Methane Generation During *In Situ* Reductive Treatment of Groundwater

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BACKGROUND

Carbon substrates that can be fermented to hydrogen and labile carbon compounds can enhance microbially-mediated reductive dechlorination of chlorinated volatile organic compounds (CVOCs) (Ballapragada, Stensel, Puhakka, & Ferguson, 1997; Smatlak, Gossett, & Zinder, 1996; Sung et al., 2003). Hydrogen is, however, also a substrate for methanogenic bacteria. The highest rates of anaerobic dechlorination of CVOCs typically occur under sulfate-reducing or methanogenic conditions (Parsons Corporation, 2004). In particular, Yang and McCarty (2000) report that the optimal concentrations of hydrogen for anaerobic dechlorination to occur range from 2 nmol/L (mid-range of sulfate reduction) to 11 nmol/L (mid-range of methanogenesis). A high concentration of hydrogen will favor methanogenesis and shift the microbial balance to the undesirable methanogens. Highly elevated concentrations of methane (greater than 5 to 10 mg/L) may indicate that the substrate is being consumed by methanogens at the expense of dechlorinating organisms (Parsons Corporation, 2004).

For *in situ* reductive bioremediation sites where production of methane is a potential health or safety hazard, additional analysis is warranted (Department of Toxic Substances Control, 2005). Methane has a solubility in water of 24.1 mg/L at room temperature (Mackay & Shiu, 1974) and methane concentration in groundwater above its solubility limit forms a gaseous phase into which CVOCs may partition from the aqueous phase (Van Breukelen, Griffioen, Roling, & Van Verseveld, 2004). The chemicals that volatilize into the gaseous phase do not undergo degradation. Consequently, CVOC “removal” may seem apparent but the overall amount of the chlorinated compounds actually degraded in the subsurface environment decreases. Furthermore, contaminant biodegradation may also be impacted by a separate gas phase occupying a part of the pore space and reducing the hydraulic conductivity of the aqueous phase (Islam & Singhal, 2004; Fortuin & Willemsen, 2005). This can lead to formation of preferential flow paths so that the contaminant plume circumvents areas of active biological activity, resulting in decreased remedial performance.

For reductive treatment of CVOCs in groundwater, factors that affect the production rate of methane in the subsurface include:

- Carbon substrate type and dosage;
- Site geochemistry (Eh, pH, concentration of electron acceptors);
- Supply of ferric iron-bearing minerals such as green rusts and other iron oxide/hydroxide minerals;
- Activity of indigenous microbial population and, if used, the added inoculum; and
- Biodegradability of the carbon substrate.

Factors that influence the potential for problematic levels of methane in the vadose zone include:

- Potential concentrations and volumes of methane that may be produced, controlled by the factors above;
- Depth to the treatment zone;
- Pathways for vapor migration, such as underground utilities;
- Advective flow rate (i.e. the ability to flush out dissolved methane); and
- Proximity to buildings and shallow impermeable layers that may cause gas buildup.

At most sites, the application of PeroxyChem's EHC® *in situ* chemical reduction reagent does not result in excessive methane accumulation; however, for some sites (e.g. injections under buildings containing explosive materials) additional consideration may be warranted. The purpose of this technical bulletin is to address concerns for such sensitive sites.

THEORETICAL CONSIDERATIONS

Essentially all commercial sources of fermentable carbon will enhance the activity of all hydrogen-utilizing microbes. However, EHC contains zero valent iron (ZVI) to uniquely elicit in situ chemical reduction (ISCR) reactions, and it is composed of a hydrophilic, solid and complex carbon source hence it generates little or no methane (< 5 mg/L) as observed in our bench-scale studies.

When compared to carbon only electron donors, EHC is less likely to generate excessive methane due to a combination of factors:

1. An active population of iron-reducing bacteria, which is promoted by the high iron content of EHC (i.e. 40% ZVI w/w), is known to inhibit methanogenesis (Lovley & Phillips, 1987; Roden & Wetzel, 1996; Van Bodegom, Sholten, & Stams, 2004). As ferrous iron is released from ZVI particles undergoing corrosion, it is subject to oxidation to ferric form and precipitates as a variety of ferric minerals. Good examples include ferrihydrite and goethite. The ferric iron in these minerals becomes the electron acceptor for iron reducing bacteria (Weber, K. A., Achenbach, L. A., & Coates, J. D., 2006) which compete with methanogens for available electron donors, thereby suppressing methane formation. Thus, stimulation of the ferric iron reducing bacteria by the iron content of EHC will, in many cases, suppress or eliminate excessive methane generation.
2. The main carbon component of EHC is insoluble, cellulose-rich, micro-scale plant fiber. As such it is hydrophilic, complex, and slowly metabolized. Since cellulose is not transported into bacterial cells, biodegradation/fermentation of the carbon component of EHC requires the presence of extracellular cellulase enzymes to hydrolytically transform EHC/cellulose into water soluble mono-and di-saccharides that can be transported across bacterial cell walls. Rather, these simple sugars can be subsequently biodegraded by other soil microorganisms that convert the sugars into CO_2 and H_2; under certain environmental conditions, CO_2 can serve as an electron sink liberating methane. Further, methane is not produced by cellulolytic bacteria.
3. EHC is added as a slurry of suspended solids typically at a concentration of less between 0.1% and 0.5% (soil weight basis), and provides a slowly-consumed, long-lasting carbon source. In contrast, molasses and emulsified oils are usually added at higher concentrations along with very rapidly biodegraded "boosters"

such as lactate, and all are chased with large volume of water to distribute the amendments *in situ*. This facilitates rapid decomposition sometimes generating large amounts of CO_2/CH_4 which can potentially accumulate.

4. As compared to the addition of molasses, lactate, and emulsified oils, the amount of carbon dioxide (CO_2) produced from EHC is limited by insoluble character and slowly-metabolized nature of EHC carbon. This effectively limits the activity of hydrogen-oxidizing methane producers. (CO_2 serves as the electron acceptor for various methanogenic bacteria which thereby generate methane.)
5. The ZVI component of EHC has a known ability to store hydrogen gas in the lattice structure, thus mediating the buildup of high levels of hydrogen gas which may stimulate excessive methanogenesis. For example, Reardon (1995) notes that researchers were able to induce over 1 L of hydrogen into 1 kg of iron by electrolytic charging.
6. Generally speaking, methanogens prefer slightly acidic pH. ISCR applications that use EHC do not favor methanogens because the high iron content of EHC results in release of alkalinity which prevents acidification in the treatment zone.

Overall, methanogens are most active in an Eh range of -200 to -250 mV. Microbiological reactions can reduce the Eh of an aquifer to about -275 to -300 mV. Because EHC uniquely contains ZVI, very low Eh conditions are established, in the range of -400 to -600 mV *in situ*, (defined herein as ISCR) which tends to favor the activity of acetogens and other hydrogen-utilizing microbes.

Theoretical calculations for methane generation can be performed for a given application considering site conditions and amendment mass loadings. Such calculations are, however, of limited value for field applications because they cannot allow for other important such as vadose zone gas migration, venting, and methane utilization. Actual field data, as presented in the next section, are of more value.

FIELD DATA

The carbon moiety of EHC is composed of plant fibers that allow it to ferment at different rates. In field projects, an initial spike in methane concentrations is sometimes observed due to the rapid fermentation of the more readily biodegraded carbon elements, elements that are desired to allow rapid reduction of the redox potential in the aquifer. Once this carbon is consumed, the more persistent, cellulose-based carbon elements are more slowly degraded, which allows for sustained activity. We have monitored soil vapor and/or dissolved methane at a few sites where EHC has been employed. In general, higher methane concentrations have occasionally been observed at sites with more permeable lithologies and where EHC was applied at higher loading rates (e.g., 0.25% EHC by soil mass) at shallower depths (e.g., 10 to 15 ft bgs).

FIELD PROJECTS

Oregon Project 1: EHC was applied at a higher loading rate (0.6% EHC to soil mass) at a shallow depth (*ca.* 10 ft bgs) into a lower permeability silty clay aquifer, the maximum amount of methane in soil gas observed to date at this site has been about 6.5 mg/m^3.

Oregon Project 2: EHC application at a higher loading rate (*ca*. 1% EHC to soil mass) into a more permeable silty sand aquifer at deeper depths (*ca.* 80 to 120 ft bgs) did not yield methane gas accumulation.

North Carolina Project 1: At a Marine Corps site in North Carolina, methane concentration was monitored in soil gas beneath a slab following EHC injection. Here, negligible methane concentrations were observed (EHC application rate *ca*. 0.1% EHC to soil mass; relatively shallow application starting at *ca*. 15 ft bgs).

North Carolina Project 2: Elevated methane was monitored in the groundwater. Interpretation of the observed methant is, however, complicated by the presence of chloroform, methylene chloride, and chloromethane in the impacted groundwater (EHC application rate between 0.2 and 0.7% EHC to soil mass; relatively shallow application starting at *ca*. 10 ft bgs). Maximum observed dissolved methane concentrations are shown in **Figure 1**, and equivalent vadose zone concentrations are shown in **Figure 2**.

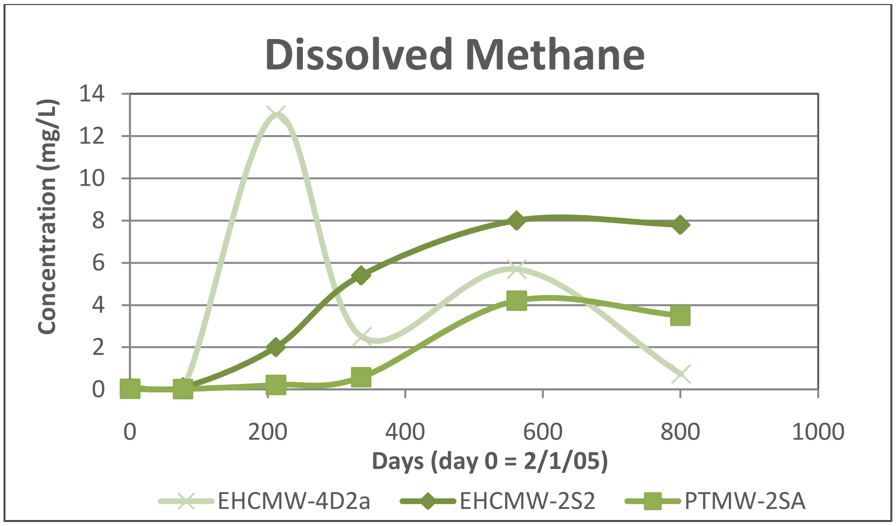

Figure 1: Observed Dissolved Methane Concentrations at North Carolina Project 2

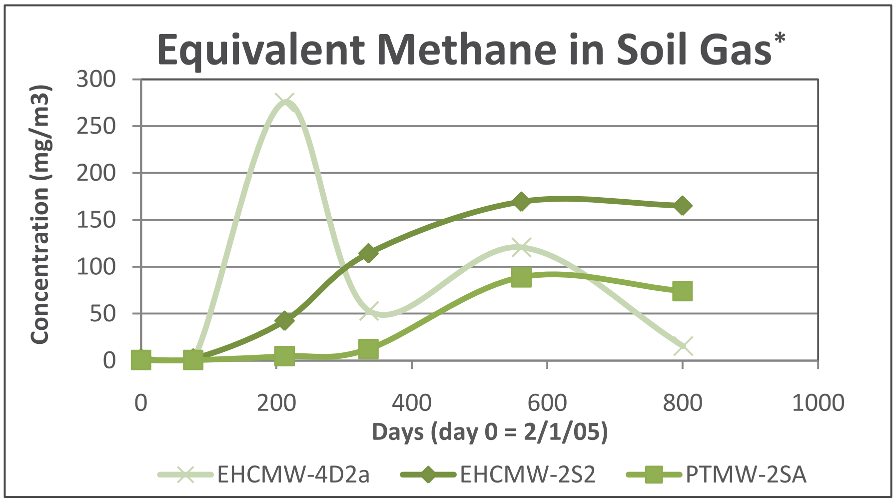

Figure 2: Calculated Vadose Zone Methane Concentrations at North Carolina Project 2
*Assumes equilibrium soil vapor-groundwater concentrations

SUMMARY

Carbon substrates used to enhance reductive dechlorination produce high concentrations of hydrogen that may support methanogenesis. High levels of methane are a potential health or safety hazard, providing a gaseous phase into which CVOCs may partition, and a partially saturated, lower hydraulic conductivity zone bypassed by groundwater flow and CVOC transport.

The high iron content of EHC (i.e. 40% ZVI w/w), results in the formation of a range of ferric minerals which serve as electron acceptors for iron reducing bacteria which compete with methanogens for available electron donors, thereby suppressing methane formation.

When compared to many simple carbon-alone electron donors, EHC, which is composed of a combination of plant-based carbon and ZVI, is less likely to generate excessive methane because it is more slowly metabolized. The first step in metabolism of insoluble carbon in EHC requires that activity of cellulolytic bacteria, which are not methane producers. Further, because EHC is generally applied at lower dosages than carbon-only substrates, carbon dioxide production (and hence methane generation) is often lower. Finally, the pH and Eh conditions generated in an EHC treatment zone are not conducive to methanogenesis.

Bench scale studies have demonstrated EHC-related methane generation of less than 5 mg/L. Routine field applications of EHC have not resulted in excessive methane accumulation. Occasionally, higher methane concentrations have been observed at sites with more permeable lithologies where EHC was applied at higher loading rates (e.g., above 0.25% EHC by soil mass) at shallower depths (e.g., 10 to 15 ft bgs). Four field examples showing methane gas measurements of zero to 6.5 mg/m3 are summarized.

Methane diffusion to the atmosphere and in situ degradation during transport may be sufficient to mitigate any safety concerns. If, however, there is potential concern regarding methane generation/accumulation at a particular site, then it is recommended that a field-scale pilot test is conducted at a location outside the sensitive area/building which can be monitored for soil gas prior to full-scale implementation within the sensitive area. Alternatively, a lower application rate (ca. 0.1%) can be used beneath the building with the option for a second application later, if required, in order to minimize the potential for methane generation.

REFERENCES

Ballapragada, P. S., Stensel, H. D., Puhakka, J. A., & Ferguson, J. F. (1997). Effect of hydrogen on reductive dechlorination of chlorinated ethenes. *Environmental Science & Technology, 31,* 1728-1734.

Department of Toxic Substances Control. (2005). Response to comments on the remedial action plan, Central Los Angeles High School #1l, First Street and Beaudry Avenue, Los Angeles. Retrieved from http://www.dtsc.ca.gov/Schools/Projects/upload/CLAHS_Ltr_RAP-Response.pdf

Fortuin, N. P. M., & Willemsen, A. (2005). Exsolution of nitrogen and argon by methanogenesis in Dutch ground water. *Journal of Hydrology*, *301*(1-4), 1-13.

Islam, J., & Singhal, N. (2004). A laboratory study of landfill-leachate transport in soils. *Water Res, 38*, 2035–2042.

Lovley, D. R. & Phillips, E. J. P. (1987). Competitive mechanisms for inhibition if sulfate reduction and methane production in the zone of ferric iron reduction in sediments. *Applied Environmental Microbiology, 53*(5), 2636-2641.

Mackay, D., & Shiu, W. Y. (1974). The aqueous solubility and air-water exchange characteristics of hydrocarbons under environmental conditions. In: Chemistry and Physics of Aqueous Gas Solutions, *Am. Soc. Test. Mat*., Philadelphia, PA, pp. 104–108.

Parsons Corporation. (2004). Principles and practices of enhanced anaerobic bioremediation of chlorinated solvents. AFCEE, NFEC, ESTCP 1-457.

Reardon, E. J. (1995). Anaerobic corrosion of granular iron: Measurement and interpretation of hydrogen evaluation rates. *Environmental Science & Technology, 29*(12), 2936-2945.

Roden, E. E., & Wetzel, R. G. (1996). Organic carbon oxidation and suppression of methane production by microbial Fe(III) oxide reduction in vegetated and unvegetated freshwater wetland sediments. *Limnology & Oceanography*, *41*, 1733-1748.

Smatlak, C. R., Gossett, J. M., & Zinder, S. H. (1996). Comparative kinetics of hydrogen utilization for reductive dechlorination of tetrachloroethene and methanogenesis by an anaerobic enrichment culture. *Environmental Science and Technology, 30,* 2850-2858.

Sung, Y., Ritalahti, K. M., Sanford, R. A., Urbance, J. W., Flynn, S. J., Tiedje, J. M., & Loffler, F. E. (2003). Characterization of two tetrachloroethene-reducing, acetate-oxidizing anaerobic bacteria and their description as Desulfuromonas michiganensis sp. nov. *Applied Environmental Microbiology, 69*(5), 2964-2974.

Van Bodegom, P. M., Sholten, J. C. M., & Stams, A. J. M. (2004). Direct inhibition of methanogenesis by ferric iron. *FEMS Microbiology Ecology, 49,* 261-268.

Van Breukelen, B. M., Griffioen, J., Roling, W. F. M., & Van Verseveld, H. W. (2004). Reactive transport modelling of biogeochemical processes and carbon isotope geochemistry inside a landfill leachate plume. *Journal of Contaminant Hydrology, 70*, 249–269.

Weber, K. A., Achenbach, L. A., & Coates, J. D. (2006). Microorganisms pumping iron: Anaerobic microbial iron oxidation and reduction. *Nature, 4*, 752-764.

Yang, Y., & McCarty, P. L. (2000). Biologically enhanced dissolution of tetrachloroethene DNAPL. *Environmental Science & Technology*, *34*(14), 2979-2984.