Application of Biodegradable Oils (VOS™) for Treatment of Chlorinated Ethenes in the Vadose Zone - 12085

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ABSTRACT

Few active remediation alternatives are available to treat residual chlorinated volatile organic compounds (cVOCs) within the vadose zone. Soil vapor extraction (SVE) can be very effective at removing cVOCs in permeable soils; however, recoveries decline substantially in low permeability zones where mass transfer is diffusion-limited. Entrapped cVOCs in these zones represent a slow but continuous source of contamination to underlying groundwater.

An ongoing field study was initiated at the Department of Energy’s Savannah River Site (SRS) to evaluate an in situ biological treatment technology to address cVOC contamination in the vadose zone. Developed by Savannah River National Laboratory (SRNL), VOS™ is a thixotropic (shear thinning) formulation of biodegradable oil, water, nutrients, buffers, and dechlorinating bacteria (Dehalococcoides sp.) that is designed to sequester and biodegrade slow-diffusing cVOCs from unsaturated, low permeable soils. Injection of 871 L (230 gal) of VOS™ resulted in a rapid and significant decrease in cVOC gas concentration, generation of cVOC daughter products, a decrease in oxygen concentration, and an increase in carbon dioxide and methane production.

INTRODUCTION

Unsaturated (vadose) zone soils contaminated with residual chlorinated volatile organic compounds (cVOCs) pose long-term threats to human health and the environment as these contaminants gradually diffuse into underlying groundwater [1]. The slow but continual transfer of contaminant mass from these unsaturated source areas adds decades to groundwater remediation schedules and millions of dollars to long-term remediation project costs [2]. Because groundwater plumes typically grow significantly larger than their sources, source treatment within the vadose zone can be a very cost-effective component of mitigating long-term groundwater impacts.

To date, there are few active remediation alternatives available to treat residual cVOCs within the vadose zone. Conventional ex situ treatment methods such as soil washing and excavation and off-site treatment/disposal can be costly, energy-intensive, and impractical for sites with extensive vadose zone contamination. In situ soil vapor extraction (SVE) is a very effective technique for cVOC recovery in permeable soils; however, efficiencies decline substantially in low permeability zones where mass transfer is generally diffusion-limited [3]. In situ biological treatment with liquid electron donor substrates, despite well-documented success for cVOC destruction in groundwater [e.g., 4, 5], can be ineffective in the vadose zone because injected substrates either migrate downward out of the treatment area or do not provide the necessary saturations to sustain long-term anaerobic biodegradation.
In recent years, scientists at the Department of Energy (DoE) at Savannah River National Laboratory (SRNL) have explored ways to address cVOC contamination in the vadose zone, particularly within low permeable soils where conventional SVE is less effective. As an outcome of their research, SRNL developed a low-cost in situ biological treatment technology, named VOS™ (Vadose Oil Substrate; US Patent No. 7,896,577), that is designed to overcome limitations of traditional aqueous organic substrates in the vadose zone. VOS™ is a thixotropic (shear-thinning) gel that is easily injected into the subsurface, where it spreads outward filling pore spaces and bringing moisture, nutrients, pH buffer, electron donor carbon (e.g., vegetable and/or mineral oil) and dechlorinating bacteria (i.e., Dehalococcoides sp.) to the contaminated zone. Ultimately, the VOS™ technology prevents continued downward migration of contaminant mass from low permeable source zones while promoting suitable conditions for long-term contaminant biodegradation of cVOCs in situ.

Field testing of VOS™ was initiated in February 2010 at the M-Area Process Sewer Line (MAPSL) site, located in the northwest portion of the Savannah River Site (SRS), approximately 2.4 km south of the 3/700 Area operations and 4.8 km east of the SRS boundary. Historically, M-Area buildings discharged process wastewaters through the MAPSL, a 76 cm (30 in.) diameter, 610 m (2,000 ft) long vitrified clay pipe, into a large settling basin. Process wastewaters contained multiple chlorinated solvents, primarily tetrachloroethylene (PCE) and trichloroethylene (TCE), with minor amounts of 1,1,1-trichloroethane (TCA). Over time, leaks developed in the MAPSL (typically at the joints) resulting in discrete point sources of cVOC contamination within the 37-40 m (~120-130 ft) thick vadose zone.

From 1995 to 2002, three active SVE units were operated at the MAPSL site (via a series of vertical and horizontal wells), resulting in the recovery of approximately 45,400 kg (~100,000 lbs) of cVOC mass from the vadose zone [6]. However, subsequent assessment work identified significant residual cVOC mass entrapped in a shallow low permeable zone, known as the Upland Unit. This unit extends to a depth of 12-15 m (~40-50 ft) below ground surface (bgs) and consists of a very low permeability (κ = 10^{-12} – 10^{-9} cm²), high porosity, and high water content mixture of sand, silt and clay (Figure 1). Most process facilities at the SRS were built on the Upland Unit, which has been shown to entrap significant cVOC dense non-aqueous phase liquid (DNAPL) over long time periods (e.g., 20-40 years since documented release) [7]. In order to prevent this residual from reaching the water table, VOS™ was field-tested as a potential treatment option for the vadose zone at the MAPSL site.

The overall objective of the study was to evaluate the ability of VOS™ to sequester and biodegrade slow-diffusing cVOCs from the Upland Unit of the MAPSL site and serve as a long-term treatment barrier to protect the underlying aquifer. A 1.8-m (6-ft) thick, higher permeability zone located immediately beneath the Upland Unit was targeted for the VOS™ injection (Figure 1). This zone was selected because 1) it was bounded by two lower permeability layers, facilitating both vertical and lateral control of VOS™ emplacement during injection and 2) its higher permeability offered greater cVOC gas diffusion into VOS™ and improved injection rates. A series of soil gas sampling ports were installed around the injection zone to evaluate the performance of VOS™ over time. Specific aims 1 - 3 were investigated as part of the field demonstration:

1) Evaluate the ease of injection, distribution, and longevity of VOS™ in the subsurface;
2) Evaluate the ability of VOS™ to sequester and degrade PCE and TCE over time; and
3) Assess the maintenance of appropriate subsurface conditions for anaerobic biodegradation of cVOCs (e.g., soil pH, total organic carbon [TOC] content, oxygen concentration in soil gas).
MATERIALS & METHODS

Demonstration Design

Three injection points, MOI-01, MOI-02, and MOI-03, were installed via direct-push technology (DPT) to distribute VOS™ immediately beneath the Upland Unit at the MAPSL site (30 – 36 ft bgs (Figure 2). The injection wells were designed with a 1.5-m (5-ft) long, 2.5 cm (1 in.) diameter metal perforated screen, emplaced within the target zone, and connected to a high-pressure hose at the surface for VOS™ injection. The screened section was surrounded by a sand pack with the remainder of the borehole sealed with cement grout to the surface.

Approximately 870 liters (230 gallons) of VOS™ were mixed on-site and stored for several days in a plastic tote lined with a 3-ply liquid liner bag (Arena Products, Inc.; Rochester, NY). Subsamples were collected from each batch to measure viscosity using a Brookfield viscometer (Model LVDVE). Once anoxic conditions were confirmed in the totes using an optical oxygen probe (Ocean Optics, Inc. Dunedin, FL), 10 L of a commercial dechlorinating culture (BAC-9™, EOS® Remediation, LLC, Raleigh, NC), containing $10^8$ gene copy number (GCN) per ml of Dehalococcoides sp., was added directly to VOS™. A 0.5 hp, 3-phase, gear pump was used to inject the inoculated VOS™ into wells MOI-01, MOI-02, and MOI-03. Flow rate and total volume injected were recorded with a Great Plains Industries Flow Meter (Model GM 4ARP-2Z).

Prior to injection, 21 soil gas sampling implants were installed at varying distances and depths around each injection point (Figure 2). Generally, two gas sampling ports were installed per borehole, at depths of approximately 35 ft bgs (MO-02A, MOM-01B to MOM-09B, MVC-06C, MOO-01, MOO-02, MOI-01 to MOI-03) and 55 ft bgs (MOM-01A to MOM-09A, MVC-06B). Depths of the sample ports were selected based on cone penetrometer technology (CPT) results during installation. Each sampling port was constructed of a 1.3-cm (0.5-in.) diameter,
15.2-cm (6-in.) long wire mesh (80 x 80) section connected to 0.6-cm (0.25-in.) diameter high-density polyethylene tubing to surface. A 15.2 cm (0.5 ft) sand filter pack was placed around each sample port followed by 30.5 cm (1 ft) of dry bentonite pellets to seal the borehole. Bentonite was hydrated for > 1 hr before grouting the borehole to the surface. The sampling ports were finished with a Swagelok cap and surface cover.

Fig 2. Locations of injection wells, soil gas implants, and soil core samples

To address Specific Aims 1 - 3, a series of soil and soil gas samples were collected before VOS™ injection (to establish baseline conditions) and at varying time points post-injection. A summary of the post-injection sampling strategy is provided in Table I.
Table I. Summary of the Post-Injection Sampling and Analysis Plan

<table>
<thead>
<tr>
<th>Aim</th>
<th>Metric</th>
<th>Method</th>
<th>Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>VOS™ saturation in soil samples</td>
<td>Moisture content, TOC</td>
<td>3 and 8 months after injection</td>
</tr>
<tr>
<td>2</td>
<td>Gas concentrations of O₂, CO₂, PCE, TCE, daughter products and light hydrocarbons</td>
<td>Field O₂ and CO₂ sensors, Gas chromatography (GC)</td>
<td>Weekly or biweekly after injection</td>
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<td></td>
<td>cVOC concentration in soil samples</td>
<td>Modified EPA Method 5021</td>
<td>3 and 8 months after injection</td>
</tr>
<tr>
<td>3</td>
<td>pH of soil samples</td>
<td>ASTM Method D4972 [8]</td>
<td>3 and 8 months after injection</td>
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</tbody>
</table>

Soil Sampling and Analyses

Two soil sampling events were performed at the MAPSL site, approximately 3 and 8 months post-injection, respectively. Soil samples were collected at 30.5-cm (1-ft) increments between 20 and 45 ft bgs from boreholes MPI-1, MPI-2, MPI-3, MPI-4, MPI-5, and MPI-6 during the first sampling event and from MPI-7, MPI-8, MPI-9, MPI-10, MPI-11, and MPI-12 during the second event (Figure 2). Select samples were analyzed for soil moisture content, TOC concentration, soil pH, and cVOC headspace concentrations. Duplicate samples were collected from all depth increments.

The technique used to prepare and analyze soil samples for cVOC analysis was a modified version of USEPA Method 5021 [9] which has been used successfully at the SRS for over 20 years. Briefly, an approximate 2 cm³ plug sample was removed for each soil core and combined with 5 ml of nanopure water in a 22 ml glass headspace vial. The vial was then sealed with a crimped Teflon-lined septum top, weighed, and stored at 4°C prior to headspace analysis. Each sample was analyzed on the HP 5890 Series II or Agilent 6890 gas chromatograph (GC) using an automated head space sampler at 75°C for equivalent water concentrations. The GC was equipped with an electron capture detector (ECD) and flame ionization detector (FID) connected to the column in parallel. The GC was calibrated using a certified standard mixture in methanol, diluted with deionized water to specific concentrations: 3, 5, 10, 100, 1,000, and 10,000 µg/L. Samples were analyzed for multiple cVOCs including PCE, TCE, 1,1,1 trichloroethane (1,1,1-TCA), cis-1,2 dichloroethene (cis-DCE), trans-1,2 dichloroethene (trans-DCE), 1,1 dichloroethene (1,1-DCE), and vinyl chloride (VC). Two reagent blanks of pure deionized water were also analyzed to ensure the transfer lines and column were adequately flushed of residual solvents between samples.

Soil concentrations (mg/kg) were calculated from the GC results using Equation 1:

\[
C_s = \frac{C_wV_w}{M_s} 
\]

(Eq. 1)

where \(C_s\) is the calculated soil concentration of analyte \(i\) (mg/kg), \(C_w\) is the aqueous concentration of analyte \(i\) (mg/L), \(V_w\) is the volume of water in the headspace vial (7.5 ml), and \(M_s\) is the mass of the soil plug added to the headspace vial (mg). This method assumes that 1) all of the analyte originally in the soil plug is transferred to the aqueous phase and 2) the mass of the soil plug is equal to the mass of a field-sampled vial minus the average mass of field blanks (containing only 5 ml deionized water).
TOC and soil pH were measured in select samples to evaluate VOS™ distribution within the subsurface. Increases in TOC and pH above baseline levels are strong indicators of VOS™ emplacement. Samples for pH measurement were collected in 40 mL vials and analyzed according to ASTM Method D4972 [8]. TOC was analyzed using an O.I. Analytical Solids TOC Analyzer in samples exhibiting pH greater than baseline levels within the VOS™ target zone (30-36 ft bgs).

Gas Sampling and Analyses
Soil gas was collected from each soil gas implant several times before VOS™ injection and on a weekly or biweekly basis after injection. Sampling was conducted using a vacuum pump connected to the terminal end of the polyethylene tubing. Effluent tubing from the pump was placed in a sealed Zip-Loc® bag with an open 20 mL glass vial and septum cap; the bag was then purged three times with soil gas. After the third purge, the bag was filled, the tubing removed, and the Zip-Loc® bag sealed. The septum-cap was crimped on the vial before opening the bag. Soil gas samples were analyzed using an Agilent 7890 GC with PLOT and molecular sieve-packed columns and an ECD, FID, and thermal conductivity detector. Samples were introduced to the GC using a Gerstel auto sampler system. The suite of analytes included cVOCs (i.e., PCE, TCE, 1,1,1-TCA, cis-DCE, trans-DCE, 1,1-DCE, and VC), oxygen, carbon dioxide, and light hydrocarbons (i.e., n-butane, ethane, ethene, methane, n-pentane, and propane).

RESULTS

VOS™ Composition
Laboratory viscosity measurements confirmed the thixotropic nature of VOS™. The average viscosity of the three subsamples increased from 520 centipoise (cP) at a shear rate of 21 sec⁻¹ to 190,600 cP at rest.

VOS™ Injection and Distribution
Approximately 288, 288, and 238 L (76, 76, and 63 gallons) of inoculated VOS™ were injected in wells MOI-01, MOI-02, and MOI-03, respectively during the study. Injection flowrates generally ranged from 7.6 to 9.5 L/min (2.0 to 2.5 gpm) for all injection wells. Injection pressures ranged from 483 to 614 kPa (70 to 89 psi) for MOI-01, 379 to 483 kPa (55 to 70 psi) for MOI-02, and 414 to 448 kPa (60 to 65 psi) for MOI-03. Decreases in injection pressure often coincided with increased flowrates, suggesting that pressure-induced fractures formed in the subsurface. The presence of fractures would allow VOS™ to propagate greater distances from the injection point, although distribution would not be uniform.

Prior to injection, the average soil pH within the Upland Unit was 3.9 ± 0.2 (S.U.). After VOS™ injection, average soil pH increased to 4.6 ± 0.3 (S.U.). As expected, the greatest increase in soil pH occurred closest to the injection point due to the presence of deposited alkaline buffer in the VOS™ formulation. At injection point MOI-1, for example, soil pH was 4.0 (S.U.) at a depth of 35 ft bgs. After VOS™ injection, soil pH at MPI-3 (located 1 ft away from MOI-1) was 5.2 (S.U.) and 5.6 (S.U.) at depths of 35 and 36 ft bgs, respectively. Soil pH at MPI-11 (4 ft away from MOI-1) and MPI-9 (7 ft away from MOI-1) were 5.0 (S.U.) and 5.3 (S.U.), respectively, at a depth of 36 ft bgs.

Likewise, TOC concentrations were significantly greater than baseline conditions (<0.001% TOC) near the injection points. At MPI-3, TOC concentrations were highest at depths of 35 and 36 ft bgs (2.2% and 1.9%, respectively), which correlates well with the pH data. Elevated TOC (up to 0.17%) was also detected at MPI-12 (located 10 ft away from MOI-1), although
measurable amounts of TOC were not detected at the closer MPI-11. These data provide strong evidence of horizontal VOS™ distribution from the injection point and suggest that transport occurs through preferential pathways or pressure-induced fractures.

**VOS™ Performance**

Performance monitoring of VOS™ was accomplished primarily through monitoring of soil gas in the vicinity of the three injection points. Figure 3 shows soil gas concentration profiles for a) cVOCs, b) oxygen and carbon dioxide, and c) light hydrocarbons at one soil gas implant, MOM-02B, located equidistant (~6 ft) from injection wells MOI-01 and MOI-02 (Figure 2). Soil gas samples were not collected from implants MOM-01A, MOM-01B, MOM-04B, and MOM-06B due to screen clogging.

**cVOC Removal in Soil Gas**

At a depth of 35 ft bgs, average baseline PCE concentrations ranged from 228 to 533 parts per million by volume (ppmv); average TCE concentrations ranged from 163 to 346 ppmv. At 55 ft bgs, average baseline PCE and TCE concentrations were 1 to 2 orders of magnitude lower (19 – 50 ppmv and 3 – 7 ppmv, respectively). cDCE, VC, and ethene concentrations were below detection at both depths.

After VOS™ injection, PCE and TCE concentrations decreased rapidly at several monitoring locations (i.e., MOM-2B, -5B, and -9B). At MOM-2B, PCE concentration decreased from 623 ppmv to 27 ppmv within 2 weeks of VOS™ injection (Figure 3a). TCE concentration followed a similar trend, decreasing from 420 ppmv to 17 ppmv over the same timeframe. Daughter products, cDCE, VC, and ethene, were detected at MOM-2B 6 to 9 weeks post-injection. Ethene was detected at most monitoring locations (at 35 ft bgs) surrounding the treatment zone, with maximum concentrations ranging from 38 ppmv (MOM-5B) to 146 ppmv (MOM-2B). The rapid decrease in PCE and TCE concentrations and widespread production of ethene are strong lines of evidence for cVOC sequestration and subsequent biodegradation within VOS™.

A gradual rebound in PCE and TCE concentration was observed over time at most 35-ft bgs monitoring locations. VC and ethene concentrations also steadily decreased, returning to near baseline levels after one year post-injection. Despite the rebound, PCE and TCE concentrations remained below baseline levels beyond 12 months post-injection at MOM-2B, MOM-5B, and MOM-9B.

For all 55-ft bgs monitoring locations, no significant decrease in PCE or TCE concentration was observed. Moreover, formation of cDCE, VC, or ethene was not detected. This is likely because vertical distribution of VOS™ was confined by a lower permeability unit (at ~36 ft bgs), separating deeper soil gas from the injected VOS™.

**VOS™ Degradation**

For biological dechlorination of cVOCs to occur, reducing conditions must be established within the treatment zone. Injection of VOS™ displaces oxygen from the pore spaces and subsequent aerobic degradation of the carbon in VOS™ drives consumption of residual oxygen within and surrounding the treatment zone.
Fig 3. Pre- and post-injection gas concentrations of a) PCE, TCE, cis-DCE, trans-DCE, VC, and ethene; b) oxygen and carbon dioxide; and c) methane, n-butane, n-pentane, propane, and ethane from soil gas implant MOM-02B.
Average baseline oxygen levels within the treatment zone ranged 18.1% (MOM-9B) to 19.5% (MOO-01); average carbon dioxide concentrations were < 2%. After VOS™ injection, a rapid decrease in oxygen concentration was observed at most 35-ft bgs monitoring points. In particular, oxygen levels decreased below 10% at MOM-9B and MOO-02 and below 5% at MOM-2B (Figure 3b) and MOM-3B within 4-6 weeks post-injection. A concomitant increase in carbon dioxide levels above 10% was observed at these locations. These data illustrate the ability of VOS™ to rapidly transition an aerobic environment to anaerobic conditions.

After 3-4 months post-injection, oxygen and carbon dioxide concentrations appeared to stabilize and, in some cases, gradually trended towards baseline levels, indicating depletion of the carbon source. Oxygen and carbon dioxide concentrations did not approach baseline levels over the course of the study, remaining below 15% and above 8%, respectively, at MOM-2B, MOM-3B, MOM-9B, and MOO-02 after one year. For all 55-ft bgs monitoring locations, no significant change in oxygen and carbon dioxide concentration was observed after VOS™ relative to baseline levels.

Significant methane was generated within the treatment zone after VOS™ injection, with maximum concentrations ranging from 991 ppmv (MOM-8B) to 6,016 ppmv (MOM-2B; Figure 3c) approximately 6 months post-injection. N-pentane was also detected within the treatment zone along with minor amounts of n-butane, propane, and ethane; these light hydrocarbons are typical breakdown products of aerobic oil decomposition [4, 5]. At MOM-2B, n-pentane levels greater than 300 ppmv were observed 3-4 months after VOS™ injection (Figure 3c). As expected, greater methane and light hydrocarbon generation was observed closer to the injection points. The production of methane and light hydrocarbons correlates well with the generation of PCE/TCE daughter products, providing strong evidence for cVOC biodegradation within the treatment zone rather than solely cVOC sequestration.

Some methane generation was detected at the 55-ft bgs implants after 4-5 months; however, maximum concentrations were generally less than 10 ppmv. Minor amounts of n-pentane (< 1 ppmv) were also detected at MOM-4A and MOM-5A one year after VOS™ injection.

DISCUSSION

The on-going pilot test for VOS™ at the MAPSL site yielded promising performance results. After VOS™ injection, a rapid and significant decrease in PCE and TCE gas concentration was realized by partitioning into VOS™. Within several weeks, daughter products were measured showing reductive dechlorination of PCE and TCE is possible, along with a complete reduction to ethene. Carbon dioxide and methane increased and oxygen decreased within the treatment area, suggesting that injection of VOS™ into an aerobic vadose zone can rapidly establish anaerobic conditions. Overall, VOS™ demonstrated the ability to maintain high saturation levels in the subsurface, sequester cVOCs from the soil by diffusion and partitioning into the oil phase, provide sufficient substrate to stimulate biological activity, and sustain biodegradation resulting in accelerated contaminant reductions.

The longevity of VOS™ in situ, however, was much shorter than expected as indicated by a gradual and partial rebound in soil gas PCE, TCE, and oxygen concentrations. Based on these data, the rate of aerobic degradation of VOS™ in situ exceeded the carbon loading within approximately 4-6 months, presumably due to fast gas diffusion of oxygen within and surrounding the VOS™ treatment zone. The aerobic ‘burn rate’ of VOS™ is based on the surface area of VOS™ once it sets up as an in-situ bioreactor in the vadose zone. Modeling
efforts are underway to evaluate the longevity of VOS™ based on several different injection scenarios. In addition, the original formulation of VOS™ has been improved to include greater carbon content and an oxygen scavenger to increase longevity.

In November 2011, an additional 2,650 L (700 gallons) of the newly formulated VOS™ (purchased from EOS® Remediation, LLC: the licensee and exclusive supplier of VOS™) was injected into one injection point (MOI-3). VOS™ was inoculated with approximately 30 L of BAC-9™ (supplied by EOS® Remediation, LLC), allowed to stand for several days, and then injected into MOI-3 at an average injection rate of 3.8 L/min (1 gpm) with injection pressures ranging from 689-862 kPa (100-125 psi). Soil gas sampling has since commenced for this second injection program and will provide a more comprehensive dataset to evaluate VOS™ longevity and dose in the subsurface.

REFERENCES


