OVER 17 YEARS OF EMULSIFIED VEGETABLE OIL APPLICATIONS: THE GOOD, THE BAD AND THE UGLY!

William Newman; RNAS Remediation Products, Brooklyn Center, MN USA

BACKGROUND

Prior to 2002, emulsified vegetable oil (EVO) electron donors for bioremediation were produced on site with high-shear mixers that made field emulsions with o droplets ranging from one to ten microns or more. In February of 2002 RNAS Remediation Products manufactured the first EVO product with sub-micron oil droplets. Approximately 10 million kilos of this EVO product has been injected hundreds of sites, providing a wealth of experience and data. Key elements of effective in situ bioremediation using EVO are described using brief case histories to illustrate effective EVO application methods as well as common problems an how to address them.

KEY PROPERTIES OF ELECTRON DONORS

HYDROGEN PRODUCTION POTENTIAL - How much potential energy does an electron donor have? Vegetable oil based electron donors provide more than double the molecular hydrogen per mass of electron donor than sugars, lactate, glycerol or cellulose based electron donors.

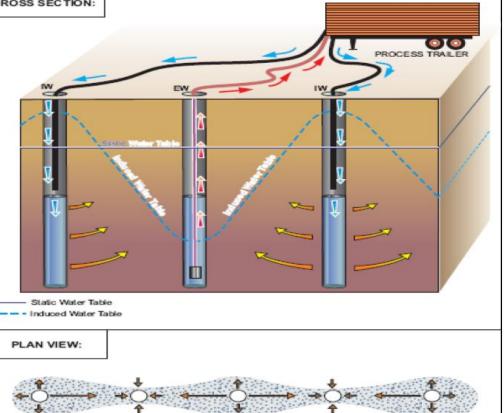
HYDROGEN PRODUCTION RATE – EVO slowly dissolves and ferments to release low concentrations of molecular hydrogen for up to several years. Molecular hydrogen concentrations of 2-11 nanomolar effectively stimulate dechlorination while limiting competition from methanogens and acetogens (Yang and McCarty

ELECTRON DONOR MOBILITY – Colloidal transport and filtration modeling by Xu et. al. suggests that particle capture by straining occurs when the ratio of the mobile particle size to porous media particle size is greater than 0.008. With a median droplet size of 0.30 microns the Newman Zone small droplet EVO products exhibit little or no straining for soil particles larger than 38 microns

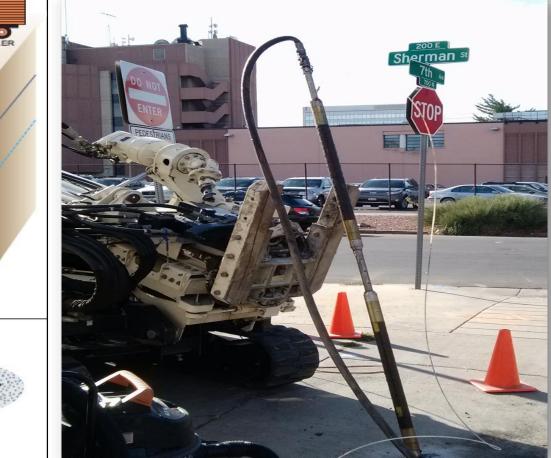
DEFAULT HYDROGEN PRODUCTIO ESTCP Substrate Design Tool

Kilos Hydrogen/Kilo (Dry Wt.)

HIGH MOBILITY EVO INJECTED IN WELLS OR USED IN



EVO DONOR LONGEVITY A ONE-AND-DONE, TOP-DOWN **CIRCULATION SYSTEMS DIRECT PUSH INJECTION**



Combustion Kilojoules/Gram

Potential Energy of Substrates

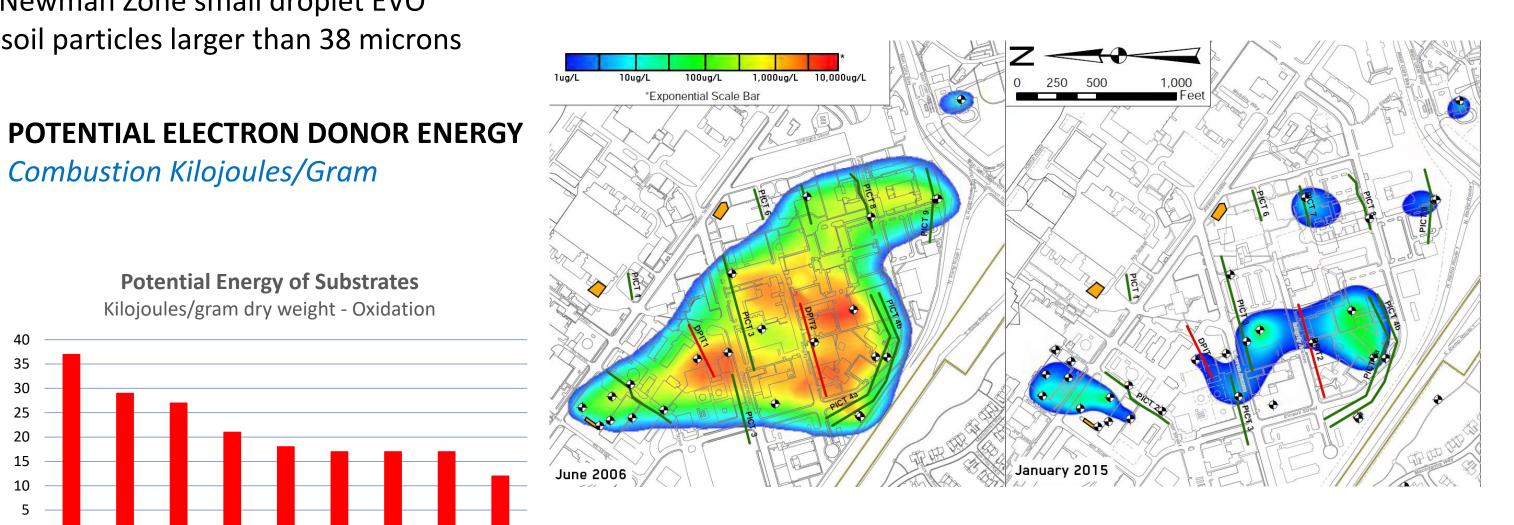
Kilojoules/gram dry weight - Oxidation

EVO MOBILITY FOR WELL INJECTIONS – THE GOOD

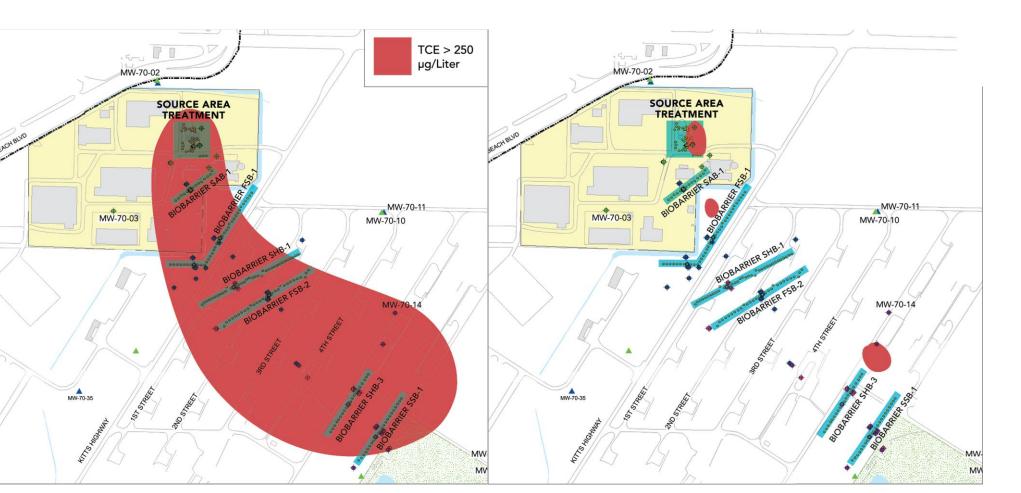
Small Droplets - High Mobility: Emulsified vegetable oil with submicron oil droplets is typically injected at 1% to 5% oil by weight and has a viscosity similar to water. Once diluted, the EVO can be injected into any formation that can take water. With minimal straining the small droplet EVO can be moved distances of 30 meters or more in some soils and fractured rock with direct injections or temporary circulation systems

Creating Large Biobarriers With Injection Wells: Large, dilute plumes with deep wells and mixed contaminant plumes including explosives, chloroethenes, chrome and perchlorate can be addressed using large volume injections or circulation between wells to install EVO biobarriers. Newman Zone EVO has been used to construct biobarriers as long as one kilometer with wells spaced 30 meters apart using large volume direct injection methods.

Temporary Circulation Between Wells – Dover AFB Area 6: At Dover AFB Area 6 temporary circulation between wells spaced 15 meters apart were used to create biobarriers in silty sands. Another EVO product with larger oil droplets was initially used but high injection back-pressures limited EVO distribution. A Newman Zone EVO product with sub-micron oil droplets greatly reduced these problems. Over 700,000 kilos of EVO was used to maintain the biobarriers to effectively treat a large TCE source area over a ten year period.



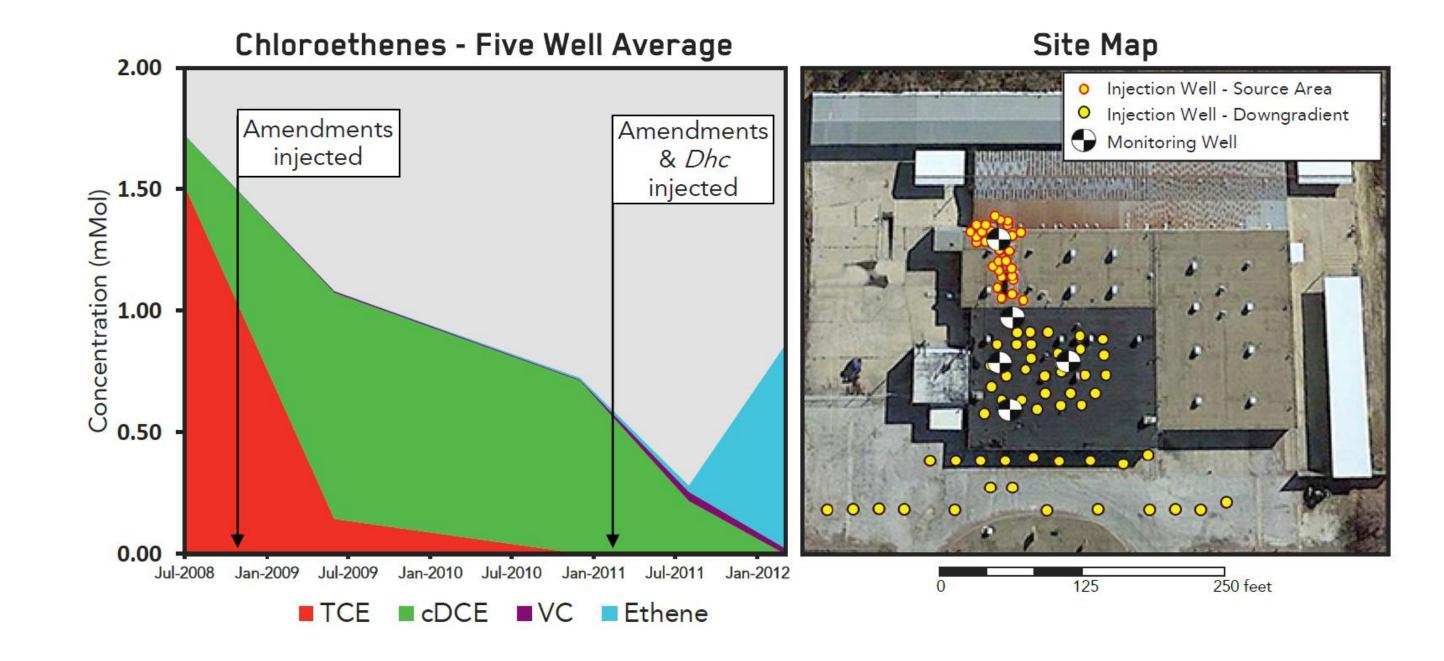
Source Area Injection Wells & Temporary Circulation Well **Biobarriers - Seal Beach Naval Weapons Station:** Direct injection into wells was used to treat the source area TCE plume. The dilute plume was treated with temporary circulation between wells spaced 15meters apart to create biobarriers. Each well used multi-elevation screens with flow paths isolated using straddle packers during injection events.



EVO, ZVI AND BIOAUGMENTATION WELL INJECTIONS – THE GOOD

EVO and zero valent iron (ZVI) have a synergistic effect that is ideal for a combined abiotic and biologica treatment approach for high concentrations of chloroethenes. Adding ZVI to injection fluids rapidly eliminates dissolved oxygen and creates a strongly reducing ORP prior to injection. This allows bioaugmentation cultures to be mixed into the bulk of the injection fluid prior to injection. The ZVI may reduce high concentrations of chloroethenes to reduce potential toxicity to microbes and increases alkalinity to help counter the acidity produced by electron donor fermentation and dechlorination.

Direct Injection of ZVI, Neutral Zone Buffer and EVO – Auto Parts Manufacturer: A ruptured degreaser at an auto parts manufacturing site resulted in a release of TCE. The shallow surficial aquifer consisted of silty sands with ground water contamination up to 500 mg/L near the site of the release and a dissolved plume that extended 200 feet down gradient of the source area with concentrations of TCE in excess of 100 mg/L. After the initial injection of Newman Zone EVO, Neutral Zone Buffer and a small micron ZVI, TCE was effectively converted to DCE but further reduction to VC and ethene was minimal. A second injection event of EVO, Neutral Zone and a bioaugmentation culture (from BCI) resulted in effective conversion of DCE to VC and ultimately ethene.

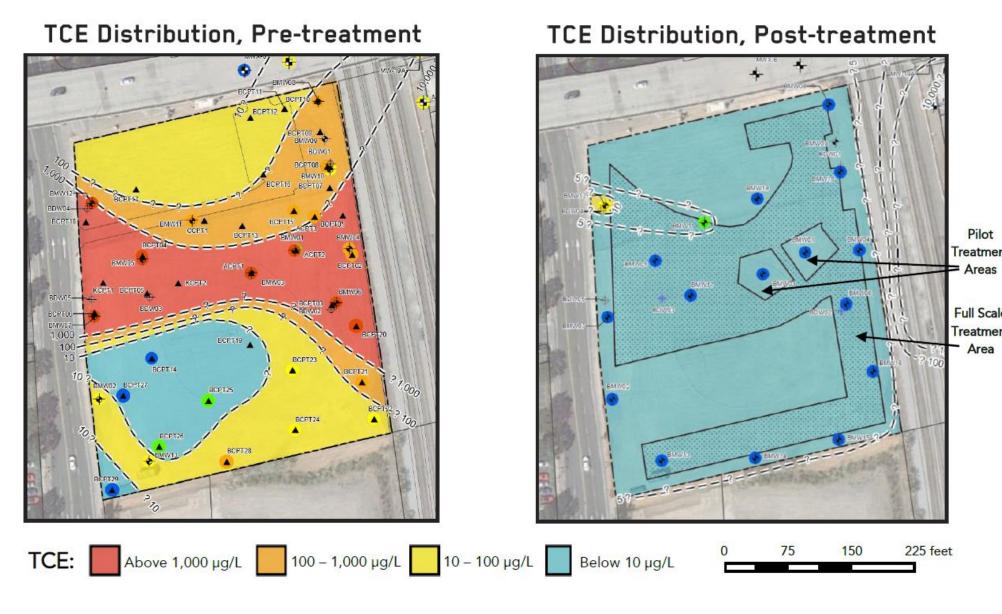


EVO LONGEVITY FOR ONE-AND-DONE INJECTIONS-THE GOOD

Direct Push Injections For Cost- Effective Treatment of Shallow Ground Water: Direct push injection methods are often ideal for contaminant source areas and dissolved plumes at depths of less than 30 meters. High resolution site characterization of contaminant profiles using membrane interface probes (MIP) combined with permeability information from hydraulic profiling tools (HPT) allows us to identify mobile dissolved contaminants and contaminated low permeability zones that slowly release contaminants by diffusion. Top-down, side-port injection methods allow for targeted injections in permeable zones that contain mobile dissolved contaminants. The use of a slow release electron donor allows a single injection event to create an active treatment zone for several years, allowing time for both advective flow and diffusion to make contaminants available in the EVO treated zones.

EVO Direct Push Injections Plus Bioaugmentation In One Injection Event: In the past bioaugmentation cultures were often injected in a separate injection event, days or weeks after electron donor injections had produced anaerobic conditions in the subsurface. The time and expense of making anaerobic chase water often limited the injection volumes used to distribute bioaugmentation cultures. Combining EVO and microiron and EVO or a low-cost oxygen scavenger like the Newman Zone OS product allows for a one-and-done injection. Electron donor, buffer, and bioaugmentation culture can be injected in a single event allowing bacteria, buffer and electron donor to be immediately distributed in the target area. EVO longevity often allows for a single injection event to complete treatment.

Direct Push Injection of EVO, Neutral Zone Buffer, Micrometal and Bioaugmentation Culture: A brownfield site with an industrial history was contaminated with PCE, TCE and associated daughter products in a sand and silty sand geology. The mobile contaminants were primarily located in high-permeability channels running across the site in an hour-glass shape. Poorly buffered soils resulted in a pre-treatment pH of as low as 5.6, too low for effective chlorethene reduction to ethene. Targeted injections using a combination of EVO, Neutral Zone buffer, a small amount of ZVI micrometal and KB-1 were performed in the sand channels using a 5-meter on center grid pattern. The EVO injections reduced CVOC concentrations by 98% and continue to maintain a favorable pH and reducing conditions.



EVO MAY BE TOO MOBILE AT SOME SITES – THE BAD

Newman Zone small droplet EVO is not significantly captured by straining in sandy soils although some adsorption of oil will always occur it may be too mobile in coarse sands and gravel with fast advective ground water flow. Newman Zone small droplet EVO injected in a coarse sand and gravel aquifer at Elmendorf AFB had poor retention and was not retained in the treatment area. Later injections using a larger oil droplet emulsion prepared on site was more effective. RNAS Remediation Products later developed a field emulsion product Newman Zone HRO to address this type of application with oil droplets of 1-10 microns and much higher oil retention in sandy soils and fractured bedrock.

BEWARE OF PREFERRENTIAL FLOW PATHS – THE UGLY

Although non-toxic, even dilute EVO is very visible as a bright white turbidity when it impacts surface waters which can be alarming to the public or property owners. Unexpected preferential flow paths in fractured bedrock and mounding during high flow injections into storm drains has resulted in EVO released into surface waters.





EVO LONGEVITY MAY CAUSE WELL FOULING – THE UGLY

Residual EVO in injection wells may form polymerized vegetable oil solids or freefatty acid "soap scum" residues that can foul well screens. Using sufficient clean "chase water" will usually eliminate this problem. Fouled well screens can usually be effectively treated with hot water and/or caustic solutions. Heavily fouled screens may be cleaned with a hydrogen peroxide or mild Fenton's reagent then bailed clean.



CONCLUSIONS

Overall EVO has proven to be a remarkably versatile slow release electron donor. By using a kinetically stable oil-inwater emulsion with sub-micron oil droplets we have greater mobility than other slow release electron donors. This mobility allows for injection methods that in the past could only be used with soluble substrates. Over the last sixteen years high resolution site characterization and targeted injection methods have improved to make in situ bioremediation more cost-effective. Bioaugmentation cultures have also become more affordable and when combined with ZVI and/or low-cost oxygen scavengers like Newman Zone OS allow for a one-and-done direct push injections of electron donor and culture at most sites.