Bench-Scale Experiments in Support of an In Situ Permeable Reactive Barrier Pilot Test: Effective Oil Retention, Biological Reduction of Perchlorate, and Metals Mobilization Using Site-Specific Soils and Groundwater

Nevada Environmental Response Trust Site Henderson, Nevada

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Responsible CEM for this Project:

I hereby certify that I am responsible for the services described in this document and for the preparation of this document. The services described in this document have been provided in a manner consistent with the current standards of the profession and, to the best of my knowledge, comply with all applicable federal, state and local statutes, regulations and ordinances.

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1.0 EXECUTIVE SUMMARY

Since 1998, an active groundwater remediation program has been underway at the Nevada Environmental Response Trust Site in Henderson, Nevada to reduce the load of perchlorate entering the Las Vegas Wash. A series of three on- and off-site well fields capture and transport perchlorate-impacted groundwater to an on-site treatment facility where the perchlorate is degraded in biological fluidized bed reactors.

While substantial perchlorate control and reduction has been achieved to date, significant perchlorate persists in groundwater downgradient of the Athens Road Well Field. Groundwater from this area continues to flow north to the Seep Area Well Field where the majority of it is captured before reaching the Las Vegas Wash. Currently, the extraction of groundwater with relatively low levels of perchlorate at the Seep Area Well Field represents up to about 60% of the total water volume treated in the on-Site water treatment plant. The Nevada Environmental Response Trust (Trust) is evaluating alternatives for the in situ treatment of perchlorate migrating in groundwater downgradient from the Athens Road Well Field to reduce the need for extraction at the Seep Area Well Field. A Permeable Reactive Barrier (PRB), which could be located in the primary subsurface channel that carries perchlorate to the Las Vegas Wash has been identified as a promising in situ alternative. The proposed PRB will biologically degrade perchlorate using injected emulsified edible oil as the electron donor substrate. In October 2010, the Nevada Division of Environmental Protection (NDEP) approved a work plan to complete two series of laboratory tests prior to installing and operating a pilot-scale PRB to test its effectiveness at reducing perchlorate concentrations in groundwater between the Athens Road Well Field and the Seep Area Well Field.

Two series of bench-scale experiments have been completed using site-specific soils, groundwater, and EOS[®] 598B42 emulsified oil. These tests were conducted to obtain critical design parameters and to investigate if metals adsorbed onto saturated soils would be mobilized by the reducing conditions brought about by the PRB. The results of batch sorption tests show that the effective retention of EOS[®] 598B42 emulsified oil onto site-specific soils is sufficient to meet or exceed the pilot test objectives. Treatability tests demonstrate that perchlorate completely degrades within 14 days without mobilizing significant amounts of arsenic or other metals in groundwater. Based upon these results, we recommend proceeding with the proposed PRB pilot test at the Site.

2.0 INTRODUCTION

Northgate Environmental Management, Inc. (Northgate) has prepared this technical memorandum on behalf of ENVIRON International Corporation (ENVIRON) for the Nevada Environmental Response Trust Site (Site) located in Henderson, Nevada. This document describes the results of bench-scale tests performed to support the design and operation of a pilot-scale in situ permeable reactive barrier (PRB) to reduce concentrations of perchlorate in groundwater between the Athens Road Well Field and the Seep Area Well Field downgradient of the Site (Figures 1 and 2). In situ PRBs using emulsified edible oil as electron donor substrates have been shown to be effective in remediating perchlorate-impacted groundwater (ESTCP, 2006-2010; ITRC, 2007; SERDP, 2006). The Site bench tests and planned PRB pilot test are described in *Work Plan to Conduct In-Situ Permeable Reactive Barrier Pilot Test for Perchlorate-Impacted Groundwater* (Northgate, 2010). These bench tests and planned PRB pilot test build upon a previous work plan developed by Shaw (Shaw, 2010).

The Site has been undergoing active remediation for groundwater contamination since 1986 (hexavalent chromium) and 1998 (perchlorate) under the oversight of the Nevada Division of Environmental Protection (NDEP). As part of the remediation program, Tronox (the former owner of the Site) installed a series of well fields, both on- and off-Site, for the capture and treatment of perchlorate-impacted groundwater associated with historical Site operations. While substantial perchlorate control and reduction has been achieved to date, elevated concentrations of perchlorate continue to be observed in groundwater monitoring wells located downgradient from the off-Site hydraulic containment wells at Athens Road. Groundwater from this area continues to flow north and discharges to the Las Vegas Wash, located approximately 6,000 feet further downgradient from Athens Road. Just before the Wash is a row of 10 extraction wells (Seep Area Well Field) that capture impacted groundwater which is then transported to an on-Site groundwater treatment system. A surface water collection system, known as the Seep Surface Collection System, is located nearer the Wash to capture intermittent surface flows downgradient of the Seep Area extraction wells, although no surface flows have occurred in past several years.

Currently, the groundwater extraction from the Seep Area Well Field represent up to about 60% of the total water volume treated in the on-Site groundwater treatment plant. The Trust is interested in evaluating alternatives for the enhanced treatment of perchlorate migrating in groundwater downgradient from the Athens Road Well Field to potentially reduce the need for extraction in the Seep Area Well Field and existing requirements for groundwater pumping and on-Site treatment, while continuing to minimize perchlorate discharge to the Las Vegas Wash.

The proposed in situ biological remediation of perchlorate involves a similar process as the above-ground fluidized bed reactor in the on-site groundwater treatment plant. Indigenous bacteria found in the subsurface can, under anoxic conditions, reduce perchlorate to chloride ions and water. To achieve these conditions, an appropriate electron donor must be provided to promote the growth of bacteria. Bacteria will initially consume dissolved oxygen as an electron acceptor, followed by various other constituents including nitrate, and chlorate. Eventually the oxidation reduction potential will be lowered to the point at which perchlorate will be used as an electron acceptor and subsequently reduced to chloride.

Based upon a review of the lithology, hydrology, and perchlorate concentrations at the Site, $EOS^{\$}$ 598B42 emulsified oil substrate was chosen as the electron donor substrate for the proposed pilot-scale PRB. Approximately 1,650 gallons of emulsion would be mixed with 180,000 gallons of push water and injected, via wells, to generate the in situ PRB. Previous analysis indicated that an effective retention ratio of 0.001 g/g must be achieved to meet the pilot test objectives outlined in the PRB pilot test work plan approved by NDEP (Northgate, 2010). Bench-scale tests were performed to determine whether this effective retention ratio can be achieved on Site-specific saturated soils. If tests indicated that the effective retention would be evaluated.

Although perchlorate is readily biodegraded under the reducing conditions generated by an in situ PRB, such conditions can also mobilize metals that are adsorbed onto the surface of saturated soils. Arsenic is present in Site groundwater above the NDEP Basic Comparison Level (BCL) and was identified as a chemical of interest in the Groundwater Assessment Report (Northgate, 2011). Arsenic is a naturally occurring element in rocks, soils, and the waters in contact with them. Arsenic in groundwater typically exists as As(V) (arsenate) or As(III) (arsenite) under oxidizing and reducing conditions, respectively. As(V) is an anionic species and tends to adsorb onto the positively-charged ferric oxyhydroxides that commonly coat the surface of most sediments. As(III) is a neutral species and tends to be mobile in groundwater (U.S. EPA, 2004). If conditions in the subsurface become reducing due to biological or chemical activity, the ferric oxyhydroxide present on the soil surfaces that bind arsenic can be reduced to ferrous iron and dissolve. This dissolution would result in a release of adsorbed arsenic, most likely as the more mobile As(III) neutral species.

Treatability and metals mobilization testing was conducted to simulate PRB conditions at the bench-scale and investigate the potential for perchlorate reduction, as well as for arsenic or other metals to mobilize from Site soils due to the reducing conditions that would occur in the PRB.

Microcosms to simulate these conditions were created by adding EOS[®] 598B42 emulsified oil substrate to site-specific saturated soils and groundwater and then sealed. These microcosms were destructively sampled over time and chemically analyzed for perchlorate reduction, dissolved metals, and general water quality parameters.

3.0 **OBJECTIVES**

Specific objectives of the bench-scale experiments reported herein include:

- Determine the effective retention of EOS[®] 598B42 and lecithin-modified EOS[®] 598B42 emulsified oil onto site-specific soils using laboratory batch testing.
- Chemically analyze the site-specific soils and groundwater to determine concentrations of metals and competing electron acceptors.
- Perform leachability tests on the site-specific soils using deionized (DI) water to determine a baseline for adsorbed metals stability.
- Establish the change in oxidation-reduction potential by adding EOS[®] 598B42 electrondonor substrate to site-specific soils and groundwater in the presence of indigenous bacteria, perchlorate, and competing electron acceptors.
- Determine the rate of perchlorate reduction in the test reactors.
- Determine the effect of oxidation-reduction potential on metals stability and
 - If dissolved metals concentrations increase, assess whether attenuation occurs as treated groundwater moves downgradient.
 - If dissolved metals concentrations decrease due to the formation of sulfides, assess the stability of these sulfides as conditions return to the aerobic pre-treatment condition.

4.0 BENCH-SCALE TESTING PROCEDURES AND RESULTS

The bench-scale testing consisted of three stages: 1) collection and analysis of site-specific soil and groundwater samples; 2) laboratory bench-scale batch testing to determine the effective retention of EOS[®] 598B42 on site-specific soils; and 3) microcosm treatability tests using site-specific soils, groundwater and EOS[®] 598B42 to determine perchlorate treatability and metals mobilization brought about by biologically-induced changes to the oxidation-reduction potential. Each of these is described below.

4.1 Soil and Groundwater Sample Collection

The oil retention and microcosm bench-scale tests required saturated soil and groundwater from the proposed PRB pilot-test location (Figure 3). On December 12, 2010, a borehole was drilled at proposed injection well location I-2 to a depth of 40 feet using an 8" hollow stem auger (HSA). Soil was logged from cuttings by an experienced field geologist (Appendix A). The water table was encountered at a depth of 27 feet below ground surface (bgs). Approximately 15 gallons of soil were collected from the saturated zone. The soils were blended and homogenized in the field. The saturated soils were then placed in three 5-gallon buckets and shipped overnight to PRIMA Environmental for chemical analysis and microcosm testing, to North Carolina State University (NCSU) for oil retention testing, and to Shaw Environmental (Shaw) for particle size analysis. Approximately 10 gallons of groundwater were collected from the open borehole and shipped via overnight delivery to PRIMA Environmental for chemical analysis and microcosm testing.

4.1.1 Soil Sample Characterization

4.1.1.1 Soil Particle Size Analysis

The soil sample was analyzed using ASTM D422, Standard Test Method for Particle Size Analysis of Soils. The soil was classified as clayey sand (SC) based on plasticity in accordance with the Unified Soil Classification System, with clay (9.0%), silt (19.4%), as well as some fine gravel (10.5%). The sand fraction included fine (18.4%), medium (26.2%), and coarse (16.5%) grained fractions.

4.1.1.2 Soil Chemical Analysis

The homogenized untreated saturated soils from the proposed PRB Site were analyzed for total and speciated metals by laboratories certified by the State of Nevada and/or accredited by the National Environmental Laboratory Accreditation Conference (NELAC).

The results of the chemical analyses of untreated soil for metals are presented in Table 1 with complete analytical reports provided in Appendix B. The soil contains 15,000 mg/kg iron, 5.4 mg/kg arsenic, 33 mg/kg chromium (total), 12 mg/kg nickel, 15 mg/kg copper, 31 mg/kg zinc, and 6.9 mg/kg lead. Other metals included in the analytical program were not detected above laboratory reporting limits.

Synthetic Precipitation Leaching Procedure (SPLP) testing using deionized water (DI) as a leaching solution was conducted on untreated saturated soils to determine a baseline for the stability of adsorbed metals prior to microcosm testing. Chemical analytic results of the SPLP leachate are also presented in Table 1 below, and the analytical reports are included in Appendix B. Most of the metals tested for were not detected in the leachate from the SPLP test above the reporting limit. The exceptions were iron and copper, which were present at 9.5 mg/L and 0.27 mg/L, respectively.

Table 1: Comparison of Untreated Soil and SPLP Results										
Test	Analytical Method	Units	Untreated Soil	SPLP (DI Water)						
Metals										
Antimony	EPA Method 6020	mg/kg or mg/L	< 1.0	< 0.1						
Arsenic (tot)	EPA Method 6020	mg/kg or mg/L	5.4	< 0.1						
Beryllium	EPA Method 6020	mg/kg or mg/L	< 1.0	< 0.1						
Cadmium	EPA Method 6020	mg/kg or mg/L	< 1.0	< 0.1						
Chromium (tot)	EPA Method 6020	mg/kg or mg/L	33	< 0.1						
Chromium (VI)	EPA Method 7199	mg/kg or mg/L	< 40	< 0.4						
Copper	EPA Method 6020	mg/kg or mg/L	15	0.27						
Iron (tot)	EPA Method 6020	mg/kg or mg/L	15,000	9.5						
Lead	EPA Method 6020	mg/kg or mg/L	6.9	< 0.1						
Mercury	EPA Method 6020	mg/kg or mg/L	< 0.2	< 0.1						
Nickel	EPA Method 6020	mg/kg or mg/L	12	< 0.1						
Selenium	EPA Method 6020	mg/kg or mg/L	< 1.0	< 0.1						
Silver	EPA Method 6020	mg/kg or mg/L	< 1.0	< 0.1						
Thallium	EPA Method 6020	mg/kg or mg/L	< 1.0	< 0.1						
Zinc	EPA Method 6020	mg/kg or mg/L	31	< 2.0						

4.1.2 Groundwater Sample Characterization

Untreated groundwater from the proposed PRB Site was analyzed for total and speciated metals, perchlorate, and other water quality parameters by laboratories certified by the State of Nevada and/or accredited by NELAC. Results of chemical analysis of the untreated groundwater are presented in Table 2 below, and the analytical reports are included in Appendix B.

Among other analytes, groundwater contained chlorate (28 mg/L), perchlorate (25.7 mg/L), chloride (2,200 mg/L), and sulfate (1,400 mg/L). Total and recoverable arsenic were identified at 0.034 mg/L and 0.0378 mg/L, respectively, and a separate analysis of arsenic speciation identified As(V) at 0.0319 mg/L and As(III) below the laboratory reporting limit. The pH of the water was 7.42 and oxidation reduction potential (ORP) was 146 mV.

Table 2: Chemical Analysis of Untreated Groundwater										
Test	Analytical	Units	Untreated							
	Method	•	GW							
Dissolved Metals										
Antimony	EPA Method 6020	mg/kg or mg/L	< 0.005							
Arsenic (tot)	EPA Method 6020	mg/kg or mg/L	0.034							
Arsenic (recoverable)	ICP-DRC-MS	mg/kg or mg/L	0.0378							
Arsenic (III)	IC-ICP-DRC-MS	mg/kg or mg/L	< 0.000074							
Arsenic (V)	IC-ICP-DRC-MS	mg/kg or mg/L	0.0319							
Beryllium	EPA Method 6020	mg/kg or mg/L	< 0.004							
Cadmium	EPA Method 6020	mg/kg or mg/L	< 0.005							
Chromium (total)	EPA Method 6020	mg/kg or mg/L	< 0.005							
Chromium (VI)	EPA Method 7199	mg/kg or mg/L	< 0.001							
Copper	EPA Method 6020	mg/kg or mg/L	< 0.01							
Iron (tot)	EPA Method 6020	mg/kg or mg/L	1.6							
Iron (II)	Hach Method 8146	mg/kg or mg/L	0.11							
Lead	EPA Method 6020	mg/kg or mg/L	< 0.005							
Mercury	EPA Method 6020	mg/kg or mg/L	< 0.001							
Nickel	EPA Method 6020	mg/kg or mg/L	0.014							
Selenium	EPA Method 6020	mg/kg or mg/L	0.01							
Silver	EPA Method 6020	mg/kg or mg/L	< 0.005							
Thallium	EPA Method 6020	mg/kg or mg/L	< 0.002							
Zinc	EPA Method 6020	mg/kg or mg/L	< 0.10							
Anionic Species and O	ther Parameters									
Chloride	EPA Method 7199	mg/kg or mg/L	2200							
Chlorate	EPA Method 300	mg/kg or mg/L	28							
Perchlorate	EPA Method 314	mg/kg or mg/L	25.7							
Nitrate	EPA Method 300	mg/kg or mg/L	8.1							
Sulfate	Hach Method 8051	mg/kg or mg/L	1400							
Sulfide	Hach Method 8131	mg/kg or mg/L	< 0.1							
DO	Probe	mg/kg or mg/L	8.5							
DOC	EPA 9060	mg/kg or mg/L	4.4							
ORP	Probe	mV	146							
рН	Probe	units	7.42							

4.2 Laboratory Bench-scale Tests

4.2.1 Oil Retention Testing

4.2.1.1 Materials and Methods

Oil loading tests were performed by the Environmental Engineering Laboratory in the Department of Civil, Construction, and Environmental Engineering Department at NCSU. Prior to testing, the homogenized aquifer material was passed through a #4 sieve to remove gravel from the sample. Approximately 89.5% of the soil was retained. Initial plans called for using column testing to determine oil sorption, but the relatively high percentage and plasticity of fine particles in the soil sample led to clogging, so batch tests were designed following collaborative discussions between NCSU, Shaw, and Northgate. The batch tests are considered to be a comparable substitute for the column tests.

Batch sorption tests were conducted by placing 40 g of moist soil into a series of 50 mL Falcon centrifuge tubes and adding sufficient tap water to cover the soil surface. These tubes were then amended with 0, 0.1, 0.4, or 1.0 mL of EOS[®] 598B42 or lecithin emulsion and then filled to the 50 mL mark with tap water. All tests were run in duplicate. The tubes were sealed and mixed to distribute the emulsion and the soil was allowed to settle overnight. The aqueous phase was decanted off and the amount of oil remaining in the aqueous phase was determined. The tubes were then refilled with water and mixed to remove any remaining liquid-phase emulsion from soil pore space. This step was repeated two additional times and the liquid was set aside to measure volatile content. Liquid and soil volatile concentrations were determined by drying at 105 degrees C followed by ashing at 550 degrees C. Oil retention was calculated as the difference between the volatile suspended solids (VSS) of the treated soil sample and VSS of the untreated control sample.

4.2.1.2 Results and Discussion

The sorption tests indicate a maximum effective oil retention ratio of 0.02 g/g for EOS[®] 598B42 and 0.06 g/g for lecithin-modified EOS[®] 598B42 (details of the sorption tests can be found in Appendix C). Overall, almost all of the oil was retained on the soil. These values exceed the minimum effective retention of 0.001 g/g required to achieve the pilot test objectives presented in the in situ PRB work plan (Northgate, 2010). These high levels of retention are likely due to the large percentage of fines (silt and clay) in the tested sample. As discussed in Section 5, these soil conditions are not expected across the entire proposed PRB.

4.2.2 Treatability and Metals Mobilization Testing

Batch tests were undertaken to gain knowledge of the behavior of arsenic and other metals in Site-specific saturated soil and groundwater exposed to an emulsified oil-based organic electrondonor substrate in the presence of perchlorate and competing electron acceptors. The perchlorate treatability and metals mobilization testing was conducted by Prima Environmental, Inc., under the direction of Dr. Cindy Schrier.

4.2.2.1 Materials and Methods

Thirteen (13) reactors containing site-specific saturated soils (700 g) and groundwater (1,850 mL) were prepared. The headspace in each reactor was approximately 200 mL to allow for gases generated by biodegradation. One of the reactors was sampled within 2 hours of set-up and served as the Time 0 reactor. The remaining reactors were divided into three sets of four: Controls, Low Dose (2 mL EOS[®]/L groundwater) and High Dose (4 mL EOS[®] 598B42/L groundwater) (Table 3). Reactors were stored at room temperature in the dark. Because the primary goal of the study was to assess metal mobility under different redox conditions, three additional reactors (one control, one low dose, and one high dose) were also prepared (using lesser amounts of soils and groundwater) and treated with the redox indicator Resazurin, which is blue under oxidizing conditions and colorless when the ORP drops below about -150 mV.

Table 3: Summary of EOS Microcosm Tests											
Test	GW	Soil	EOS Dose	Resazurin	Total Vol	Sample Time					
TESL	mL	g	mL/L	Resazurin	mL						
Time 0	1740	700	0	no	1750	0					
Control A	1740	700	0	no	1750	2 days					
Control B	1740	700	0	no	1750	6 days					
Control C	1740	700	0	no	1750	14 days 41 days -					
Control D	1740	700	0	no	1750						
Control R	249	100	0	yes	250						
EOS-Low A	1740	1740700217407002		no	1750	2 days					
EOS-Low B	1740			no	1750	6 days					
EOS-Low C	1740			no	1750	14 days					
EOS-Low D	1740			no	1750	41 days					
EOS-Low R	w R 249 100 2		2	yes	250	-					
EOS-High A	1740	700	4	no	1750	2 days					
EOS-High B	1740	700	4	no	1750	6 days					
EOS-High C	1740	700	4	no	1750	14 days					
EOS-High D	ligh D 1740 700 4		4	no	1750	41 days					
EOS-High R 249 10		100	4	yes	250	-					

Periodically, at 2, 6, 14 and 41 days, one reactor from each test condition was destructively sampled and the aqueous phases analyzed for:

- Total dissolved metals
 - As (tot), Be, Cd, Cr, Cu, Fe, Pb, Hg, Ni, Se, Ag, Tl, and Zn
- Metals speciation
 - As (III), As (V), Cr (VI), and Fe (II)
- Anionic species
 - Chloride (Cl⁻), chlorate (ClO₃⁻), perchlorate (ClO₄⁻), nitrate (NO₃⁻), sulfate (SO₄⁻ 2), and sulfide (S⁻²)
- Water chemistry parameters
 - Dissolved oxygen (DO), dissolved organic carbon (DOC), oxidation redox potential (ORP), and pH

Note that sampling times were based in part on the color of the second, similar set of reactors that contained the Resazurin redox indicator. These indicator reactors were sealed for the duration of the study and were not sampled. Sample times for the first set of reactors were 48 hours after set-up, once the redox indicator lightened in the EOS[®] 598B42-amended reactors (6 days), after the redox indicator turned colorless in the EOS[®] 598B42-amended reactors (14 days), and after 41 days. The testing was concluded at T+41 days after analysis of the T+14 day results showed removal of nitrate, chlorate, and perchlorate below detectable levels and reducing conditions. Due to the constant influx of electron acceptors such as dissolved oxygen, nitrate, chlorate, and perchlorate, the reducing conditions of the T+41 microcosms are not expected to be representative of those in an operating PRB at the Site. The tests are summarized in Table 4.

4.2.2.2 Results and Discussion

The concentrations of perchlorate, chlorate and other parameters after treatment with EOS[®] 598B42 are shown in Table 4. Complete analytical reports are provided in Appendix B. Treatment with either a low or high dose of EOS[®] 598B42 rapidly degraded both chlorate and perchlorate, although degradation was faster with the higher dose. No change in either parameter was observed by Day 2 in the low dose test, but perchlorate had decreased from 25,100 μ g/L at Time 0 to 5,560 μ g/L by Day 6 in the low dose test and was completely removed by Day 14. Similarly, chlorate decreased from 26,000 μ g/L in the Time 0 sample to 1,100 μ g/L in the Day 6 low dose test and was below 100 μ g/L by Day 14. For the high dose test, perchlorate was

unchanged by Day 2, but below the reporting limit of $3.0 \ \mu g/L$ by Day 6, while chlorate was below the reporting limit of $10 \ \mu g/L$ by Day 2. There were no significant changes in the control.

The decrease in perchlorate and chlorate is presumably due to biodegradation since DO, nitrate and (to some extent) ORP also decreased during the first 14 days of the test. By Day 2 for both EOS® tests, DO decreased from 8.3 mg/L to below 1 mg/L and nitrate (as nitrogen) decreased from 11 mg/L to between 1.8 and 2.0 mg/L. ORP was steady through Day 6, ranging from 74 mV to 128 mV, but then declined to between -208 and -189 mV by Day 14 and to between -348 and -337 mV by Day 41. The pH decreased by up to about 0.5 pH units in both EOS® tests relative to the control suggesting that some volatile fatty acids were generated due to microbial activity. Sulfate concentrations did not seem to change much relative to the controls; however, the sulfate concentrations were variable. Sulfide was not detected in any of the samples until Day 41, at which time relatively high concentrations (6,750 mg/L to 12,600 mg/L) were detected in the EOS[®] 598B42-amended tests. The presence of sulfide is consistent with the highly negative ORP values measured at Day 41.

The concentrations of metals after exposure to EOS[®] 598B42 are shown in Table 4. Treatment of site-specific soils and groundwater with EOS[®] 598B42 did not significantly mobilize arsenic, except possibly in the Day 41 tests. The Day 41 high-dose EOS[®] 598B42-amended test contained 0.072 mg/L total arsenic compared to 0.024 mg/L in the control. Analysis of the speciation data suggests that thio-arsenite complexes are being formed under these strongly reducing conditions. Nickel concentrations in the Day 6 and Day 14 tests were slightly elevated compared to the control tests, but decreased by Day 41, likely due to the formation of insoluble nickel sulfides. Copper concentrations increased slightly (up to 0.019 mg/L) in both EOS® tests by Day 2, but concentrations were less than 0.01 mg/L in the remainder of the test. Selenium concentrations were steady through day 14, but decreased from about 0.022 mg/L at Time 0 to less than 0.005 mg/L by Day 41. As discussed in Section 5, it is unlikely that highly negative ORP or sulfide generation will occur in the pilot study due to the continual inflow of groundwater with electron acceptors (dissolved oxygen, nitrate, chlorate, and perchlorate) that are energetically preferable to sulfate.

Table 4: Summary of Microcosm Perchlorate Treatability and Metals Mobilization Test Results															
- .	Analytical	Units	Control				EOS - Low				EOS - High				
Test	Method		Time 0	Day 2	Day 6	Day 14	Day 41	Day 2	Day 6	Day 14	Day 41	Day 2	Day 6	Day 14	Day 41
Dissolved Metals															
Antimony	EPA Method 6020	mg/L	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Arsenic (tot)	EPA Method 6020	mg/L	0.037	0.032	0.03	0.03	0.024	0.039	0.032	0.029	0.028	0.036	0.033	0.028	0.072
Arsenic (recoverable)	ICP-DRC-MS	mg/L	0.0336	0.0274	0.0247	0.0275	0.0256	0.033	0.026	0.0258	0.0507	0.032	0.028	0.026	0.0655
Arsenic (III)	IC-ICP-DRC-MS	mg/L	< 0.000074	< 0.000074	0.00015	< 0.000044	< 0.00011	0.00369	0.024	0.0205	0.0218	< 0.000074	0.0257	0.0166	0.00102
Arsenic (V)	IC-ICP-DRC-MS	mg/L	0.0287	0.0242	0.0234	0.0227	0.0185	0.025	0.00103	< 0.0016	0.00114	0.00262	0.00108	0.00052	0.00143
Beryllium	EPA Method 6020	mg/L	< 0.004	< 0.004	< 0.004	< 0.004	< 0.004	< 0.004	< 0.004	< 0.004	< 0.004	< 0.004	< 0.004	< 0.004	< 0.004
Cadmium	EPA Method 6020	mg/L	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Chromium (tot)	EPA Method 6020	mg/L	< 0.005	< 0.005	< 0.005	0.0064	0.0051	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Chromium (VI)	EPA Method 7199	mg/L	< 0.01	0.001	< 0.001	0.001	0.0059	0	< 0.001	0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Copper	EPA Method 6020	mg/L	< 0.01	< 0.01	< 0.01	0.011	< 0.01	0.017	0.018	< 0.01	< 0.01	0.019	< 0.01	< 0.01	< 0.01
Iron (tot)	EPA Method 6020	mg/L	2.0	2.0	2.3	2.2	1.9	2.2	2.3	2.3	2.0	2.3	2.2	2.5	2.1
Iron (II)	Hach Method 8146	mg/L	0.01	< 0.01	0.03	0.03	< 0.02	0.01	0.05	0.14	< 0.02	0.01	0.05	0.3	0.04
Lead	EPA Method 6020	mg/L	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Mercury	EPA Method 6020	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Nickel	EPA Method 6020	mg/L	0.011	0.011	0.012	0.012	0.012	0.016	0.017	0.018	< 0.01	0.019	0.018	0.023	0.011
Selenium	EPA Method 6020	mg/L	0.022	0.022	0.023	0.025	0.023	0.025	0.022	0.015	<0.005	0.025	0.024	0.021	<0.005
Silver	EPA Method 6020	mg/L	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Thallium	EPA Method 6020	mg/L	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
Zinc	EPA Method 6020	mg/L	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10
Anionic Species and W	/ater Quality Param	eters													
Chloride	EPA Method 7199	mg/L	2.2	2.2	2.6	2.7	3	2.2	3.1	2.2	2	2.2	3	2.3	2
Chlorate	EPA Method 7199	mg/L	26	26	26	27	30	26	1.1	< 0.05	< 0.05	< 0.01	< 0.10	< 0.05	< 0.05
Perchlorate	EPA Method 314	mg/L	25.1	23.1	22	24.8	22.6	22.3	5.56	< 0.003	< 0.003	23.7	< 0.003	< 0.003	< 0.003
Nitrate	EPA Method 7199	mg/L	11	10	10	10	10	1.8	< 0.25	< 0.25	< 0.25	2	< 0.25	< 0.25	< 0.25
Sulfate	Hach Method 8051	mg/L	1450	1350	1500	1300	1800	1300	1700	1300	1550	1450	1600	1350	1150
Sulfide	Hach Method 8131	mg/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	6.75	< 0.01	< 0.01	< 0.01	12.6
DO	Probe	mg/L	8.3	8	7.9	7.8	7.8	1	1	0.8	1.7	0.8	0.7	0.5	1.9
DOC	EPA 9060	mg/L	3.8	3.4	3.7	2.8	3.7	27	14	12	24	160	110	48	170
ORP	Probe	mV	54	70	143	138	140	74	128	-189	-348	94	116	-208	-337
рН	Probe	units	7.52	7.46	7.37	7.43	7.41	7.26	6.93	7.03	7.2	7.02	6.7	6.91	6.82

5.0 SUMMARY, CONCLUSIONS, AND NEXT STEPS

Laboratory bench testing demonstrated that the addition of emulsified oil (EOS[®] 598B42) to sitespecific soils and groundwater can stimulate indigenous bacteria to anaerobically biodegrade perchlorate without significant mobilization of arsenic. Addition of 2 to 4 mL EOS[®] 598B42 per liter of groundwater led to the removal of perchlorate to below the laboratory reporting limit within 14 days with no significant mobilization of arsenic or other metals. The ORP continued to decrease after all perchlorate was removed, reaching -337 to -348 mV by Day 41, but still no significant metals mobilization occurred. Dissolved arsenic concentrations in the EOS[®] 598B42treated reactors were similar to concentrations in the controls except for the Day 41 high dose EOS® test which had about 3 times as much arsenic (0.072 mg/L) as in the control (0.024 mg/L). Arsenic speciation analysis indicates that the dissolved arsenic in the control reactors was present as arsenate (As(V)). The reducing conditions in the EOS[®] 598B42-amended reactors led to formation of arsenite (As(III)). The strongly reducing conditions in the Day 41 tests appear to have led to the formation of thio-arsenite complexes. We do not expect that ORPs in the Day 41 tests will be achieved in the field due to a constant flux of dissolved oxygen, nitrate, chlorate, and perchlorate entering the PRB.

Bench testing also indicates that EOS[®] 598B42 emulsified oil retention on the tested Site soils is more than adequate to meet the pilot test design criteria without the addition of lecithin. The percentage of fines (silt and clay) present in the tested soil (28%) was higher than anticipated and may not be representative of the entire pilot study PRB area. However, oil retention in the bench test exceeded the minimum required by more than an order of magnitude, so retention should be sufficient even with much lower fine percentages.

Based on the results of the bench testing, Northgate recommends going forward with the field pilot test as specified in the work plan (Northgate, 2010). As described in the work plan, soil samples will be collected every five feet from each borehole during installation of the pilot test injection and monitoring wells, and the field geologist will describe and classify the soil according to the Unified Soil Classification System. If soil with less than 5% fines predominates in the injection interval for any of the three injection locations, lecithin will be added to the EOS[®] substrate injected at that location.

As specified in the work plan, slug tests will be performed on several wells (all three injection wells and two monitoring wells selected based on lithology) to determine local hydraulic conductivity (K). A 2-to-4-hour step-rate injection test will also be conducted on one or more of the injection wells. If similar lithologies are observed in all three injection wells, an injection test will only be performed on I-2; however, if lithology varies among locations, tests will be



conducted in the well with the highest estimated K and the well with the lowest estimated K. The well water level and injection pressure will be monitored during the step-rate injection test(s). The results of the slug and injection tests will be analyzed to determine appropriate injection rates for the EOS[®] solution to achieve the desired minimum radius of influence of 30 feet. As described above, the homogenized soil from the boring at the proposed I-2 location contained a higher percentage of fines than expected, so the hydraulic conductivity may be lower than originally expected. If this proves to be the case across the width of the proposed PRB, one or more additional injection points may be installed to provide assurance that sufficient electron donor will be available, achieving PRB pilot test design goals.

With NDEP approval, the Trust will initiate the in situ PRB pilot study as planned. Based on the schedule presented in the work plan (Northgate, 2010), establishing the well network, collecting baseline data, and EOS[®] emulsion injection is estimated to take approximately 8 weeks. Six months of performance monitoring and preparation of the pilot test report will follow. Based on this schedule, it is anticipated that the pilot test report would be submitted to NDEP approximately 40 weeks after pilot test initiation.



6.0 **REFERENCES**

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FIGURES

APPENDICES Provided on CD