Creation of Passive Biobarriers Using Emulsified Oil: A Summary of Multiple Field Applications

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ABSTRACT: Emulsified vegetable oil (EVO) was successfully used as a long-term electron donor for stimulation of bioremediation of chlorinated chemicals in four field trials completed under a variety of site conditions. During the field trials, a number of factors impacting the successful application of EVO were evaluated, including: (*i*) the achievable radius of injection and vertical distribution of the EVO around the point of injection; (*ii*) potential for sustained oil mobility; (*iii*) EVO injection method; (*iv*) impacts to secondary groundwater quality; (*v*) oil longevity and associated breakdown products; and (*vi*) the effectiveness of the EVO at achieving complete dechlorination of all contaminants present under varying geochemical conditions. From the trials, it was concluded that EVO is an effective electron donor for chlorinated methanes, ethanes and ethenes, where the required microorganisms are present, in a wide range of geochemical environments. Effective distribution of EVO was found to be impacted by soil permeability, soil heterogeneity, nearby extraction of groundwater, and use of injection wells with proper seals and of sufficient diameter. Hydrolysis of the EVO resulted in transient formation of elevated organic concentrations in the groundwater; however, the formed organic constituents readily biodegraded once sufficient biomass developed, thus mitigating the impact to secondary groundwater quality. Methane formation was generally low, and sulfate reduction may be stimulated in some environments. Longevity of the EVO has been demonstrated to be a minimum of 12 months, even where high contaminant mass flux and groundwater velocity result in a higher electron donor demand.

INTRODUCTION

This paper discusses observations and knowledge gained from the use of EVO at multiple field sites under a range of site conditions. An overview of EVO is presented first, followed by a summary of four field applications and the resulting observations of the effectiveness of EVO and its impact on the aquifer at each site.

OVERVIEW OF EVO

At many sites, groundwater contamination is being treated *in situ* under ambient groundwater flow conditions by injecting sparingly soluble electron donors , which either sorb to the soil or are immobilized in pore throats (Soo and Radke, 1986), to provide a sustained long-term supply of electron donor for stimulation of microbial growth and contaminant biodegradation. These donors are often used to form permeable biobarriers, which treat groundwater passively as it flows through the biobarrier. Successful utilization of biobarriers is contingent upon effective lateral distribution of the electron donor across the zone of contamination to create a barrier to further contaminant mass flux downgradient, while minimizing the alteration of the hydraulic regime flowing

through the permeable barrier to avoid short-circuiting of groundwater around the barrier. The cost and effectiveness of emplacing long term donors *in situ* is highly impacted by the lifespan of the donor and the achievable radius of injection (ROI) of the electron donor around the point of injection.

Commercially available oil emulsions typically consist of water, vegetable oils (often soybean oil) and food-grade surfactants combined to create an oil-in-water emulsion using high-energy mechanical mixing. Soybean oil is a complex mixture of long-chain fatty acid glycerol triesters, which are biologically hydrolyzed over time and biodegraded to form shorter-chain fatty acids such as acetate, hexanoate, propionate and butyrate (Lalman and Bagley, 2000). Other breakdown products such as ketones, aldehydes and alcohols are suspected, but have not been confirmed to date (GeoSyntec unpublished data).

GeoSyntec has successfully constructed permeable biobarriers at several sites with varying site characteristics, including geology profiles (silty clay aquitards to peaty sands), a range of contaminants (including perchlorate and multiple chlorinated chemicals), contaminant loadings (from >800 mg/L total volatile organic compound (VOC) loading to <0.5 mg/L), and groundwater velocities (from <10 ft/year to >500 ft/yr). Despite the successful stimulation of bioactivity, we have identified a number of fundamental aspects of the application and use of emulsified oil not yet adequately defined that may be critical to cost-effective biobarrier construction, including the following:

- Oil injection and well installation techniques;
- Achievable radius of influence under different site conditions;
- Impact on soil permeability;
- Mobility of the oil emulsion post-injection;
- Longevity of donor for various contaminant mass flux loading and groundwater velocity combinations;
- The ability of the emulsion to promote complete and stable dechlorination;
- Breakdown products of the oil emulsion and impacts to secondary groundwater quality; and
- Electron donor mass loading from the oil emulsion.

Included below is a discussion of four field demonstrations of oil emulsion application in a wide range of site conditions, addressing the findings of the above factors.

FIELD DEMONSTRATION RESULTS

Test Site 1. A pilot test was conducted to evaluate EVO as the electron donor for bioremediation of a mixed VOC plume at a former industrial site in California, containing fine-grained sand with some silt, and a horizontal gradient ranging from 0.001 to 0.003 m/m. The plume has elevated concentrations (40 mg/L) of 1,2-dichloroethane (1,2-DCA), as well as somewhat lower concentrations of trichloroethene (TCE), cis-1,2-dichloroethene (cis-1,2-DCE) and vinyl chloride (VC). In addition, this aquifer has elevated sulfate concentrations (up to 800 mg/L), which was expected to increase the electron donor demand significantly.

EVO with 4% lactate was mixed with site groundwater and injected into the formation using six pre-existing injection points (5 cm PVC wells) with ten foot screens. The 8 hour injection was completed over two days, with a total of 220 kg (500 liters) of soybean oil injected at a 1% saturation. These injection points formed a semi-circle around a downgradient monitoring well, and groundwater samples were collected from both this monitoring well and two of the injection wells to monitor the progress of the pilot test over a six month period. During the EVO injection, suction was observed at the injection points due to the proximity to the downgradient monitoring well, which was used for the source of the dilution water. EVO was likely smeared towards the extraction well in an ovoid distribution around each injection point, as indicated by recovery of low levels of tracer and emulsion in the extraction well at the end of the injection period, resulting in incomplete lateral coverage.

Results from pilot testing indicated an increase in anaerobic microbial activity associated with the biodegradation of VOCs. Sulfate concentrations decreased to near the detection limit. Substantial decreases in 1,2-DCA and cis-1,2-DCE concentrations were also observed, coincident with corresponding increases in ethene concentrations. EVO breakdown products of acetate, propionate and butyrate, as well as acetone, were observed in groundwater samples. Bioaugmentation was not required to promote complete dechlorination at this site, suggesting the requisite organisms were present.

During the second half of the pilot test, organic measurements [total organic carbon (TOC), biochemical oxygen demand (BOD) and chemical oxygen demand (COD)] and volatile fatty acid (VFA) concentrations declined rapidly with a corresponding partial rebound of 1,2-DCA concentrations. These results indicated that the more soluble electron donor (lactate) had been exhausted in the pilot test area and insufficient lateral coverage of the oil emulsion was achieved. Methane production was limited throughout the pilot test. Hydrogen sulfide off-gasing was observed during groundwater sampling events in the early part of the pilot test. Metals mobilization was not observed over the pilot. It was clear from the pilot test that a full-scale biobarrier approach would require a more extensive injection zone, and potentially repeated injections to maintain the biobarrier due to the substantial electron donor demand posed by the high sulfate concentrations at this site.

Test Site 2. Two pilot tests were conducted to evaluate the effectiveness of EVO under both passive (*i.e.*, ambient groundwater flow) and active conditions (*i.e.,* groundwater was continually injected into a well that had been previously charged with EVO) for bioremediation of a highly mobile, mixed VOC plume at an industrial site in Australia. The site consists of a heterogeneous, highly conductive (K = 20 to 30 m/day), sandy aquifer with peat and clay layers. The plume contains >90% 1,2-DCA mass (ranging from 200 mg/L upwards of >3,000 mg/L), combined with VC (up to 160 mg/L), and 1,1,2,2-tetrachloroethane, chloroform (CF), carbon tetrachloride, all other chlorinated ethenes and 1,1,2-trichloroethane in the low mg/L concentration range. The aquifer can be described as naturally anaerobic and reducing (-50 mV oxidation-reduction potential background), high sulfate (>1,000 mg/L in places), with elevated chloride concentrations (>500 mg/L) and low pH (4.5 to 5.5) likely related to elevated concentrations of naturally produced acetic acid (up to 250 mg/L).

In each pilot test, EVO was mixed with site groundwater and then injected into the formation through permanent injection wells at targeted oil saturations of 1% (active) and

5% (passive). Reductions in soil permeability and clogging were not observed in either pilot test during injection activities. In the active pilot test, continuous injection of groundwater at a rate of about 38 L/min has occurred over a period of 12 months without any visible change in soil permeability or biofouling of the injection well. Oil distribution in the passive test was observed to a minimum 4.5 m radius around the well, and an unknown portion of the oil mass was observed to remain mobile and flow downgradient at least 33.5 m. Mobile oil was not observed in the 1% oil active trial, which may either be related to higher soil organic content or lower oil mass.

Groundwater samples were collected every six weeks from upgradient (one well nest in the passive test, the mixed effluent in the active test) and three downgradient well nests (two to three wells screened at variable depths per nest) in each pilot test, plus the injection well in the passive test, over a twelve month period to date. During this period, the maximum reduction in total VOC concentrations, observed 3 to 6 months post-injection, was 96% to 99% in each trial. After 4 to 6 months, minimally sorbing compounds such as 1,2-DCA and VC were observed to desorb preferentially, sometimes causing transient peaks (as much as an order of magnitude above influx levels), followed by slowly increasing desorption of more strongly sorbing compounds such as tetrachloroethene (PCE) and TCE. Concurrent with the initial VOC biodegradation and subsequent desorption was substantial ongoing production of daughter products VC, ethene and methane. All contaminants were observed to biodegrade.

The predominant breakdown product of the oil was found to be acetate, with propionate and hexanoate also observed in the 5% oil trial. Long-chain fatty acid, alcohol, ketone and aldehyde production was not monitored. Upon stimulation of sufficient biogrowth, the pH was found to increase to >6 in downgradient monitoring wells, likely due to biodegradation of the organic acids. Minimal sulfate reduction was observed, and this did not occur until the majority of the contaminants were biodegraded. The resulting sulfide production was mitigated through precipitation of iron sulfide, which also mitigated dissolved iron production (dissolved iron concentrations ranged from a few mg/L to 29 mg/L where sulfate reduction had not yet occurred). Methane production was also fairly low (typically <2 mg/L, to a maximum of 8 mg/L). The oil appears to be persisting after 12 months, although there may be indications that the lower concentration oil (1%) may be nearing depletion (non-detect VFA concentrations).

Test Site 3. Two pilot tests were conducted to evaluate the effectiveness of EVO as an electron donor for the bioremediation of a stable VOC plume located in shallow and deep groundwater aquifers at an industrial site in New England. The shallow groundwater zone is comprised of fine and medium sand with some gravel and minor peat lenses. The deep groundwater zone is characterized by a medium sand and gravel layer that is coarsely interbedded with silt and fine sand. The two aquifers are separated by a non-cohesive silt layer that pinches out downgradient of the test areas. Hydraulic conductivity testing of the shallow and deep groundwater zones provided estimates of 1.8 to 3.6 m/day and 3.6 to 61 m/day, respectively.

For the majority of the plume, approximately 75 to 85% of the concentration of total dissolved VOCs is comprised of 1,1,1-trichloroethane (1,1,1-TCA) and its biodegradation daughter products: 1,1-dichloroethane (1,1-DCA), and chloroethane (CA). Up to 16% of the total dissolved VOC concentration is comprised of TCE and its biodegradation

daughter products; cis-1,2-DCE, VC and ethene. Other VOCs of concern are methylene chloride, 1,2-dichlorobenzene and 1,4-dichlorobenzene; concentrations of these organic compounds appear localized within the dissolved shallow groundwater plume. Recent concentrations of 1,1,1-TCA in the shallow source area ranges between 6.5 mg/L and 9.9 mg/L. The concentration of TCE in the shallow source area ranges between 0.10 mg/L and 0.15 mg/L. Sulfate was detected at concentrations ranging from 5 to 25 mg/L.

The deep zone pilot test area was comprised of a groundwater recovery well, three 5 cm diameter monitoring wells and three 5 cm diameter injection wells. The injection wells were oriented perpendicular to groundwater flow and to the line created by the monitoring wells to form a "T". Groundwater was pumped from the recovery well to create a forced gradient through the pilot test area over the duration of the pilot test.

A 0.5% solution of EVO in groundwater was injected over four days to provide an estimated ROI at each well of approximately eight feet. Groundwater was extracted from two of the three amendment wells to provide dilution water while the diluted emulsion was injected into the remaining well. EVO was detected as far downgradient as the recovery well (>13 m downgradient). Monitoring continued for ten months after EVO injection. 1,1,1-TCA and sulfate were not detected in the pilot test area after the first three months of electron donor addition. Additionally, 1,1-DCA increased and then decreased to non-detectable levels during the first three months and chloroethane was detected sporadically. After an initial increase in TOC concentration to approximately 162 mg/L in the first monitoring well, TOC concentrations decreased to below baseline concentrations (<40 mg/L) after the third week of monitoring. Acetate and propionate were the main by-products of oil degradation. Sulfate concentrations began to rebound in the seventh month after EVO injection. 1,1,1-TCA was also detected sporadically in the eighth month after EVO injection. The anaerobic and reducing conditions conducive to reductive dechlorination were maintained at least six months after injection of the EVO.

The shallow zone pilot test was comprised of a row of seven monitoring wells aligned with the groundwater flow direction. Groundwater was extracted at 8 L/min from the furthest downgradient well to create a forced gradient toward this well throughout the pilot test. Two injections of 1,556 L of EVO were performed targeting 2% by volume EVO; the first injection was performed using a 1.9 cm diameter well that was installed using direct push technology, the second injection was performed using a conventional 5 cm diameter PVC well installed using hollow stem auger and was followed with injection of 1,515 L of groundwater. A reduction in permeability was observed at the first well post-injection, although the well was later successfully rehabilitated through injection of heated water and steam. No reduction of permeability was observed with the second injection. Bioaugmentation using a known dechlorinating culture (12 L of KB-1^{TM} provided by SiREM Labs) was performed mid-way through the first injection. The milky color associated with dissolved EVO in groundwater was observed in all of the downgradient monitoring wells one month after injection.

One week after the first EVO injection, TOC increased to 1,200 mg/L, but steadily decreased to 120 mg/L over the next six months. Acetate and proprionate were consistently detected over the six month monitoring period in all of the monitoring wells at concentrations of 200 to 400 mg/L and up to 600 mg/L respectively. The propionate decreased to non detectable levels after 6 months. Valerate was detected at low concentrations. Baseline concentrations of total VOC concentrations ranged from 7.2 to

19.4 mg/L. Within the first six months, all 1,1,1-TCA in the well located eight feet upgradient of the injection point was reduced to chloroethane. Downgradient monitoring wells all show varying degrees of 1,1,1-TCA dechlorination to 1,1-DCA and CA. Ethene concentrations have begun to increase in the farthest downgradient monitoring well and in the extraction well.

Test Site 4. Three pilot tests (Areas 1, 2 and 3) were conducted to evaluate the effectiveness of EVO for bioremediation of three VOC groundwater plumes located in a silty sand and clay interbedded aquitard at a former industrial site. The zone of interest ranged from the water table (nominally 9.7 m bgs) to a depth of approximately 18.3 m bgs. For the majority of the plume, approximately 95% of the concentration of total VOCs is comprised of TCE and its biodegradation daughter product cis-1,2-DCE. Recent concentrations of TCE in the pilot test areas ranged between 0.10 and 5.8 mg/L.

The Area 1 pilot tested various well construction techniques (hollow stem versus direct push) and means to effectively amend EVO to the target interval of interest (various EVO concentrations and injection equipment). Five spatially separated injection wells were installed each with a monitoring well network comprised of upgradient and downgradient wells to carefully assess the achieved ROI. Sodium bromide (conservative tracer) was co-injected with the EVO to evaluate the maximum potential ROI. The evaluation of injection well types concluded that conventional well completions were preferable (less prone to surface leaks related to seal failures). Bromide was not detected more than 4.5 m downgradient nor more than 2.1 m upgradient. The estimated achieved ROI was conservatively estimated as 2.3 m. No difference in ROI was observed with oil concentrations varying between 0.25% and 0.5%.

For the remaining two pilot tests, conventional 5 cm hollow stem auger wells were used as injection wells and the target oil injection concentration was 1% (oil by volume). In Area 2, the treatment design consisted of multiple biobarriers with an estimated 10 year travel time between injection rows. The injections wells within each row were off-set to encourage a more continuous barrier. In Area 3, the injection well layout was a closely-spaced grid of injection wells to target a localized source area. In total, just over 18,700 kg of soybean oil and 1,850 kg of lactate was amended to 53 injection wells. In Areas 2 and 3, each injection well was bioaugmented with two to three liters of KB-1^{TM}.

To ensure that the area of treatment influence was defined in Areas 2 and 3, sentinel wells were installed upgradient and downgradient of the targeted treatment zone. The oil emulsion did not mobilize beyond the targeted treatment zone and thus the impacts of the treatment was confined to the targeted area, as indicated by the lack of change in the VOCs or geochemistry in the sentinel wells over the pilot test monitoring period. Several performance monitoring wells (PMWs) were installed within each pilot test area to monitor the performance of the treatment throughout the pilot tests and determine the achievable ROI. These PMWs were installed outside of and within the anticipated ROI, as well as at the intersection of the ROI for two injection wells. Given the heterogeneities in the site geology, the achieved ROI was likely variable with depth and location. Based on monitoring well placement, the ROI is expected to be at least 3 m in Area 2 and possibly 4.5 m in Area 3, which had a slightly higher hydraulic conductivity.

Monitoring occurred on a quarterly basis after electron donor addition was completed for a range of parameters including VOCs, dissolved hydrocarbon gases, anions, TOC,

VFAs, COD, BOD, and dissolved metals. Within three months, reducing conditions were present in all but one performance monitoring well (indicating this well was outside of the achieved ROI). VOC concentrations declined substantially three to six months post-injection and have remained low in Area 3 over the monitoring period (one year). Methane concentrations peaked in the first six to nine months and have either been stable or decreasing from this point. The addition of this quantity of EVO to a tight formation resulted in transient detections of 2-butanone, 2-hexanone and acetone. These compounds are likely biodegradation intermediates of the EVO and have been shown to deplete within the pilot test area.

A single soil gas probe was installed in each pilot test area to monitor the potential for vadose zone impacts. After one year, detectable concentrations of methane, carbon dioxide and reduced concentrations of oxygen were observed in the vadose zones overlying the pilot test areas. Hydrogen sulfide has not been detected in the samples collected. Soil gas results measured to date have not exceeded local action level criteria.

The mobility of the emulsion post injection was believed to be very limited. The ultimate longevity of the EVO has not been determined, but conditions of high TOC and reduced concentrations of VOCs have been observed for over 18 months in Area 1, and 12 months in Areas 2 and 3. Bioaugmentation resulted in complete dechlorination at Areas 2 and 3 within 3 months, whereas after 18 months at Area 1, where bioaugmentation was not performed, VC is the terminal biodegradation product.

DISCUSSION

The following observations and conclusions may be drawn from the experiences of EVO application at these four sites:

- The achievable emulsion ROI is dependent upon the soil type, permeability and heterogeneity, with ROIs of 2.1 to 3 m observed in heterogeneous silty clay environments, and 2.4 to >4.5 m in more permeable sandy soils. Heterogeneity in the soil is suspected to have caused uneven vertical distribution of the oil emulsion in the pilot tests of Test Site 4. Some variation in oil breakthrough with depth was also observed at Test Site 2, which was also significantly heterogeneous.
- Permanent well installations generally provide better injection properties for oil emulsion injection. Failures of direct push wells were observed, resulting in short-circuiting of the emulsion to surface. Significant reductions in permeability were also observed in the smaller direct push wells.
- In the sand and gravel environments, a portion of the oil emulsion was observed to remain mobile to at least 30 m downgradient of the point of injection. The percentage of the original injected volume that remained mobile is unknown at this time; however, sustained biodegradation around the point of injection indicates that some mass remained within the targeted ROI.
- Observed breakdown products of the oil emulsions are predominantly acetate, with propionate, butyrate and hexanoate also observed at lower concentrations. Suspected breakdown products include transient formation of ketones such as 2-butanone, 2-hexanone and acetone. Also suspected is the formation of alcohols such as isopropanol and perhaps aldehydes.
- Impacts to secondary groundwater quality were observed and will need to be monitored during future pilot tests and any full-scale implementations. Methane

production was generally low at all sites (typically up to a few mg/L). Transient increases of BOD, TOC and VFAs were observed at all sites, but upon growth of sufficient biomass, BOD, TOC and VFA concentrations decreased as the fatty acid breakdown products were biodegraded. The low methane concentrations may be a result of elevated concentrations of long-chain fatty acids (e.g., linoleic acid) which have been demonstrated to inhibit methane formation (Lalman and Bagley, 2000), or at Test Sites 1 and 2, may have been related to inhibitory concentrations of chlorinated chemicals.

- At Test Sites 2, 3 and 4, the oil emulsion persisted for a minimum of 12 months. Monitoring at Test Site 1 did not extend beyond 6 months. At Test Site 2, the 1% oil emulsion was predicted to last at most only a few months due to the high groundwater velocity and contaminant mass flux demand (based on an assumed 2X stoichiometric demand); however, it appears to have persisted for 12 months.
- Emulsified oil promotes complete and continuing dechlorination of a multiple of chlorinated compounds (including chlorinated ethenes, ethanes and methanes), where the required microorganisms are present (bioaugmentation was beneficial in both cases where it was applied). EVO does not appear to inhibit biodegradation of any contaminant, and appears to biodegrade under a wide range of geochemical conditions, including low pH (as low as 4), high sulfate, and high chloride environments.
- Adequate lateral distribution of the EVO across the plume is essential to provide a barrier to contaminant mass flux downgradient. To achieve this lateral coverage, an understanding of the achievable ROI, accounting for soil heterogeneity, at each site is required. While dilution of the EVO with groundwater is preferred over the use of a clean water supply, the groundwater extraction well should be carefully situated to avoid impacting the lateral distribution of the EVO around the injection well.

CONCLUSIONS

EVO has been demonstrated to be an effective long-term electron donor for stimulation of biodegradation of a number of contaminants in a wide range of geological and geochemical environments. Site-specific determinations of the achievable ROI are required, and the impact of soil heterogeneity on vertical EVO distribution must be considered. Unknowns include donor longevity and the relation to groundwater velocity and mass flux, factors impacting EVO mobility and mass retained in the targeted treatment zone, impact to soil permeability throughout the treatment duration, breakdown products and their persistence, and methods for detecting continuing EVO presence once bioactivity is established.

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