

NDEP Comment	Response to Comment
Specific Comments	
<p>1. Specific Comment #1 Section 1.1, Page 6. The report states that one of the objectives of the study is to provide understanding of the technology in several field applications as shown on Figure 1.1. Please comment on how the results of the study would inform a decision about the approaches shown on Figure 1.1. The simulations in the study appear to be more applicable to setup "C" in Figure 1.1 than to the other applications.</p>	<p>The results from this study's simulations, including the derived kinetic parameters, are applicable to all three scenarios even though they may appear to be closest to setup C. The laboratory derived perchlorate reduction rates are used to inform the likely outcomes from a field study; the field study would be used to confirm the laboratory results, provide information necessary for evaluating feasibility of a full-scale application, and provide information necessary for full-scale design. In all three scenarios, perchlorate reduction would be expected with half-lives on the order of a few days. A final design of the technology would be based on biogeochemical, hydrogeological, infrastructure, and cost considerations.</p> <p>Note that responses to comments in relation to field testing, as presented above and in the remainder of this document, have been prepared commensurate with the Trust's decision to suspend further evaluation of bioelectrochemical technology at this time; however, the Trust may elect to pursue field testing of bioelectrochemical technology at a later date, pending the results of the Trust's ongoing evaluation of other remediation technologies.</p>

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<p>2. Specific Comment #2 Section 2.1, First Paragraph. Literature research performed in support of this study showed that heterotrophic bacteria reduced perchlorate twice as fast as autotrophic bacteria. In this study, there is some use of heterotrophic bacteria when carbon sources such as acetate are used; however, the study focuses primarily on autotrophic bacteria. What is the rationale for focusing on stimulation of this class of bacteria?</p>	<p>Demonstrating the use of hydrogen as an electron donor specifically for perchlorate reduction (and other co-contaminant electron acceptors) was an essential microbiological component of this study to demonstrate proof-of-concept for bioelectrochemical treatment. The focus on autohydrogenotrophs stemmed from the need to establish that electrochemical treatment could stimulate this type of the metabolism. The final activity of autotrophic versus heterotrophic bacteria during remediation would need to be established in-situ. Moreover, there are potential advantages to using hydrogen to stimulate autotrophic perchlorate reduction: 1) autotrophs tend not to create as much biomass as heterotrophs, potentially reducing risk of clogging, and 2) autotrophs are not as metabolically diverse as heterotrophs, so using hydrogen as an electron donor could minimize the unintended reduction of competing electron acceptors.</p>
<p>3. Specific Comment #3 Section 2.2. The equations in this section as well as Figure 2 show oxygen being generated from the hydrolysis of water as well as hydrogen. Was this oxygen added along with the hydrogen to the tests in this study and was any effect from the oxygen observed?</p>	<p>The electrochemical reactor was equipped with a proton exchange membrane to prevent oxygen from being introduced into the cathodic chamber that generates the hydrogen. The efficacy of the membrane was tested by analyzing the gas composition coming from the cathodic chamber; oxygen was not detected. In addition, all electrochemically-treated water holding tanks were kept under a hydrogen headspace to minimize the amount of atmospheric oxygen that may have been inadvertently introduced. Therefore, the presence of oxygen should not have affected the bioelectrochemical treatment tests.</p>

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<p>4. Specific Comment #4 Section 2.2, Top of Page 10. This section states that a benefit of in situ hydrogen generation is enhanced efficiency due to avoiding the growth of non-target bacteria competing for electron donor. Do the microbial analyses performed in support of this study show this?</p>	<p>Yes, the microbial analyses performed qualitatively support this idea. The qPCR assays discussed in Section 3.7 are not able to distinguish autohydrogeneotrophic versus heterotrophic bacterial populations; however, the microbial community composition results presented in Section 3.7 discuss the microbial taxa identified and the plausibility of autohydrogenotrophs in the taxa reported. The results indicate that the microbial community became more enriched (i.e., a lesser number of "generalist" microbes that likely consume electron donor without reducing perchlorate) along the flow path when exposed to electrochemically-treated water saturated with dissolved hydrogen.</p>
<p>5. Specific Comment #5 Section 3.2.1. Please provide the rationale for using a synthetic groundwater rather than using site groundwater for these tests. Would the presence of inorganic carbon that may have been reduced to acetate by the electrode have made a difference to the study? Were potential interactions with other chemical contaminants in site groundwater considered?</p>	<p>Synthetic groundwater was used primarily because laboratory-scale testing would have consumed thousands of liters of site groundwater, which was not practically feasible to transport. In addition, a synthetic formulation inherently lessens the experimental variability, thus laboratory-scale experiments are more controlled. The presence of inorganic carbon in the site groundwater may have been cathodically-reduced to acetate and other organic molecules, but without additional field testing, the exact quantities remain to be determined. Potential interactions with other chemical contaminants in the site groundwater were considered, but only analyses of bulk carbon and anions were performed. The potential effects of these other contaminants are not known but could be elucidated during a field test.</p>
<p>6. Specific Comment #6 Section 3.3.2. What was the recipe used for the synthetic water used for the electrochemical batch testing? Is the synthetic water used here same as it in the Table 3 (Synthetic groundwater recipe for initial column testing)?</p>	<p>Yes, the recipe for electrochemical batch testing was the same as in Table 3; however, as specified in Section 3.3.2, the amount of bicarbonate varied between 500-1000 mg/L.</p>

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<p>7. Specific Comment #7. The high TDS water is common at the NERT project area and it is a challenge for the service life of electrodes. What are the solution for this challenge if the field application is conducted?</p>	<p>The most common (and practical) approach to keep electrodes clean is to periodically switch the polarity, which leads to acidic conditions at the original cathode, dissolving inorganic scale such as carbonates.</p>
<p>8. Specific Comment #8 Section 3.3.3.2. Please speculate on the nature of the gelatinous precipitate and on whether it would be likely to form if this treatment was performed in situ and what would be the effect on the groundwater if it did form.</p>	<p>The gelatinous precipitate visually resembled hydroxide flocs. While no chemical or physical analyses were performed on these flocs, it was noted that the flocs only formed in the cathodic chamber, where the pH increased. In a controlled reactor, these flocs could be periodically removed during maintenance. We do not have information specific to how these flocs would behave in an in-situ application; the flocs could accumulate, be transported downgradient, and/or may redissolve depending on the specific aqueous geochemistry. The floc formation in the laboratory experiment demonstrates the importance of evaluating location-specific geochemistry for any in-situ application; it may be that floc formation can be mitigated under defined conditions identified at certain areas of the site.</p>
<p>9. Specific Comment #9 Section 3.3.3.2, Page 20. Please discuss the differences observed between the results of the electrochemical batch tests between the site groundwater and the synthetic groundwater and comment on what this might mean for an in situ application.</p>	<p>Generally, the results observed between the site and synthetic groundwater were similar in nature. The hydrogen saturation appeared to be slightly higher in the site groundwater compared to the synthetic groundwater, but this observation does not lead to a conclusion that this condition is repeatable. The most important finding is that hydrogen saturation can be reliably achieved in the site groundwater under varying conditions. The site groundwater appeared to have a greater buffering capacity (i.e., ability to withstand drastic changes in pH) compared to the synthetic groundwater. This increased buffering capacity in site groundwater would be advantageous for an in-situ application.</p>

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<p>10. Specific Comment #10 Section 3.4.3, Figure 13. Perchlorate and chlorate show a sharp decrease from greater than baseline levels to non-detect levels between days 37 and 57. Additional data points between these days would have been interesting to see.</p>	<p>Noted.</p>
<p>11. Specific Comment #11 Section 3.4.3, Figure 13. Concentrations of chlorate, perchlorate, nitrate, and nitrite are very high on day 10. Was there any issue with the analytical run on that day?</p>	<p>This question is assumed to be in reference to the third panel in Figure 13 (the hydrogen only microcosms). The increase in concentrations for all measured anions appeared to be systematic, so it is likely there was an underlying issue with the instrument for those analyses. The results were reported as measured.</p>
<p>12. Specific Comment #12 Section 3.5.2. Please discuss the expected effect of electrochemical treatment on groundwater pH if applied in situ.</p>	<p>As observed in the electrochemical batch tests, the pH of the treated water on the cathodic side of the membrane inevitably increases because protons are consumed in the generation of hydrogen (the pH on the anodic side of the membrane decreases due to the production of protons). The pH of groundwater is anticipated to behave similarly, however, given the observations in the columns and sand tank, the soil would likely offer some buffering capacity, thus keeping the overall environmental pH from significantly changing. This process is the same as for other reductants, such as zero-valent iron (ZVI), where Ramboll's experience with this reductant demonstrates that while pH of groundwater may increase near the downgradient interface of a ZVI system, the pH returns to ambient within a short distance (feet) due to the natural geochemical conditions of the aquifer.</p>

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<p>13. Specific Comments #13 Section 3.5.3. Please explain some inconsistency between the results from the Batch Microcosm Testing and the Column Testing.</p>	<p>The batch microcosms and flow-through columns were experimentally distinct, one being a batch mode, the other being a flow-through mode. Given these differences, it is not surprising that differences in results were observed. First, the residence time in the microcosms was significantly longer compared to the columns, thus greater time was permitted for microbial biomass to “adapt” to the geochemical conditions. In addition, excess electron donors were supplied to the microcosms from the start, therefore, the metabolic activity in the microcosms was likely to be higher compared to the columns from the start of the experiment.</p>
<p>14. Specific Comment #14, Figure 27. To what extent was the hydrogen consumed by the column vs being lost to the atmosphere?</p>	<p>Measures were taken to keep the electrochemical reactors and columns airtight (e.g., silicone or rubber gaskets were used for sealing the reactors, tubing was zip-tied to any fittings to prevent leaks, PTFE tape was used on all column fittings, and any sampling ports were fitted with valves to keep ports closed to the atmosphere). The amount of hydrogen lost to the atmosphere is expected to be negligible compared to the amount of hydrogen consumed in the columns.</p>
<p>15. Specific Comment #15, Figure 31. Why did the influent pH in the Electrochemical Treatment column jump around so much?</p>	<p>The pH variability can be attributed to daily electrochemical treatment, which increases the pH as an effect of the electrochemical treatment, and experimental operation variability in terms of electrochemical treatment times.</p>
<p>16. Specific Comment #16, Figure 38. The hydrogen in the water pumped into the sand tank was largely consumed within the first 6 inches of the tank. Does this imply that if water is infused with hydrogen gas and then pumped into the groundwater that the hydrogen will be gone very quickly?</p>	<p>The sand tank results, while informative, cannot be directly scaled to a field-scale setting, though a similar pattern would likely be observed in a field-scale application. Several factors are known to influence hydrogen transport and consumption in the subsurface; field-scale testing would need to be designed to specifically monitor and evaluate hydrogen transport and consumption as a key performance metric.</p>

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<p>17. Specific Comment #17, Section 3.6.3. This soil-sand mixture was inoculated with de-watered sludge obtained from functioning FBRs at the NERT site prior to being placed into the sand tank and the ORP ranged from -240 mV to -277 mV during the recirculation mode. This condition is enough for the perchlorate reduction without introducing hydrogen. How do you quantify the perchlorate reduction from the biodegradation only and the electrochemical degradation?</p>	<p>Perchlorate is highly stable towards direct electrochemical reduction and is thus used as common electrolyte in electrochemical applications. It is therefore reasonable to assume that all perchlorate was biologically reduced.</p>
<p>18. Specific Comment #18, Section 3.6.3. The perchlorate, chlorate and nitrate reduction mostly occurred in the first 24 inch from the influent side of the sand tank. It is unlikely that the layout for the field implementation is different from the sand tank laboratory setup. How to count for this potential difference if the field pilot test is planned?</p>	<p>If perchlorate, chlorate and competing electron acceptors are consumed through this remedial technology faster than can be determined in the field, even while using high-resolution sampling, this would simply be a success. However, the extent of treatment could be temporarily lowered to detect and quantify the electron acceptors and ultimately to derive kinetics. Based on the derived kinetics, the treatment process could then be optimized at the field-scale so as to avoid wasting energy input.</p>
<p>19. Specific Comment #19, Section 3.6.3. "The microbial community appeared to become less diverse and more enriched with respect to certain microbial families with distance along the flow path". It would be nice to see that this observation is confirmed in the field application.</p>	<p>Noted. Based on the results of the microbial community analyses, this comment illustrates the need to incorporate microbial community characterization and monitoring in any in-situ biological remedy implemented at the site.</p>
<p>20. Minor Correction Specific Comment #20 Section 3.6.3, Paragraph below Figure 41. The statement "In light of the excellent perchlorate reduction achieved at the 7-day residence time with perchlorate as the primary electron donor" should be revised to read "In light of the excellent perchlorate reduction achieved at the 7-day residence time with perchlorate as the primary electron acceptor"</p>	<p>Noted.</p>