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Long-term sustainability of reductive dechlorination reactions at chlorinated solvents sites

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Abstract

The sustainability of biodegradation reactions is of interest at Type 1 chlorinated solvent sites where monitored natural attenuation is being considered as a remedial alternative. Type 1 chlorinated solvent sites are sites undergoing reductive dechlorination where anthropogenic substrates (such as landfill leachate or fermentable organics in the waste materials) ferment to produce hydrogen, a key electron donor. A framework is provided that classifies Type 1 chlorinated solvent sites based on the relative amounts and the depletion rates of the electron donors and the electron acceptors (i.e., chlorinated solvents). Expressions are presented for estimating the total electron donor demand due to the presence of solvents and competing electron acceptors such as dissolved oxygen, nitrate, and sulfate. Finally, a database of 13 chlorinated solvent sites was analyzed to estimate the median and maximum mass discharge rate for dissolved oxygen, nitrate, and sulfate flowing into chlorinated solvent plumes. These values were then used to calculate the amount of hydrogen equivalents and potential for lost perchloroethylene (PCE) biodegradation represented by the inflow of these competing electron acceptors. The median and maximum mass of PCE biodegradation lost due to competing electron acceptors, assuming 100% efficiency, was 226 and 4621 kg year^{-1}, respectively.

Background

Sustainability is a key factor governing the long-term effectiveness of natural attenuation. The United States National Research Council (NRC) describes sustainability as occurring when the mechanisms that destroy or immobilize contaminants are sustainable for as long as the source area releases the contaminants to the groundwater (NRC 2001). While the US Environmental Protection Agency's Monitored Natural Attenuation (MNA) Directive does not refer to sustainability directly, it does conclude that the effectiveness of MNA in the near and long term should be demonstrated to the EPA (or other overseeing regulatory authority) through: (1) sound technical analyses that provide confidence in natural attenuation's ability to achieve remediation objectives; (2) performance monitoring; and (3) contingency remedies where appropriate (US EPA 1999).

Sustainability can be estimated using a mass-balance analysis to estimate the long-term destruction rates of contaminants by natural attenuation processes (NRC 2001). At fuel hydrocarbon sites, the mass balance approach indicates that four out of five key biodegradation reactions are likely to be continuous and renewable at most sites. Electron acceptors such as O_2, NO_3^-, and SO_4^{2-} are transported to the contaminated zone *via* the influx of upgradient groundwater into the source zone where fuel hydrocarbons serve as electron donors. Methanogenesis is likely to be sustainable for long-time periods because it produces CH_4 from hydrogen and carbon dioxide or acetate in zones where other electron acceptors have been effectively depleted. Of the five most commonly evaluated fuel biodegradation reactions, only the reduction of ferric iron (Fe^{3+}) is non-renewable. Ferric iron is found on the matrix of the water-bearing unit and is slowly consumed as the iron reduction reaction proceeds.

At sites with chlorinated aliphatic compounds undergoing naturally-occurring biological reductive dechlorination reactions, the contaminants are not electron donors but serve as electron acceptors. This has significant implications for evaluating the sustainability of chlorinated solvent reactions. Reductive dechlorination at solvent sites is controlled by the availability of electron donors from two potential sources: (i) donor that is supplied to groundwater from man-made sources, such as fuels that were released into the subsurface at the same time solvents were released (termed a Type 1 site), or (ii) donor that is delivered to the

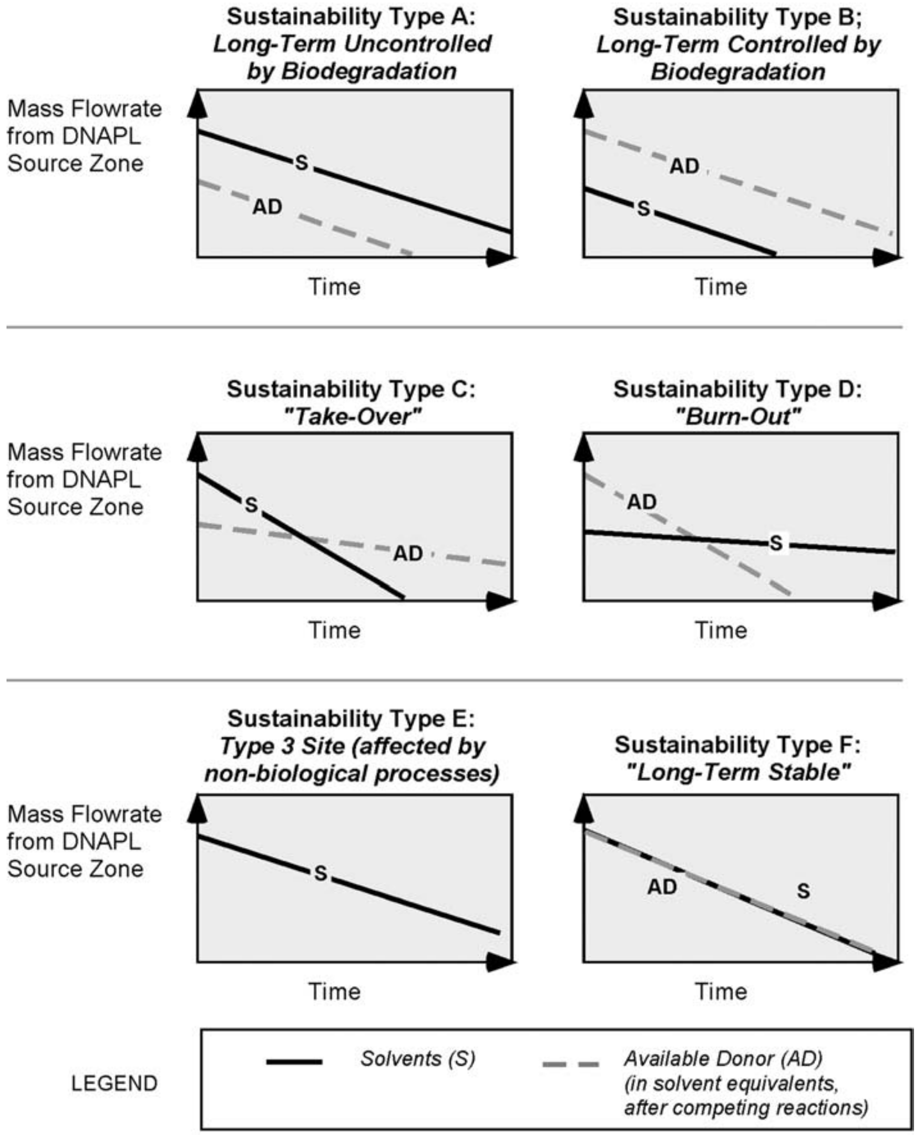

Figure 1. Example of different sustainability types for natural attenuation processes at chlorinated solvent sites.

source zone by groundwater that is rich with naturally-occurring organics (termed a Type 2 site) (Wiedemeier et al. 1999).

For a Type 2 solvent site, the reductive dechlorination reactions are likely to be sustainable indefinitely unless the supply of naturally occurring organics to upgradient groundwater is somehow interrupted. Unfortunately, a review of two chlorinated solvent plume databases (Aziz et al. 1999; Wiedemeier et al. 1999) suggests that Type 2 solvent sites are relatively rare compared to Type 1 solvent sites or Type 3 solvent sites (sites with no active reductive dechlorination processes).

At Type 1 sites, however, there is a concern that the supply of electron donor may not be sustainable over the long-time frames required to manage chlorinated solvent source zones. In contrast to fuel sites, the driving force behind biodegradation (the electron donor) is in finite supply and can, in theory, be exhausted over time. If electron donor depletion occurs, this 'burn-out' will cause once stable or shrinking plumes to expand. To describe the potential for 'burn-out' in more detail, a conceptual framework for the sustainability of biological reductive dechlorination reactions is provided below.

Type 1 site conceptual model

At most chlorinated solvent sites, the dissolved solvent plume originate from dense nonaqueous phase liquid (DNAPL), which has migrated from a surface or near-surface release point to the saturated zone. Although some plumes originate from the release of dissolved constituents alone to the saturated zone and some plumes may originate only from waste materials on the surface or in the unsaturated zone, these conditions are relatively rare (Wiedemeier et al. 1999).

At a Type 1 chlorinated solvent site, an anthropogenic electron donor plume mixes with a dissolved chlorinated solvent plume to form conditions suitable for reductive dechlorination. The electron donors can be introduced to groundwater in two general ways: (1) mixing of two different plumes from two different sources; or (2) mixing of fuels and solvents during the original release events to form DNAPLs containing both fuels and solvents.

Sustainability conceptual framework

The sustainability conceptual framework presented here plots chlorinated solvent availability and electron donor availability over time. Electron donor is expressed as equivalents of donor that is available to fuel reductive dechlorination reactions after accounting for competing reactions. The framework assumes that the concentration of solvent and donor will both decline over time as the source is attenuated. Based on this framework, a site can be classified into one of six different sustainability types. Examples of the six different sustainability types are shown in Figure 1 and are described below.

Sustainability Type A: The available donor ('AD') is always present in lower available equivalents than the solvent ('S'), resulting in a solvent plume that is uncontrolled by biodegradation over the short term and long term.

Sustainability Type B: The available donor ('AD') is always present in higher available equivalents than the solvent ('S'), resulting in a solvent plume that is controlled by biodegradation over the short term and the long-term.

Sustainability Type C ('*Take-Over*'): The available donor ('AD') starts out with lower available equivalents than the solvent ('S'), but the rate of concentration decline for solvents is greater than the rate of decline for the donor. Therefore at some point in the future biodegradation will 'take over' control of the plume and the plume will eventually stabilize and shrink.

Sustainability Type D ('*Burn-Out*'): The opposite of 'Take-Over', where the decline in donor concentrations is greater than the decline in concentrations in solvents. Therefore a plume that is controlled in the beginning of the plume's lifetime becomes uncontrolled at some point in the future, resulting in an expanding plume.

Sustainability Type E: This curve describes a Type 3 solvent site, where no donor is available. The plume is uncontrolled by biodegradation.

Sustainability Type F: This curve describes the case where solvent and donor both exhibit the same decline curve, resulting in a long-term stable condition. This condition is unlikely at actual sites.

Sustainability Types B, C, and F are sustainable over the lifetime of a chlorinated solvent plume undergoing reductive dechlorination. Sustainability Types A, D, and E are not sustainable. The linear decline curves on each graph in Figure 1 are conceptual only; the actual decline curve will likely have a more complicated pattern than a constant decline.

To apply this sustainability framework to a particular site, three types of information are needed: (i) the mass of donor and solvents that will be introduced to groundwater; (ii) the mass discharge rate of donor and solvent into groundwater over time; and (iii) the stoichiometry of reactions of donor with solvents, competing electron acceptors, and other reactions. Some tools are now being developed to evaluate the mass of contaminants in source zone and estimate the mass discharge overtime (e.g., Farhat et al. 2004). In practice, estimating (i) and (ii) above will entail significant uncertainty (i.e., orders of magnitude). A method to estimate the stoichiometry of key reactions is presented below.

Sustainability mass balance calculations

Lumped reaction method

Common practice at enhanced reductive dechlorination sites is to add at least 25–100 g of donor to dehalogenate 1 g of chlorinated solvent (Wiedemeier 1999; Yang & McCarty 2002). This ratio considers stoichiometry and addresses competition from other electron acceptors such as O_2, NO_3, and SO_4^{2-} and from methanogenesis. Therefore, the total mass of the donor that will be available to sustain the reductive dechlorination reactions should be at least 25–100 times the total mass of chlorinated solvents in the source zone. To make this type of mass balance calculation, estimates of the solvent mass in the source zone (e.g., in the DNAPL or the mass in a landfill) and the mass of donor (either in the DNAPL, as an LNAPL, or from a landfill) are required.

Use of simple ratios does not account for different mass discharge rates that would result in a Type D burnout condition, but does help to estimate the minimum amount of donor required to dechlorinate solvents present in a Type 1 source zone. This method also does not consider nonbiological attenuation processes (i.e., dispersion, sorption, and abiotic reactions) that will contribute to control the plume. A more detailed analysis would require knowledge of the change in mass discharge of donor and solvent into groundwater over time.

Separate reaction method

In theory, the stoichiometry of reductive dechlorination reactions can be used to estimate the mass of the donor required to sustain reductive dechlorination. Although this approach has many practical difficulties, the separate reaction approach is summarized below. This approach below is based on the stoichiometry of dissolved hydrogen as the electron donor.

First the stoichiometry of dechlorination of the chlorinated solvents must be considered to determine the amount of electron donor required. For the complete dechlorination of PCE to ethene, 1 g of dissolved hydrogen gas (H_2) is needed to completely dechlorinate 21 g of PCE, assuming 100% conversion. For TCE, *cis*-DCE, and VC, the ratios of hydrogen to solvent are 1:22, 1:24, and 1:31, respectively.

The stoichiometry for competing electron acceptors is shown below and can be used to calculate the total mass of hydrogen required to consume competing electron acceptors.

(i) Every 16 g of dissolved oxygen can consume the equivalent of 2 g of dissolved hydrogen based on the stoichiometry of water formation. The total mass of dissolved oxygen that will react with the donor can be estimated by multiplying the mass discharge of dissolved oxygen entering the source zone (in units of mass per time) by the time period where chlorinated solvents are being dissolved from the source zone to groundwater (i.e., the lifetime of the source zone).

(ii) Every 21 g of nitrate can consume the equivalent of 2 g of dissolved hydrogen based on the stoichiometry of nitrate reduction. The total mass of nitrate that will react with the donor can be estimated using the same method as used for dissolved oxygen above.

(iii) Every 20 g of sulfate can consume the equivalent of 2 g of dissolved hydrogen based on the stoichiometry of sulfate reduction. The total mass of sulfate that will react with the donor can be estimated using the same method as used for dissolved oxygen above.

(iv) Every 56 g of bioavailable ferric iron (Fe^{3+}) consumed represents the equivalent of 1 g of dissolved hydrogen consumed. The total mass of ferric iron on soil in the source zone that will react with the donor can be estimated by estimating the concentration of bioavailable iron using methods summarized by Kennedy et al. (2002) and multiplying by the mass of saturated soil in the source zone.

(v) Every 2 g of methane produced represents the equivalent of 1 g of dissolved hydrogen consumed. The total mass of methane can be estimated by multiplying the mass discharge of methane leaving the source zone by the time period where chlorinated solvents are being dissolved from the source zone to groundwater.

(vi) Every gram of BTEX that is fermented results in the production of between 0.25 and 0.4 g of H_2 (Wiedemeier et al. 1999). Fuel hydrocarbons such as BTEX compounds are common electron donors at Type 1 solvent sites, as fuels and solvents are often disposed together.

Therefore, the minimum mass of required donor (H_2) to sustain reductive dechlorination over the entire lifetime at a Type 1 chlorinated ethene site will be:

$$\begin{aligned}\mathrm{Mass}_{H_2} = {} & \frac{\mathrm{Mass}_{PCE}}{21} + \frac{\mathrm{Mass}_{TCE}}{22} + \frac{\mathrm{Mass}_{DCE}}{24} \\ & + \frac{\mathrm{Mass}_{VC}}{31} + \frac{\mathrm{Mass}_{O_2}}{8} + \frac{\mathrm{Mass}_{NO_3^-}}{10.5} \\ & + \frac{\mathrm{Mass}_{SO_4}}{10} + \frac{\mathrm{Mass}_{Fe^{3+}}}{56} + \frac{2 \cdot \mathrm{Mass}_{CH_4}}{1}\end{aligned}$$

As with the lumped reaction method, the separate reaction method does not consider different mass discharge rates that would result in a Type D burnout condition. It only incorporates the minimum amount of donor required to dechlorinate solvents present in Type 1 source zone. The separate method also does not consider nonbiological attenuation processes, such as dispersion, sorption, and abiotic reactions, which will also act to control the plume. It also does not explicitly incorporate hydrogen utilization *via* acetogenesis (He et al. 2002) but overestimates the hydrogen demand from methanogenesis as some methane will be generated by the breakdown of acetate.

Impact of competing electron acceptors on sustainability

The transport of O_2, NO_3^-, and SO_4^{2-} into source zones at Type 1 chlorinated solvent sites is an important electron donor sink that can reduce the long-term sustainability of natural attenuation. As an example, a database of 13 chlorinated solvent plumes was evaluated to estimate an upper-range electron donor demand due to competing electron acceptors entering the source area in incoming groundwater (Table 1).

The flow rate through a volume occupied by a representative chlorinated solvent plume was estimated by multiplying groundwater seepage velocity by the plume width, plume thickness, and by an estimated porosity of 0.3. This approach results in an average flow rate for the 13 chlorinated solvent sites of 2.9×10^7 l year^{-1}, with a range of 1.3×10^5–1.5×10^8 l year^{-1} (Table 2). The median value is nine times smaller than the average, indicating a skewed distribution where several sites with extremely large flow rates increase the average relative to the median.

This flow rate was then multiplied by the concentration of dissolved oxygen, nitrate, and sulfate observed in clean groundwater flowing into the chlorinated solvent plume volume (Table 1) to yield the mass discharge rate for each of the competing electron acceptors. As seen in Table 2, the median mass discharge rates are 11 kg year^{-1} for dissolved oxygen, 5 kg year^{-1} of nitrate, and 89 kg year^{-1} of sulfate. Again, a few sites from the 13-site database have much larger mass discharge rates, with maximum values of 179 kg year^{-1} of dissolved oxygen, 235 kg year^{-1} of nitrate, and 1753 kg year^{-1} of sulfate.

Using the stoichiometry outlined previously for these three competing electron acceptors, the introduction of 11 kg year^{-1} of dissolved oxygen, 5 kg year^{-1} of nitrate, and 89 kg year^{-1} of sulfate into the source zone per year is equivalent to the consumption of 10.7 kg year^{-1} of dissolved hydrogen (i.e., 10.7 = (11)•(2/16) + (5)•(2/21) + (89)• 2/20)). If one assumes that 0.3 g of hydrogen is produced per gram of organic that is fermented, then the competing electron acceptors result in an organic electron donor demand of approximately 36 kg year^{-1}. At a site with significant mass discharge rate of incoming competing electron acceptors, such as the largest site in Table 2, equivalent

Table 1. Selected hydrogeologic, plume, and background groundwater characteristics from 13 chlorinated solvent sites (Appendix A, Weidemeier et al. 1999)

Site	Type of chlorinated solvent plume upgradient – down-gradient portion of plume	Concentration of clean ground-water flowing into site (mg l^{-1})			Site characteristics		
		Dissolved Oxygen	Nitrate	Sulfate	Groundwater seepage velocity (m/year^{-1})	Median plume width (m)	Plume thickness (m)
Shaw AFB, SC – OU-4	1–1	9	1.2	20.4	42	168	1.5
Wurtsmith AFB, MI – OT-41/SS-42	1–1	9.9	6.02	13.6	89	30	3.0
MacDill AFB, FL – Site OT-24	1–1	1.54	2.46	77	11	107	6.1
Offutt AFB, NE – Fire Training Area	1–1	3.3	1.52	391	2	137	9.1
Fairchild AFB, WA – FT-1	1–1	7.95	2.4	13.1	10	91	3.0
Rickenbacker ANGB, OH – HWSA	1–1	13.4	9.1	938	8	18	3.0
Westover ARB, MA – Current FTA	1–1	8.93	5.57	76.7	6	76	15.2
Westover ARB, MA – Zone 1	1–1	10.75	9.5	36.8	32	366	15.2
Plattsburgh AFB, NY – FT-002	1–3	10	30	20.3	42	625	18.3
Offutt AFB, NE – Building 301	3–2	7	23.2	25	46	427	15.2
Cape Ca0veral AS, FL – FT-17	1–2	1.2	0.72	224.5*	34	122	4.6
Columbus AFB, MS – LF-06	1–3	5.1	6.7	50	457	168	1.5
Hill AFB, UT – OU-1	1–3	8	21	204.5*	18	427	12.2
Median		8.0	6.0	50	32	137	6.1
Mean		7.4	9.2	161	62	212	8.3

Notes: Type 1: Reductive dechlorination at site due to anthropogenic electron donors. Type 2: Reductive dechlorination at site due to naturally-occurring electron donors. Type 3: No or minimal biological reductive dechlorination at site.

* Average of range of reported values.

Table 2. Mass discharge rate of competing electron acceptors into chlorinated solvent plumes

Site	Flowrate through plume	Mass discharge rate into plume (kg year^{-1})		
	$n = 0.3$ (l year^{-1})	Dissolved oxygen	Nitrate	Sulfate
Shaw AFB, SC – OU-4	3.2E + 06	29	4	66
Wurtsmith AFB, MI – OT-41/SS-42	2.5E + 06	68	41	93
MacDill AFB, FL – Site OT-24	2.1E + 06	1	2	65
Offutt AFB, NE – Fire Training Area	7.7E + 05	1	0	61
Fairchild AFB, WA – FT-1	8.4E + 05	6	2	10
Rickenbacker ANGB, OH – HWSA	1.3E + 05	8	5	548
Westover ARB, MA – Current FTA	2.2E + 06	4	3	37
Westover ARB, MA – Zone 1	5.4E + 07	27	24	91
Plattsburgh AFB, NY – FT-002	1.5E + 08	32	97	66
Offutt AFB, NE – Building 301	9.0E + 07	25	82	89
Cape Canaveral AS, FL – FT-17	5.8E + 06	3	2	593
Columbus AFB, MS – LF-06	3.5E + 07	179	235	1753
Hill AFB, UT – OU-1	2.9E + 07	11	29	287
Median	3.2E + 06	11	5	89
Mean	2.9E + 07	30	41	289
Maximum	1.5E + 08	179	235	1753

mass of hydrogen would be much greater at 220 g hydrogen per year. This is roughly equivalent to 734 kg year^{-1} of an organic donor, such as BTEX.

The hydrogen consumed by the competing electron acceptors represents a potential pool of donor for reductive dechlorination. If all this hydrogen was utilized by dechlorinating bacteria instead of the competing electron acceptors, approximately 226 kg year^{-1} of PCE could be completely dechlorinated to ethene assuming median site conditions, and 4621 kg year^{-1} of PCE could be completely dechlorinated to ethene at the site with largest mass discharge rate of oxygen, nitrate, and sulfate. It is unlikely that all the excess hydrogen would be diverted to dechlorinators alone, but this calculation does show the magnitude of the competition for electron donor from the incoming mass discharge rate of dissolved oxygen, nitrate, and sulfate at Type 1 sites. At some sites, the competition may be an important constraint on the effectiveness of using monitored natural attenuation as a remedial alternative.

Passive method to enhance natural attenuation

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. A second method, developed by the Air Force Center for Environmental Excellence (AFCEE) and the authors, involves the delivery of dissolved hydrogen directly to the subsurface (Newell et al. 2001a). However, the analysis of the sustainability of natural attenuation at Type 1 solvent sites suggests a third method of increasing the effective supply of electron donor to dechlorinating bacteria. By permanently interrupting the transport of competing electron acceptors (oxygen, nitrate, and sulfate) to chlorinated solvent plumes, more electron donor is preserved for beneficial reductive dechlorination reactions. This can be achieved by either: (i) diverting clean groundwater around a chlorinated solvent source zone using either a physical barrier such as a slurry wall upstream of the solvent site source zone, or (ii) operating a hydraulic containment system upstream of the source zone (Newell et al. 2001a, b; see Figure 2). Diversion of competing electron acceptors would have the same benefits as electron donor addition, without the

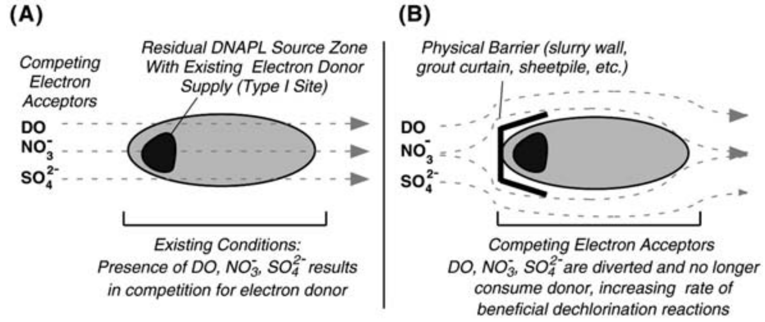

Figure 2. (A) Type 1 chlorinated solvent site undergoing natural attenuation and (B) with passive enhanced natural attenuation system *via* electron acceptor diversion. Pumping wells upgradient of the source area forming a stagnant zone downgradient of the source can be used in place of the physical barrier (Newell et al. 2001).

addition of any substrates to the subsurface. This process would be more beneficial at the sites with a large mass discharge rate of competing electron acceptors relative to the estimated mass of chlorinated solvents in the DNAPL source zone.

Conclusions

Aerobic, denitrifying, and sulfate-reducing bacteria compete with dechlorinating bacteria for electron donor at Type 1 chlorinated solvent sites. At some sites, this competition is likely to reduce the mass of chlorinated solvents destroyed by natural attenuation processes by hundreds or even thousands of kilograms per year. By diverting these electron donors around Type 1 chlorinated solvent plumes, the efficiency of natural attenuation processes may be increased. This diversion could be accomplished by the construction of physical or hydraulic barriers upstream of the chlorinated solvent plume.

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