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Evaluation of Central Plateau Remediation Alternatives: Interim Status Report

September 2018

C Bagwell
AR Lawter
KJ Cantrell
CF Brown

U.S. DEPARTMENT OF
ENERGY

DISCLAIMER

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Executive Summary

Several comingled groundwater contaminant plumes exist in the Hanford Central Plateau and are currently targeted by ongoing remedy efforts (i.e., pump-and-treat [P&T]). However, across much of the Central Plateau, the deep vadose zone is also expected to serve as a long-term source of contaminant flux to the groundwater. Contaminant transport in the groundwater and vadose zone often occurs at vastly different time scales. Remedial action is needed in the near term to address existing groundwater contamination, but for some waste sites, long-term vadose zone source control may be needed. The overall remediation strategy for the Central Plateau will require the development of remedial alternatives that consider the coupled groundwater and vadose zone system.

This report documents laboratory efforts initiated in FY18 to screen potential remedial technologies for comingled contaminant plumes in the Central Plateau. Specifically, these studies evaluated gas-phase remediation approaches for the deep vadose zone and evaluated co-contaminant impacts on biological attenuation processes. When possible, laboratory studies were performed with sediment collected from the UP-1 or ZP-1 Operable Units to better represent site-specific conditions. Bench-scale testing included gas phase bioreduction to evaluate soil respiratory response and contaminant reduction potential to gaseous and vaporized liquid substrates, and CO_2 injection for carbonate coating development to evaluate co-precipitation of iodine and uranium and iodine in carbonate minerals via dissolution and re-precipitation caused by injection of CO_2.

Results of the gas phase bioreduction work indicated that after 3 weeks of incubation, the majority of substrates tested were microbiologically consumed and soil respiration was sufficiently enhanced to chemically reduce Hanford deep vadose zone sediments without macro- and micro-nutrient amendments. The substrate utilization was also faster and more consistent at higher volumetric water contents, but the low water content and the discontinuity of aqueous films connecting pore spaces characteristic of the deep vadose may limit diffusive transport as well as the mobility of microbial populations. Water availability is a crucial consideration and key to the success for any biostimulation strategy employed for the deep vadose zone. The results for the sediment samples used in the testing indicate that Hanford's deep vadose zone likely has adequate conditions (e.g., nutrients) to support in situ microbial remediation processes.

CO_2 treatment of calcite or Ringold sediments in double de-ionized (DDI) water was found to remove only minor amounts of iodine; however, when vadose zone pore water was used, iodine removal was much greater in the initial stages of the experiment. While the iodine concentrations rebounded after reaching maximum removal at the beginning of the test, 25% to 50% removal was demonstrated and shows some potential for this approach. Additionally, ~60% of iodine was removed from solution in DDI water when Cold Creek Unit sediments were present, demonstrating the importance of different lithologies on contaminant uptake. Injection of CO_2 was ineffective at removing uranium from solution and increased uranium solubility when Ringold and Cold Creek sediments were present. While these results do not support the continued evaluation of CO_2 injection for uranium treatment, CO_2 treatment may be useful as part of a two-step remediation approach to armor contaminants precipitated by redox approaches. For instance, future tests should apply this approach, including chemically reduced conditions for mixtures of contaminants (e.g., ^{99}Tc, U, and Cr) with monitoring of the release of contaminants of concern as the reactors slowly oxidize.

Acknowledgments

Acronyms and Abbreviations

CCU	Cold Creek Unit
COC	contaminant of concern
COPC	contaminant of potential concern
DDI	double de-ionized
DOE	U.S. Department of Energy
NQAP	Nuclear Quality Assurance Program
OU	operable unit
Q-XRD	quantitative X-ray diffraction
SPW	synthetic perched water
VZPW	vadose zone pore water
vWC	volumetric water content
XRD	X-ray diffraction

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1.0   Introduction

Nearly 2 trillion liters (450 billion gal.) of liquid waste have been released into the subsurface at the Hanford Site as a byproduct of nuclear weapons production by the U.S. Department of Energy (DOE) and its predecessors. Much of this discharge occurred within the Central Plateau (Figure 1), a 200 km^2 (75 mi^2) area that includes approximately 800 waste sites (Truex et al. 2018). Associated operations discharged large volumes of water and waste effluent into the hundreds of disposal sites, which included cribs, trenches, ponds, and some reverse wells. Additional sources of contamination include liquids leaked from underground waste storage tanks and their associated infrastructure. Contamination from these sources has spread into the vadose zone, with some of the more mobile contaminants reaching the groundwater. Significant quantities of both mobile and relatively immobile contaminants remain in the vadose zone and are a potential long term risk to further groundwater contamination. Contaminants of concern (COCs) within the Central Plateau vadose zone and groundwater include technetium-99 (^{99}Tc), uranium (U), nitrate (NO_3^-), chromium (Cr), cyanide (CN^-), and iodine-129 (^{129}I). Brief descriptions of these deep vadose zone contaminant source areas are provided in Wellman et al. (2011).
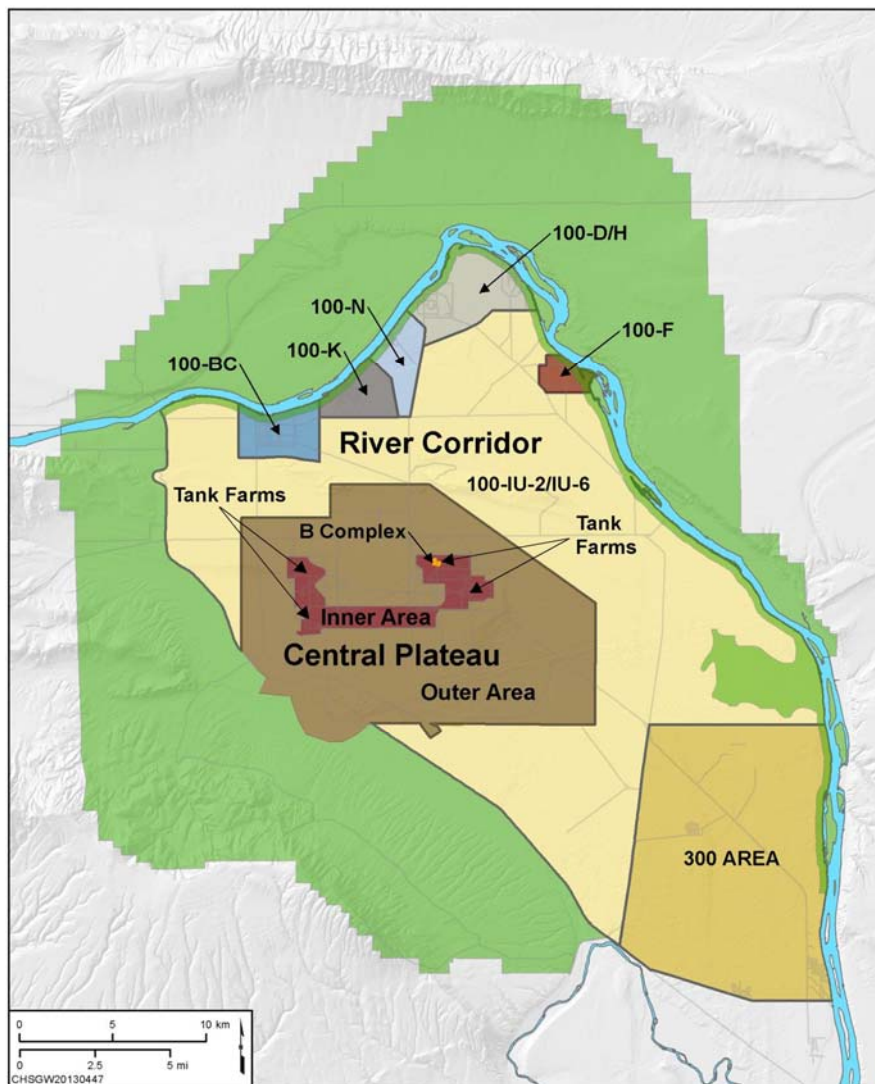

Figure 1. Location of the Hanford Site and Central Plateau (from SGW-58147).

The Tri-Party Agencies (DOE, U.S. Environmental Protection Agency, and Washington State Department of Ecology) established several milestones that direct remediation activities in Hanford's Central Plateau, including Milestone M-015-110B, *Submit Corrective Measures Study & Feasibility Study Report and Proposed Plan/Proposed Corrective Action Decision for the 200-DV-1 OU to Ecology*; Milestone M-015-84, *Complete remedial investigation of 200-WA-1 and 200-BC-1 operable unit waste sites in accordance with the 200-WA-1 and 200-BC-1 RI/FS Work Plan*; Milestone M-015-91B, *Submit Feasibility Study Report(s) and Proposed Plan(s) for the 200-BC- 1 and 200-WA-1 operable units (200 West Inner Area) to EPA*; and Milestone M-015-92B, *Submit RCRA Facility Investigation/Corrective Measures Study & Remedial Investigation/Feasibility Study Report and Proposed Corrective Action Decision/Proposed Plan for the 200-EA-1 OU (Central Plateau 200 East Inner Area) to Ecology* (Ecology 2003). Collectively, these milestones direct DOE to (1) evaluate remedy options for vadose zone continuing sources and groundwater units and (2) provide the technical basis to assess their performance as long-term remedial alternatives to pump-and-treat for Central Plateau contaminants of concern.

Remediation options are limited for much of the deep vadose zone contamination within the Central Plateau due to its considerable depth, coupled with challenges posed by the physical and hydrogeologic properties of the vadose zone and aquifer (Dresel et al. 2011; Truex et al. 2017a,b). Key factors that must be considered include (a) much of the contamination has traveled to a depth of 200 feet (or more) below ground surface (Truex et al. 2017a; Figure 2), making deployment of remedial treatment technologies challenging; (b) the vadose zone within the Central Plateau contains thin lenses of fine-grained sediments that promote the lateral migration of contaminant plumes (Figure 3); and (c) many plumes contain mixtures of contaminants, necessitating the need for a systems-based approach for remediation to ensure technologies targeted at one or more COCs do not cause deleterious impacts on other co-located contaminants.

Initial laboratory efforts were conducted in FY18 to screen potential in situ remedial alternatives to address the complex biogeochemistry of contaminant mixtures within the Central Plateau's vadose zone and groundwater. These initial studies evaluated gas-phase remediation approaches and evaluated co-contaminant impacts on biological attenuation processes. These activities targeted approaches for ^{99}Tc, U, NO_3, Cr, and CN. Evaluation of ^{129}I in the vadose zone is also included; however, technologies for ^{129}I contamination in groundwater are reported separately associated with work for the 200-UP-1 Operable Unit (OU) (Szecsody et al. 2018). Specifically, initial technology investigation included gas phase bioreduction and CO_2 injection for carbonate coating development. Results from these tests will support future assessment of remedial alternatives to address the specific contaminant mixtures that serve as continuing sources in the Central Plateau.
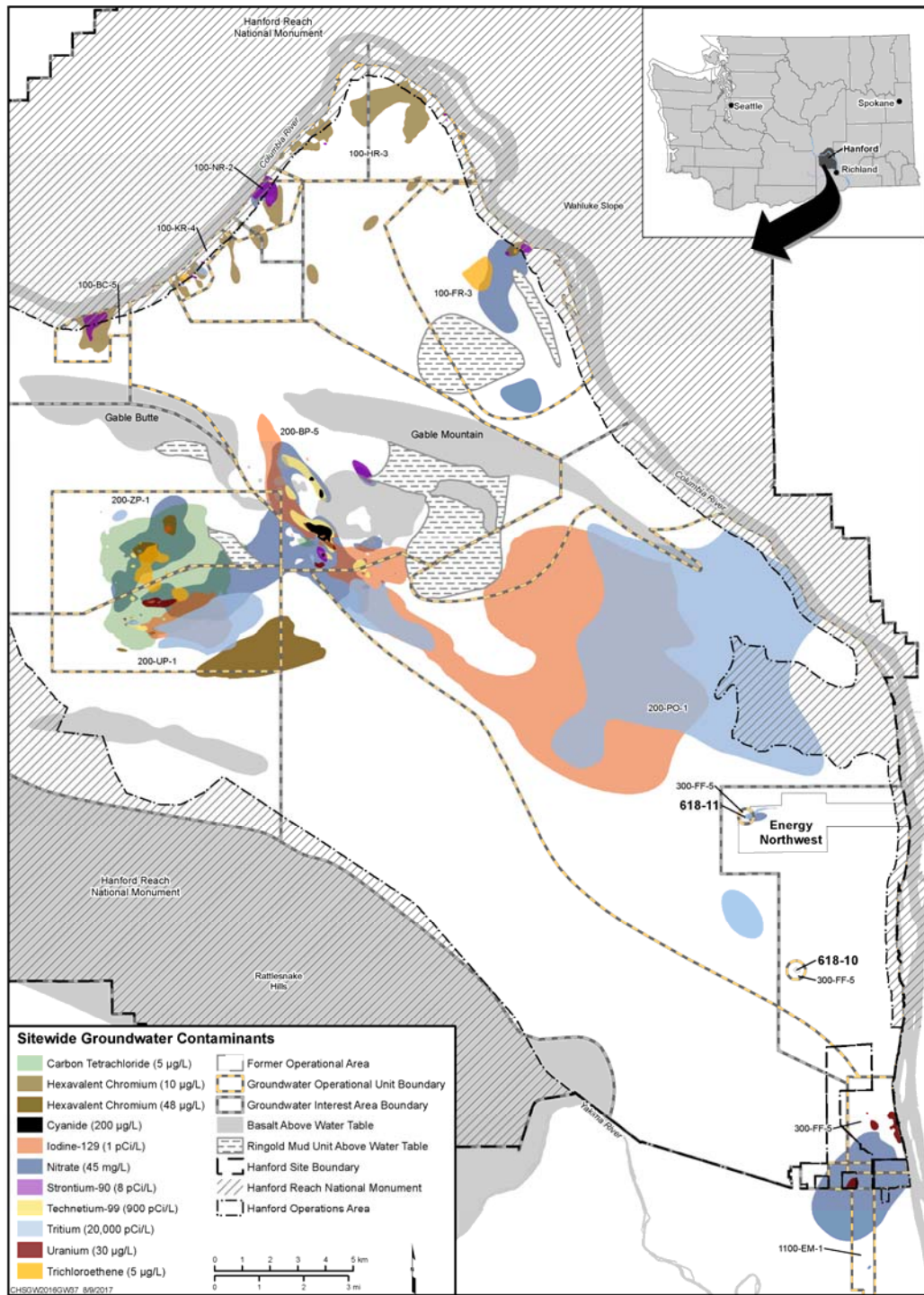
Figure 2. Groundwater contaminant plumes and regions of the Hanford Site (from DOE/RL-2016-67).

Figure 3. Central plateau geology (from DOE/RL-2016-67).

1.1 Gas Phase Bioreduction

In previous work, Brockman et al. (2004) conducted bench-scale studies to evaluate the feasibility of injecting gas phase hydrocarbons and nutrients into the deep vadose zone at Hanford to stimulate microbial bioremediation. Sediments from the 216-Z-9 Trench were amended with a gas mixture containing equal amounts of methane, ethane, propylene, propane, and butane, along with gaseous nitrogen in the form of N_2O. Phosphorous was added as an aqueous solution of triethyl phosphate (which could be delivered to the vadose zone as a vapor). Results indicated that 80% of the sediments degraded at least one of the hydrocarbon compounds, and 20% to 45% of the sediment samples showed the ability to biodegrade a specific hydrocarbon. More than three hydrocarbons were degraded in 70% of the sediments.

The organic carbon sources that were utilized the most generally had higher carbon numbers; 44% of butane was used, followed by 42% of propylene, 31% propane, and 22% ethane. Methane degradation was not observed in any of the sediments. Gaseous nitrogen and phosphorus did not stimulate removal of gaseous C sources compared to no addition of N and P; however, the microbial community appeared to have adequate levels of sediment-associated N and P to convert large amounts of hydrocarbon utilization to cell mass. A pattern explaining the ability of the microbial community in the sediments to utilize the gaseous hydrocarbons could not be identified.

In a more recent study (Evans et al. 2011), liquefied petroleum gas (injected as 79% N_2, 10% H_2, 10% LPG, 1% CO_2), which is composed primarily of propane, propylene, butane, and butylene in various mixtures, was demonstrated to be effective for nitrate/nitrite degradation in a field test site in California. Nitrate/nitrite concentrations were reduced by over 90%. LPG is an inexpensive and readily available hydrocarbon substrate for use with stimulating gas phase microbial reduction.

The results of Brockman et al. (2004) and Evans et al. (2011) suggest that the use of gaseous hydrocarbons to increase microbial populations may be viable for an in situ treatment approach in Hanford deep vadose zone sediments. This work also has potential application to Central Plateau contaminant remediation. The creation of reducing conditions within the vadose zone could immobilize in situ hexavalent chromium, technetium, and uranium.

1.2 CO_2 Injection for Carbonate Coating Development

CO_2 gas injection into unsaturated sediment results in an acidic pH as low as 5.4, and is dependent on the water content, with lower water content resulting in a lower pH (Szecsody et al. 2010). Exposing sediments to 100% CO_2 increases carbonate concentrations in the sediment pore water relative to natural conditions. Both the increased carbonate and acidic pH are expected to increase uranium mobilization by forming more Ca-U-CO_3 aqueous complexes and reducing adsorption. Other minerals, such as iron oxides, are also likely partially dissolved at lower pH. After the CO_2 is allowed to dissipate, the pH increases, resulting in precipitation of uranium and other phases.

Szecsody et al. (2010) conducted experiments in which sediment columns were exposed to 100% CO_2 for 1 month. The sediment was then flushed with air for 2 months. Sequential extractions conducted on sediments from the column indicated that there were substantial uranium surface phase changes. Apparent changes were decreases in adsorbed and carbonate associated uranium, with a corresponding increase in silicate/oxide uranium (8% to 33%). During the 1-month treatment with CO_2 gas, there was a substantial increase in uranium mobilization (which may be an issue for field-scale application).

In a separate set of experiments, the sediment pH with just CO_2 treatment (i.e., no flushing with air) showed a slow increase to natural pH conditions (i.e., pH was 7.3 by 3 months). These results demonstrated that in a field scenario, it is possible that a single treatment of just CO_2 gas without a subsequent pH neutralization step could be used.

In recent work by Truex et al. (2017a), they found that the majority of iodine in sediments from the 200-DV-1 OU was associated with precipitates (likely carbonates), and that iodine mobility would be controlled by dissolution processes. Other work by Zhang et al. (2013) has identified evidence of iodine coprecipitation with calcium carbonate. These findings have spurred recent efforts by Szecsody et al. (2018) to quantify iodate incorporation into calcite. Their results indicate that up to 70% of iodate can be removed from solution during calcite precipitation under Hanford-relevant conditions.

1.3 Scope, Report Content, and Organization

This report documents batch-scale laboratory screening tests that support evaluation of remediation approaches for continuing sources of contamination within the Central Plateau at Hanford. Evaluated contaminant immobilization technologies are presented in Sections 2 and 3. Section 2 presents interim results for a gas phase bioreduction approach. Section 3 presents initial evaluation of using CO_2 gas injection to immobilize contaminants, either through incorporation into a secondary precipitate or by coating the contaminants with a less soluble mineral. Section 4 contains a summary of all results to date and recommendations for future activities. A description of the quality assurance program is presented in Section 5.

2.0   Gas Phase Bioreduction

The principal contaminants present in deep vadose sediments throughout the Hanford Central Plateau include chromium, technetium, iodine, and uranium. Nitrate is also present in relatively high concentrations. In oxic conditions typical of deep vadose zone sediments, these contaminants exist as highly mobile chemical species, and thus signify a persistent source term for long-term groundwater contamination. Consequently, a number of stabilization strategies are being pursued to chemically reduce co-located contaminants to less mobile species and then sequester them in place. In addition, direct microbial degradation of nitrate is also possible. Stimulation of indigenous microorganisms to reductively immobilize mixtures of inorganic contaminants in deep vadose sediments is not a novel concept, but has not been thoroughly investigated for the Hanford Site.

Microorganisms are present in Hanford deep vadose sediments in reasonably high numbers ($10^6 – 10^7$ cells/g soil, (Brockman et al. 1992, 2004; Fredrickson et al. 1993; Truex et al. 2014, 2017a); however, catabolic activity is exceptionally low due to low resource availability. It is widely assumed that organic carbon, nutrients, water availability, as well as other environmental factors limit microbial physiology and activity in deep vadose sediments (Holden and Fierer 2005). It is presumed that if these limitations can be overcome, microbial activity can be stimulated, thus creating reduced zones for contaminant degradation or immobilization. The delivery of gaseous electron donors and nutrients into the vadose zone has been demonstrated as an effective biostimulation strategy for the degradation of organic and inorganic contaminants (Brockman et al. 1995; Evans and Trute 2007; Evans et al. 2011; Evans 2012), but the feasibility of the approach for inorganic contaminants has not been explored. Preliminary screening experiments were conducted to evaluate the potential for using gaseous or volatile substrates to stimulate vadose soil respiration, and thereby lower the redox potential of the system sufficiently to demonstrate promise as a reductive technology for inorganic contaminant immobilization or for direct degradation of nitrate.

2.1   Experimental Methods

The concentrations and relative proportions of co-mingled contaminants in deep vadose sediments will have a strong influence on subsurface soil respiration and ultimately dictate the rate and extent to which soil redox can be lowered microbiologically to immobilize radionuclides. Based on the redox ladder of oxidation-reduction potentials (Table 1), the order and progression of terminal electron acceptors (and key contaminants) can be predicted based on thermodynamic reduction by microbiological respiration. This interpretation is an oversimplification of the actual chemical complexity and heterogeneity of subsurface environments (Holden and Fierer 2005); however, a redox sensitive colorimetric dye can be used as a proxy to evaluate the potential of different gaseous substrates to stimulate soil respiration and qualitatively estimate the reduction potential of soils containing mixtures of inorganic contaminants (e.g., Wildung et al. 2000).

Table 1. Oxidation Reduction Potentials (Lide, 2003.

Electron acceptor pairing	E_0(mV)
Cr(VI)/Cr(III)	+1340
O_2/H_2O	+1229
Fe(III)/Fe(II)	+770
Tc(VII)/(IV)	+740
NO_3/N_2	+740
NO_3/NO_2	+430
U(VI)/U(IV)	+170
Resazurin	+70
Resorufin	-51
SO_4/HS^-	-220
CO_2/CH_4	-240

Preliminary screening experiments were conducted in sealed test tubes using representative subsurface lithologies that broadly capture the 200 Area deep vadose zone. Experiments were performed at volumetric water contents (vWC) of 4% and 8% to evaluate soil respiratory responses at varying degrees of pore-scale water connectivity and water film thickness. Previous calculations have established that columns of Hanford sediment at ~5% vWC would be effectively composed of hydraulically disconnected pores, while at ~10% vWC pore spaces would be hydraulically connected, thus allowing motility facilitated microbial colonization (Brockman et al. 2004).

Pre-weighed representative materials were dried to a constant weight in a laboratory incubator at 60°C to determine the relative moisture content of the sediments. All experiments utilized synthetic vadose zone pore water (VZPW) to adjust sediment moisture content to 4% and 8%. The synthetic perched water (SPW) recipe used for this sub-task is provided in Table 2 (Table 1.0; PNNL-24297).

Table 2. Vadose Zone Porewater (VZPW) Simulant Recipe (from Serne et al. 2015).

Order to Dissolve	M	Reagent	MW	g/L
1	0.012	$CaSO_4*2H_2O$	172.1723	2.0661
2	0.0017	NaCl	58.4430	0.0994
3	0.0004	$NaHCO_3$	84.0068	0.0336
4	0.0034	$NaNO_3$	84.9948	0.2890
5	0.0026	$MgSO_4$	120.3660	0.3130
6	0.0024	$MgCl_2*6H_2O$	203.3034	0.4879
7	0.0007	KCl	74.5515	0.0522

Adjust pH to 7.0 to 7.2 with sodium hydroxide or sulfuric acid

After VZPW addition, 5 g of representative 200 Area sediment was transferred to sterile glass tubes fitted with a butyl rubber septa and screw caps. Two UP-1 sediments were selected for this investigation. Core C9632 (B3B0C6) was taken from a depth of 315 feet within the footprint of a Cr^{6+} plume. The second core under investigation was C9607 (B3H7W1), which was taken from a depth of 340 feet within the footprint of nitrate (NO_3), technetium (^{99}Tc), carbon tetrachloride (CT), and trichloroethene (TCE) plumes. The first core provided evaluation of the suitability of gaseous substrates to support sediment respiration. The second core qualified the relative strength of each substrate to sequentially and systematically progress down the redox ladder (Table 1), thereby reducing mixtures of contaminants prior to colorimetric reaction of resazurin.

The following gaseous (200 µL) and volatile substrates (100 µL) (analytical grade, Sigma-Aldrich) were qualitatively tested for stimulating respiratory response in Hanford deep vadose sediments: H_2, ethanol, methanol, pentane, butyrate, dimethyl sulfoxide (DMSO), butyl acetate, ethyl acetate, propane, cyclopropane, butane, methane, ethane, butyrate, propylene, and a custom gas mix (15 ppm each of methane, ethane, ethylene, acetylene, propane, propylene, propyne, n-butane in N_2 gas). The headspace was briefly flushed (2 sec) with a pure Ar gas stream prior to substrate delivery. Liquid donors were inoculated onto sterile filter pad disks placed atop the sediment column and allowed to vaporize during incubation. Controls included using glucose as a substrate (positive control), no added exogenous organic substrate (reliant upon autochthonous organic carbon supplies), and heat killed (negative control). All sediment trials were conducted at room temperature and in the dark.

The screening investigations incorporated resazurin (1 mg/L) as a colorimetric indicator to permit visualization of oxygen consumption and reduced zone formation within the vadose zone sediments. Resazurin (E_0 = 70 mV) is a non-toxic, water soluble, redox sensitive dye that irreversibly changes from blue to pink (resorufin) when exposed to microbial respiration under aerobic to microaerophilic

conditions (Wildung et al. 2000). Further reduction transforms resorufin (E_0 = -51 mV) to colorless hydroresorufin. Therefore, resazurin color transformation is proportionally correlated to microbial respiration rate in prepared 200 Area sediments and will allow for convenient visualization of spatial heterogeneity and soil respiratory response in soils. By relating these responses to established redox couples, inferences can be drawn as to the potential of representative 200 Area sediments to reductively immobilize vadose zone contaminants [Cr(VI), Tc(VII), U(VI), and NO_3] in response to the injection of gaseous substrates and vaporized liquids.

2.2 Results

Experimental responses of Hanford sediment core C9632 (B3B0C6) to various gaseous and volatile substrates are shown in Table 3. Qualitative color development was scored according to the visual reaction of resazurin from blue to pink to colorless. Based on the oxidation-reduction potentials shown in Table 1, the reduction of resazurin from blue to pink is interpreted to indicate that all residual oxygen was consumed, Cr^{6+} is reduced to Cr^{3+}. Experimental trials with the second Hanford sediment core C9607 (B3H7W1), which contains a more complex mixture of constituents (NO_3, Tc^{99}, CT, and TCE) have been established, but experiments are ongoing and will be documented in a future report.

Table 3. Qualitative utilization of gaseous or volatile organic substrates by Hanford sediment (core C9632) at two volumetric water contents.

Substrate	5 Days		13 Days		19 Days	
vWC	4%	8%	4%	8%	4%	8%
Ethyl Acetate	-/-	-/+	-/-	-/+	-/-	-/c
Ethanol	-/-	-/-	-/-	+/+	+/-	+/+
DMSO	-/-	-/-	-/-	-/-	-/-	-/-
Butyrate	+/+	+/+	+/+	+/+	c/c	c/c
Pentane	+/+	+/+	+/+	+/+	+/c	+/c
Gas Mix (8)	-/-	-/-	+/-	+/+	+/-	+/+
Methane	-/-	-/-	+/-	+/+	+/-	+/+
Hydrogen	-/-	-/-	+/+	+/+	+/c	+/+
Propane	-/-	+/-	-/-	+/+	-/-	+/+
Methanol	-/-	+/-	+/-	+/+	+/+	+/+
Ethane	-/-	+/+	-/-	+/+	+/+	+/c
Butane	-/-	+/+	-/-	+/+	+/+	c/c
Propylene	-/-	+/-	+/+	+/+	+/+	+/+
Butyl Acetate	+/+	+/-	c/c	c/c	c/c	c/c
Glucose (+)	+/+	+/+	+/+	+/+	+/+	+/+
No added S (-)	-/-	-/-	-/-	-/+	-/-	-/+
Sterile Controls	-/-	-/-	-/-	-/-	-/-	-/-

All experimental tubes were spiked with 2 µl of 1 g/L resazurin stock and incubated in the dark at room temperature. The following notation was used to report color development: '-' means the resazurin is blue (oxidized); '+' means resazurin was reduced to resorufin which is colored pink; and 'c' means the resorufin was further reduced to colorless, hydroresorufin. Results are reported for biological duplicates at 4% and 8% vWC, respectively.

2.3 Discussion

This study provides a comprehensive investigation of gaseous and volatile substrates to stimulate soil respiration and achieve chemical reduction of Hanford deep vadose sediments. After 3 weeks of incubation, the majority of substrates tested were microbiologically consumed and soil respiration was sufficiently enhanced to chemically reduce Hanford deep vadose sediments. No colorimetric reaction (i.e., chemical reduction) was observed for any of the negative controls (biotic or abiotic).

The addition of VZPW invoked the strongest microbial response from Hanford subsurface soils. Substrate utilization was generally favorable for 4% and 8% volumetric water contents; however, the microbial response was faster and more consistent at 8% volumetric water content. The water content values are typical of values in sandy (4%) and silty (8%) portions of the vadose zone. This result underscores the importance of aqueous thin films and pore-scale water connectivity in supporting a strong microbiological response (Brockman et al. 2004). Low water content and the discontinuity of aqueous films connecting pore spaces is typical of deep vadose sediments and will limit diffusional transport as well as the mobility of microbial populations (Holden and Fierer 2005). Water availability will be a crucial consideration and key to the success for any biostimulation strategy employed for deep vadose sediments.

Macro- or micro-nutrient amendments were not necessary to stimulate soil microbial respiration. The results for the sediment samples used in the testing indicate that Hanford's deep vadose zone likely has adequate conditions (e.g., nutrients) to support in situ microbial remediation processes. Ongoing studies with the second Hanford sediment will provide a better evaluation of the availability of these resource pools to sustain microbial activity for the reduction of complex contaminant mixtures. As a biostimulation strategy, nutrient amendments may need to be carefully considered for sustained activity and to increase the treatment zone of influence in deep vadose sediments (e.g., Brockman et al. 1995).
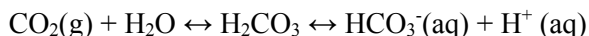
3.0 CO_2 Injection for Carbonate Coating Development

Based on previous co-precipitation studies (Zhang et al. 2013; Szecsody et al. 2017; Truex et al. 2017a,b; Qafoku and Icenhower 2008; Qafoku et al. 2017; Podder et al. 2017; Montes-Hernandez et al. 2007; Zachara et al. 2007a,b; Catalano et al. 2008), it is hypothesized that dissolved contaminants can be sequestered into calcium carbonates via co-precipitation mechanisms. Iodine incorporation into calcite under saturated conditions has been demonstrated (Szecsody et al. 2018; Zhang et al. 2013); however, fewer data are available for other Central Plateau COCs and for use of a gaseous source of CO_2. For example, a review of the literature failed to identify any studies targeting ^{99}Tc immobilization via calcite precipitation, and efforts focused on uranium sequestration have failed to identify the mechanism leading to uranium removal during calcite precipitation (Kelly et al. 2003).
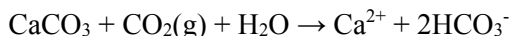
Co-precipitation of COCs in carbonate minerals via dissolution and re-precipitation caused by injection of CO_2 into the subsurface has been identified as a potential mechanism of sequestration for Central Plateau contaminants. As CO_2 is injected into the vadose zone or aquifer, carbonate minerals within the sediment dissolve. After gas injection, the CO_2 perturbed system returns to its initial state and precipitation of calcite and other soil minerals occurs.

Szecsody et al. (2010) found that exposing sediments to 100% CO_2 increases carbonate concentrations in the sediment pore water relative to natural conditions. Higher carbonate concentrations are expected to increase uranium mobilization by forming more Ca-U-CO_3 aqueous complexes. After the CO_2 is allowed to dissipate, the pH increases, resulting in precipitation of uranium and other phases. Sequential extractions conducted on sediments from their column experiments indicated that there were substantial uranium surface phase changes, including decreases in adsorbed and carbonate associated uranium, with a corresponding increase in silicate/oxide uranium (8% to 33%). During the 1-month treatment with CO_2 gas, there was a substantial increase in uranium mobilization (which may or may not be a concern for field-scale application).

A number of experimental and modeling studies conducted with soil and subsoil materials have shown a decrease in aqueous pH of up to 3 units when these materials were exposed to excess CO_2 gas, as discussed in Harvey et al. (2013), Qafoku et al. (2017), and references therein. The dissolution of the CO_2 gas in soil water results in an increase in aqueous phase proton concentrations following the chemical reactions:

$$CO_2(g) + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^-(aq) + H^+(aq)$$

The following reaction describes the dissolution of carbonate minerals, such as calcite, in the presence of excess CO_2 gas (Harvey et al. 2013):

$$CaCO_3 + CO_2(g) + H_2O \rightarrow Ca^{2+} + 2HCO_3^-$$

After injection of CO_2 stops, the pH in the system increases, allowing precipitation of $CaCO_3$ minerals, which may immobilize COCs through incorporation into the mineral matrix or coating the COCs with a carbonate mineral, thereby limiting its contact with the aqueous phase.

A series of experiments were initiated to determine the feasibility and effectiveness of using CO_2 to sequester contaminants in situ. Batch experiments were used to determine if uranium and iodine could be removed through dissolution and re-precipitation of carbonate minerals following CO_2 injection. Uranium and iodine were chosen for initial testing with Hanford sediments because they are the most likely COCs to be effectively immobilized using CO_2 gas injection.

3.1   Experimental Methods

Sediments used for testing were collected in Pasco, WA, from the middle Ringold unit and Cold Creek Unit (CCU). Prior to use, the sediment (Ringold or crushed CCU) was sieved to < 2 mm, dried, and analyzed using quantitative X-ray diffraction (XRD) for bulk mineralogy. Batch experiments were conducted in high-density polyethylene (HDPE) bottles containing 2 g of commercially available calcite (Sigma Aldrich, A.C.S.) or 5 g of sediment, along with 100 mL of double de-ionized (DDI) water VZPW (Table 2), or SPW (Table 4). See Table 5 for the test matrix. The batch reactors were fitted with lids that have an inlet to allow injection of CO_2, as well as an outlet to avoid the buildup of pressure (Figure 4). Inside the reactor, the inlet tube extended into the solution, but did not reach the bottom of the reactor where the solid was located. The CO_2 flowed through a hydration bottle prior to entering the batch reactors to minimize solution loss due to evaporation. A sample was collected from each reactor prior to CO_2 injection (this sample served as the Time = 0 sample). CO_2 injection occurred for ~24 hours. After CO_2 injection ended, samples were collected at approximate intervals of 2 and 6 hours and 1, 3, 7, 14, 21, 28, 42, and 49 days. Samples were filtered (0.2 µm) and submitted for analysis by inductively coupled plasma mass spectrometry for trace element analysis and inductively coupled plasma optical emission spectrometry for major elemental analysis, with an emphasis on Ca analysis. Ca concentrations were used to determine if and when carbonates were dissolving and/or re-precipitating based concentration changes. Solution pH was measured in the reactors after each sampling. Previous studies (Lawter et al. 2015a, 2015b; Wang et al. 2017) have shown that pH and aqueous Ca concentrations (presumably due to carbonate dissolution) tend to reach steady values in <7 days (and many reached steady values in <1 day) of CO_2 injection. After 43 or 49 days, one replicate from each test was filtered using a 0.45 µm vacuum filter to collect solids. Solids were then analyzed for changes via quantitative XRD (Q-XRD). Results from Q-XRD analysis will be reported in a subsequent report.

Table 4. Synthetic perched water recipe, for 1 L of solution.

Chemical	Mmol/L	g/L
NaHCO$_3$	10.7079	0.8995
KHCO$_3$	0.3095	0.0310
MgSO$_4$·7H$_2$O	2.7031	0.6662
CaSO$_4$·2H$_2$O	0.5608	0.0965
Na$_2$SO$_4$	1.7441	0.2477
NaCl	3.3006	0.1929
Add 100 µL of 2M HCl to 1L solution to lower pH to ~8.2		

Controls were used throughout each set of batch experiments, and consisted of batch reactors that contained the same solution, COC spike(s), and solids used in the experiment, but without exposure to CO_2. Additional controls that included the same solution, COCs, and CO_2 injection, but no solids, were also included.
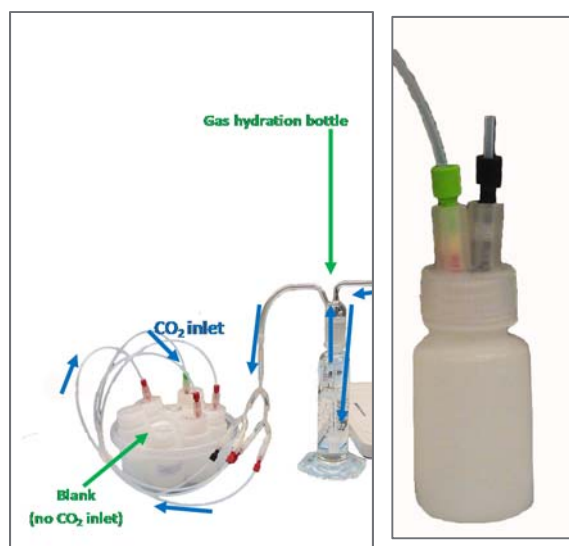
Figure 4. CO_2 injection setup.

Table 5. Test matrix.

Test ID	Solution Used	COPC Spike Added	Solids
1815 T1	DDI water	Iodine (1 ppm)	$CaCO_3$, Ringold
1815 T2	DDI water	Uranium (1.5 ppm)	$CaCO_3$, Ringold
1815 T3	Synthetic VZPW	Iodine (1 ppm)	$CaCO_3$, Ringold
1810 T1	DDI water	Iodine (1 ppm)	Cold Creek Unit (CCU)
1810 T2	DDI water, SPW	Uranium (1 ppm)	Cold Creek Unit (CCU)

3.2   Results

Controls for iodine were stable. For example, the control containing I-spiked DDI water with CO_2 injection but without any solids had average I concentrations of ~1000 ppb (Figure 5 and Figure 6). The controls with solids and no CO_2 injection demonstrated a pH that decreased from 9.6-9.9 at time 0 to 8.7-9.0 at days 47 and 49 (Figure 5 and Figure 6). After an initial increase of 200 ppm of Ca in the CCU controls (Figure 5) and 300 ppm of Ca in the calcite and Ringold controls (Figure 6), the Ca concentrations were also similar, ~50 to 60 ppm Ca 42 days post-CO_2 injection. Aqueous uranium was not stable in two of the control samples containing U-spiked DDI without solids. In those controls, uranium concentrations fluctuated between 1.3 ppm and 680 ppb for the duration the test (Figure 7). Because metals like uranium have limited stability in unpreserved (i.e., unacidified) solutions, the loss of dissolved uranium during these tests may be due to sorption on the bottles or 0.2 μm filters. Increases in uranium concentrations in control samples with CO_2 injection were perplexing and indicate that uranium may have been present as a trace contaminant in the calcite.
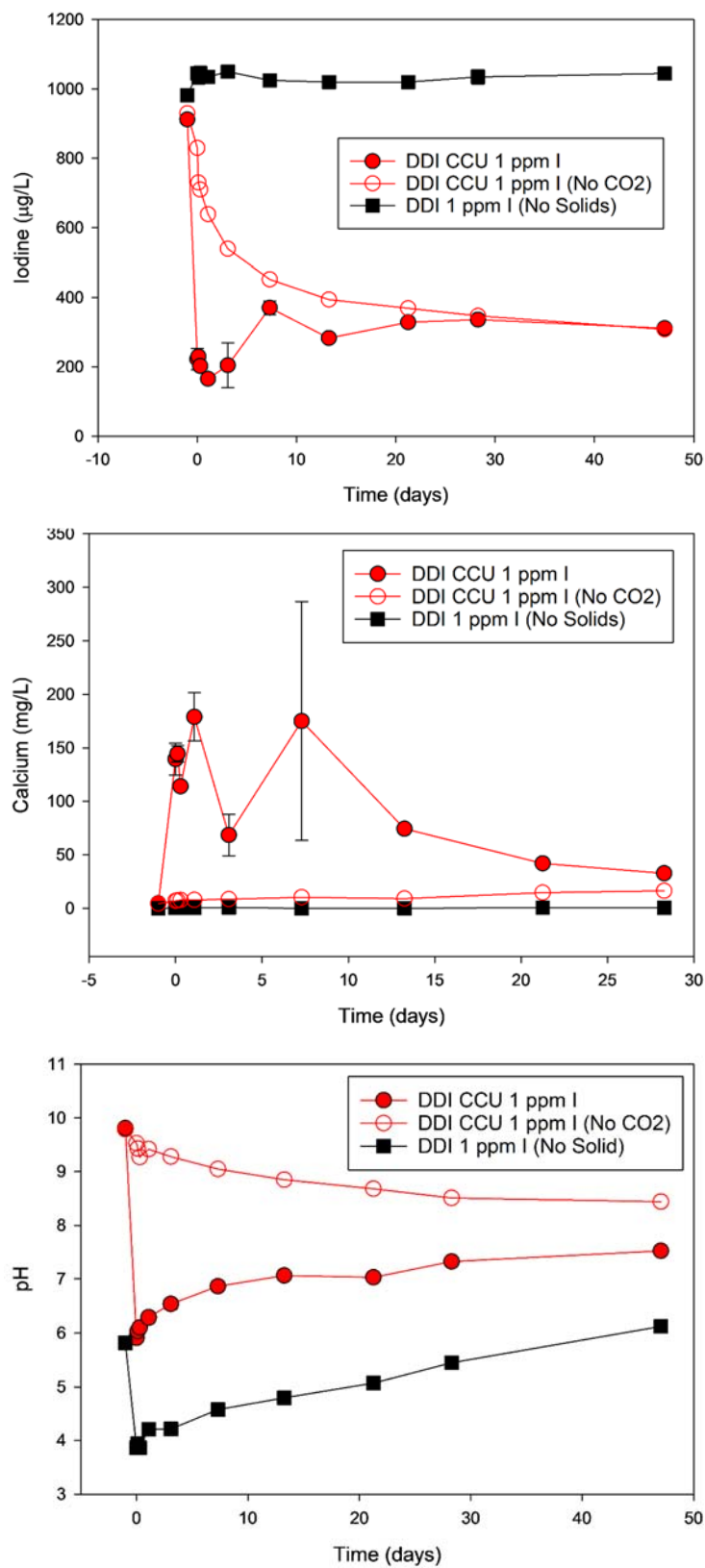
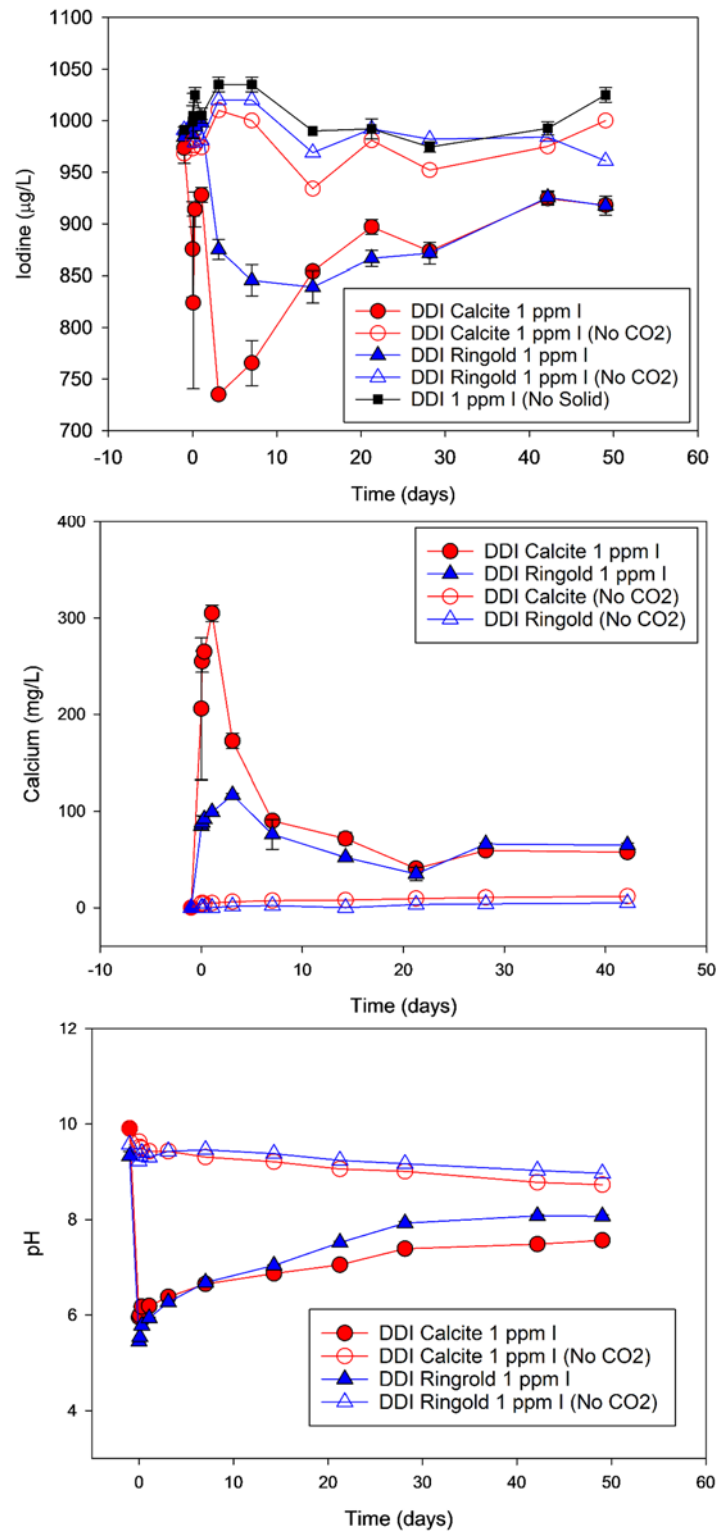**Figure 5**. a) I, b) Ca, and c) pH data for test 1810 T1.

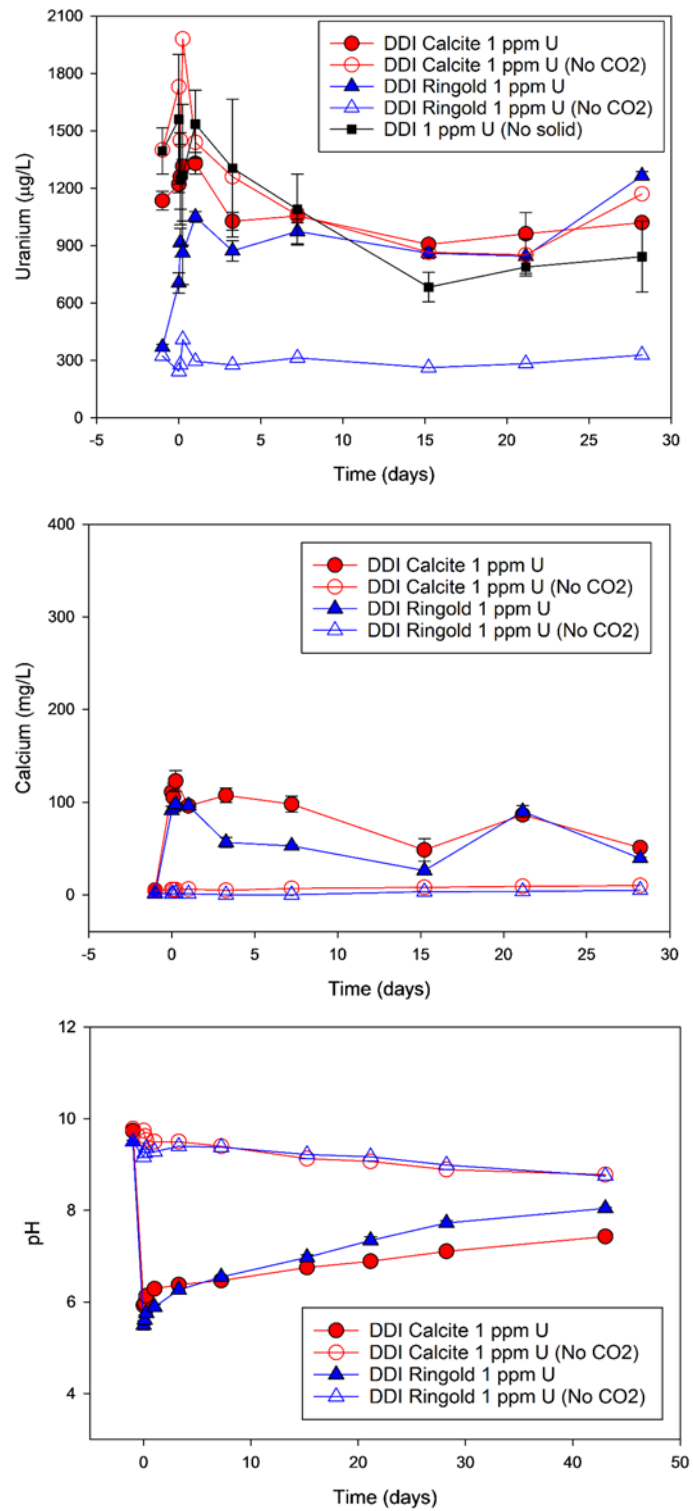**Figure 6**. a) I, b) Ca, and c) pH data for test 1815 T1.

Figure 7. a) U, b) Ca, and c) pH data for test 1815 T2.

The pH of the calcite and Ringold sediment experiments in 1815 T1 were similar, with the CO_2-injected tests increasing from pH 5.5-6 at time 0 (immediately following CO_2 injection) to pH 7.6-8.1 49 days after CO_2 injection (Figure 6). Approximately 60% of iodine was removed from solution in the reactors containing CCU sediment (Figure 5), reaching a minimum solution concentration of 312 ppb after 47 days. However, only a small amount of iodine was removed from solution in both the calcite and Ringold sediment experiments. For calcite in DDI water, the aqueous I concentration reached a minimum of 735 ppb 3 days after CO_2 injection, and in the Ringold test, iodine reached a minimum of 839 ppb 14 days after CO_2 injection. Aqueous I concentrations in both reactors with calcite and Ringold sediment then increased, reaching a concentration of 918 ppb by day 49.

Calcite reactors with synthetic VZPW (test 1815 T3) reached an aqueous I concentration of ~500 ppb by the first post-CO_2 injection sampling (time 0), indicating 50% removal (Figure 8). For Ringold sediments, I concentrations decreased slowly to a minimum of 760 ppb, 7 days after CO_2 injection. In both experiments, iodine concentrations increased after 7 days, with final concentrations of ~900 ppb at day 28. Controls without solids and without CO_2 injection remained at the 1000 ppb spike concentration throughout the test with only minor analytical variation in measured concentrations.

The Ca concentration in VZPW controls containing no solids remained at ~480 ppm, while the calcite and Ringold sediment experiments reached a maximum Ca concentration of 760 ppm and 575 ppm, respectively, at 1 day post-CO_2 injection (Figure 8). The pH was similar for all experiments (pH 9), except for the 1815 T3 controls that did not receive CO_2 injection (pH 7.5). This is likely due to the buffering capacity of the VZPW relative to the DDI water used in the other two tests.

In test 1815 T2 with DDI, aqueous uranium concentrations in the Ringold sediment control (i.e., no CO_2 injection) were about 300 ppb (ranging from 240-410 ppb) for the duration of test 1815 T2 (Figure 7). However, in the Ringold sediment with CO_2, aqueous uranium concentration increased over time from 300 ppb to more than 1.2 ppm. These results indicate that uranium is likely complexing with carbonate dissolved from the sediment, thereby promoting its solubility. In DDI with calcite, aqueous uranium concentration behavior with CO_2 injection was similar to what was observed for both controls, indicating CO_2 injection had no effect on uranium solubility under these test conditions.

In the uranium-spiked experiments with CCU sediment (test 1810 T2), aqueous U concentrations remained near 960 ppb in the SPW reactor that received CO_2 without sediments, and around 830 ppb with CCU solids, but no CO_2 injection (Figure 9). The aqueous U concentrations in the reactors with SPW, CCU sediments, and CO_2 injection initially decreased after CO_2 injection, corresponding with the lowest solution pH measured during the test, but subsequently increased as solution pH slowly increased due to calcite dissolution, resulting in uranium concentrations of approximately 700 ppb by day 7 (Figure 9). The lowest uranium concentration observed in reactors containing CCU sediment was in the reactor containing DDI water and CCU sediments with no CO_2 injection. Uranium solution concentrations in this reactor continued to decrease, from 650 ppb at time 0 to 320 ppb at day 14. Uranium removal was likely due to uranium-adsorbing to phyllosilicates present in the CCU sediments (Qafoku and Icenhower 2008). In comparison, uranium solution concentrations containing CCU sediment and SPW were approximately a factor of 2 higher, demonstrating the importance of aqueous chemistry on uranium solubility. Overall, these results indicate that CO_2 injection had little effect on aqueous uranium concentrations.
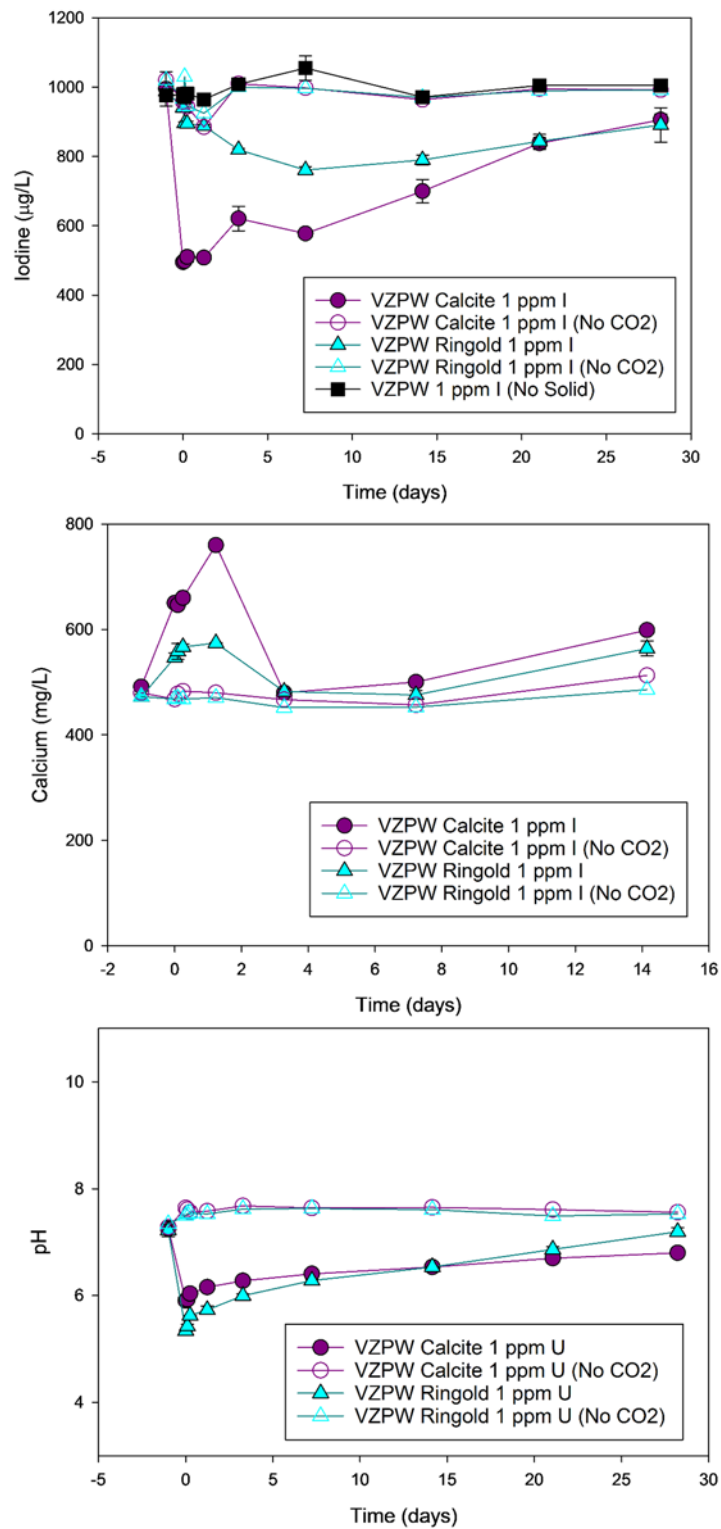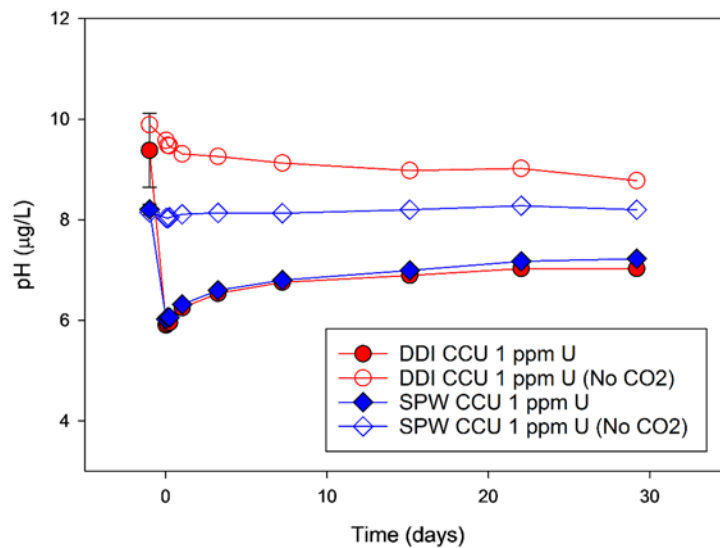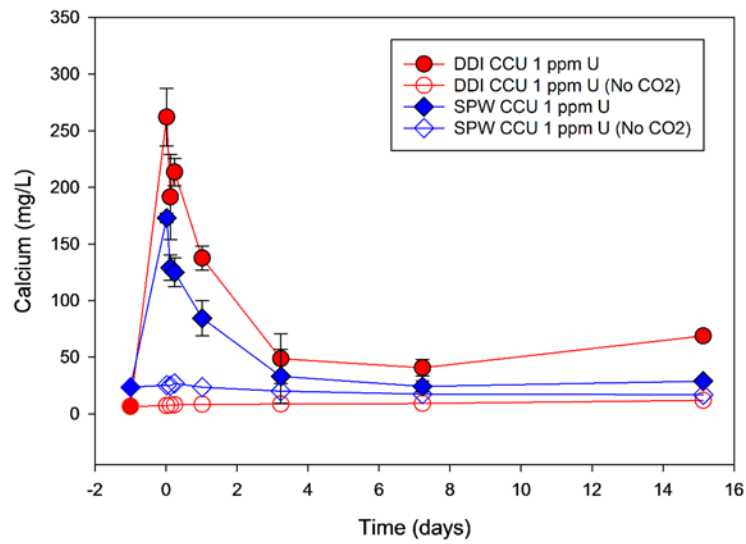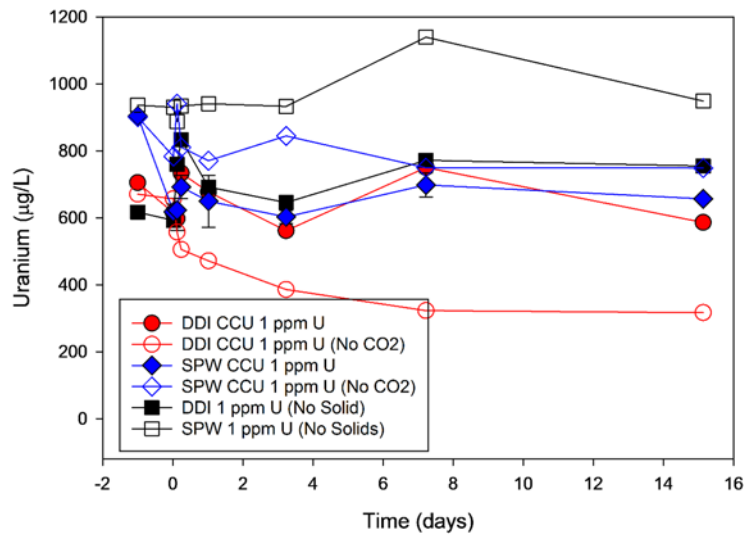
Figure 8. I, Ca, and pH data for test 1815 T3.

Figure 9. a) U, b) Ca, and c) pH data for test 1810 T2.

3.3 Discussion

Injection of CO_2 demonstrated 25% to 60% removal of aqueous iodine from solution. For uranium, CO_2 injection was ineffective and increased uranium solubility in reactors containing Ringold and CCU sediments. While these results do not support the continued evaluation of CO_2 injection, if improvements are made, the approach may be useful as part of a two-step remediation approach. With a two-step approach, a reductant would be added to the system to promote reduction of redox sensitive contaminants, such as ^{99}Tc, chromium, and uranium. This step would then be followed by injection of CO_2 to dissolve carbonate minerals present in the sediment. The final step would be to either flush CO_2 from the system using an inert gas (e.g., nitrogen), or to allow the system to slowly equilibrate with atmospheric gas. Once the solution pH returns to circa neutral, carbonate minerals precipitate and armor the reduced contaminants, thereby limiting their interaction with dissolved oxygen.

4.0   Conclusions

This report documents initial laboratory efforts to screen potential remedial technologies for comingled contaminants in the Central Plateau. Specifically, these initial studies evaluated gas-phase remediation approaches and evaluated co-contaminant impacts on biological attenuation processes. Bench-scale testing included gas phase bioreduction to evaluate soil respiratory response and contaminant reduction potential to gaseous and vaporized liquid substrates, CO_2 injection for carbonate coating development to evaluate co-precipitation of iodine and uranium in carbonate minerals via dissolution and re-precipitation caused by injection of CO_2.

Results of the gas phase bioreduction work indicated that after 3 weeks of incubation, the majority of substrates tested were microbiologically consumed and soil respiration was sufficiently enhanced to chemically reduce Hanford deep vadose zone sediments. Additionally, it was determined that macro- or micro-nutrient amendments were not necessary to stimulate soil microbial respiration. The results for the sediment samples used in the testing indicate that Hanford's deep vadose zone likely has adequate conditions (e.g., nutrients) to support in situ microbial remediation processes.

Results from CO_2 gas injection tests indicated that solution composition has a big impact on iodate removal by calcite. Little aqueous iodine was removed in DDI water in reactors containing calcite or Ringold sediment after the CO_2 treatment, but 25% to 50% was removed in the tests using VZPW. Additionally, ~60% of iodine was removed from solution in DDI water when CCU sediments were present, demonstrating the importance of different lithologies on contaminant uptake. Injection of CO_2 was ineffective at removing uranium from solution. While these results do not support the continued evaluation of CO_2 injection for uranium treatment, CO_2 treatment may be useful as part of a two-step remediation approach to armor contaminants precipitated by redox approaches.

5.0   Quality Assurance

The results presented in this report originate from work governed by the Pacific Northwest National Laboratory Nuclear Quality Assurance Program (NQAP). The NQAP implements the requirements of the DOE Order 414.1D, *Quality Assurance*, and 10 CFR 830 Subpart A*, Quality Assurance Requirements*. The NQAP uses ASME NQA-1-2012, *Quality Assurance Requirements for Nuclear Facility Applications*, as its consensus standard and NQA-1-2012 Subpart 4.2.1 as the basis for its graded approach to quality.

Two quality grading levels are defined by the NQAP:

Basic Research - The required degree of formality and level of work control is limited. However, sufficient documentation is retained to allow the research to be performed again without recourse to the original researcher(s). The documentation is also reviewed by a technically competent individual other than the originator.

Not Basic Research - The level of work control is greater than basic research. Approved plans and procedures govern the research, software is qualified, calculations are documented and reviewed, externally sourced data is evaluated, and measuring instrumentation is calibrated. Sufficient documentation is retained to allow the research to be performed again without recourse to the original researcher(s). The documentation is also reviewed by a technically competent individual other than the originator.

The work supporting the results presented in this report was performed in accordance with the *Basic Research* grading level controls.

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