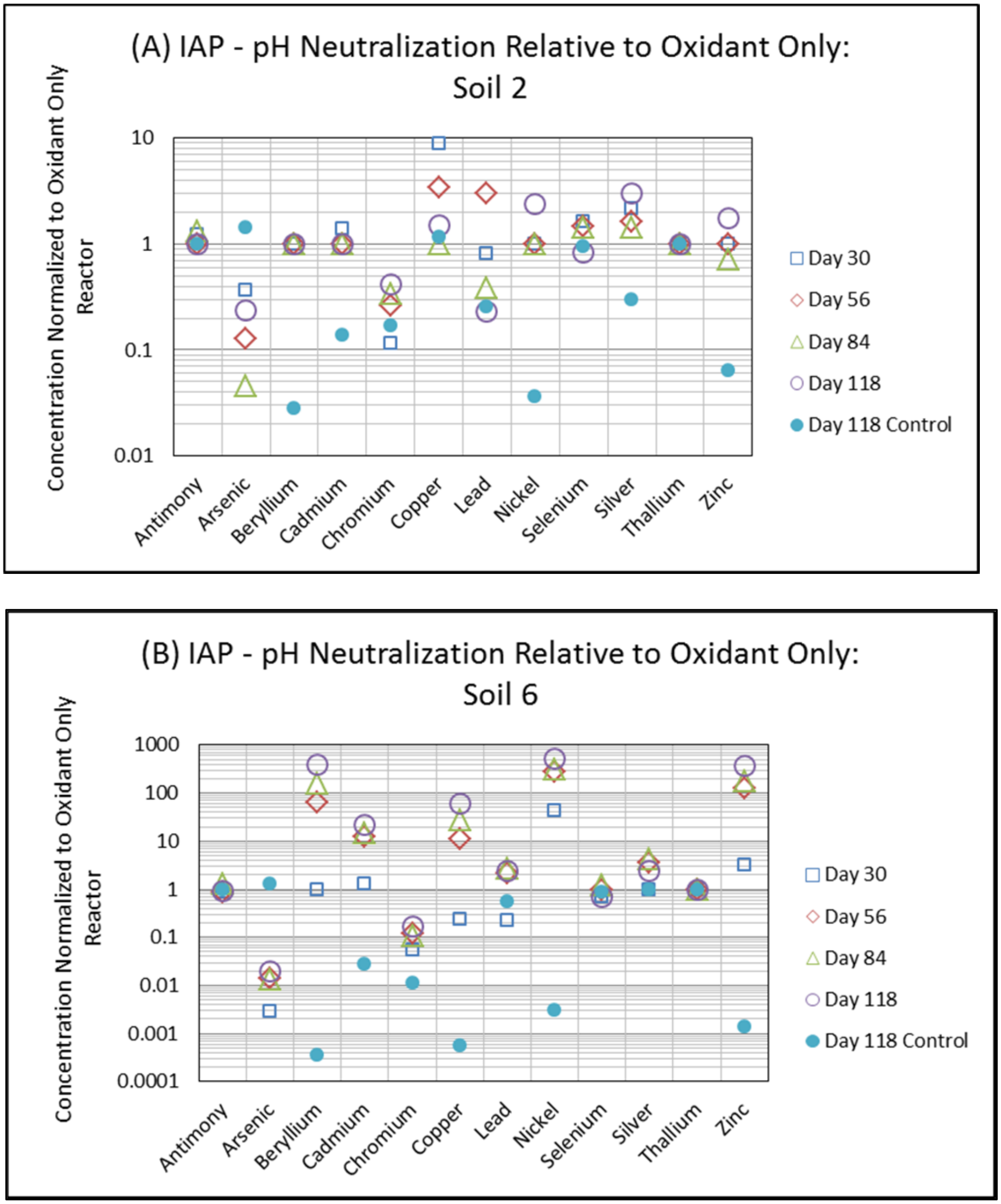


Figure 4.4.62 Post-Treatment Chemical Stabilization of IAP System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Chemical Co-treatment with pH Neutralization (A,B), sulfide mixture(C,D) for both Soil 2 and 6

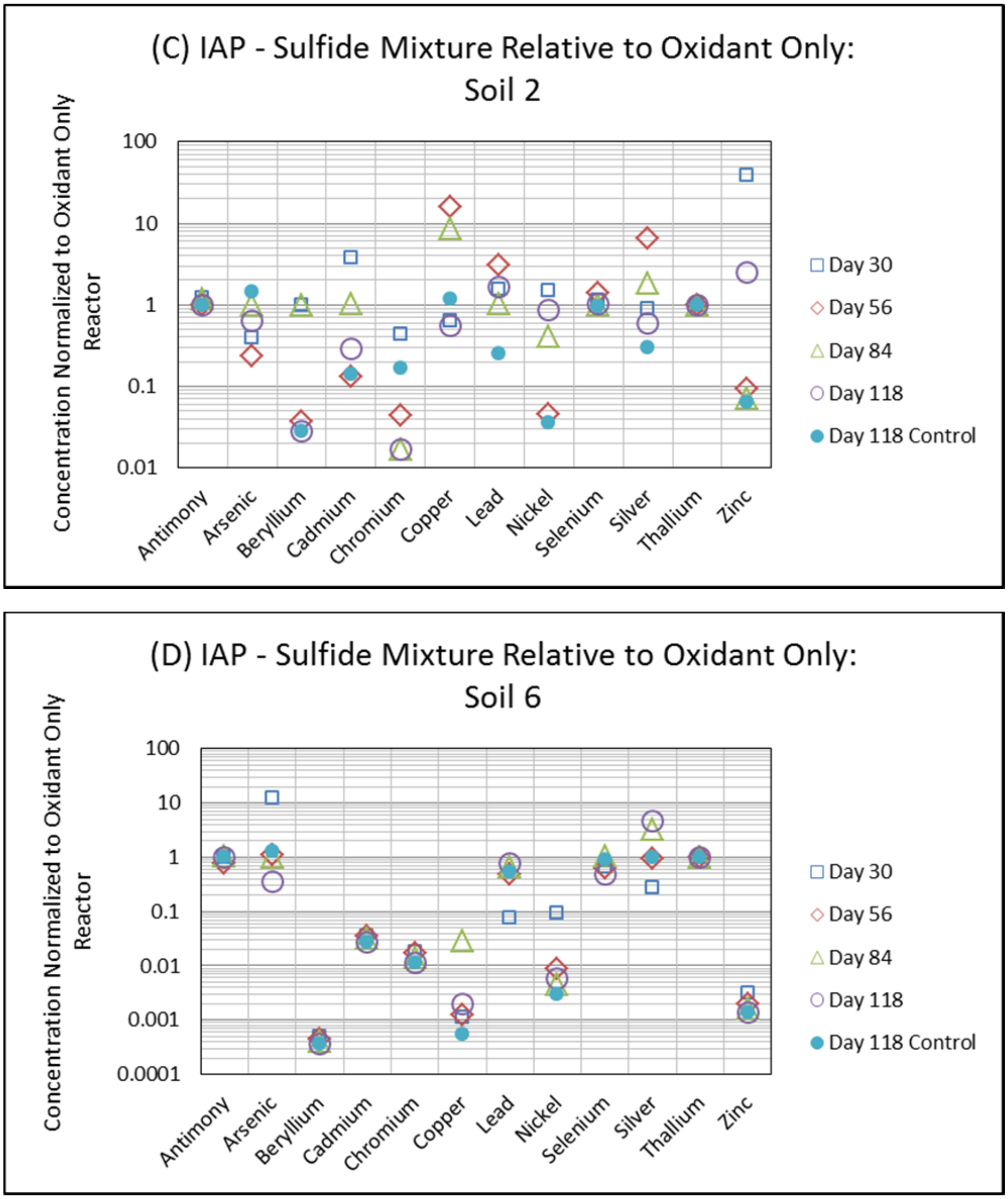


Figure 4.4.62 (cont.) Co-Treatment Chemical Stabilization of IAP System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Chemical Co-treatment with pH Neutralization (A,B), sulfide mixture(C,D) for both Soil 2 and 6

Catalyzed Hydrogen Peroxide. Figure 4.4.63 presents the concentrations of the selected priority pollutant metals in reactors treated with CHP only, normalized to the metal concentrations found in the control reactor (water only) for each respective time point for Soils 1, 2, and 6. Data indicate that concentrations of priority pollutant metals including Be, Cd, Cr, Cu, Ni, and Zn were greater in reactors treated with CHP compared to the control reactors for Soil types 1, 2, and 6.

Figure 4.4.63 shows the concentration of priority pollutant metals in reactors with amendments added after 28 days of contact with CHP, normalized to the concentrations in CHP only reactors. These amendments were allowed 2 days of contact with the ISCO reagents and soils, and on Day 30, the concentrations of metals were assessed. Results for Soil 1 indicate that concentrations of Be, Cr, Cu, and Zn were typically lower in reactors receiving one of the treatment conditions compared to the respective concentrations in the CHP only reactor. Neutralization of system pH also reduced Cd and Ni concentrations by greater than 90 percent for Soil 1. In the Soil 2 system, both the presence of sulfide and neutralizing the system pH reduced Cd, Cu, and Zn concentrations from CHP only levels. In the Soil 6 system, the concentrations of certain metals increased compared to CHP only; however, even after only 2 days, Cd, and Zn had decreased compared to the CHP only.

Based on these results, the test conditions of bicarbonate, lactate, and sulfide addition and pH neutralization were selected for further evaluation over additional time points to evaluate their longer term impacts of on metals mobilization with CHP. The additional evaluation involved collecting data from time points after 30, 56, 84 and 118 days of contact with CHP in the presence of Soil 2 and Soil 6. Additional evaluation was not conducted on Soil 1 it was depleted during the screening tests

Figure 4.4.65 shows the changes of pH and ORP during the experiment. The addition of CHP to the system reduced the pH to pH 4 for each soil type. The addition of sulfide increased the pH above 10 for both systems, while the neutralization of the pH kept the system between pH 6 and pH 9 throughout the experiment. Reactors treated with bicarbonate and lactate had similar pH values as the CHP only system. Addition of lactate or bicarbonate or the neutralization of the pH resulted in similar ORP values as the control and CHP only reactors for both soil types. The addition of sulfide to reactors treated with CHP resulted in more reductive conditions for both soil types until Day 118 for Soil 2, by which time the ORP was similar for all test conditions.

Figure 4.4.66 presents the concentration of priority pollutant metals in CHP reactors for each of the selected test conditions, normalized to the respective concentrations in CHP only reactors at Days 30, 56, 84, and 118. The results for pH neutralization systems are presented in Figure 4.4.66A and B. The data show that by Day 118, the metals concentrations in reactors where pH was neutralized for both soil types were less than the CHP only reactors or similar to the concentrations observed in the control reactors on Day 118 for all the selected metals with the exception of Cu and Soil 2. The data show that this effective treatment typically occurred by Day 30 for Soil 6, but required the full 118 days (90 days post pH neutralization) for several metals in the presence of Soil 2.

The results of reactors treated with sulfide are presented in Figure 4.4.66C and D. The data show that the concentrations of Sb, As, Se, Ag, and Tl in both the reactors treated with sulfide and the Day 118 control were similar to the concentrations observed in the Day 118 CHP only reactor, even after some variation over the experimental timeframe. For Soil 2, the concentration of several metals, specifically Be, Cr, Cu, Ni, and Zn, showed significant variability, typically due to small changes in concentrations near the detection limit. For Soil 6, where the metal concentrations in the CHP only reactor were typically higher, treatment with sulfide resulted in significant reductions of Be, Cd, Cr, Cu, Ni, and Zn to concentrations near the control.

Shown in Figure 4.4.66E and F, the addition of lactate in an attempt to stimulate biotic activity generally showed little to no change in metals concentrations compared to the CHP only reactors. As shown in Figure 4.4.66G and H, the addition of bicarbonate showed a reduction in concentration of several metals by approximately 60 percent by Day 118, indicating modest treatment compared to the results achieved by pH neutralization and sulfide addition.

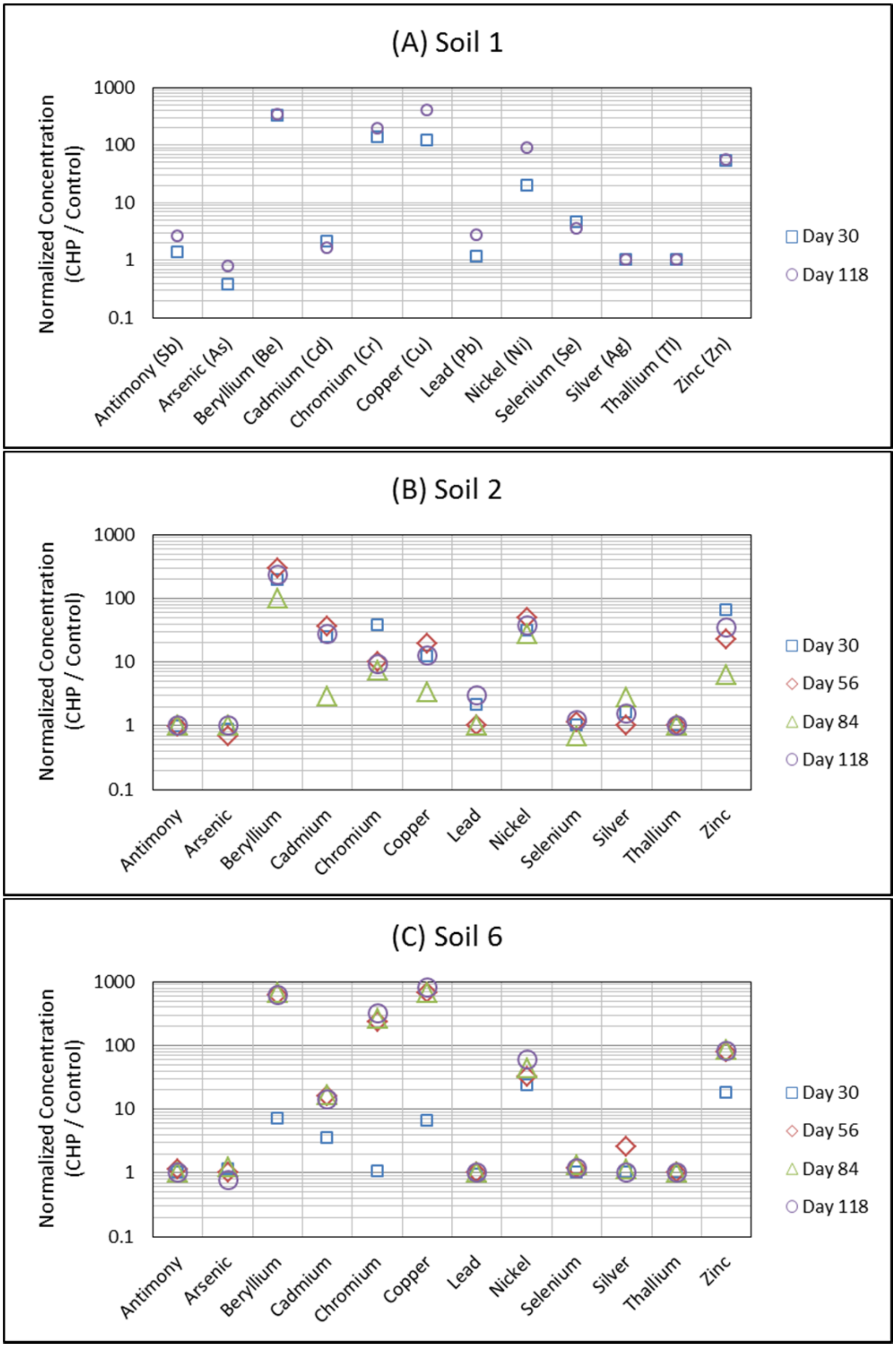


Figure 4.4.63 Post-Treatment Chemical Stabilization: Normalized concentration of metals for reactors with CHP applied versus control conditions (no CHP treatment).

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C)

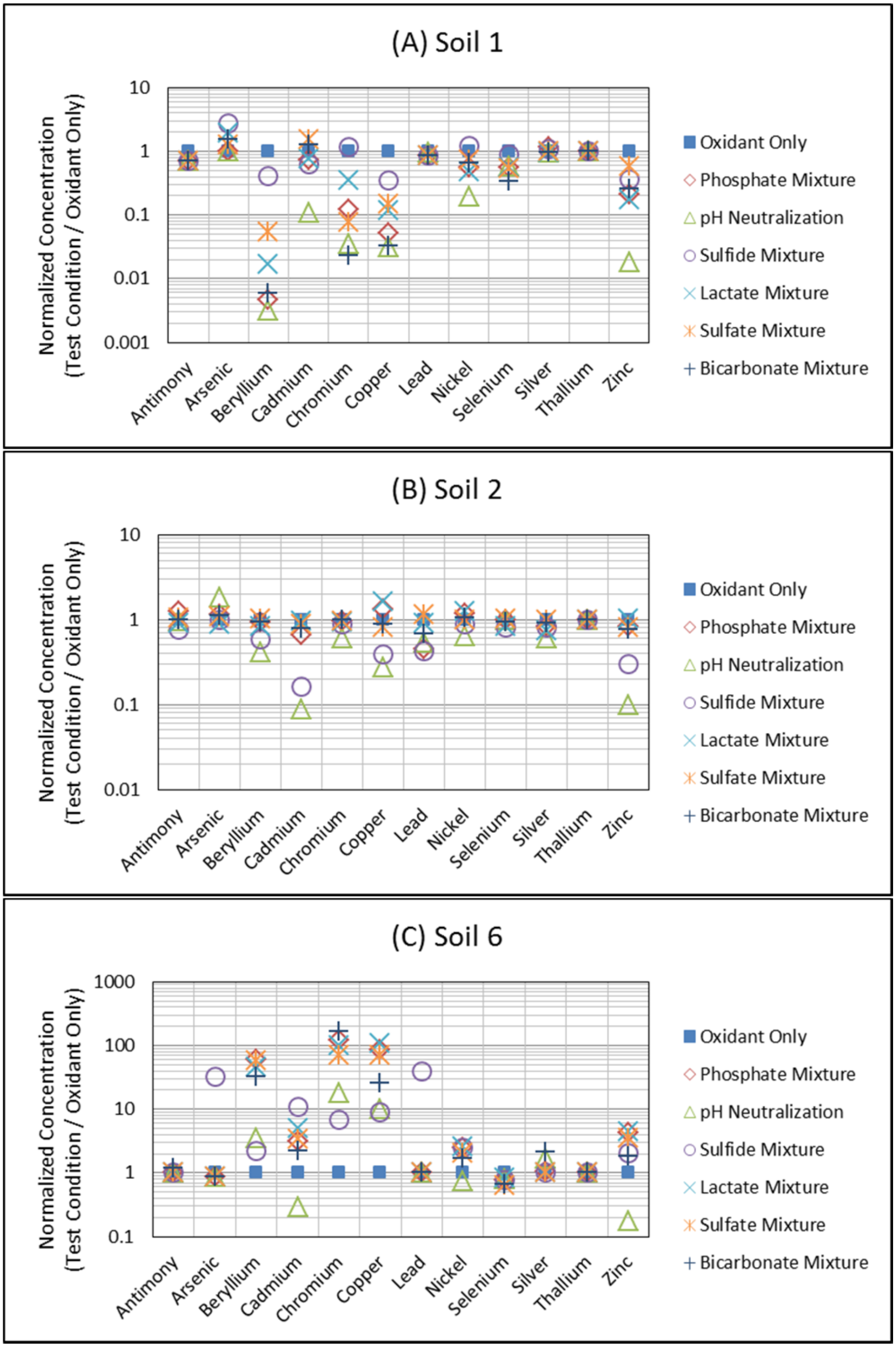


Figure 4.4.64 Post-Treatment Chemical Stabilization of CHP System: Select normalized metal concentrations for 6 chemical treatment options.

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C).

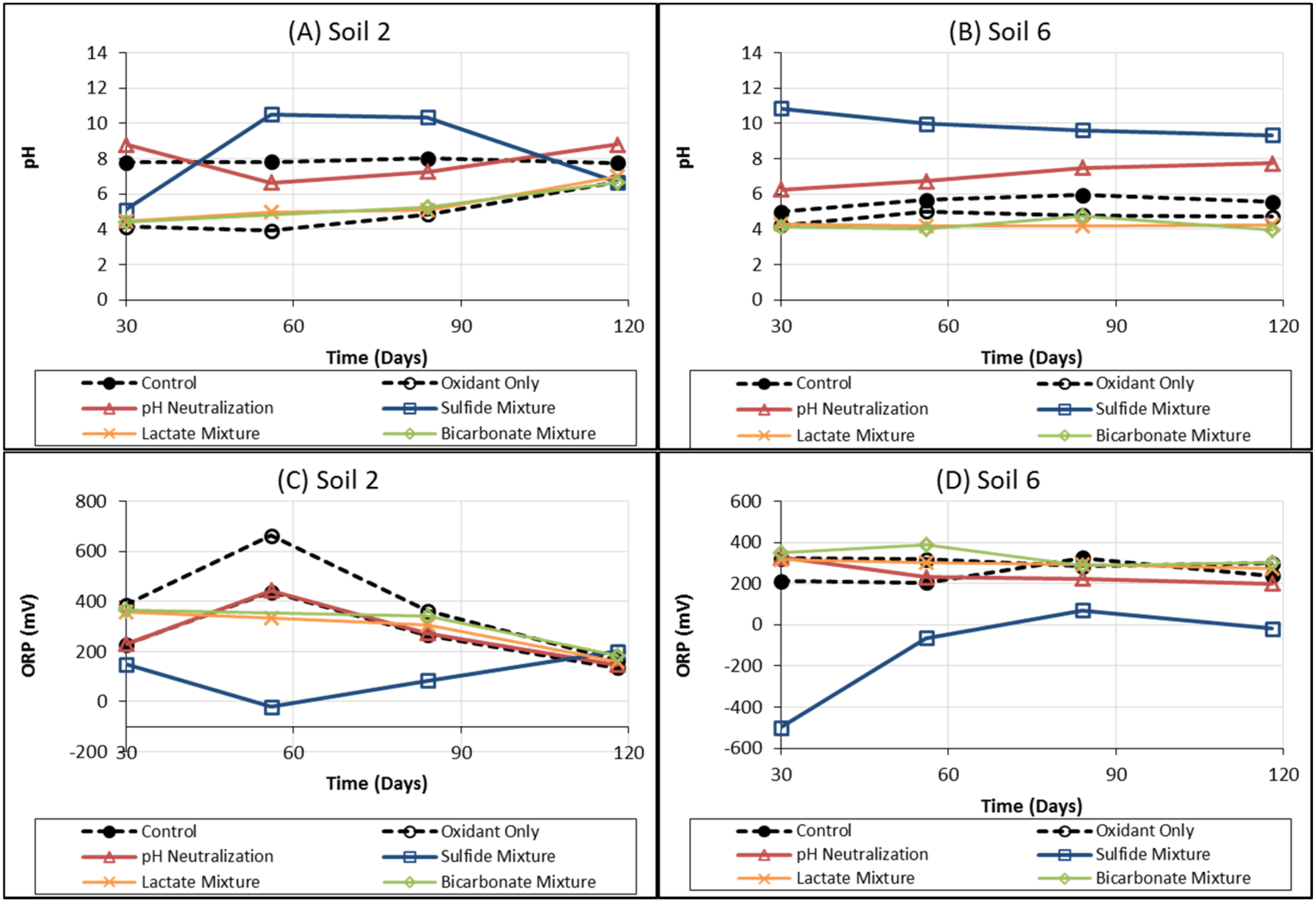


Figure 4.4.65 Post-Treatment Biological Stabilization of CHP System: Geochemical parameters at 2, 28, 56, and 90 days
Note: Soil 2 (A, pH, C, ORP) and Soil 6 (B, pH, D, ORP)

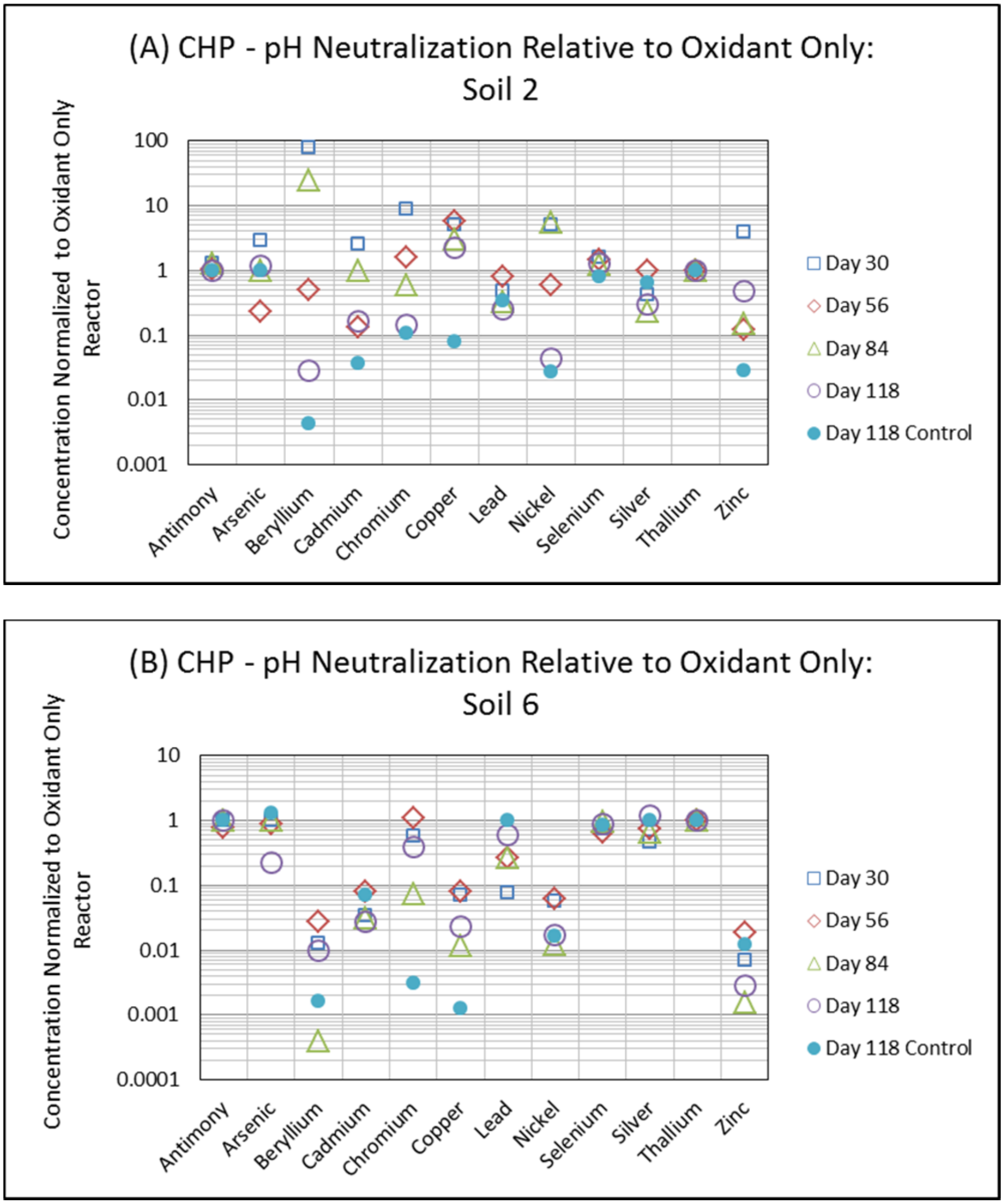
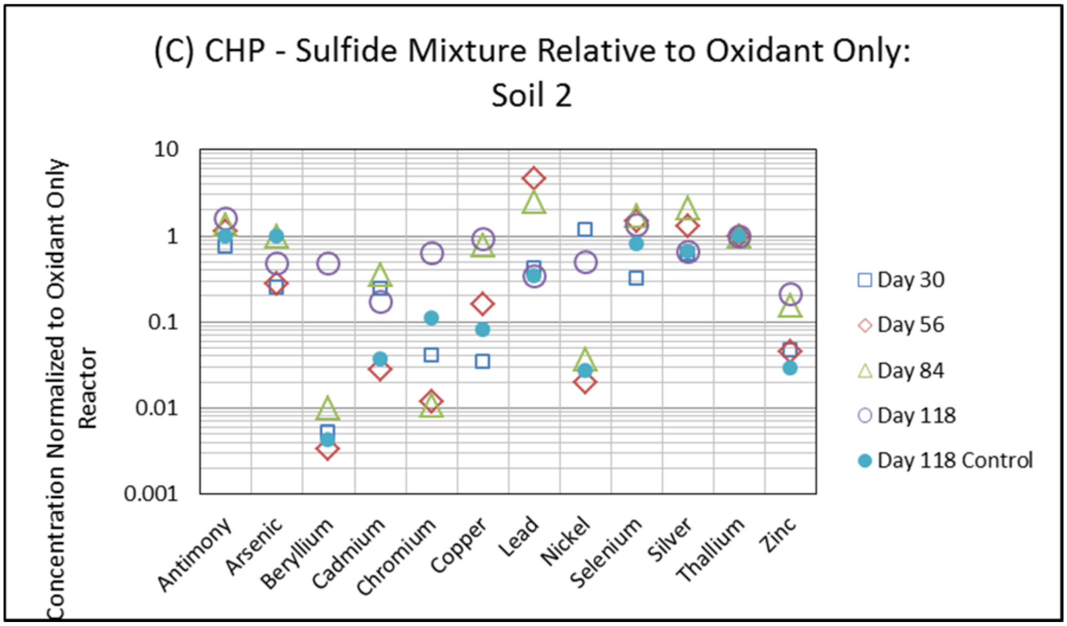


Figure 4.4.66 Post-Treatment Chemical Stabilization of CHP System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Chemical Post-treatment with pH Neutralization (A,B), sulfide mixture(C,D), Lactate(E,F) and Bicarbonate (G,H)



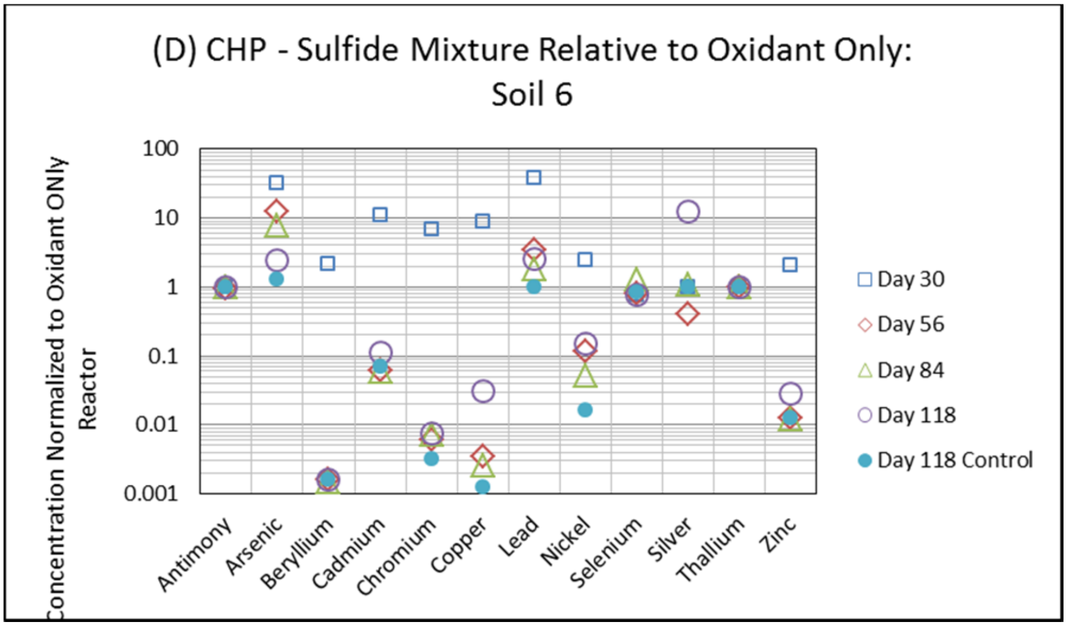
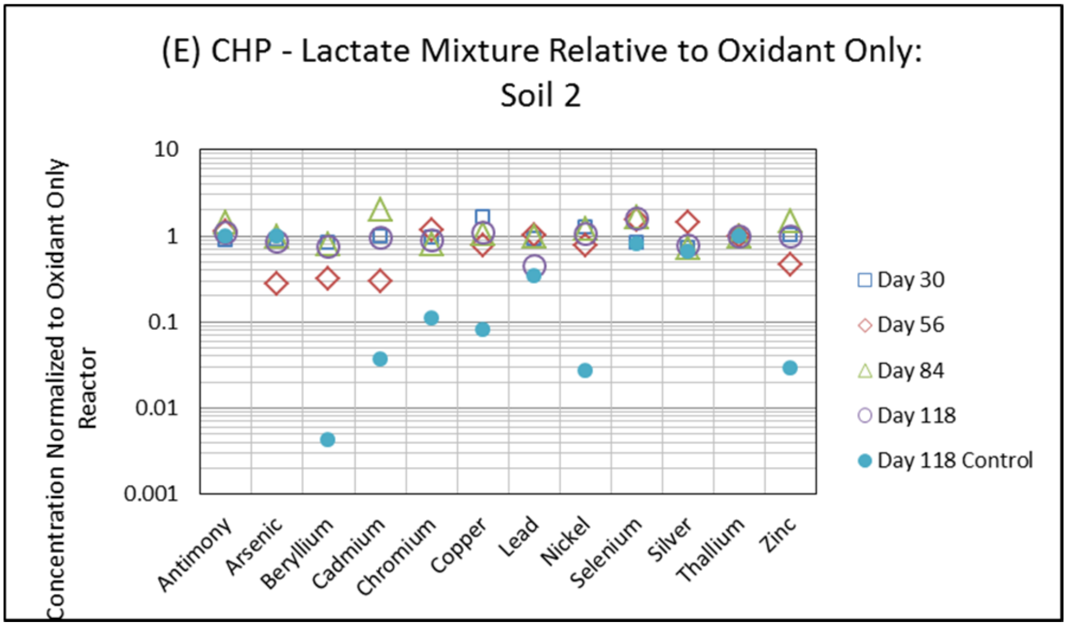


Figure 4.4.66 (cont.) Post-Treatment Chemical Stabilization of CHP System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Chemical Post-treatment with pH Neutralization (A,B), sulfide mixture(C,D), Lactate(E,F) and Bicarbonate (G,H)



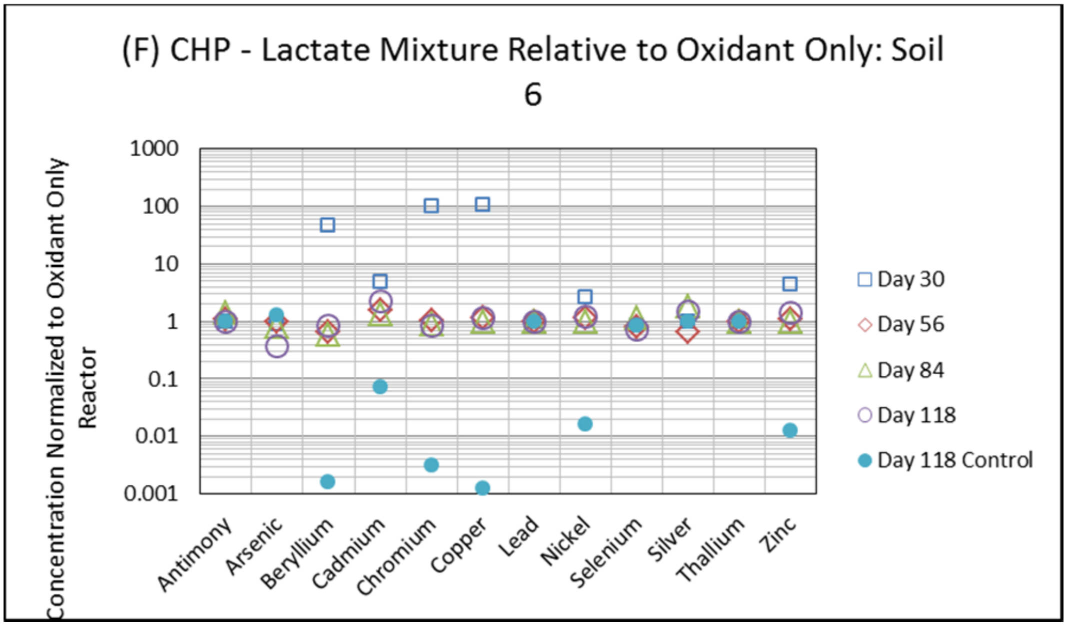
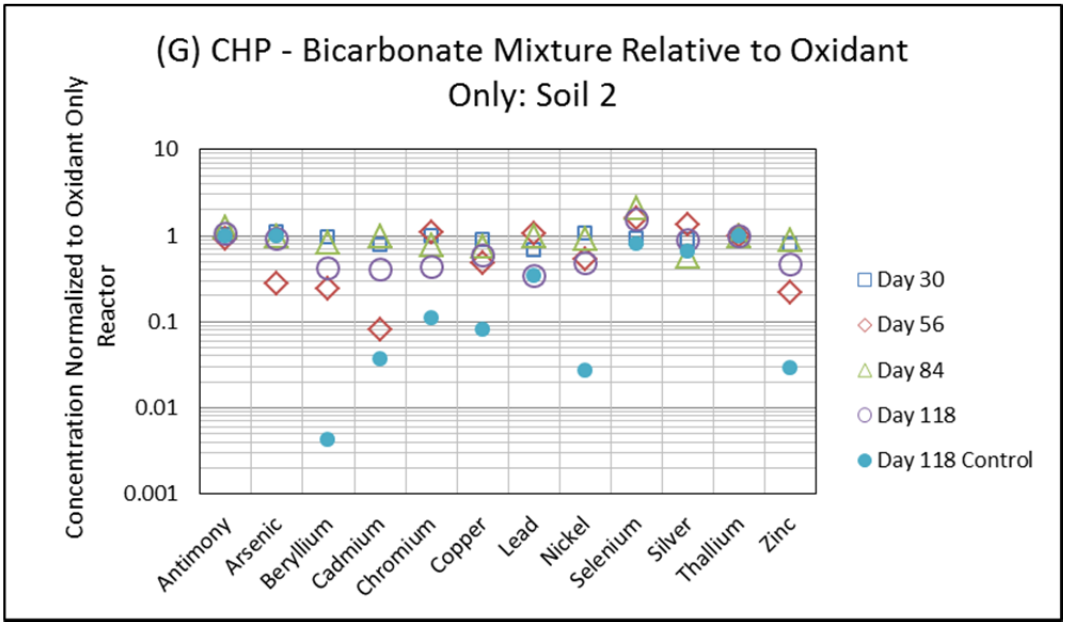


Figure 4.4.66 (cont.) Co-Treatment Chemical Stabilization of CHP System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Chemical Post-treatment with pH Neutralization (A,B), sulfide mixture(C,D), Lactate(E,F) and Bicarbonate (G,H)



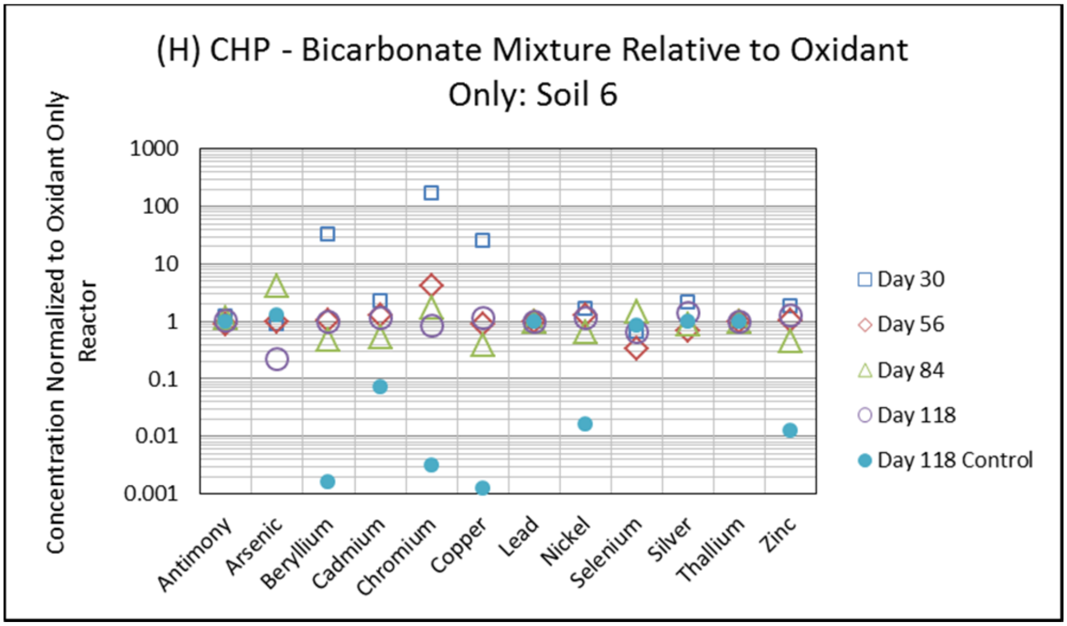


Figure 4.4.66 (cont.) Co-Treatment Chemical Stabilization of CHP System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Chemical Post-treatment with pH Neutralization (A,B), sulfide mixture(C,D), Lactate(E,F) and Bicarbonate (G,H)

Potassium Permanganate. The evolution of metals from each soil type varied more with soils treated with $KMnO_4$compared to other ISCO technologies, such as CHP. Figure 4.4.67 presents the concentrations of the selected priority pollutant metals in reactors treated with $KMnO_4$ only, normalized to the respective metal concentrations found in the control reactor (water only) for each respective time point for Soils 1, 2, and 6. In the Soil 1 system, $KMnO_4$ addition mobilized Cr and Cu, but reduced both Cd and Ni concentrations. The addition of $KMnO_4$ to Soil 2 mobilized six metals, including Be, Cr, Pb, Se, Ag, and Tl, while in Soil 6, only Cr, Ag, and Tl mobilized significantly. Conversely, Cu concentrations decreased with the addition of $KMnO_4$ in the Soil 2 system, and Ni decreased in the Soil 6 system.

Figure 4.4.68 shows the concentration of priority pollutant metals in reactors with amendments added after 28 days of contact with $KMnO_4$, normalized to the respective concentrations in $KMnO_4$ only reactors. These amendments were allowed 2 days of contact with the ISCO reagents and soils, and on Day 30, the concentrations of metals were assessed. Most critically, the data show that Cr was reduced by the sulfide treatment for each soil type. The addition of sulfide also resulted in the increase of Pb and Ni in Soil 1, the increase of Zn in Soil 2, and the increase of As and Ni in Soil 6. Each treatment technology reduced the concentration of Be in Soil 2 and Ag, and Tl in Soil 6 while the addition of lactate resulted in lower concentrations of Pb, Ag, and Tl in Soil 2 and Ag in Soil 6.

Based on these results, sulfide addition was selected as the test condition for further evaluation over additional time points to evaluate their longer term impacts of on metals mobilization with $KMnO_4$. The additional evaluation involved collecting data from time points after 30, 56, 84 and 118 days of contact with $KMnO_4$ in the presence of Soil 2 and Soil 6. Additional evaluation was not conducted on Soil 1 it was depleted during the screening tests.

Figure 4.4.69 shows the changes of pH and ORP during the experiment. Potassium permanganate had minimal effect on pH, but increased system ORP to over 600 mV with both soil types. Addition of sulfide caused the pH to rise over pH 12 and the ORP to reduce as low as -572 mV in the Soil 6 system and as low as -298 in the Soil 2 system. Both systems saw a consistent rise in ORP from Day 30 to Day 118, with the ORP ending up at -171 mV for Soil 6 and +224 mV for Soil 2.

Figure 4.4.70 presents the concentration of priority pollutant metals in $KMnO_4$ reactors with the sulfide addition, normalized to the respective concentrations in $KMnO_4$ only reactors at Days 30, 56, 84, and 118 for each soil type. For both soil types, the metals concentration after 118 days in reactors treated with sulfide on Day 28 were either lower than $KMnO_4$ only reactors and in most cases, similar to the control reactors with the exception of Ni, which increased in both reactors with sulfide treatment, and As, which increased in the presence of Soil 6. These increases may be related to the elevated pH caused by the addition of sodium sulfide. For example, in the Soil 2 reactors treated with sulfide, the pH returned to similar to the control and $KMnO_4$ only reactors by Day 118, and also had concentrations of As less than the both the control and $KMnO_4$ only reactors. This is in contrast to Soil 6 where the pH remained elevated over the course of the experiment and the concentration of As increased with time.

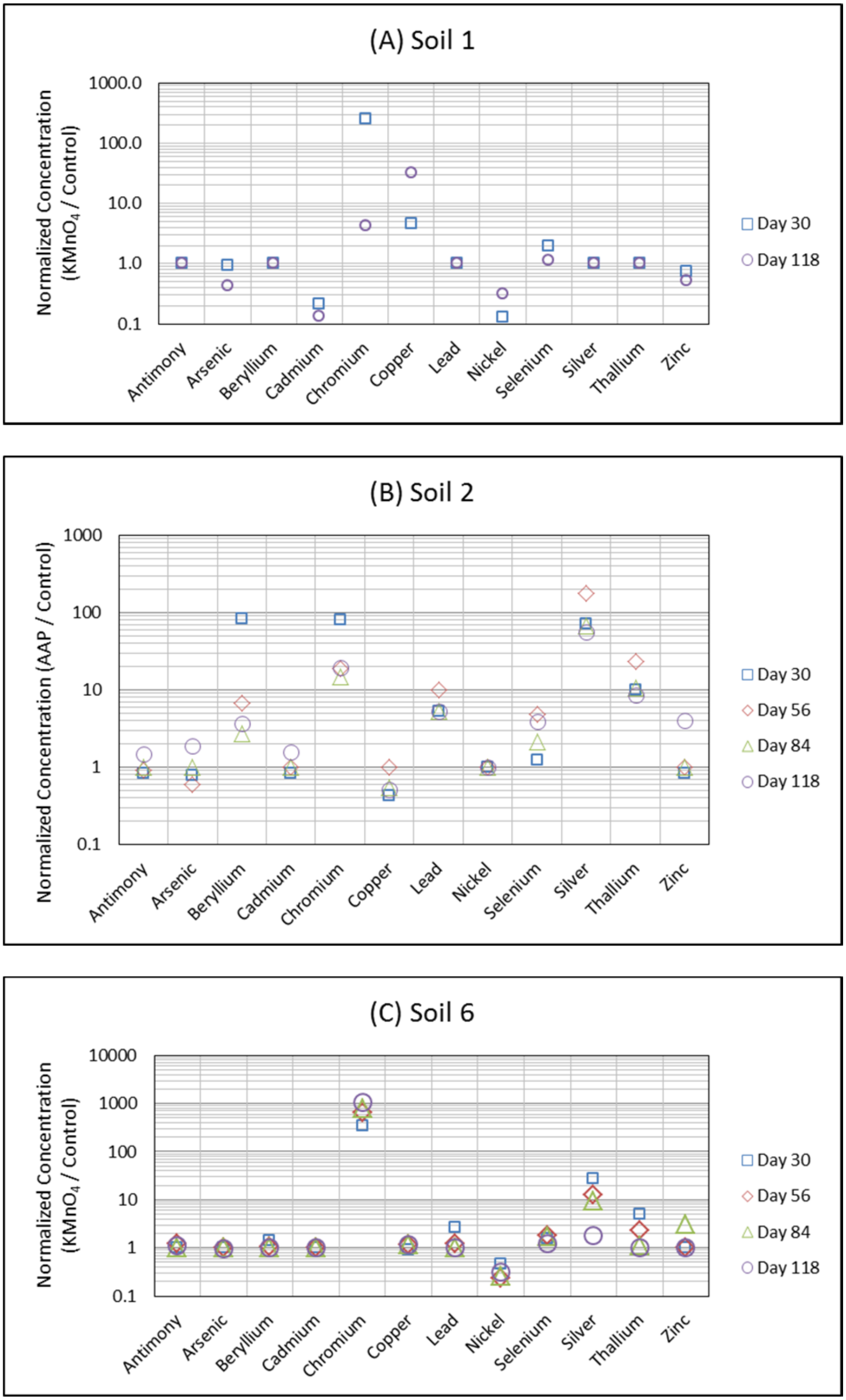


Figure 4.4.67 Post-Treatment Treatment Chemical Stabilization: Normalized concentration of metals for reactors with PM applied versus control conditions (no PM treatment).

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C).

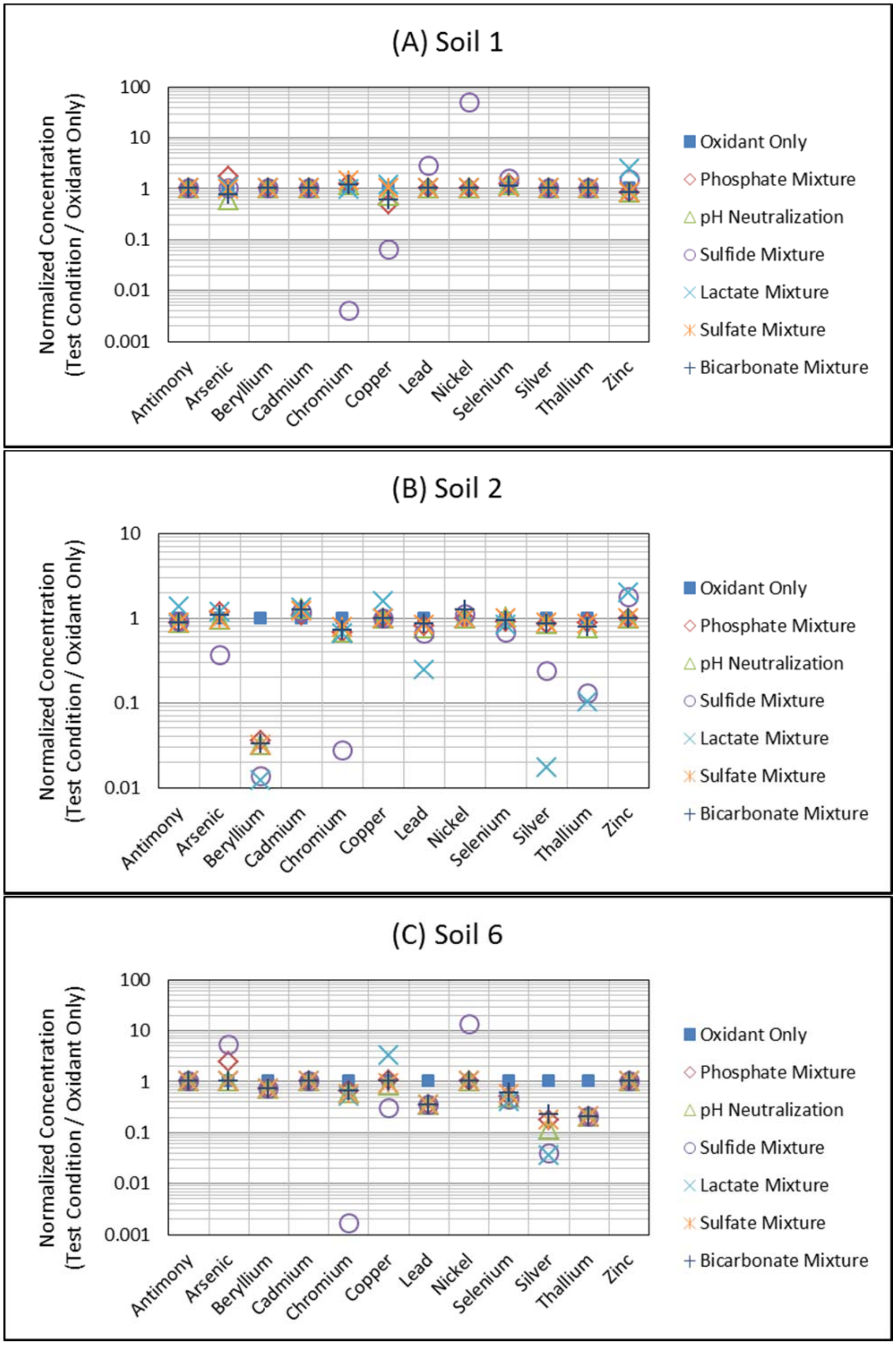


Figure 4.4.68 Post-Treatment Chemical Stabilization of PM System: Select normalized metal concentrations for 6 chemical treatment options.

Note: Soil 1 (A), Soil 2 (B), and Soil 6 (C).

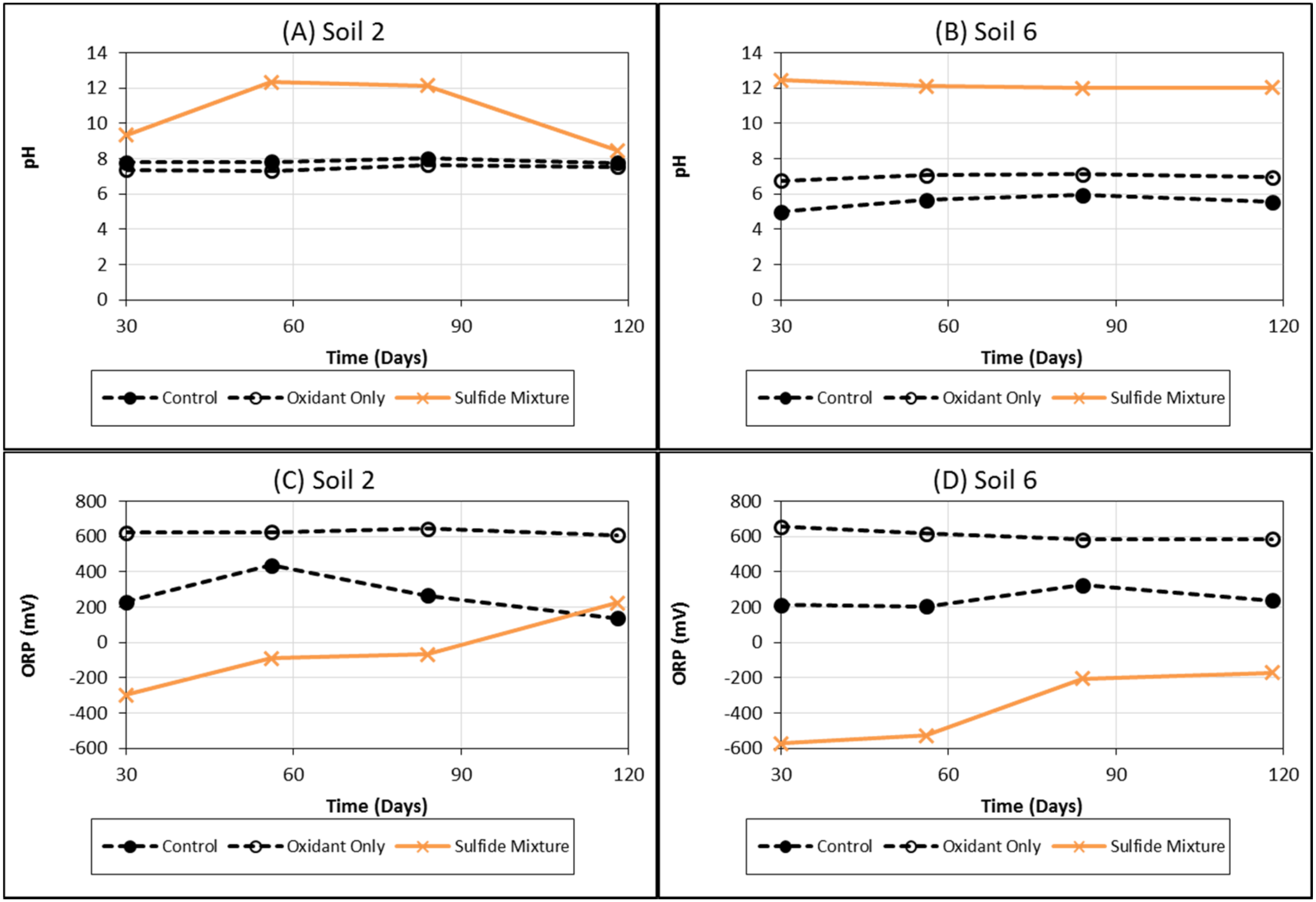


Figure 4.4.69 Post-Treatment Chemical Stabilization of PM System: Geochemical parameters at 2, 28, 56, and 90 days

Note: Soil 2 (A, pH, C, ORP) and Soil 6 (B, pH, D, ORP.

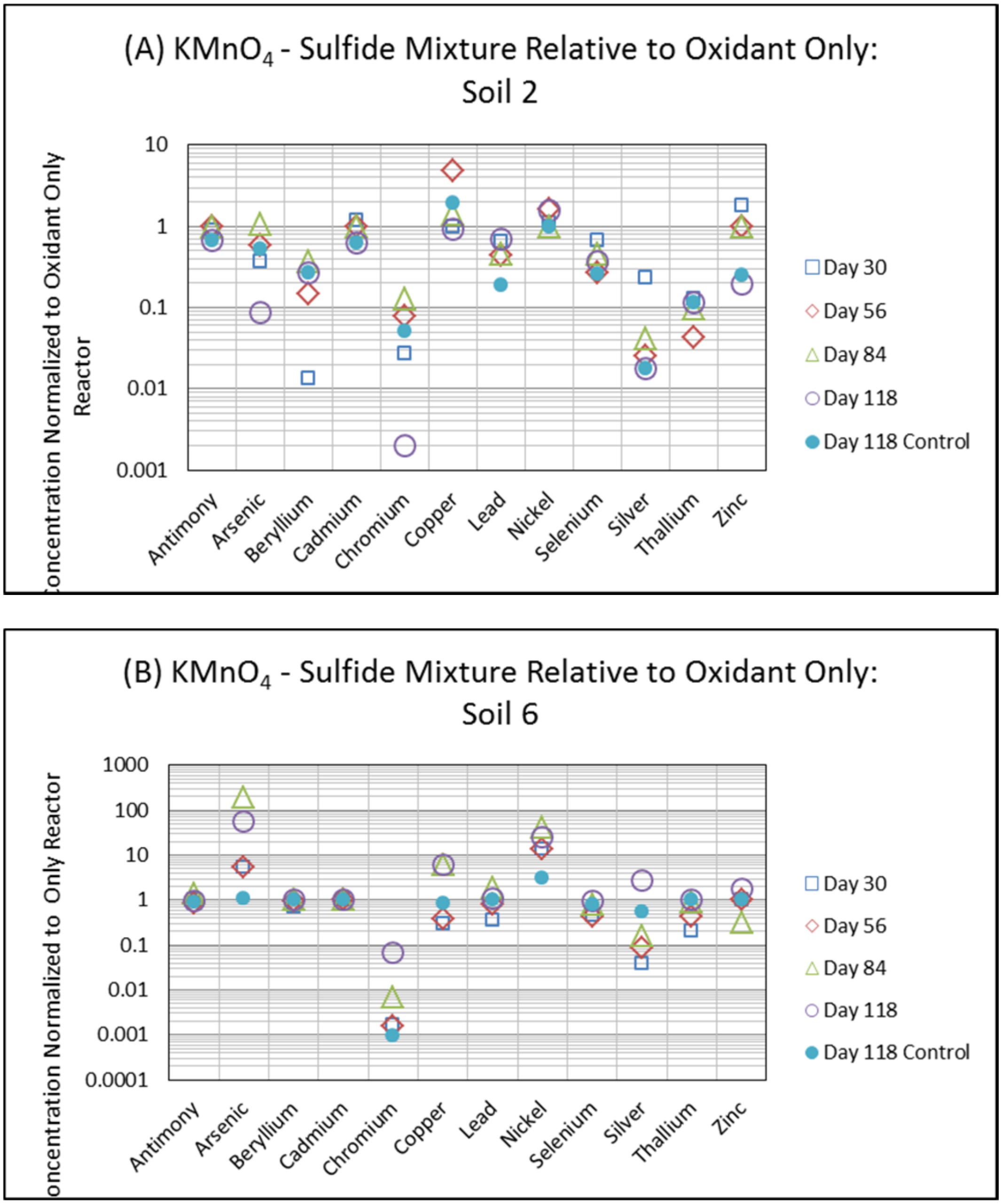


Figure 4.4.70 Post-Treatment Chemical Stabilization of PM System: Select normalized metal concentrations at 2, 28, 56, and 90 days

Note: Chemical Post-treatment with sulfide mixture (A,B)

CONCLUSIONS AND IMPLICATIONS

SUMMARY OF SPECIFIC CONCLUSIONS

Task 1: Pre-Experimental Evaluation

A total of 89 case studies were identified as field implementation sites to populate the database. Majority of the sites were commercial (drycleaner sites), followed by the Navy (7 sites), DOE (5 sites), Army (4 sites) and Air Force (2 sites). The most commonly observed oxidant in the database was permanganate (56 sites), followed by hydrogen peroxide (55 sites) and sodium persulfate (19 sites). In some of the sites, treatment involved the use of multiple oxidant types. Among the sites, only one site used calcium peroxide and ozone was used at 15 sites.

Several sites used multiple injection strategies for the injection event to maximize the subsurface distribution of the oxidant (e.g., a combination of recirculation and permanent wells or a combination of direct push technology and direct injection using temporary wells). The majority of injections were performed using permanent wells. Among the different delivery methods, the most common oxidant delivery method was direct injection (85 sites). Direct push (12 sites) and recirculation (11 sites) were employed less frequently. The other category included the use of trenches, gravity feeding, garden sprayers, soil mixing techniques and pneumatic fracturing for injection methods.

Metals were monitored in 21% of the case studies (19 out of the 89 case studies). There is a potential to observe more sites with elevated metals concentrations if more sites were monitored for metals. In several cases where metal was monitored, the concentration of metal was not reported in the documents available. An increase in metals concentration was observed in 63% of the case studies (12 out of 19 case studies). Chromium (total and hexavalent), iron, manganese and arsenic were the four most frequently observed mobilized metals in these 12 sites.
Amongst the RCRA and PP metals, chromium (MCL = 0.1 mg/L) and arsenic (MCL = 0.01 mg/L) were observed most frequently. A total of 10 sites out of the 12 sites had metals that exceeded the maximum contaminant levels (MCLs).

Overall, based on the available data (sites more than three monitoring events) at the 12 sites, mobilized metal indicates a decreasing trend after an ISCO injection. The duration of the metal increases were highly site specific.

A similar study by Krembs (Krembs, 2008) indicated that metal was monitored in 23 sites out of 242 sites (9.5%). For 57% of the case studies that monitored metal concentrations, transient increases were noted as a result of ISCO (sample size = 23). Similar to the results in this project, the duration and severity of metal increases is highly site specific, and was generally limited to the ISCO target zone.

Correlations between groundwater quality parameters (such as pH and oxidation reduction potential) with the mobilized metals were not possible due to the lack of data. The remaining tasks in this project will discuss the correlation of these parameters in detail.

Task 2: Evaluation of ISCO Technologies and Mobilization of Metals

Task 2 involved the testing of native soils from ISCO sites to develop a fundamental understanding of metals release as a result of three common ISCO approaches (i.e., persulfate, permanganate, and hydrogen peroxide oxidation). First, batch leaching studies have been completed on ten site soils, nine of which were exposed to six ISCO chemistries and the tenth (that was acquired at a later time) to four oxidant conditions at the natural pH of these materials (note, that the pH of the treated soils had been significantly impacted by the oxidant chemistry applied). Note, that the number of oxidant chemistries tested significantly exceeded the originally planned three conditions. Oxidant conditions evaluated included permanganate, unchelated and chelated hydrogen peroxide, unchelated and chelated iron-activated persulfate, and alkaline-activated persulfate. In addition, experiments have been conducted to develop a dose-response curve for the same six ISCO conditions for soil #1.

Results of the metal mobilization screening experiments showed that the leaching of metals depended on soil type, ISCO chemistry, and the metal in question. Several metals were released at elevated levels in each oxidant system compared to control batches, but more metals were mobilized in the catalyzed hydrogen peroxide and persulfate systems than in the presence of permanganate. In general, catalyzed hydrogen peroxide seemed to have the biggest impact on metals release in terms of number of metals mobilized in over one third of the soils tested, followed by the various persulfate chemistries. The application of permanganate resulted in the least metals release, with most of the observed metals mobilization originating from the reagent itself in the form of impurities.

Differences in metals mobilization were also observed within the various catalyzed hydrogen peroxide and persulfate chemistries; the citric acid chelating agent contributed to metals release in both oxidant systems. When comparing the impact of the various persulfate chemistries, iron activation resulted in more metals release than alkaline activation. In general, dissolved metal concentrations increased with the addition of higher oxidant dose.

Most priority metal contaminants (Ag, As, Ba, Be, Cd, Cr, Cu, Pb, Sb, and Zn) exceeded the background in at least two thirds of the site soils tested for select ISCO chemistries. Of these, the ones that exceeded the MCL in over two thirds of the site soils included As, Be, Cd, Pb, and Sb. This release was ISCO chemistry specific. For example, As only mobilized at levels above the MCL in the alkaline-activated persulfate and the chelated catalyzed hydrogen peroxide systems, and Cd and Sb were only released in excess of the MCL in the presence of hydrogen peroxide. On the other hand, Pb release exceeded the MCL in the presence of both chelated and unchelated catalyzed hydrogen peroxide and iron-activated persulfate, and with the exception of the unchelated iron-activated persulfate, so did Be when the same ISCO chemistries were applied. Finally, permanganate only mobilized Cr and Ba above background levels in over one third of the sites tested. There were no MCL exceedances in the presence of this oxidant in any of the site soils. Cr mobility was impacted by all of the oxidant chemistries tested. This is an important finding, since the release of Cr in the form of highly soluble Cr(VI) is a potential concern for contaminated site managers.

This task also involved the pH-dependent leaching evaluation of select soils (i.e. soils #1, 2, and 4) and ISCO conditions (i.e. permanganate, chelated iron-activated hydrogen peroxide and persulfate, and alkaline-activated persulfate). In these experiments, the pH o the oxidant exposed soil slurry was adjusted to various levels in the range of pH 3 to 11 to identify cases when factors other than the pH were responsible for metals release. The pH-dependent leaching studies revealed that while the release of most metals was controlled by pH, the mobilization of select metals was determined by ISCO chemistry. In the latter case, metals mobilization either increased or decreased in the presence of the oxidant and this phenomenon was both ISCO chemistry and soil specific. ISCO chemistry related release has primarily been observed in soils #1 and 2. Metal mobilization in soil #4, a coarser soil with significantly higher organic content than soils #1 and 2 (see Table 2.1), was dominated by pH effects. In terms of ISCO chemistry, alkaline-activated persulfate affected the release of the highest number of metals, followed by iron-activated persulfate and hydrogen peroxide. Permanganate altered the leaching of the least number of metals, most of which were released in smaller quantities compared to background in the presence of this oxidant. The increased or decreased release of metals in the presence of oxidants typically occurred in specific pH ranges, and sometimes the same ISCO chemistry would mobilize a given metal either above or below background levels depending on the pH.

Finally, geochemical speciation modeling was conducted using the LeachXS modeling platform to study controlling solid phases and elucidate processes responsible for the release of metals in instances when pH was not the controlling factor. Metals release from soil #1 in the presence and absence of alkaline-activated persulfate and catalyzed hydrogen peroxide has been evaluated. With an understanding of which phases or aqueous species are controlling metals release, suitable alterations to the ISCO process may be developed and tested. The more fundamental understanding of controlling solid phases enables prediction of successful chemical additives that would likely reduce aqueous phase concentrations; this testing was the focus of Task 4.

The modeling work revealed that besides pH and ORP conditions, secondary effects such as the formation of organic complexes and the dissolution of iron oxides and other minerals also contributed to the release of select metals in soil #1. Metals whose release was primarily controlled by the formation of organic complexes included Cd, Cr, and Ni. The same was observed for Cu in the presence of catalyzed hydrogen peroxide, while in the alkaline-activated persulfate chemistry this metal leached due to the dissolution of cuprous ferrite. Another metal whose release was impacted by both organic and mineral phases was Pb in the alkaline-activated persulfate system. On the other hand, the mobilization of As and V was purely determined by the dissolution of mineral phases (observed in the alkaline-activated persulfate chemistry).

Task 3: Evaluation of Post-ISCO Recovery/Return to Baseline Conditions.

Our results demonstrate that metals release due to contact with an ISCO regent is site-specific (aquifer specific) and metal specific. This observation reinforces the recommendation that all sites should be initially screened for the presence of metals, especially if there is knowledge of historical uses and/or suspected prior metals releases that could have a legacy in the subsurface.

In some cases, metals may become mobilized despite efforts to better characterize the site and institute pre-emptive measures to mitigate the potential for mobilization of metals during ISCO application. In cases where metals of concern were not detected in pre-ISCO characterization, these metals are likely to be attenuated and immobile under the natural groundwater conditions. Consequently there are site-specific factors that must be evaluated and considered before deciding upon any potential mitigation plan to address metals impacts. For example, no mitigation may be necessary if the target area is a large distance from the nearest receptor (or property boundary), and the rates of attenuation exceed the potential for metals to reach a potential receptor (or property boundary). However, should the target area be in close proximity to a surface water or drinking water receptor, and/or threaten to move across a *down-gradient* property boundary, active mitigation of mobilized metals may be warranted.

In the instance where metals have been mobilized due to ISCO application, a site-wide approach should be created to strategically develop a robust conceptual model of metals fate and transport in order to evaluate the need for mitigation. The site-wide characterization strategy can be approached in a similar framework for most ISCO sites where the aim is to understand the physical setting and the dominant processes controlling metal transport behavior.

The translation of these results to field-scale implementation is done through strategic site-characterization where metals are known to be present, or suspected of being present, and therefore potentially mobilized during ISCO application. The general approach for site characterization for an ISCO site where metals may be mobilized contains the following elements:

- Site layout, including target area and historical inventory of chemicals released.
- Hydrologeologic environment and transport potential, including groundwater velocities and distance to points-of-compliance (e.g., drinking water receptor or property boundary).
- Background geochemical conditions of groundwater aquifer
- Lateral and vertical distribution of metals
- Selection of mitigation technologies (Task 4) and applicability of technology to site-specific conditions.
- Metal stability under post-ISCO conditions

Task 4: Mitigating Metals Mobilization as a Result of the Application of ISCO.

The presented data indicates that metals were mobilized above the control for each ISCO technology tested. The data also show that in many instances, the mobilized metal concentrations in reactors with only the respective ISCO technology returned to near the control within 90 days without any additional treatment. This indicates that mobilized metals may be a temporary phenomenon and that as site conditions return to near baseline the metals will return to their original equilibrium concentration.

The variability within the observed responses of each soil type indicate the complex chemistries involved in metals mobilization. This observation within this controlled data set supports the concern that issue of metals mobilization following the application of ISCO may be site specific and soil dependent. This also suggests that measures may need to be taken during the addition of ISCO reagents to help mitigate the potential or duration of metals mobilization.

The data show that citrate and acetate were effective in mitigating the mobilization of evaluated metals during the application of IAP. The addition of acetate with IAP consistently helped maintain metal concentrations close to those observed in the control reactors. The addition of acetate and citrate were similarly beneficial to the application of CHP in reducing metals concentrations. While with IAP some of the metals concentrations were reduced within 2 days, with CHP, several of the concentrations remained elevated within 2 days but steadily declined until approximating those observed in the control reactors by Day 90. The addition of lactate to $KMnO_4$ also reduced the observed mobilization of metals. For example, Cr was observed to be steadily increasing over the 90 day duration of the tests in the reactors with $KMnO_4$ only but approximated the control reactors in the systems that contained lactate with the $KMnO_4$. No additive intended to stimulate biotic activity was deemed successful enough to warrant addition evaluation for AAP.

The apparent trade off to mitigating the mobilization of metals in ISCO systems with electron donors such as lactate, acetate and citrate is an observed general tendency toward a decrease in treatment efficacy. In many instances the impact was minimal and in other instances the decrease in treatment efficacy may still be acceptable to the ISCO designer and associated stakeholders.

IMPLICATIONS FOR FUTURE RESEARCH AND IMPLEMENTATION

Future Research

While the current project significantly advanced the present knowledge on metals mobilization issues in ISCO applications, there are several outstanding questions that should be addressed in future research. For example, results of this investigation revealed that both ISCO treatment and soil characteristics have a significant impact on metals release. However, the specific soil properties that influence the leaching of metals have not been clearly identified. Possible correlations between metals release and grain size or total soil organic carbon content were evaluated, but no such relationships had been identified. A more refined set of soil property parameters should be identified and tested to determine the factors that most significantly impact the mobilization and fate of metals in ISCO applications. One such example could be the humic acid fraction of the SOM and the pH-dependent humic fraction of the DOC content, both of which were input parameters in the geochemical speciation model used in this work (due to lack of measured values, literature based assumptions were used in the present study). Similarly, knowledge of the iron and aluminum (hyrd)oxide content of oxidant treated soils would be beneficial in the geochemical modeling work. The less superior model fit achieved in the oxidant treated soils in the current project was most likely due to not having information about how SOM and iron- and aluminum (hydr)oxides were influenced by exposure to significant changes in geochemical conditions. In reality, both the organic content and mineral phases are likely to change due to exposure to the oxidant, and therefore, it is hypothesized that experimental SOM fractionation and iron- and aluminum (hydr)oxide content determination in the oxidant treated soils would improve the model fit and increase the confidence of the results. In addition, an increased understanding is needed on the nature of DOC that results form partial oxidation of SOM in the presence of oxidizing agents. Furthermore, the present study only evaluated release mechanisms in the presence of alkaline-activated persulfate and catalyzed hydrogen peroxide using geochemical modeling. A similar analysis should also be performed for other oxidant chemistries.

Implementation

One of the aims of this project was to bridge the gap between academic research and practical application. A guidance manual has been developed for practitioners to aid contaminated site managers in assessing potential metals mobilization issues and in designing mitigation measures at their sites. This guidance manual outlines a set of detailed steps that practitioners should follow and also presents testing protocols. In addition, an interactive ISCO site database has been developed using both survey and literature data with a focus on metals mobilization related issues. While such a guidance manual and database will serve as valuable resources to site managers who want to evaluate metals release issues, these tools do not replace knowledge that could be gained in actual field studies that would test the performance of mitigation measures developed in this project. Therefore, it is recommended that the most effective mitigation measures identified in the current project are evaluated in a field demonstration.

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APPENDICES