

## Novel Method to Enhance Chlorinated Solvent Biodegradation by the Use of Barriers

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**Abstract:** Physical containment has several advantages for managing chlorinated solvent plumes, but is not considered at many sites because of the perception that it does not remove or destroy contaminant mass. Because of this perception, other remediation approaches that do remove mass are often favored, even if they remove it slowly (such as natural attenuation) or are expensive (long-term pumping).

Our biodegradation research indicates that barrier systems will result in increased contaminant destruction at many chlorinated solvent sites. Chlorinated solvent biodegradation occurs when *electron donors* (carbon substrates that form dissolved hydrogen) are utilized by naturally-occurring dechlorinating bacteria in the subsurface to consume *electron acceptors* (the chlorinated solvents). This process occurs naturally at many sites (when source materials contain both solvents and electron donors), and can be enhanced by supplementing the electron donor supply. However, our research shows that the efficiency of naturally-occurring and enhanced biodegradation is compromised by the transport of *competing electron acceptors* (i.e., dissolved oxygen, nitrate, and sulfate) to solvent biodegradation zones via the flow of clean upgradient groundwater through the source.

By constructing a low-cost, low-permeability containment barrier upgradient of a chlorinated solvent source zone, three benefits will be realized: 1) competing electron acceptors will be diverted away from the source zone, thereby increasing the rate of naturally-occurring bioremediation; 2) the plume will shorten dramatically, greatly reducing long-term monitoring costs; and 3) the plume will be controlled without pumping. Calculations based on a 14-site database show that such a barrier system will be inexpensive, reliable, and have the potential to increase the rate of naturally-occurring chlorinated solvent biodegradation by an order of magnitude at a typical chlorinated solvent site undergoing natural attenuation.

**Introduction:** Hydrogen is now widely recognized as a key electron donor required for the biologically-mediated dechlorination of chlorinated compounds. In this process, hydrogen acts as an *electron donor* and halogenated compounds such as chlorinated solvents act as *electron acceptors*, becoming reduced in the reductive dechlorination process. At sites where natural dechlorination is occurring, organic substrates such as aromatic hydrocarbons (BTEX), landfill leachate, or other non-chlorinated organics are fermented by indigenous bacteria to provide a source of dissolved hydrogen. The hydrogen is then utilized as an electron donor by naturally occurring dechlorinating bacteria to achieve reductive dechlorination of chlorinated compounds.

The dechlorinating reaction only occurs in the appropriate geochemical environment, i.e., deeply anaerobic conditions where concentrations of competing electron acceptors are low. In addition to low dissolved oxygen concentrations, there should be low concentrations of nitrate and

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moderate to low concentrations of sulfate, as many bacteria will preferentially use these compounds over chlorinated solvents as electron acceptors. Almost all of the oxygen and nitrate, and in some cases some of the sulfate, must be consumed through reaction with source-zone electron donors (non-chlorinated organic substrates and/or hydrogen) before the appropriate geochemical environment is produced.

To accelerate the natural dechlorination process for the purpose of bioremediation, numerous research groups have focused on methods to increase the supply of electron donors to the dechlorinating bacteria. Most researchers and technology developers add indirect electron donors (such as lactate, molasses, mulch, etc.) that ferment in-situ to produce hydrogen or employ the direct addition of hydrogen. A third method of increasing the effective supply of electron donor to dechlorinating bacteria, discussed below, may provide significant cost and operational advantages compared to the other two methods.

**Technology Description:** By permanently interrupting the transport of competing electron acceptors (oxygen, nitrate, and sulfate) to chlorinated solvent plumes, more electron donor (i.e., organic substrates and/or dissolved hydrogen) is preserved for beneficial reductive dechlorination reactions. This approach involves constructing a low-cost barrier upgradient of a chlorinated solvent source zone to reduce the transport of competing electron acceptors into the source zone (Figure 1). Our initial calculations (below) show that such an Enhance Reductive Dechlorination Zone (ERDZ) would be inexpensive, reliable, and have the potential to increase the rate of natural biological attenuation processes by an order of magnitude at some sites.

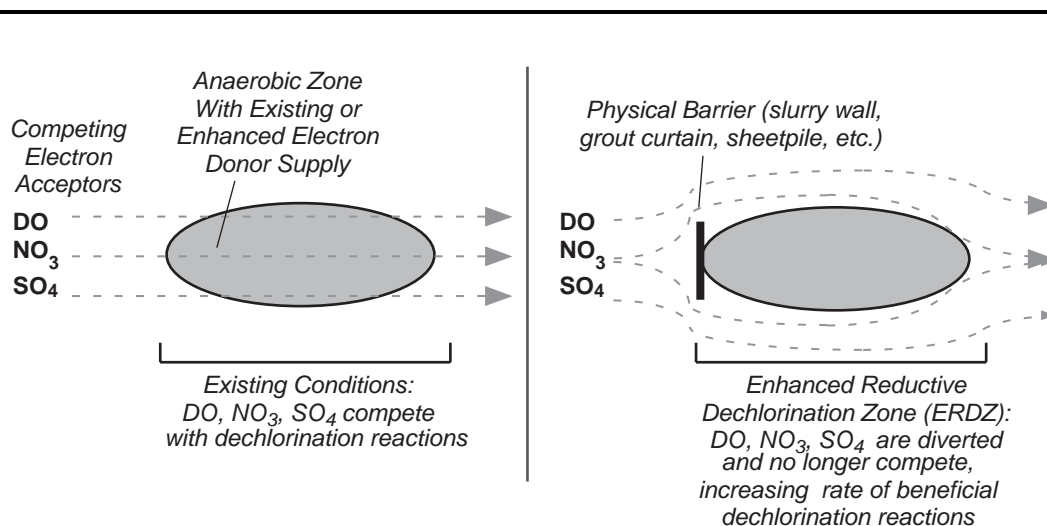


FIGURE 1. Conceptual model of Enhanced Reductive Dechlorination Zone (ERDZ) barrier. (Note that a hydraulic barrier pumping clean groundwater upgradient of the plume is an alternate configuration)

**Destruction Performance:** By diverting the transport of competing electron acceptors (oxygen, nitrate, and sulfate) around a contaminated groundwater zone, the electron donor supply to the beneficial reductive dechlorination reactions is significantly increased. For example, evaluation of a 14-site chlorinated site database in Wiedemeier et al. (1999) indicates the potential effectiveness of an ERDZ approach. Key plume parameters from this database are shown below:

Median plume/source width: 400 ft	Median Background D.O.: 8.0 mg/L
Median seepage velocity: 110 ft/yr	Median Background NO <sub>3</sub> : 5.8 mg/L
Median saturated thickness: 40 ft	Median Total Chlor Solvents in Source: 1.5 mg/L

Assuming a porosity of 0.3, a representative specific discharge through a chlorinated solvent source zone is equivalent to  $15 \times 10^6$  L/yr of flow. Approximately 120 kg of dissolved oxygen and 87 kg of nitrate flow into a representative source zone per year, where they compete for electron donor. One method to account for the potential amount of lost reductive dechlorination to competing electron acceptors is to assume that every 16 kilograms of dissolved oxygen can consume the equivalent of 2 kilograms of dissolved hydrogen (based on the stoichiometry of water formation), and that every 50 kilograms of nitrate can consume the equivalent of 4 kilograms of dissolved hydrogen (based on the stoichiometry of nitrate reduction). Therefore, the introduction of the 120 kilograms of dissolved oxygen and 87 kilograms of nitrate into the source zone per year is equivalent to the consumption of 22 kilograms of dissolved hydrogen per year (i.e.,  $22 = (120) \cdot (2/16) + (87) \cdot (4/50)$ ). Finally, using the accepted stoichiometry whereby 1 kg of hydrogen has the potential to completely dechlorinate 21 kilograms of PCE, then an additional 462 kg of PCE could be completely dechlorinated to ethene per year assuming no loss to other mechanisms.

By comparison, naturally-occurring reductive dechlorination processes in a source zone at a typical chlorinated solvent site may be on the order of tens of kilograms per year. Using the BIOCHLOR natural attenuation model with the site data above and a typical biodegradation rate coefficient for chlorinated solvents from the BIOCHLOR database (0.63 per year) (Aziz et al., 2000), it is estimated that only 20 kilograms of solvents are naturally biodegraded per year in a 400 ft by 200 source zone.

Therefore, merely diverting the competing electron acceptors away from the source zone has the potential to increase the biodegradation of chlorinated solvents in the source zone of a representative chlorinated solvent site from about 20 to 482 kilograms per year, greater than a 20-fold increase in the naturally occurring biodegradation rate. The diversion of competing electron acceptors can be performed in a number of ways, but most likely can be achieved by the construction of a physical barrier upstream of the source zone using conventional geotechnical barrier techniques (slurry wall, grout curtain, etc.).

In summary, by constructing a low-cost, low-permeability containment barrier upgradient of a chlorinated solvent source zone, three benefits will be realized: 1) competing electron acceptors will be diverted away from the source zone, thereby increasing the rate of naturally-occurring bioremediation; 2) the plume will shorten, greatly reducing long-term monitoring costs; and 3) the plume will be controlled without pumping. Such a barrier system will be inexpensive, reliable, and have the potential to significantly increase the rate of chlorinated solvent biodegradation at a typical chlorinated solvent site already undergoing natural attenuation.

#### References:

Wiedemeier, TH, Rifai, HS, Newell, CJ, and Wilson JT (1999) *Natural Attenuation of Fuel Hydrocarbons and Chlorinated Solvents*, John Wiley and Sons, New York, New York.