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Sequestration and Treatment of Vadose Zone Solvents using Edible Oils

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ABSTRACT: Edible oils have emerged as an effective treatment amendment for a variety of contaminants. When applied to chlorinated volatile organic compounds (cVOCs) in the saturated zone, edible oils have been shown to enhance anaerobic bioremediation and sequester the contaminants. However, edible oils have not been applied to the vadose zone for contaminant treatment. Soybean oil was injected into the vadose zone in M-Area at the Department of Energy's (DOE) Savannah River Site (SRS) as a research study to evaluate the effectiveness of edible oils for solvent sequestration and the ability to change a vadose system from aerobic to anaerobic to initiate reductive dechlorination. The proposed use of this technique would be an enhanced attenuation/transition step after active remediation. The goals of the research were to evaluate oil emplacement methods and monitoring techniques to measure oil placement, partitioning and degradation. Gas sampling was the cornerstone for this evaluation. Analyses for cVOCs and biotransformation products were performed. Overall, the cVOC concentration/flux reduction was 75-85% in this vadose zone setting. Destruction of the cVOCs by biotic or abiotic process has not yet been verified at this site. No reductive dechlorination products have been measured. The deployment has resulted in a substantial generation of light hydrocarbon gases and geochemical conditions that would support cometabolism.

INTRODUCTION

The clean-up of many contaminated sites is proceeding based on the assumption of a period of active treatment followed by some form of enhanced attenuation or monitored natural attenuation (MNA). At many facilities, extensive vadose zones exist and have become contaminated with chlorinated solvents and pose a long term groundwater threat. In permeable sediments, soil vapor extraction (SVE) can be very effective at removing chlorinated solvents. However, when lower permeability zones are contaminated, SVE is less effective and remediation time is controlled by slow diffusion. Under these conditions, use of edible oils could provide a cost-effective alternative for treatment of slowly emanating, residual contaminants. When properly applied, edible oils could serve to: (a) physically sequester chlorinated solvents, reducing their mobility and (b) stimulate biological degradation of the contaminants to less toxic and/or further biodegradable compounds. The goals of this study were to evaluate these processes.

Edible oils have been used extensively for enhanced anaerobic bioremediation and sequestration of chlorinated solvents and related contaminants in the saturated zone. However, there is little or no experience in treatment of vadose zone contaminants with edible oils. Developing vadose zone targeted methods to mitigate contaminant release rates from low permeability, diffusion controlled zones will reduce the flux into groundwater and result in shorter timeframes for final site closure and/or transition to final MNA paradigms.

SITE DESCRIPTION

The site chosen for this study is near building 320-M that was formerly used as a metals processing facility. The solvent contamination at this site is associated with a solvent cleaning sump in the building and the M-Area Inactive Process Sewer Line (MIPSL) that was a system of vitrified clay sewer lines used to convey process wastes from fabrication facilities to nearby basins and tributaries. Point source type 'leaks' occurred at pipe connections, junctions and manholes. Sediments were contaminated with cVOCs; primarily trichloroethylene (TCE) and perchloroethylene (PCE). Characterization work has shown that the majority of cVOC contamination associated with these releases is located between 18 and 20 feet (5.5 and 6 m) below the sewer line. This zone, known as the Upland Unit, is a low permeability formation that has proven to entrap cVOCs for extended periods of time (30-50 years). The Upland Unit is between 22 ft thick on the southwest side and 28 ft thick on the northeast side (6.7 and 8.5 m) of the test site. A more permeable sandy unit is below the Upland Unit and the water table is located at approximately 130 ft (39.6 m) depth.

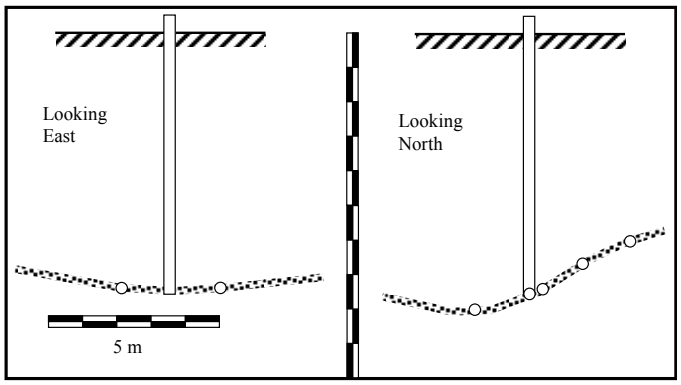

FIGURE 1. Measured and interpreted fracture 4-F cross sections.

To emplace oil in the Upland Unit, a previously installed hydraulically induced sand filled fracture was used. The fracture has an average thickness of 0.4 inches (0.01 m), radius of 15 ft (4.5 m) and depth of 24.3 ft (7.4 m) and contains 1350 lbs (610 kg) sand. The fracture orientation is shown in Figure 1 (Riha, et. al., 2005). The test site layout is shown in Figure 2 where the 'P' designations are gas sampling ports; 4-F is the fracture injection well and 1-IN is a vertical injection well (5 ft screen length). The depths in the figure are the midpoint for the sample port or injection point. It is likely both wells are connected to the sandy unit below the Upland Unit.

The test site is not in a solvent release source area but contains a significant gas plume associated with nearby releases. Initial concentrations were greater than 400 ppmv TCE.

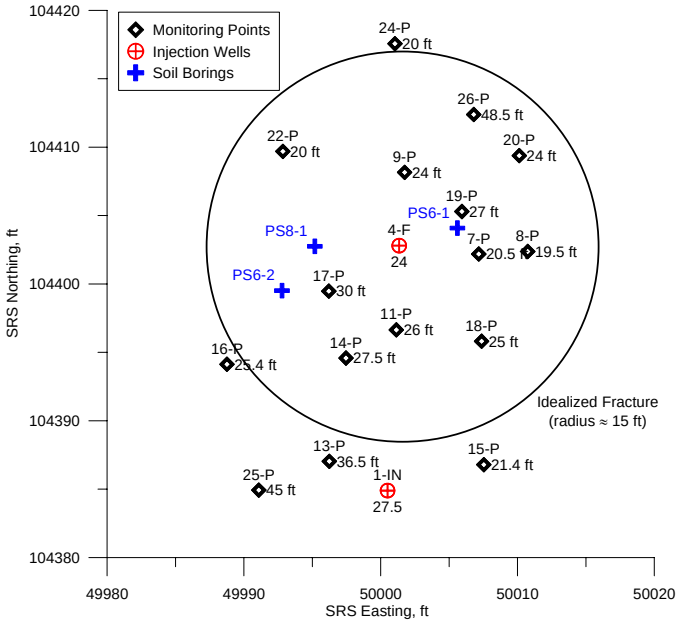

FIGURE 2. Test site layout.

MATERIALS AND METHODS

The field studies included installing monitoring points, injecting soybean oil and other amendments, monitoring soil gas and collecting and analyzing soil samples. In addition, two cone penetrometer test (CPT) logs were collected to aid in understanding the geology and flow paths of the injected oil. Monitoring points were installed in boreholes created with the DOE/SRNL CPT truck. These points were constructed of rolled up stainless steel cloth connected to ¼ inch nylon tubing with a crimp fitting. Monitoring points have a sand pack and were isolated between depths with bentonite pellets. The boreholes were sealed to the surface with a cement grout.

Seven drums (385 gal – 1460 L) of neat soybean oil were gravity fed into the fracture well 4-F on 3/14/06 and 3/16/06 (Figure 3). Oil flow quickly reached a steady state rate of 0.5 gallon per minute (gpm) (1.9 Lpm). An additional five drums (275 gal – 1040 L) were gravity fed into vertical well 1-IN on 4/4/06 with an oil flow rate of 1.5 gpm (5.7 Lpm).

Additional injections were completed on 1/12/07 to further stimulate bioactivity. Neat soybean oil with a phosphorous amendment and water addition with a pH buffer was used for the vertical well 1-IN. EOS®, a commercially available emulsified soybean oil product with other nutrients, along with phosphorous amended neat soybean oil, was used for the fracture well 4-F. The phosphorous amendment created a carbon to phosphorous ratio of 100:1. The purpose of the pH buffer was to attempt to increase the soil pH from around 5 to greater than 6; a range more suitable for microbial activity. These injection details are provided in Table 1.

FIGURE 3. Neat soybean oil injection.

TABLE 1. 1/12/07 Injection Details.

Vertical Injection Well FRC-1N	Fracture Injection Well FRC-4F
110 gal soybean oil with 0.2% (0.25 gal) triethyl phosphate (TEP) as a phosphorous source	5 gal EOS® 598B42 concentrate diluted with 15 gal buffered (TSP) water (20 gal total)
25 gal water with 5 g trisodium phosphate [Na_3PO_4 (TSP)] as a pH buffer	55 gal soybean oil with 0.2% TEP as a phosphorous source
Injection Sequence: 10 gal H_20, 55 gal oil, 10 gal H_2O, 55 gal oil, 5 gal H_2O. (135 gal total)	Injection Sequence: 5 gal EOS, 15 gal oil, 5 gal EOS, 15 gal oil, 5 gal EOS, 15 gal oil, 5 gal EOS, 10 gal oil. (75 gal total)

Gas sampling was the cornerstone for this evaluation. Analyses for cVOCs and biotransformation products were performed including CO_2 (carbon dioxide), O_2, (oxygen) TCE, PCE, cis-DCE (cis-dichloroethylene), vinyl chloride and gaseous breakdown products of soybean oil (pentane, butane, propane, ethane, ethene, and methane). Samples for CO_2, O_2, and TCE were collected in 1 L Tedlar® bags and analyzed on an Innova Model 1312 infra-red photo-acoustic spectrometer (IRPAS). An Apogee Model O2S oxygen sensor was connected to the outlet of the IRPAS for O_2

measurements. Gas samples were also collected in 20 ml crimped septum top vials for gas chromatography (GC) analysis of the cVOCs and light hydrocarbons. The Agilent Model 6890 GC contained a 60 m GS-GASPRO PLOT column and electron capture detector (ECD) and flame ionization detector (FID) in parallel. A Tekmar autosampler was used to inject the samples into the GC.

Soil samples were collected using the DOE/SRNL CPT truck and a Vertek (ARA, Inc.) wireline soil sampler. Soil cVOC analysis was conducted using the SRNL modified method 5021 for GC headspace analysis. Soybean oil content was measured by analyzing soil samples for total carbon using an OI Analytical Solids TOC Analyzer. The detection limit for soybean oil was approximately 200 mg_{oil}/kg_{soil}. Soil pH measurements followed ASTM method D4972.

RESULTS AND DISCUSSION

Gas and soil analysis results are used to evaluate the effectiveness of the treatment of cVOCs in the vadose zone with soybean oil. The processes evaluated include the estimation of oil location, the decrease in cVOC concentration (sequestration and degradation) and the generation of subsurface conditions that could induce reductive dechlorination in this vadose zone setting. In theory, treatment of vadose zone cVOCs with edible oils should be similar to applications in the saturated zone. Biological activity would consume oxygen and then release anaerobic fermentation products of the oil (hydrogen and acetate) that are used by common dechlorinating bacteria to reduce TCE and PCE to cis-DCE.

Oil Distribution. The distribution of the oil is inferred from gas measurements (CO_2, O_2 and TCE) and a limited number of soil samples. In general, the oil appears to have saturated the fracture and moved downward and towards the southwest. After moving downward, the data indicate the oil is distributed in a zone between 30 and 35 ft. Lithology logs show this zone contains sand with interbedded, thin fine grained layers that controlled the distribution of the injectants. The distribution of oil is shown in Figure 4 for soil boring PS6-1 conducted on 9/7/06. Additional borings had similar distributions of injectants relative to the fine grained zones.

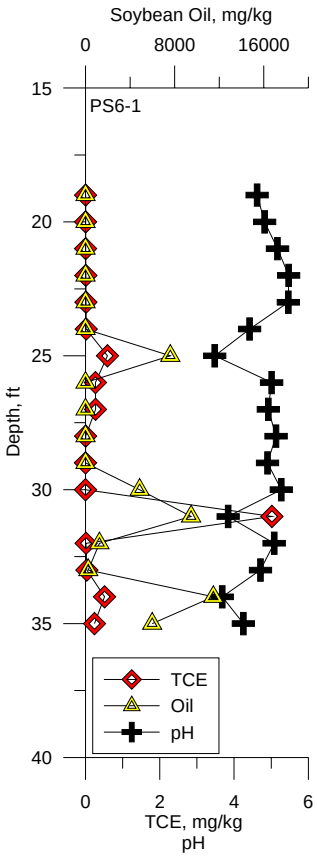

FIGURE 4. PS6-1 soil analysis results.

cVOC Trends. Immediately after oil injection, cVOCs present in the vicinity of the oil began to partition into the oil phase resulting in a decrease in TCE gas phase and aqueous concentration. See Figure 5. The sequestration reduces the mass flux to the underlying aquifer. The average TCE concentrations in the treatment area decreased from approximately 200 ppmv to 30 ppmv; an 85% reduction in concentration and resulting flux to the groundwater. In the oil zone (17-P) the concentration decreased from approximately 300 to 10 ppmv (97%). In monitoring point 26-P, at a depth of

approximately 50 ft and originally considered a background monitoring point, the TCE concentration decreased from 400-200 ppmv (50%). The fast gas diffusion in the vadose zone appears to play a significant role in sequestering the contaminants into the soybean oil treatment zone with a zone of influence larger than the oil bearing zone. Increased TCE soil concentration correlating with higher oil concentration provides evidence of the partitioning and sequestration of the gas phase TCE into the oil phase (Figure 4). No daughter products related to dechlorination of TCE were detected.

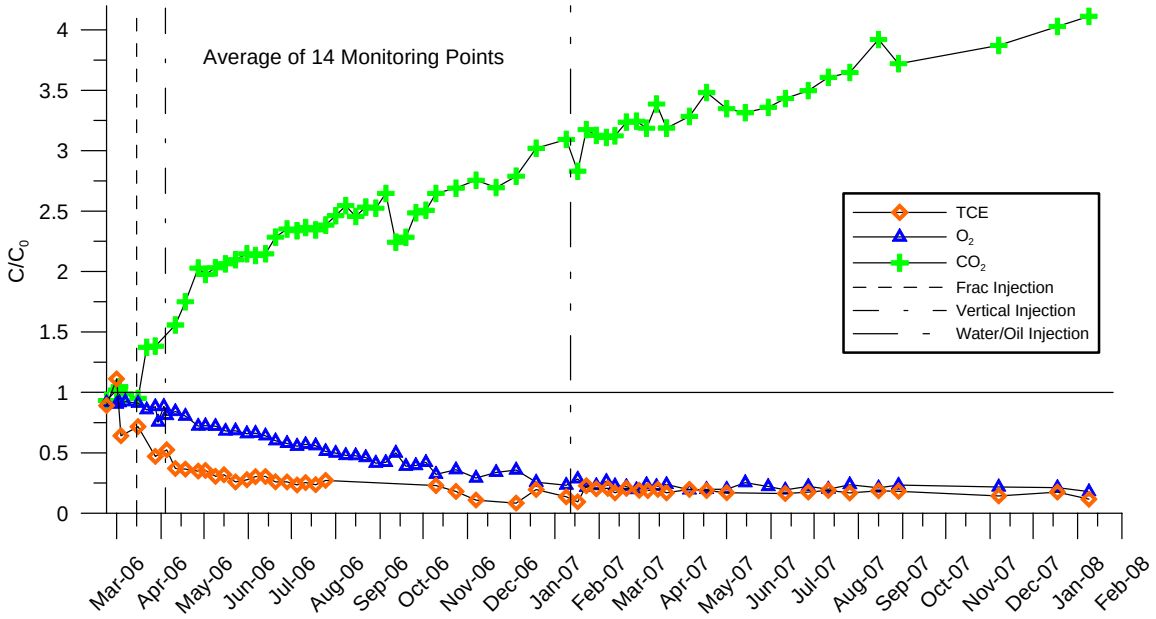

FIGURE 5. Average gas concentration trends.

Biological Activity Trends. O_2 and CO_2 measurements were used to evaluate biological activity in the test area. The initial average decrease in O_2 was approximately 0.05%/day for the first 10 months after the initial neat oil injection. In the oil bearing zone, O_2 reduction rates were 0.1 %/day for the first 7 months and then were measured at less than 1%. The O_2 levels are likely lower because of the slow response/equilibration of the galvanic cell oxygen meter at very low concentrations. The O_2 concentrations were nearly constant after the additional injection of oil, water and nutrients. This equilibrium could indicate an increase in biological activity with the other additives and that a balance has been reached between oxygen utilization and diffusion into and out of the treatment zone.

Initial average CO_2 production rates were 0.03%/day for the about the first month after the initial injection and then were fairly constant at 0.005%/day. Rates in the oil treatment zone and overall average rates were similar. These O_2 and CO_2 rates are low compared to bioventing results for aerobically remediating hydrocarbons (Leeson and Hinchee, 1997). Although one goal is to remove the oxygen, these initial rates may indicate an initial small population of microbes and/or limited consortia of the correct microbes for degradation of the soybean oil.

The gaseous breakdown products of the soybean oil (pentane, butane, propane, methane, ethane and ethene) were measured to aid in interpreting the oil degradation and

bioactivity (Figure 6). Overall, the trends show an increase in the generation of these gases and then a decrease as the oxygen is depleted and these products are consumed and/or diffuse away from the treatment zone. The methane increased from a background concentration of about 4 ppmv to an average of 30 ppmv. The methane levels increased and have remained relatively steady after the second injection consistent with localized methanogenesis and other lactate/oil degradation related impacts.

If strongly reducing methanogenic conditions have been created, it would indicate the progression of a microbial community capable of anaerobic respiration and fermentation of the soybean oil. Under these conditions, the soybean oil would ferment to hydrogen and acetate and lower amounts of the gaseous breakdown products would be produced. These products would in turn provide carbon and energy for reductive dechlorination under the correct conditions (AFCEE, 2007).

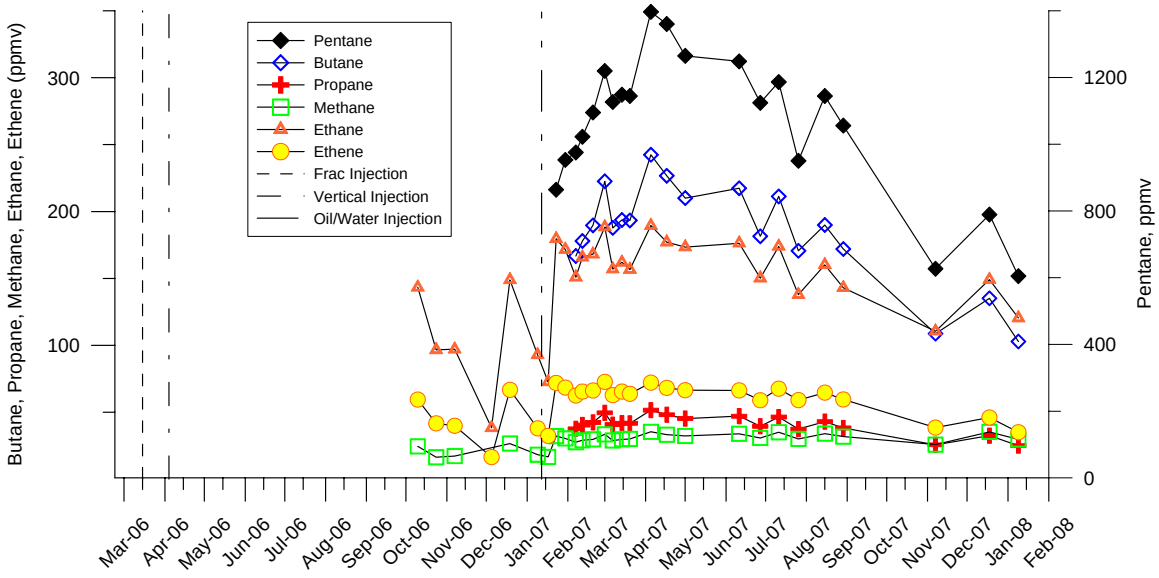

FIGURE 6. Gaseous breakdown products of soybean oil.

Oil Degradation Rates. Soybean oil degradation rates were calculated following protocols for soil bioventing for hydrocarbons (Leeson and Hinchee, 1997). The biodegradation rates were estimated from O_2 utilization and CO_2 production rates, the stoichiometric relationship for oxidation of soybean oil ($C_{56}H_{100}O_6 + 78O_2 \rightarrow 56CO_2 + 52H_2O$) and representative soil parameters (air filled porosity and bulk density). Initial O_2 utilization rates during the first few months after injection were on the order of 0.1 %/day and CO_2 production rates were 0.03% /day.

After equilibration, CO_2 production rates have remained fairly constant at 0.005%/day. Average O_2 concentrations have remained between 4-5% in the treatment zone; a level at the lower limit for aerobic degradation of hydrocarbons (Leeson and Hinchee, 1997) but likely too high to generate strong reducing conditions. Current aerobic degradation rates of the soybean oil are in the range of 3-10 $\mu g_{oil}/kg_{soil}$-day (or 1 to 4 mg_{oil}/kg_{soil}-year). Based on these degradation rates, the oil in the treatment zone is calculated to last for hundreds of years, providing a long-term flux reduction and treatment zone.

TCE Degradation. Degradation products of TCE were not detected in any of the soil or soil gas samples so reductive dechlorination cannot be verified. However, daughter products, which do not partition as readily into the soybean oil, could be rapidly degraded in the more oxygenated zones of the treatment area. Due to the relatively fast O_2 diffusion in the vadose zone, strongly reducing conditions do not appear to have been created. In addition, pH levels have decreased from 5 (native pH levels) to about 4 in the treatment zone, even after the addition of a pH buffer. The TCE, oil and pH distribution after the addition of the buffer is shown in Figure 7 (core collected 1/17/08). pH levels below 6 are detrimental to methanogenic and dechlorinating bacteria. Fermenting bacteria that prefer low pH levels can produce undesirable byproducts from the oil including organic acids that can further lower the pH (AFCEE, 2007). In the vadose zone, these acids will not be readily mobilized as in groundwater systems. Additional injections of a pH buffer are being considered.

Cometabolic TCE degradation is probable in the more oxygenated treatment zone in the presence of the methane, propane, ethene, etc. that are being produced from the degradation of the soybean oil. Methods to confirm cometabolism in the vadose zone are currently being developed for application to this site. These methods include nucleic acid amplification and sequencing, enzyme activity probes, and compound specific stable isotope analyses.

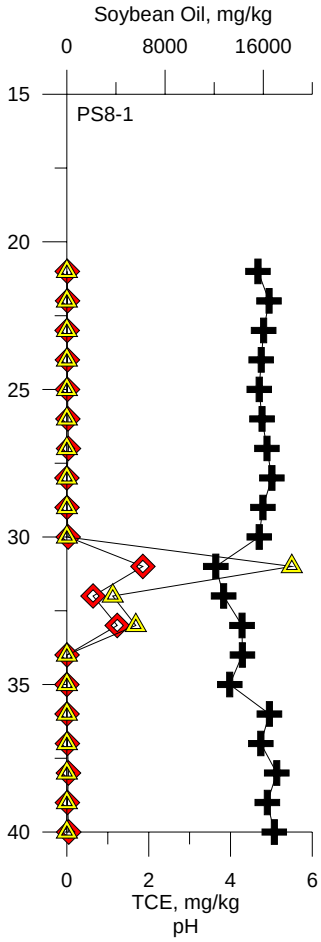

FIGURE 7. PS8-1 soil analysis results.

Limitations of Edible Oil in the Vadose Zone. The limitations of emplacing oil in the vadose zone as a treatment process for cVOCs in this study include 1) oil distribution, 2) slow microbial growth and progression, 3) pH reduction, 4) possible inability to achieve strong reducing conditions and 4) adequate means to measure cVOC degradation. The oil distribution does not appear to be a significant problem at this site due to the presence of finer grained layers that allowed the oil to spread and the fast diffusion of the cVOCs to the oil for sequestration and flux reduction.

The slow microbial growth is likely due to an initial small microbial community, low water saturation, nutrient availability and decreases in the pH. The low viscosity fluids such as edible oils and water tend to migrate downward and leave low saturations in the vadose zone. The low saturations leave an air permeability that can allow O_2 to diffuse into the treatment zone and prevent strongly reducing conditions needed to induce complete reductive dechlorination. The air/water/oil saturations at the site were estimated based on water and oil content measurements and site specific soil parameters. These distributions are shown in Figure 8 and show high air filled porosity in the oil treatment zone. To overcome these limitations, a thixotropic oil and water substrate coined VOS™ (“Vadose Oil Substrate”, patent pending) is under development. VOS is

designed to be easily injected and then to maintain its location with a high water and oil saturation in the vadose zone. Specific amendments (buffers, nutrients, microbes) in the VOS can be tailored to specific vadose zone conditions. In essence, VOS sequesters the cVOCs by diffusion and partitioning and creates an efficient bioreactor for degradation of the contaminants for long-term enhanced attenuation and flux reduction.

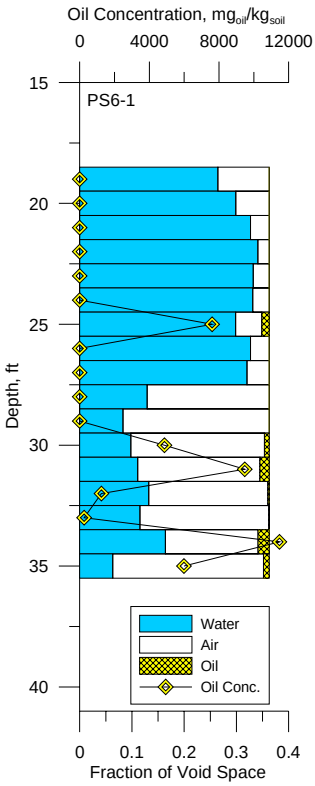

FIGURE 8. Soil air, water and oil saturations.

CONCLUSISONS

In this pilot study, the soybean oil effectively sequestered the TCE from a nearby source and reduced the concentration and resulting flux to groundwater by 85%. The degradation of the soybean oil is slow and is currently estimated to last for hundreds of years; providing long-term attenuation of flux to the groundwater. The addition of the oil did reduce the O_2 levels significantly and there likely are some anaerobic areas in the treatment zone. TCE dechlorination is not indicated based on the absence of breakdown products and is likely not occurring due to the current unfavorable geochemistry and apparent slow progression of the microorganisms. Conditions are favorable for cometabolic degradation of the cVOCs with a fairly constant, although low, production of methane and other co-metabolites.

Valuable information has been gained on the application of edible oils in vadose zone settings. The fast diffusion of gasses in the vadose are beneficial for sequestering cVOCs but are likely detrimental to creating strongly reducing conditions supportive of reductive dechlorination. The pH in the vadose zone is difficult to control because soluble organic acids (fermentation products) are not readily mobilized from the treatment area. The information gained from this study led to the development of an improved substrate (VOS) to overcome the limitations realized from emplacing neat edible oils in the vadose zone for sequestration and remediation of cVOCs.

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