

Application of Soybean Oil Carbon Substrate to Soil Excavations to Enhance Biodegradation of Chlorinated Ethenes

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ABSTRACT

Emulsified Oil Substrate (EOS[®]) was applied using an innovative application technique to enhance the reductive dechlorination of dissolved chlorinated ethenes at two RCRA sites at Seymour Johnson Air Force Base in Goldsboro, NC. The mixed source mass, consisting of chlorinated ethenes and petroleum hydrocarbons, was removed through excavation. The removal of the source mass may have resulted in the elimination of a significant percentage of the anthropogenic carbon and thereby inhibited biodegradation of the residual chlorinated ethenes. Therefore, an emulsified oil product was applied to a gravel infiltration bed constructed in the bottom of the excavation. The emulsion was diluted, spray applied and followed by chase water. The excavation was backfilled and compacted. Wells in the area were monitored for continued biodegradation and a series of direct push samples were taken to evaluate the distribution of the oil and the resulting aquifer chemistry. Analytical results and field measurements collected three months after the application confirmed the presence of reducing conditions in the treated aquifer. The results also showed significant dechlorination of the residual mass.

INTRODUCTION

The goal of this EOS[®] application was the continuation of reducing conditions already present at the two RCRA sites. Solid Waste Management Unit 64 (SWMU 64) – Engine Shop is the former location of an Oil/Water Separator (OWS) in a grassy area approximately 45 feet west of Building 4810. Maintenance activities within Building 4810 included wheel cleaning, lubrication, and tire replacement. Wheel rims were reportedly cleaned using a jet washer, which is the primary source of wastewater discharges. The OWS was removed in 2000.

The site designated SWMU 86/87 AOC A is a combination of sites located in close proximity and consists of the former location of two above-ground storage tanks (ASTs) used for storage of waste oil and waste fuel (SWMU 86), the former site of an uncurbed concrete pad that was used to transfer oil from 55-gallon drums stored on the concrete pad (SWMU 87), and the former site of two 55-gallon drums containing Southeastern Lab C-4 fuel additive (AOC A).

At both sites, a source area consisting of petroleum and chlorinated hydrocarbons, as well as an associated groundwater plume extending from the source zone, had been delineated during the site investigations. The soil source area for each site was remediated through excavation of contaminated soil for offsite disposal. Both excavations extended to groundwater. The preferred remedy for groundwater was previously determined to be monitored natural attenuation (MNA). Natural attenuation had been monitored semiannually during the two years preceding the source

removal. The excavation eliminated much of the source mass including most of the petroleum hydrocarbons that may have been contributing to the reducing conditions at the site. The changes entailed by the soil removal may have been detrimental to the reducing conditions that are favorable to reductive dechlorination. This may slow biodegradation of the residual primary contaminants of concern, the chlorinated ethenes. Therefore, the addition of a carbon substrate to enhance reductive dechlorination was recommended. The substrate selected for application as a bioremediation enhancement was an emulsified plant-based oil (EOS598B42), which has a low viscosity, is easily applied at ambient temperatures, and is designed to spread through the subsurface. The emulsified oil was added in July 2005 as part of the soil excavation task. Two well sampling events and a round of direct push sampling have been performed since the application was complete.

THEORY OF APPLICATION

When applied to the water table surface, EOS® is distributed into the aquifer by the mounding/recharge forces of the applied solution and the subsequent force of the applied backfill. Since diluted EOS® has a viscosity similar to ambient groundwater, the material is distributed into the aquifer through the natural dispersion processes. The travel distance depends on site-specific geology and hydraulic conditions. For SWMU 64 and 86/87, a distribution throughout the top two-three feet of the excavated area was expected. The gravel bed was used to ensure equal distribution of the product into the aquifer below the excavation. In the days following the surface application, the EOS® flows with the groundwater until it adheres to the aquifer matrix, thus forming a permeable subsurface treatment cell in and below the former contaminant source area. Once in place, the emulsion slowly ferments to release fatty acids and hydrogen directly into the aquifer. This process enhances reductive dechlorination by providing food and nutrients to the native bacteria and by providing hydrogen for the reductive process.

DETAILS OF APPLICATION TECHNIQUE

The soil remediation entailed excavation of the contaminated soil to the water table in the source zone. The addition of the substrate while the excavation was open eliminated the need for the injection wells and pumping systems normally required for an *in-situ* application. Additionally, the application directly into the open excavation simplified the regulatory approval process by eliminating the need for an injection permit. The emulsified oil was determined to be the most amenable substrate for this type of application due to ease of injection, substrate longevity and material cost. The fatty acids in these oils are slowly broken down to hydrogen and acetate, providing a long-lasting source of reducing power for reductive dechlorination. The substrate selected for application as a bioremediation enhancement was an emulsified plant-based oil (Emulsified Oil Substrate), which has a low viscosity, is easily applied at ambient temperatures, and is designed to spread through the subsurface.

One of the design considerations was the ability to move the material away from the application point. The EOS® delivery process was designed to maximize the substrate distribution. Two key components of this process were the preparation of the excavation and

substrate delivery method. As part of the source removal soil was removed into the top of the water table and a trench was constructed into the water table. The trench in the open pit was backfilled to slightly above the groundwater surface with pea gravel. The gravel layer was installed to provide an infiltration gallery for application of the oil substrate. Since the gravel is highly permeable and has low EOS® sorption capacity, the gallery provided an ideal *in-situ* reservoir for the substrate during the infiltration process. The mixing method was a batch process where EOS® and potable water were prepared in a container. The diluted emulsion was applied evenly by spraying it into the gravel layer, followed by additional potable water and Vitamin B12. The excavation was backfilled with appropriate clean fill and compacted.

Specifically for SWMU 64, the area of excavation was approximately 15 feet by 23 feet and the depth of the excavation ranged from 5 to 7.5 feet deep. Approximately 132 tons of contaminated soil was removed for offsite disposal. At the bottom of the excavation, a trench was cut running the length of the excavation about 2 feet wide and 1.5 feet deep and backfilled with pea gravel. One drum of EOS® 598 B42 was diluted with 220 gallons of potable water. The Vitamin B12 was mixed with approximately 100 gallons of chase water.

Specifically for SWMU 86/87 AOC A, an estimated 349 tons of contaminated soil was excavated and transported off-site for disposal. The final excavated hole was approximately 20 ft by 60 ft at the surface and 12 ft by 42 ft at the bottom. The depth of the excavation ranged from 12 ft to 15 ft. Following the excavation, the trench (3 ft x 60 ft x 3 ft deep) in the bottom of the open pit was backfilled with pea gravel. One drum of EOS®598B42 was diluted with 245 gallons of potable water. The Vitamin B12 was mixed in 100 gallons of chase water.

DATA EVALUATION SUMMARY

The results of sampling the monitoring wells installed in and downgradient of the former source area were evaluated. Samples from these wells were analyzed for contaminants of concern and indicators of biologically mediated attenuation during four sampling events conducted prior to the remedial action. A sampling event was conducted approximately three months after the excavation and EOS® application. Post remedial samples from the historical wells were evaluated to determine the influence area and the resulting water chemistry. An additional sampling event as well as a direct push technology investigation to obtain samples in and around the application area were conducted ten months after the application. The results from the direct push sampling events at the two sites indicated that volatile organic compound concentrations had decreased but remained above cleanup standards. At both sites, TOC concentrations (subtracting contaminant and background) indicated an adequate continuing carbon source after 10 months. Groundwater velocity at both sites is <10 feet/year, so down gradient affects within the time period of this evaluation were not anticipated. Overall, the conditions favorable to reductive dechlorination were maintained at both sites.

CONCLUSIONS

The available site data for SWMU 64 are summarized in Table 1. At SWMU 64, dissolved contaminant mass decreased substantially after excavation but TOC was maintained significantly above background. The volatile fatty acids, propionic acid and acetic acid, indicators of soybean oil fermentation, were detected in the source area. The hydrogen concentration almost doubled to 2.3 nM in October 2005, then dropped off slightly to 1.8 nM in May 2006. Also at SWMU 64, the accumulation of 1,2 cis-DCE seen prior to oil addition has been mitigated in the source well. Direct push results also indicate that some partitioning of contaminants into the applied oil may have occurred.

The available site data for SWMU 86/87 AOC A are summarized in Table 2. At SWMU 86/87 AOC A, due to presence of a concrete structure, wells were not placed in the source area prior to structure removal for excavation. A well located about 7 feet laterally from the edge of the application trench contained increased dissolved contaminant mass, possibly indicating the extent of lateral spread. TOC was maintained significantly above background in the source area.

Dramatic decreases in contaminant concentrations were observed at SWMU 64, but residual concentrations continue to exceed the applicable regulatory limits. The addition of EOS® was warranted and degradation is ongoing. The innovative application of emulsified oil immediately following the source excavation provided a cost effective long term remedy.

Although decreases in contaminant concentrations were not readily seen at SWMU 86/87 AOC A likely mostly attributable to well location, several parameters indicate that natural attenuation is still occurring.

Table 1
Summary of Source Area Data for SWMU 64

	January - June 2005 Baseline Data	October 2005 Post Remedy	May 2006 Post Remedy
NA Scoring	Strong evidence of reductive dechlorination	Strong evidence of reductive dechlorination.	Strong evidence of reductive dechlorination.
DO	<0.5 ppm	0.8 ppm	0.38 ppm
ORP	-50 mV	-60 mV	-78 mV
Hydrogen	1.2 nM	2.3 nM	1.8 nM
TOC	72-92 mg/L	25 mg/L	21 mg/L
BTEX	1.2 mg/L	0.03 mg/L	0.054 mg/L
TCE	270 µg/L	24 µg/L	1 µg/L
cis-DCE	49,000 µg/L	45 µg/L	87 µg/L
Volatile fatty Acids	Not Detected	Propionic Acid 6.6 mg/L	Acetic Acid 31.6 mg/L

Table 2
Summary of Source Area Data for SWMU 86/87 AOC A

	January - June 2005 Baseline Data	October 2005 Post Remedy	May 2006 Post Remedy
NA Scoring	Good evidence of reductive dechlorination	Good evidence of reductive dechlorination.	Adequate evidence of reductive dechlorination.
DO	<0.5 ppm	0.45 ppm	1.9 ppm
ORP	-20 to -50 mV	-34 mV	-37 mV
Hydrogen	2-3 nM	Not detected	2 nM
TOC	6.7 mg/L	11 mg/L	18 mg/L
BTEX	0.003 mg/L	0.413 mg/L	1.076 mg/L
TCE	24 µg/L	14 µg/L	3.2 µg/L
cis-DCE	45 µg/L	94 µg/L	97 µg/L

LESSONS LEARNED

This innovative application of an organic carbon substrate has provided valuable data for addressing residual groundwater concentrations after the source area is excavated. It is often difficult to predict whether excavation alone will be sufficient to achieve the remedial objectives. The conservative phased approach, where the source area is removed followed by assessment and remediation of the residual groundwater contamination, may not be the appropriate strategy of many sites. For these sites, the application of EOS® as part of the source removal was a low cost and low risk approach for reducing the long term cleanup cost. Additionally, post excavation data confirmed that groundwater concentrations of the contaminants of concern remain above the cleanup standard. Therefore an active remedy was required at these sites. The results indicate that the reductive zone below the excavation was re-established. The lessons learned from the EOS® application at SWMU 64 and SWMU 86/87 AOC A are provided for the benefit of other practitioners.

- 1) Construction realities often result in uneven excavation surfaces. Emulsion distribution may be enhanced with the application of thicker gravel layer and/or greater trench depth.
- 2) Using a greater volume of dilution water may provide a greater driving force for emulsion distribution into the subsurface.
- 3) The pre-excavation groundwater concentration data used for the substrate dosing design will likely be different than the actual post excavation concentrations. Engineering judgment should be used to adjust the design as needed.
- 4) An injection permit was not required for this application due to specific North Carolina rules. Regulatory considerations may make this application process more or less attractive in a different state.