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Appendix E. Case Studies

E-1. In Situ Biological and Chemical Reduction of Hexavalent Chromium and Perchlorate

Location
Black Mountain Industrial Complex, Henderson, Nevada

Reference Material
Groundwater Bioremediation Treatability Study Results Report

Contaminants
Hexavalent chromium and perchlorate

Regulatory Phase
Remediation investigation and feasibility study (RI/FS); bench and pilot study

Amendment(s)
Emulsified vegetable oil (EVO), industrial sugar wastewater, a mixture of EVO and industrial sugar wastewater, and molasses and calcium polysulfide

Remedial Technology
In situ bioremediation and chemical reduction with source control

Site Description and Approach

Site Description:
Alluvial and lacustrine sediments

Approach:
The main objective of the study was to evaluate the feasibility of remediating perchlorate in groundwater via bioremediation using injection wells. The site has been through pump and treat since 2001. The perchlorate mass removal efficiency in the downgradient plume area is very low because of much less concentration of perchlorate and much higher groundwater production rate compared to the source area. The in situ bioremediation treatability study provided information supporting the final remedy selection. This treatability study is one of several planned treatability studies. The test site was chosen because of its relatively low perchlorate concentration and fast groundwater flow velocity. The study followed detailed site characterization, bench-scale study, and field implementation. All required permits, such as a property access permit and a UIC permit, were obtained for the study. Monthly progress reports and milestone presentations of the results were implemented to monitor project progress and to make necessary modifications.

Optimization/Lessons Learned
A CSM based on detailed or high-resolution site characterization is strongly suggested. The clay has required more attention because of its critical role in hydraulic properties and binding properties with injected substrates. Groundwater flow velocity is one of the most important parameters and must be determined before the injection. Besides targeted contaminants, other chemicals subjected to biodegradation were well defined and their behaviors and equivalent electron donors determined during the bench-scale study. The substrate injection will be done multiple times. Parameters such as dissolved oxygen, ORP, targeted contaminant concentrations, total organic compounds, and porosity are frequently monitored. The effectiveness is quantified against the baseline conditions defined during the site characterization.

Summary of Results
The test site is predominantly gravel and sand, with minor fractions of silt and clay. Groundwater flow velocity averaged 32 feet per day (geometric mean value determined from hydrogeological testing). Bench-scale studies (both batch microcosm and column tests) were performed and indicated that EVO has the ability to create and sustain reducing conditions in groundwater and that native microorganisms can use the EVO to biodegrade perchlorate quite effectively. Nitrate biodegradation (denitrification) generally preceded perchlorate biodegradation; however, in the presence of the carbon substrate and once microbial acclimation occurred, both of these were simultaneously biodegraded. Column studies, which simulated field groundwater flow conditions, demonstrated that perchlorate biodegradation also occurred effectively at high

velocity flow rates. Because of the presence of nitrate in groundwater, nitrogen supplementation as a micronutrient was not deemed necessary. However, the augmentation of phosphorus as a micronutrient was shown to reduce acclimation time for the onset of perchlorate biodegradation.

Three injection wells were installed in a single transect configuration in the field test area. In addition to the injection wells, a network consisting of nine monitoring wells was installed at locations both upgradient and downgradient of the injection well transect to determine the effectiveness of the groundwater bioremediation treatability study. Following completion of well installation, two carbon substrate injection events were performed approximately 3 months apart. Weekly, biweekly, and monthly groundwater monitoring was performed throughout the study following injections. Results from the field treatability study indicated that groundwater is quite amenable to bioremediation of perchlorate and other electron acceptors and co-contaminants such as chlorate and nitrate via the addition of EVO. The injection of EVO created an anaerobic biologically active zone of enhancement within the TTZ that resulted in perchlorate biodegradation.

Also, as observed in the laboratory studies, denitrification occurred very rapidly and was comparable to perchlorate biodegradation. Perchlorate biodegradation followed denitrification and, once initiated, the two reductive processes were observed to occur concurrently at locations that recorded the most significant geochemical response to carbon substrate injections. Several of the monitoring wells attained perchlorate reductions greater than 90% during the study. The zone of influence of perchlorate biodegradation extended up to 250 feet downgradient of the injection transect. First-order perchlorate biodegradation rate constants were estimated to be between -0.25 day^{-1} and -0.51 day^{-1} under optimal conditions. Due to these high biodegradation rates, perchlorate concentrations decreased very rapidly in several wells following microbial acclimation. Mass removal estimates were calculated using the lower, midrange, and higher estimates of hydraulic conductivity, gradient, and total porosity. This resulted in an estimated perchlorate mass removal during the study that likely ranged from 4.1 to 17.4 pounds per day. These rates equate to a total perchlorate mass removal during the 6-month time frame of 689–2,923 pounds.

E-2. Strontium-90 Apatite Permeable Reactive Barrier

Location
Hanford, Richland, WA

Reference Material
Calendar Year 2016 Annual Summary Report for 100-NR-2 Groundwater Remediation

Contaminant
Sr-90

Regulatory Phase
Full-scale, pilot-scale, and monitoring

Amendment(s)
Calcium chloride, trisodium citrate, sodium phosphate, calcium-citrate-phosphate

Remedial Technology
Permeable reactive barrier

Site Description and Approach

Site Description:
Fluvial—lacustrine and glaciofluvial sediments

Approach:
Jet injection of phosphate solution during pilot hole drilling phase in fluvial-lacustrine and glaciofluvial sediments; injection of preformed apatite with the phosphate solution as a carrier fluid; precipitation of additional apatite from the phosphate solution, potentially using the preformed apatite as a seed crystal to initiate precipitation; adsorption of Sr-90 by the apatite surface (new Sr-90 migrating into the treated zone from upgradient sources resulting from fluctuations in river stage); apatite recrystallization with Sr-90 substitution for calcium (permanent); radioactive decay of sequestered Sr-90 to Y-90 to Zr-90 in apatite.

Optimization/Lessons Learned
Decreasing 100 mM phosphate formula to 40 mM to reduce initial Sr-90 mobilization, increase injection volume proportionally to achieve at least 3.4 mg apatite per gram of sediment; phased deep and shallow zone injections from upriver wells to downriver wells; river stage affects injection emplacement.

Summary of Results
Sr-90 concentrations have been reduced by 71–98%.

E-3. Rapid Site Closure of a Large Gas Plant Using In Situ Bioremediation Technology in Low Permeability Soil and Fractured Rock

Location

Hanford, Richland, Washington

Reference Material

Site Closure of a Large Gas Plant Using In situ Bioremediation Technology in Low Permeability Soil and Fractured Rock

Contaminants

LNAPL and aqueous BTEX

Regulatory Phase

State remedial action plan

Amendment(s)

BOS 200

Remedial Technology

In situ granular activated carbon with cultured microbes, electron acceptors, and nutrients

Site Description and Approach

Site Description:

Subtle facies changes in overlying, low permeability soil and thin-bedded planes with complex fractures in highly weathered bedrock resulted in solute concentration that varies by orders of magnitude in distances of only several millimeters.

Approach:

The site was subdivided into six regions, based on constituent concentrations. Treatment was implemented in three phases over a 15-month period. Approximately 4,800 injections were completed at 1,230 locations throughout the 30-acre plume. The remedy consisted of 185,875 pounds of carbon slurry, 5,650 pounds of supplemental sulfate (gypsum), and 352 gallons of microbes.

Optimization/Lessons Learned

None Available

Summary of Results

The initial remedial action plan prepared by the previous contractor and submitted to the state was to install a soil vapor extraction and groundwater recovery and treatment system. Instead, an in situ carbon-based injection program was set up to expedite remediation for pending property sale. The remedy included granular activated carbon injected with cultured microbes (facultative microorganisms), electron acceptors (nitrate and sulfate), and nutrients (phosphorus and nitrogen) designed to biodegrade BTEX compounds. A high-resolution quantitative data assessment was used to characterize plume strength and geometry. The revised CSM was used to apply continuous soil and groundwater data to develop a discrete remedial design and inject carbon-based slurry into the complex low permeability subsurface in six regions of the 30-acre site based on constituent concentrations. The treatment took place in three phases over 15 months with complete confirmatory and performance borings to observe remedy distribution and evaluate effectiveness of remedy, adjusting subsequent injections while using analysis of groundwater samples and calculating mass reduction. This iterative sequence was completed until the cleanup goals were achieved.

E-4. Performance of Injected Powdered and Liquid Activated Carbon at a Petroleum Hydrocarbon Site

Location

Unknown

Reference Material

Activated Carbon-Based Technology for In Situ Remediation

Contaminants

LNAPL & DNAPL; BTEX

Regulatory Phase

Comparison study

Amendment(s)

Powdered and liquid activated carbon activated with sulfate or other oxygen-releasing compounds

Remedial Technology
Subsurface injection

Site Description and Approach

Silty sand aquifer

Optimization/Lessons Learned
Geochemical and microbial monitoring of the groundwater over 24 months indicated clear difference in behavior of the groundwater chemistry over short and long term.

Summary of Results
None Available

E-5. Lawrence Livermore National Laboratory—Annual Groundwater Report

Location
Multiple

Reference Material
Lawrence Livermore National Laboratory, Groundwater Project 2014 Annual Report

Lawrence Livermore National Laboratory Compliance 2018 Annual Monitoring Report Site 300

Contaminants
Aqueous VOCs

Regulatory Phase
Treatability test

Amendment(s)
Zero-valent iron

Remedial Technology
ISCR with source control

Site Description and Approach

Site Description:
Multiple hydrostratigraphic units were evaluated for each LLNL site. The sites include low permeability silt- and clay-rich sediments, depending on the site.

Approach:
In 2007, DOE/LLNL developed the Source Area Cleanup Technology Evaluation Team approach to identify targeted remediation strategies for plume sources using technologies via treatability studies based on:

- systematic characterization and cataloging of representative macroscopic features of each source area (for example, dimensions of the source area footprint, representative hydraulic conductivity, mean ambient hydraulic gradient) as permitted by the available data
- development of a compartmental screening model based on those data that capture the salient VOC mass and concentration-controlling parameters characteristic of the source areas
- utilizing the compartmental model to simulate the potential response of source area VOC distribution to various source area remediation approaches that correspond to changes in key model parameters (for example, mechanical fracturing to increase average hydraulic conductivity)

Optimization and Lessons Learned
A point to be learned is that LLNL is using source area cleanup technology evaluation to determine use of ZVI in the hotspot source area but similarly has been using in situ bioremediation at Heliport source area as well as thermal and fracturing methods in efforts to remediate complex subsurface source areas and groundwater zones. LLNL subsurface is composed of many subsurface zones, which LLNL evaluated as hydrostratigraphic units, adding to complexity of subsurface groundwater and contaminant transport. In the case of the ZVI site, use of a solar-powered purging system in multiple wells to reduce the time frame necessary to obtain ZVI-impacted groundwater samples by inducing a steeper groundwater gradient between the ZVI panels and performance monitor wells to attempt to increase the in situ remediation was implemented as a result of continuously optimizing performance when possible.

Summary of Results
Contractor installed the ZVI emplacement system over an area approximately 45 feet long and 45 feet wide, between

approximately 55 and 75 ft bls. Wellhead pressure and electrical resistance tomography were monitored to track installation of the panels. Construction of the ZVI emplacement system commenced on September 15, 2014, and was completed on September 30, 2014. The ZVI multi-azimuth grid installed in the TFC hotspot source area included the following materials and processes:

- nine emplacement boreholes with two 5-foot expansion casings (that is, upper and lower) installed to a depth of approximately 75 ft bgs using the mud-rotary drilling technique
- seven resistivity strings with five receivers each, for a total of 35 receivers installed to a depth of approximately 75 ft bgs using a direct push drilling rig
- injection of 21 tons of granular ZVI, about 33% in the upper zone and 67% in the lower zone, and application of a total of approximately 5,820 gallons of inclusion fluid during the emplacement process

Video-logging and redevelopment of area wells following ZVI emplacement indicate that there were no adverse impacts to existing wells as a result of the implementation process. Postimplementation sampling for VOC analysis, dechlorination daughter products, metals, and general minerals began in November 2014 and continued in 2018. Groundwater field parameter measurements, including dissolved oxygen, specific conductance, ORP, pH, and temperature, also continued in 2018.

E-6. Oxidant Surface Eruption During Direct Push Injection

Location
Anonymous

Reference Material
Internal distribution only

Regulatory Phase
None reported

Amendment(s)
Sodium permanganate

Remedial Technology
Subsurface injection

Site Description and Approach

Direct Push Injection

Optimization/Lessons Learned
Direct push equipment was used to inject sodium permanganate into a shallow groundwater system at a U.S. Air Force base in California. The site soils were compactable and had low to moderate hydraulic conductivity. Oxidant flow rates were near zero at low injection pressure and the contractor increased pressures until reagent delivery rates increased. As a result, eruptions of the oxidant occurred at the ground surface. Postinjection sampling showed that nearly all the reagent missed its intended target zone in the groundwater, accumulating instead in the overlying unsaturated zone.

Summary of Results
None available

E-7. TerraVac Under EPA's Demonstration Program Conducted SVE in the Source Area

Location
Groveland, Massachusetts

Reference Material
[Draft Final Source Area Re-evaluation Report Groveland Wells Nos. 1 & 2 Superfund Site 2006]

Contaminant
Aqueous and NAPL trichloroethylene (TCE)

Regulatory Phase
SVE was ineffective and ISCO was subsequently demonstrated. No source control, but further investigation led them to treat the source.

Amendment(s)

Potassium permanganate

Remedial Technology

Insitu chemical oxidation

Site Description and Approach

At the conclusion of the ex situ test, an in situ soil mixing and chemical oxidation test was performed. A treatment area of approximately 470 square feet was divided into a grid with eight cells. Soil was excavated to around 5 feet. Potassium permanganate was used to treat 90 cubic yards of shallow soil. The excavated soil was treated with potassium permanganate and mixed with water in the excavation using an excavator. Each grid did achieve some remediation, but not completely. In some cases, the post-treatment samples had higher concentrations of TCE than the pre-treatment samples (that were taken from the same area).

Optimization/Lessons Learned

Between 2004 and 2006, EPA performed a comprehensive source area investigation, underground storage tank (UST) removals, and chemical oxidation treatment pilot studies that were documented in the Source Area Re-evaluation Report. The report concluded that the initial SVE remedial action had been largely ineffective and that significant source area contamination remained (soils contaminated with TCE up to 52,000 ppb). Groundwater in the source area had TCE contamination as high as 160,000 ppb.

Summary of Results

Costs were compared for in situ chemical oxidation for both saturated and unsaturated soils and using ERH for both. The conclusion was that chemical oxidation would cost about $2 million more than ERH and would be conducted over 5 years, whereas ERH would take about 1 year. EPA chose ERH over chemical oxidation for the site based on the results of the Source Area Re-evaluation, including cost estimates for various remedial options. In 2007, EPA issued an Explanation of Significant Differences (ESD) for the source control remedy modifying it to include ISTT along with SVE to address soil and groundwater contamination remaining on the Valley Manufacturing property within the source area. [“Final Remedial Action Report, Groveland Wells Numbers 1 and 2 Superfund Site – Operable Unit 2.” Noblis Engineering, Inc., September 20, 2011, page 6, unavailable.]

E-8. Unusual Dichloroethylene Isomerizations and External Nitrate Input to Help Decipher in Situ Pilot Test Outcomes

Location

Urban Gulf Coast, Florida

Reference Material

Importance of Unusual Dichloroethylene Isomer and Sewer Leakage to an In situ Remediation: Studer, J., 2017. 17th International Contaminant Site Remediation Conference, September 10-14, Melbourne

Contaminant

VOCs

Regulatory Phase

This pilot study represents an interesting example where outcomes from a field pilot test of an in situ groundwater treatment technology strayed significantly from expectations.

Amendment(s)

None reported

Remedial Technology

Biogeochemical Reductive Dechlorination

Site Description and Approach

Site Description:

Shallow and deep weathered limestone bedrock zones at a depth of 40 meters.

Approach:

The pilot goal was to test biogeochemical reductive dechlorination (BiRD) to accelerate remediation. 7,425 liters of reagent solution was pressure-injected into each zone.

Optimization/Lessons Learned

In depth analysis identified rapidly rising nitrate concentrations and high trans-1,2 DCE to cis-1,2 DCE ratios as two quite unusual site features that led to the conclusions that

- injectate emplacement was highly preferential to the detriment of treatment at the central monitoring wells
- in situ biogenic ferrous sulfide production with complete dechlorination treatment did occur in the limestone but native partial dechlorination of TCE was also stimulated
- nitrate originating from a previously unknown overlying sewer leak was preventing the shallow zone near the central monitoring well from transitioning into deep reducing conditions necessary for sulfate reduction, a prerequisite to BiRD

Summary of Results
The pilot test involved a shallow injection zone and a deeper injection zone within a variably weathered limestone harboring a TCE and DCE groundwater plume. Natural biodegradation was slowly degrading the TCE to DCE but mineralization was not apparent. A bench treatability study demonstrated in situ biogenic ferrous sulfide production and TCE and DCE transformation without VC production. A reagent formulation identified from the bench study was the basis for 7,425 liters of reagent solution pressure-injected into each zone. The central monitoring well in the shallow zone did not respond to injection even after 9 months. The central monitoring well in the deep zone did not immediately respond but eventually injectate components were detected due primarily to diffusion and TCE and DCE concentrations declined without VC production. This was perplexing given that the central monitoring well screens were only 4.6 meters from multiple injection well screens. Further explanation of the site in the Clu-IN 2017 reference states that unsuspected sewer leakage introduced nitrogen to the alluvium, resulting in maximum detected NO_3 of 120 mg/L in shallow bedrock. Following discovery and repair of the sewer break, in depth analysis aided by bench study insights suggested that BiRD can be a good match for the bedrock if an improved reagent distribution process is implemented allowing transition into deep reducing conditions necessary for sulfate reduction, as BiRD requires.

E-9. In Situ Bioremediation and Soil Vapor Extraction at the Former Beaches Laundry & Cleaners

Location
Jacksonville Beach, Florida

Reference Material
In situ Bioremediation and Soil Vapor Extraction at the Former Beaches Laundry and Cleaners

Contaminants
PCE, TCE, cis-1,2 DCE, and VC

Regulatory Phase
Florida RCRA process

Amendment(s)
Potassium lactate and denatured alcohol

Remedial Technology
Excavation, co-solvent flushing, and enhanced bioremediation with source control

Site Description and Approach

Site Description:
The soil profile at the site consists of silty, fine to very fine-grained sand with shell fragments from surface to 40–50 feet bgs. Underlying the surficial sands is approximately 3 feet of clayey sand followed by 12–15 feet of clay overlying clayey sand. The maximum depth evaluated in the site investigation was 65 feet bgs. The shell fragments and carbonate sand grains found in the subsurface increased the buffering capacity of the soil. There are three groundwater zones at the site: shallow, intermediate, and deep.

Approach:
Three pilot injections of Fenton’s reagent (hydrogen peroxide and ferrous iron catalyst) were conducted from July 1999 to August 2000 and did not significantly reduce VOC concentrations in groundwater. Therefore, a revised remedial action plan consisting of a phased approach was implemented. The phased approach included excavation of contaminated soil followed by use of the SVE system to accelerate the removal of mass from the source area. A total of 244 tons of contaminated soil was excavated from the northeast corner of the Beaches building. Following soil excavation, the SVE system began operation on February 7, 2007 to address remaining soil contamination in the vadose zone of the site. Florida Department of Environmental Protection approved the soil excavation work plan, which recommended placing 11 horizontal SVE wells in the excavated area to allow subsequent treatment of soil containing less than 17 mg/kg of PCE to be left in place near

building bearing walls.

Groundwater treatment consisted of in situ enhanced bioremediation to expedite the bioremediation process of the plume through the addition of nutrient amendments (potassium lactate and denatured ethanol). Implementation of the final 2006 remedial action plan for the enhanced bioremediation injection system was initiated by constructing six new injection wells spaced approximately 12 feet apart along the northern and eastern edges of the northeast corner of the building; each well contained screened injection points at three different depths. The 2006 remedial action plan also specified the use of three existing monitoring wells as additional injection points and the use of the 11 SVE wells as surface-level injection points. A total of 21 vertical injection points were used, including seven well points between 10 and 20 feet bgs, seven at 20–30 feet bgs, and seven at 30–45 feet bgs. In addition the 11 SVE wells were used to inject into the first 3 feet of soil. Only five of the 11 SVE wells were used during the first and third injections, and the other six wells were used during the second and fourth events. All of the 11 SVE wells were used during the fifth and sixth events. During the enhanced bioremediation, January to June 2008, a total of 77,400 gallons of potassium lactate and ethanol solution was injected into the groundwater and flushed with 10,800 gallons of water over a 6-month period, at depths ranging from 2 to 45 feet. In 2009 the SVE system was shut off.

Optimization/Lessons Learned

Baseline and postinjection monitoring was conducted at the site for both the SVE and enhanced bioremediation system. The goals of the revised remedial action plan were to reduce PCE, TCE, cis-1, 2 DCE, and VC contaminant concentrations in the soil to below Florida State Cleanup Target Levels, and to reduce the groundwater contaminant concentrations to below the Florida Natural Attenuation Default Criteria (FNADCs). Once the FNADC were achieved, it is anticipated that natural attenuation will reduce the contaminant concentrations to below FSCTLs. Samples collected from the influent of the SVE system indicated that PCE and methane concentrations were below the detection limit; therefore, the SVE system was shut down and converted to a passive system in March 2009. Groundwater concentrations of PCE and TCE continued to exceed the FNADCs at several locations within the aquifer based on sampling in July 2008. Analytical results indicate that the phased remedial action at the site resulted in significant reductions in contaminant concentrations that were continuing to decrease.

Summary of Results

Soil excavation: The source removal goal of removing all materials with PCE concentrations above 17 mg/kg was accomplished in the southern and western portions of excavation.

Soilvapor extraction: The SVE vapor influent concentrations were successfully reduced to below the detection limits. The SVE system was shut down during the injection and the SVE lateral wells were used for injection wells.

Enhanced bioremediation: To decrease costs, the existing SVE, injection and monitoring wells were used to inject the amendment. Ball valves were installed on the SVE wells to prevent the amendment slurry from entering the SVE system piping inside the trailer. Based on the analytical results from the first four injections, the remedial action plan was modified to increase the amount of potassium lactate used in the injection. In addition, the injected volume was increased by an additional 300 gallons of water per well to distribute more carbon from the amendment in the intermediate and deep zones of the aquifer. Increasing the mass of electron donor in the bioremediation injection system increases the production of methane. The SVE system will provide the engineering control to address excessive methane generation. The potassium lactate and denatured ethanol amendments were effective in accelerating the biodegradation of PCE and PCE degradation products. The total VOC reduction ranged from 65 to 99% in the shallow zone wells. More targeted injections for the intermediate and deeper levels are needed to enhance the reductive dechlorination at the site. The addition of vertical injection wells upgradient of the site helped further enhance the capability to deliver electron donor to source areas with elevated VOC concentrations. Use of existing horizontal SVE wells for the bioremediation injections helped lower the cost to implement the series of injections.

E-10. LNAPL Remediation Combining Mobile Dual Phase Extraction with Concurrent Injection of a Carbon-Based Amendment: Little Mountain Test Facility

Location

Hill Air Force Base, Utah

Reference Material

Site WR111 Little Mountain Test Facility Final Status Report Draft Final 2018

Contaminant

Aqueous and NAPL benzene and trimethylbenzene compounds (1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene)

Regulatory Phase

Chemically oxidized granular activated carbon (COGAC) was selected for injection based on results of a bench-scale treatability test. This amendment uses ISCO, biostimulation, and carbon adsorption.

Amendment(s)

Chemically oxidized granular activated carbon (COGAC)

Remedial Technology

Mobile dual phase extraction (DPE) and ISCO with biostimulation. Combined aggressive petroleum mass removal (free product and dissolved phase) by mobile dual phase extraction with concurrent injection of carbon combined with chemical oxidants and oxygen-generating compounds to promote natural attenuation of residually entrapped mass.

Site Description and Approach

Site Description:

Silty fine to medium sand, silty clay, and clay. Groundwater is approximately 17 ft bgs. From lower to upper in the stratigraphic sequence: slate, greenstone, and tillite.

Approach:

Over this 1-acre site, 48 extraction points were installed with 118 surrounding injection points in a systematic grid fashion. The temporary injection points were advanced with a 2.25-inch DPT rod. The goal of this project was to transition from initial chemical oxidation to longer term aerobic bacterial growth combined with carbon adsorption. ISCO uses sodium persulfate catalyzed by calcium peroxide to produce persulfate radicals with the ability to oxidize contaminants for days or weeks. Biostimulation is promoted by residual nutrients from the ISCO activity and the degradation of calcium peroxide into hydrogen peroxide, which provides the groundwater with elevated dissolved oxygen to enhance aerobic biological activity. The activated carbon itself provides both adsorption sites for organic contaminants to minimize desorption rebound as well as a substrate for the growth of contaminant-degrading bacteria. A 12% COGAC solution was prepared in a large mixing truck and pumped directly into each injection point. COGAC was injected using a bottom-up procedure. Concurrently, groundwater and LNAPL were extracted through 1-inch schedule 40 PVC pipe. A vacuum trailer was used to remove groundwater and LNAPL, and the extracted water was stored in a frac tank for later disposal. The mobile DPE was conducted concurrently with injection, just beyond the typical ROI. Over 15 pounds of amendment (for each pound of contaminant mass) was injected and evenly distributed throughout the treatment area. The placement of injection and extraction points was designed and field-adjusted to achieve hydraulic capture and control.

Optimization/Lessons Learned

Amendment distribution was vastly improved by combining mobile DPE vacuum (at extraction points) with amendment injection (at nearby injection points), thereby increasing sweep efficiency of amendment delivery through promotion of enhanced pressure gradients. Visual observations, collection of cores at injection points, and daily monitoring of the location, movement, and thickness of LNAPL were completed. . Results presented will elaborate on these findings as well as other performance metrics.

Summary of Results

Concurrent implementation of mobile DPE and injection of COGAC resulted in effective distribution of the amendment throughout the smear zone area and near-complete elimination of measurable free phase LNAPL. Initial post-treatment study data indicate decreasing trends in dissolved phase benzene and benzene compounds.

E-11. Eastern Surplus Company Superfund Site, Southern Plume: Meddybemps

Location

Washington County, Maine

Reference Material

[Examples of Groundwater Remediation NPL Sites, USEPA 542-R-18-002]

Contaminants

Chlorinated VOCs including PCE and TCE, metals including manganese and lead, and PCBs; highest concentrations in groundwater included 6,700 ppb PCE (northern plume) and 1,100 ppb PCE (southern plume). NAPL suspected in northern plume.

Regulatory Phase

Post-ROD, 5-year review, ESD. Bench-scale and pilot study worked in southern plume but northern plume concentrations increased. As part of ESD, bench- and pilot-scale tests changing from in situ chemical oxidation to enhanced in situ bioremediation.

Amendment(s)

Enhanced in situ bioremediation

Remedial Technology
Soil excavation and waste removal, pump and treat, ISCO with sodium permanganate injections, with most recent in situ bioremediation.

Site Description and Approach

Site Description:
Overburden consisting of stratified beds of gravel, sand, and mixed sands and silt, and shallow bedrock. There are two distinct plumes, northern representative of conditions post-EISB is in bedrock, while the southern plume migrated underneath the southern area of the site in overburden and shallow bedrock.

Approach:
The Record of Decision includes pump-and-treat systems for northern and southern plumes with ISCO, which worked primarily in the southern plume but not efficiently in the northern plume. In 2010, EPA with the concurrence of MEDEP shut down the southern extraction system and in 2011 under MEDEP the southern system was decommissioned.

With PCE and TCE concentrations remaining elevated in the northern plume, EPA and MEDEP agreed to conduct a bench-scale test to assess the applicability of bioremediation as a viable alternative to ISCO. Based on applications at other sites, EISB offered extended residence time for the injection material and improved degradation of the residual VOCs present in the bedrock fractures and rock matrix. In 2011, site groundwater and rock matrix material from a newly installed well were used to run a 49-day bench-scale test. The bench test results suggested that complete dechlorination from PCE to ethene could be achieved using site groundwater, an electron donor (for example, vegetable oil), a proprietary culture of *Dehalococcoides* (Dhc), organic soluble substrate (lactate), and mineral amendments.

After implementation of the bench-scale then pilot-scale investigation of EISB, EPA issued the ESD to change the in situ oxidation treatment to an in situ bioremediation treatment, leading both agencies to agree to a pilot-scale implementation. The operation of the northern extraction system was suspended, and four wells were used to inject EISB mixture. The pilot test consisted of two application events within the approximately 50-foot-diameter target area. During each application, groundwater from four pilot test area wells was extracted, stored in aboveground tanks, mixed with mineral amendments and Dhc bacteria, and then reinjected. Finalization of the ESD has led to the implementation of a source control full-scale bioremediation effort. The design for the full-scale effort was completed in September 2018 and mobilization for the full-scale implementation was expected to occur in November 2018.

Optimization/Lessons Learned
The southern contaminated groundwater plume was successfully treated using a conventional pump-and-treat system supplemented by the injection of sodium permanganate (ISCO) to accelerate degradation of contaminants. As a result of this approach, combined with source removal during the Non-Time-Critical Removal Action, the approximately 1.5-acre southern plume was cleaned up to drinking water standards, and extraction wells located within the southern plume were shut down in late 2010. Remediation continues, however, within the northern plume, where concentrations are still above MCLs due to the more complex geology and higher (DNAPL range) initial concentrations in groundwater.

Summary of Results
PCE concentrations in 1.5-acre southern plume reduced from 1,100 ppb to below cleanup level. Chlorinated VOC concentrations in northern plume are still above cleanup levels. Current site use includes a major archaeological research site for the history of the Passamaquoddy people.

E-12. Hollingsworth Solderless

Location
Fort Lauderdale, Florida

Reference Material
[Examples of Groundwater Remediation NPL Sites, USEPA 542-R-18-002]

Contaminants
Chlorinated VOCs including TCE, cis1, 2-DCE, and vinyl chloride in groundwater; TCE in soil; highest concentrations in groundwater included 4,300 ppb TCE, 10,000 ppb cis-1, 2-DCE, and 6,000 ppb vinyl chloride.

Regulatory Phase
Post-ROD and ESD, using ROD amendment for in situ ERD. Pilot study followed by additional injections result in ROD amendment.

Amendment(s)

Potassium lactate and DHE bacteria

Remedial Technology

Soil excavation and off-site disposal, groundwater pump and treat with air stripping, SVE, in situ ERD with potassium lactate and bacteria injections

Site Description and Approach

Site Description:

Site overlies Biscayne aquifer, which is highly permeable, unconfined, and composed of a fine- to medium-grained sand, sandstone, and limestone sequence.

Approach:

The cleanup approach in the ROD included excavation, ex situ aeration, and replacement of soil in the area of excavation. The ROD also specified extraction, treatment with air stripping technology, and reinjection of groundwater into the aquifer. Due to water levels reaching historically highs in the late 1980s, the soil excavation and replacement were changed to in situ SVE operated from January 1991 to July 1991, when the soil cleanup level of TCE concentrations less than 1 ppm was achieved. The groundwater treatment system ran from 1992 to 1994, when the system was removed because it was ineffective. However, groundwater rebound resulted in a 2001 ESD for additional soil removal in two distinct areas (south and west drain field areas). Groundwater monitoring showed decreased VOCs in the shallow groundwater but no similar decline in deeper groundwater. A pilot study was initiated for south and west drain fields from 2005 to 2007 using potassium lactate injections and bioaugmentation. The study demonstrated success in reducing VOC concentrations. A 2008 ROD amendment was completed for a site remedy of in situ ERD with potassium lactate injections.

Optimization/Lessons Learned

The initial groundwater remedy removed up to 55 pounds of contaminants each day. Over 300 tons of contaminated soils were removed. Chlorinated VOC concentrations in groundwater were reduced up to 98% in just over 2 years using ERD. Vinyl chloride is the only remaining groundwater contaminant detected above cleanup levels.

Summary of Results

The combination of excavation/removal and pump and treat was also used frequently at the sites that achieved significant progress toward groundwater restoration presented in the USEPA report Examples of Groundwater Remediation at NPL Sites, May 2018. At the Hollingsworth Solderless site, it was determined that a pump-and-treat system was no longer effective at decreasing concentrations of TCE, cis-1, 2-DCE, and vinyl chloride after 2 years of operation. After a successful pilot test of in situ bioremediation, an ROD amendment was issued in 2008 modifying the site remedy from pump and treat to in situ bioremediation (that is, enhanced reductive dechlorination).

E-13. Former Industrial Site Characterization and Remediation in Fractured Rock

Location

Greenville, South Carolina

Reference Material

Characterization and Remediation in Fractured Rocks

Contaminants

TCE; cis-1, 2-dichloroethene; vinyl chloride

Regulatory Phase

Pilot test and full scale

Amendment(s)

ZVI and potassium permanganate

Remedial Technology

Permanganate solid slurry injection for ISCO in source area. ZVI solid slurry injection for ISCR in plume area.

Site Description and Approach

Site Description:

The site is underlain by saprolite that grades into competent bedrock. The saprolite is heavily oxidized, relatively low permeability silt, sand, and clay, with varying degrees of relict bedrock structures and quartz veining. The transition from saprolite to competent rock is a partially weathered rock zone that is visually similar to the saprolite but marked by greater density and more abundant rock fragments. The upper bedrock exhibits varying degrees of fracturing and weathered zones in a matrix of mica schist and gneiss, feldspar gneiss, and granite. The depth to rock ranges from approximately 90 feet bgs in the source area to as shallow as 6 feet in the plume area.

Approach:

Since investigations began in 1996, site characterization has been conducted in multiple phases and has used traditional monitoring wells and a range of additional tools.

Field pilot tests of ZVI in the plume area and permanganate in the source area were conducted in 2011. Borings were advanced immediately after the injection to assess physical reagent distribution, and groundwater was monitored for 2 years following the pilot. Based upon the pilot test results, a full-scale design was implemented in 2013. A total of 83 tons of potassium permanganate blended with sand was injected via 87 discrete vertical intervals in 14 injection wells over the course of the pilot- and full-scale ISCO remedial action. A total of 725 tons of ZVI was injected via 368 discrete vertical intervals in 62 injection wells in three barriers across the plume, over the course of the pilot- and full-scale ZVI remedial action. The full-scale remedial actions were conducted from July 2013 to July 2014. An additional 5,208 gallons of 5.3% sodium permanganate solution was injected by gravity feed at two well locations in September 2015 to address a small portion of the site that was not effectively treated during the full-scale injection.

Direct push and hand-auger soil sampling was conducted where possible to delineate shallow soil. Traditional hollow-stem auger drilling was used in the saprolite. Air, mud rotary, and core drilling were used in the bedrock. FLUTe liner was used for DNAPL screening. Discrete-interval sampling tools, passive diffusion bags, and HydraSleeve samplers were used primarily to provide vertical delineation in the source area. Passive diffusion bags were also used for an in-stream assessment. Summa canisters and Dräger tubes were deployed for indoor air and soil vapor characterization. Screening-level grab groundwater samples were collected during sonic drilling of wells for reagent injection using the Isoflow discrete-interval sampling system developed by Boart Longyear. The overall remedial evaluation, implementation, modification, and performance assessment for the remedial actions since 2011 (the permanganate ISCO and ZVI remedial actions) were developed based upon guidance in the Integrated DNAPL Site Strategy document (2011c). Remedial evaluation began with an assessment of remedial objectives. The absolute objective was to restore the overburden and bedrock aquifer to drinking water standards.

Optimization/Lessons Learned

Pilot test results were used to optimize the full-scale remedial design. Procedures were developed to assess field observations and results daily to continuously refine the site conceptual model and to optimize the design to match site conditions during construction. Ongoing remedy performance and progress toward (or achievement of) the functional and absolute objectives are evaluated with an extensive groundwater monitoring program. Additional injections have been conducted based upon the results to address small areas exhibiting rebound and requiring further treatment. The large plume area, limited plume access, concentrated source area, and dual-zone (saprolite/bedrock) aquifer system pose special challenges. Remedial designs and objectives are often based on differentiation between overburden and bedrock with little consideration of the transition zone between these regions. A valuable lesson learned at this site was the importance of the partially weathered rock transition zone between saprolite and bedrock. This zone exhibits significant vertical and lateral variability and has a hydraulic conductivity that averages about one order of magnitude higher than the saprolite. The variability required ongoing assessment and remedial design modification during construction.

Summary of Results

Results to date have generally met expectations based upon the REMChlor and PREMChlor modeling predictions with respect to source and plume concentration reductions. A few locations in the source area have required additional injection to address rebound, and plume-area monitoring wells located distally from the ZVI barriers have not yet exhibited reductions because sufficient time (relative to transport velocity) has not passed. Permanganate breakthrough from the source area to one boring location in the closest ZVI barrier has been observed in the latest sampling events. The baseline represents the condition prior to the 2011 pilot test. Overall groundwater TCE concentrations (through January 2016) have been reduced by >99.9% in 12 of 15 monitoring wells, and by 99.4%, 99.0%, and 73.8% in the remaining three wells. The poorest performance (73.8% reduction) is in a well located within the former tank excavation and reflects rebound following >99.9% removal immediately after the remedial action. Additional sodium permanganate injection is planned for this location. The core of the plume (10,000 mg/L to a maximum of 96,000 mg/L TCE) has contracted significantly, with remaining TCE concentrations <2,230 mg/L. Results for MW-33, the plume monitoring well exhibiting the highest baseline TCE concentration, have been reduced by 99.2% from a maximum of 110,000 mg/L one week after the field pilot test in May 2011 to 905 mg/L in the latest sampling event (January 2016) (Figure11-3). The concentration of cis-1, 2-dichloroethene (formed as an intermediate degradation product from TCE) exhibited initial increases from the baseline (<2,000 mg/L) to a maximum of 43,000 mg/L, and has subsequently degraded to 1,650 mg/L.

E-14. Naval Submarine Base Kings Bay, Site 11

Location

Camden County, Georgia

Reference Material

Naval Submarine Base Kings Bay Site 11

Contaminants

Aqueous PCE, TCE, DCE, and vinyl chloride

Regulatory Phase

Georgia Environmental Protection Division RCRA corrective action

Amendment(s)

Fenton's reagent

Remedial Technology

Pump and treat (P&T), ISCO (Fenton's reagent), biostimulation, monitored natural attenuation (MNA). No source control included.

Site Description and Approach

Site Description:

Marginal marine sediments of barrier island and back-barrier lagoon origin. Permeable sand underlying the site exists between 32 and 42 ft bgs and is underlain and overlain by finer grained sand and clay of back-barrier lagoon origin, characterized by lower hydraulic conductivity. A layer of organic-rich sand overlies the aquifer.

Approach:

In November 1998, two extraction wells and six process monitoring wells were installed along with 23 specially designed injection wells that were placed in and around the source area. The monitoring wells were sampled twice each day and analyzed for pH, specific conductance, alkalinity, iron, sulfate, sulfide, dissolved hydrogen, and dissolved oxygen, as well as any change in contaminant concentrations. The modified Fenton's reagent containing 50% hydrogen peroxide was injected in two phases. Phase 1 of the ISCO treatment focused on the central part of the contaminant plume, while phase 2 focused on the downgradient areas that were not treated during phase 1.

The modified Fenton's reagent containing 50% hydrogen peroxide was injected in two phases. Phase 1 of the ISCO treatment focused on the central part of the contaminant plume, while phase 2 focused on the downgradient areas that were not treated during phase 1. Following phase 2, during which 21 new injectors were added, elevated contaminant concentrations (1,700 µg/L) were detected outside the plume near one of the injectors used during phase 1, indicating the presence of a previously unidentified contamination source area. Thus, two more phases were added to the treatment process. The last treatment phase was administered in November 2001.

Optimization/Lessons Learned

Because adding Fenton's reagent to an aquifer can change both the geochemistry and the microbial population, monitoring was performed. Measurements in one monitoring well showed an increase in dissolved oxygen from nondetect before injection to > 7 mg/L after injection. Also, microbial activity decreased after each injection. Dissolved hydrogen concentrations indicated that the injection of the ferrous iron activator had shifted the microbial activity from sulfate- and iron-reducing to a more purely iron-reducing environment. To reverse this trend, a solution of emulsified vegetable oil (35% soybean oil with lecithin and 65% water) was injected into the aquifer after phases 3 and 4 to return the subsurface environment to an anaerobic state and potentially restore some of the sulfate-reducing activity that increases PCE and TCE degradation. Microbial activity generally rebounded within a few months of each Fenton's reagent injection.

Summary of Results

In all, about 48,000 gallons of 50% hydrogen peroxide solution and a similar volume of ferrous sulfate catalyst were injected into the aquifer—principally in the more permeable zone between 32 and 42 ft bgs. In addition, about 25,000 gallons of the emulsified vegetable oil solution were injected following Fenton's reagent application phases 3 and 4. The plume size shrank by about 70%. Levels of total chlorinated hydrocarbons in the most contaminated area decreased from nearly 200,000 µg/L in 1999 to 120 µg/L in 2002. Currently, chlorinated hydrocarbon levels range from <1 to 13.9 µg/L. As of May 2003, no additional exceedances of MCLs occurred in any of the off-site monitoring wells, and many of the on-site monitoring wells had no measurable levels of contaminants. As a result, the P&T system was shut off 2 months after the phase 2 ISCO treatments, and MNA has been implemented as the final corrective action for the landfill. There was no need for further treatment with UV oxidation. Shutting down the P&T system slowed the transport rate of contaminants downgradient, which increased the effectiveness of the biodegradation process.

Since 1999, two long-term monitoring programs have been conducted at Site 11, including monitoring as required by the RCRA permit and performed in accordance with the associated Groundwater Monitoring Plan (GWMP) (Bechtel 1999), and monitoring conducted by the United States Geological Survey (USGS) in coordination with the Navy to evaluate the effectiveness of natural attenuation processes in reducing contaminant concentrations (USGS 2009). The RCRA permit required that monitoring begin in 1999, and the monitoring program was adjusted several times based on the exit strategy provided in the GWMP and other recommendations from the Georgia Environmental Protection Division. The USGS monitoring was conducted from 1999 to 2009 at a number of designated wells. The study confirmed the effectiveness of natural attenuation processes at Site 11 (USGS 2009). After the completion of the USGS study, these USGS monitoring wells were not sampled in 2010. Groundwater was sampled in 2011, and a new sentinel well was installed in 2012. Optimization reports have been performed, and the site is currently under a monitored natural attenuation phase.

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