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PROTOCOL FOR ASSESSING THE NATURAL ATTENUATION OF CHLORINATED ETHENES IN GROUNDWATER DRAFT ACTING AS FINAL NAS CECIL FIELD FL
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PROTOCOL FOR ASSESSING THE NATURAL ATTENUATION OF CHLORINATED ETHENES IN GROUND-WATER SYSTEMS

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--DRAFT--

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1.0 Introduction

Field and laboratory studies in the last ten years have demonstrated that the chlorinated ethenes perchloroethene (PCE), trichloroethene (TCE), dichloroethene (DCE), and vinyl chloride (VC) are subject to a variety of biodegradation processes. These processes can include reductive and oxidative pathways, and can transform chlorinated ethenes to environmentally innocuous carbon dioxide (CO_2) and chloride (Cl^-). In some hydrologic systems, these processes can effectively "treat" contaminated ground water and return it to pristine conditions without human intervention. If it can be reliably shown that natural attenuation processes are sufficient to protect sensitive receptors from contamination, then it is appropriate that they be included in Remedial Action Plans (RAPs) submitted for regulatory approval. Including natural attenuation can result in more effective and more cost-efficient remedial actions.

This document lays out a protocol for assessing the efficiency chlorinated ethene natural attenuation in ground-water systems. In particular, it identifies (1) the key ground-water quality data needed to assess natural attenuation, (2) a framework for interpreting this data, and (3) suggests a format for presenting this data to regulatory agencies.

1.1 Background Information

The microbial degradation of chlorinated ethenes is complex. Under some redox conditions, these compounds can serve as *electron donors* in microbial metabolism. This is to say that microorganisms can use them as a source of energy and electrons. Under other redox conditions, chlorinated ethenes serve as *electron acceptors*, where microorganisms use them as a sink for electrons. In addition, these compounds can be degraded by various cometabolic processes as well.

Under anoxic conditions, highly chlorinated ethenes such as PCE and TCE are subject to reductive dechlorination according to the sequence:

$$\text{PCE} \Rightarrow \text{TCE} + \text{Cl} \Rightarrow \text{DCE} + 2\text{Cl} \Rightarrow \text{VC} + 3\text{Cl} \Rightarrow \text{ethylene} + 4\text{Cl} \quad (1)$$

However, the *efficiency* of dechlorination differs for methanogenic, sulfate-reducing, Fe(III)-reducing, or nitrate-reducing conditions. Dechlorination of PCE and TCE to DCE is favored under mildly reducing conditions such as nitrate- or Fe(III)-reduction (4) whereas the

transformation of DCE to VC, or the transformation from VC to ethylene seems to require the more strongly reducing conditions of methanogenesis (5,6,7).

Under oxic conditions, DCE and VC can be oxidized to CO_2:

$$DCE + 2O_2 \Rightarrow \underline{2CO_2 + 2H^+ + 2Cl^-} \qquad (2)$$

and

$$VC + 2O_2 \Rightarrow \underline{2CO_2 + H^+ + Cl^-} \qquad (3)$$

In natural ground-water systems, complete degradation of chlorinated ethenes is favored by sequential anoxic- oxic conditions:

anoxic (either methanogenic, sulfate-reducing, or Fe(III)-reducing conditions) $\Rightarrow$ oxic conditions

PCE, TCE $\Rightarrow$ DCE and VC DCE, VC $\Rightarrow$ $2CO_2$ and Cl^-

The key to assessing the natural attenuation of chlorinated ethenes, therefore, is an accurate delineation of redox conditions in ground-water systems.

1.2 Delineating Redox Processes in Ground-Water Systems

The most common electron-accepting processes in ground-water systems are oxygen-, nitrate-, Fe(III)-, sulfate-, and carbon dioxide-reduction (methanogenesis). The stoichiometry of these processes can be represented by the generalized equations:

$$O_2 + CH_2O \Rightarrow CO_2 + H_2O \qquad (4)$$

$$4NO_3 + 4H^+ + 5CH_2O \Rightarrow 4NO_2 \Rightarrow 2N_2 + 5CO_2 + 7H_2O \qquad (5)$$

$$4Fe(OH)_3 + CH_2O + 8H^+ \Rightarrow 4Fe^{2+} + CO_2 + 11H_2O \qquad (6)$$

$$2CH_2O + SO_4^{2+} + H^+ \Rightarrow 2CO_2 + HS^- + 2H_2O \qquad (7)$$

$$2CH_2O \Rightarrow CH_4 + CO_2 \qquad (8)$$

Based on these equations, it is possible to logically deduce which microbial processes predominate in a ground-water system.

If dissolved oxygen is present in ground-water at concentrations greater than 0.5 mg/L, then oxygen reduction (equation 4) will be the predominant microbial process. If dissolved oxygen concentrations are less than 0.5 mg/L, but nitrate is present at concentrations greater than 1 mg/L, nitrate reduction (equation 5) will be the predominant microbial process. Because nitrite (NO_2) is an unstable intermediate product of nitrate reduction (equation 5), the presence of

measurable NO_2 concentrations are indicative of nitrate reduction. If ground water lacks dissolved oxygen, nitrate, or nitrate, but concentrations of Fe^{2+} are greater than 0.5 mg/L, Fe(III) reduction (equation 6) will be the predominant process. If ground water lacks Fe^{2+} but contains concentrations of sulfate greater than 1 mg/L and hydrogen sulfide greater than 0.05 mg/L, then sulfate reduction (equation 7) will be the predominant process. Finally, if the water lacks dissolved oxygen, nitrate, Fe^{2+}, sulfate, and hydrogen sulfide, but contains concentrations of methane greater than 0.2 mg/L, then methanogenesis (equation 8) will be the predominant process. This logic is summarized in Figure 1.

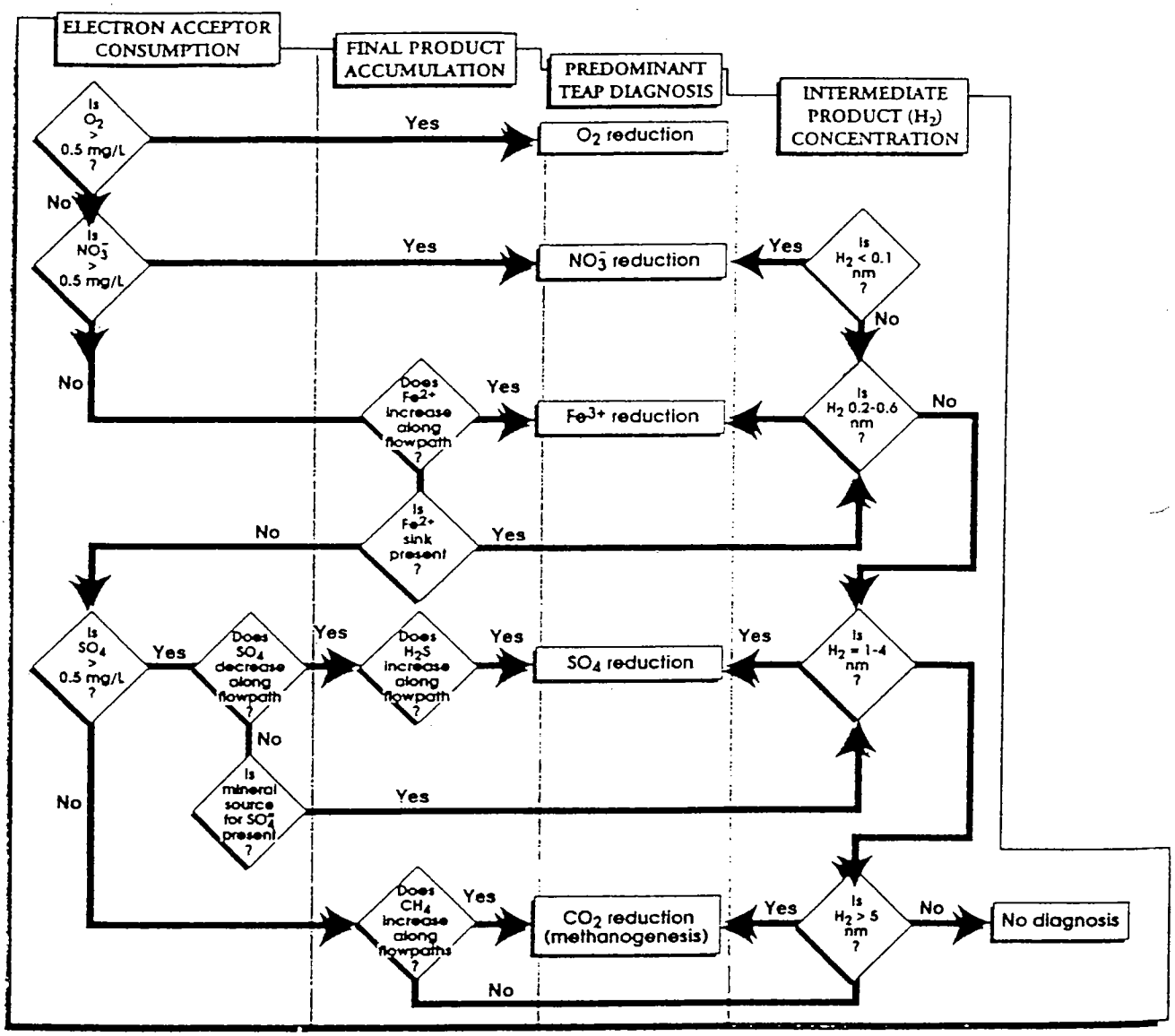

Figure 1.--*Flowchart for deducing redox processes in ground-water systems*

In practice, this methodology often encounters uncertainties. Many products of microbial metabolism, such as Fe^{2+}, H_2S, and methane can be transported by ground-water flow. In some cases where such transport is significant, it is difficult to determine the exact redox zonation with this water-chemistry information. In these cases, concentrations of dissolved hydrogen gas (H_2) can be used to evaluate ambient redox processes (Fig. 1). Fermentative microorganisms in ground-water systems continuously produce H_2 during anoxic decomposition of organic matter. This H_2 is then consumed by respiratory microorganisms that may use Fe(III), sulfate, or CO_2 as terminal electron acceptors. In microbial ecology, this process is referred to as interspecies hydrogen transfer. Significantly, Fe(III)-, sulfate-, and CO_2-reducing (methanogenic) microorganisms exhibit different efficiencies in utilizing H_2. Fe(III) reducers are relatively efficient in utilizing H_2 and thus they maintain lower steady-state H_2 concentrations (0.2 to 0.8 nM H_2) than either sulfate reducers (1-4 nM H_2) or methanogens (5-15 nM H_2). Because each terminal electron accepting process has a characteristic H_2 concentration associated with it, H_2 concentrations can be an indicator of predominant redox processes in ground-water systems.

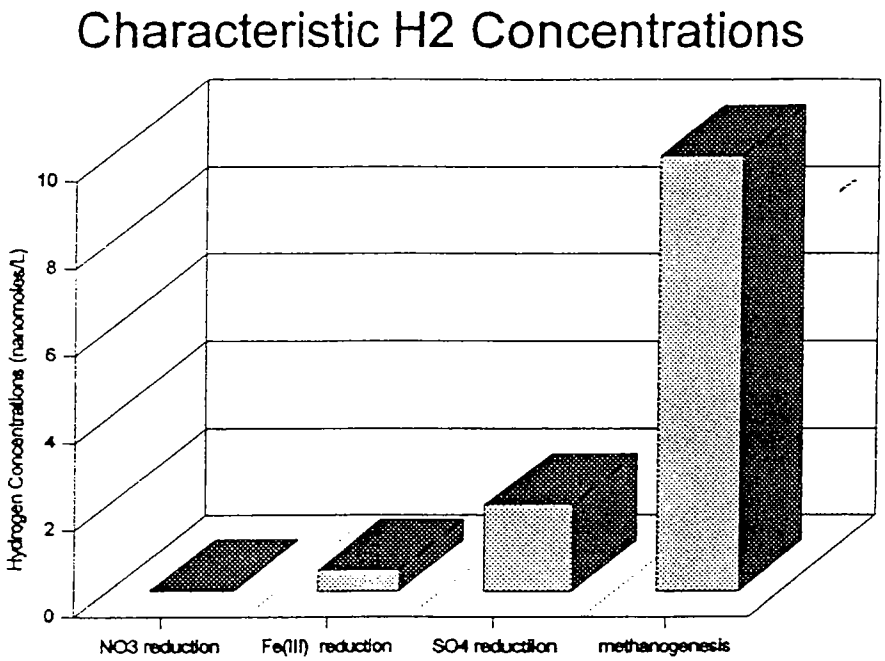

Figure 2.--*Hydrogen concentrations characteristic of different predominant redox processes in aquatic sediments and ground-water systems.*

In order to determine the zonation of microbial processes with this methodology, the following data need to be gathered (Table 1):

Table 1.--Ground-water chemistry parameters needed to evaluate redox processes.

Analytical Parameter	Field or laboratory parameter	Method of analysis
Dissolved oxygen (DO)	field	meter, field kit titration
Nitrate (NO_3)	laboratory	Ion Chromatography
Nitrite (NO_2)	laboratory	Ion Chromatography
Dissolved ferrous iron (Fe^{2+})	field	Field kit spectrophotometer
Sulfate (SO_4)	laboratory	Ion Chromatography
Hydrogen sulfide (H_2S)	field	Field kit spectrophotometer
Dissolved Methane (CH_4)	laboratory	GC FID[1]
pH (units)	field	meter
Eh (redox potential)	field	meter
Dissolved Hydrogen (H_2)	field	gas chromatography[2]

[1] Protocol for measuring methane is given in Appendix I.
[2] Protocol for measuring methane is given in Appendix II.

Of these parameters, the most important--and often the most difficult measurement to make--is dissolved oxygen. Dissolved oxygen concentrations determine whether reductive dehalogenation--or aerobic oxidation of VC or DCE--are feasible. This is a very skill-intensive parameter to measure in the field, and extreme care must be taken to avoid oxygenation of water sample prior to analysis. Dissolved oxygen meters (Table 1) are convenient, but cannot measure low (<0.2 mg/L concentrations). Dissolved oxygen kits are more difficult to use, but can accurately distinguish between truly anoxic ground water and low concentrations of dissolved oxygen. Concentrations of nitrate, nitrite, and sulfate are most efficiently measured in the laboratory. Samples for nitrate and nitrite should be chilled to 4°C in the field, and analyzed within 48 hours. Hydrogen sulfide and Fe^{2+} are most efficiently measured in the field with appropriate field kits (Table 1). Samples for methane analysis need to be collected according to the field and laboratory protocol given in Appendix I. Measurements of oxidation-reduction potential made with platinum electrodes are not amenable to quantitative interpretation, but serve as a useful check on dissolved oxygen measurements. Dissolved hydrogen measurements should be made in the field according to the protocol given in Appendix II.

In addition to redox-sensitive parameters, a full suite of dissolved cation and anion data should be collected at each well. The microbially active anions (nitrate, nitrite, and sulfate) are needed as discussed above. Dissolved chloride gives a quantitative indication of overall amounts of chlorinated solvent degradation. The major and minor cations can give ancillary information on

microbial conditions (phosphate, calcium, potassium), as well as giving a quantitative indication of analysis accuracy. For example, if molar quantities of anions and cations do no balance within 10%, this may indicate analytical errors. The suite of anions and cations that should be measured, together with the most common analytical methods are given on Table 2.

Table 2.--Major and minor cations and anions

Analytical Parameter	Field or laboratory parameter	Method of analysis
Dissolved calcium (Ca^{2+})	laboratory	ICP[1], IC[2], or AA[3]
Dissolved magnesium (Mg^{2+})	laboratory	ICP, IC, or AA
Dissolved sodium (Na^{+})	laboratory	ICP, IC, or AA
Dissolved potassium (K^{+})	laboratory	ICP, IC, or AA
Dissolved Ammonium (NH_4)	laboratory	ICP, IC, or AA
Dissolved Chloride (Cl^{-})	laboratory	IC
Dissolved Bromide (Br^{-})	laboratory	IC
Dissolved Phosphate (PO_4)	laboratory	IC
Dissolved inorganic carbon	laboratory	IC
Temperature (°C)	field	thermometer

[1] Inductively Coupled Plasma Spectroscopy
[2] Ion Chromatography
[3] Atomic Absorption Spectroscopy

1.3 Contaminant Concentrations as indicators of Reductive Dechlorination

Concentrations of chlorinated ethenes their degradation products give a direct indication of the presence or absence of microbial dechlorination processes. As such, any ground water-sampling campaign designed to elucidate ongoing microbial processes should include analysis of these parameters. The parameters that are most readily interpreted in this context are given in Table 3.

Table 3.--Analytical Data for chlorinated ethenes, soluble petroleum hydrocarbons, and possible degradation products needed to evaluate intrinsic bioremediation.

Analytical Parameter
trans Dichloroethene
cis Dichloroethene
Trichloroethene (TCE)
Perchloroethene (PCE)
Vinyl Chloride
benzene
toluene
xylene
ethylbenzene
Dissolved organic carbon

1.4 Step-by-Step Methodology for Assessing the Redox Conditions in Ground-Water Systems.

The precise methodology for assessing redox processes in ground-water systems will vary from site to site depending on ambient conditions. Nevertheless, the following steps can be taken in sequence to delineate ambient microbial redox processes in ground-water systems:

Step 1-- Place sufficient PVC-cased monitoring wells at the to delineate the areal and vertical extent of ground-water contamination. Perform slug tests or pumping tests to determine distribution of hydraulic conductivity.

Step 2--Measure water levels in the wells, prepare a potentiometric map, and determine directions of ground-water flow and hydraulic gradients. Use measured hydraulic conductivity data, hydraulic gradient data, and estimates of aquifer porosity to determine rates of ground-water flow using Darcy's Law:

$$v = \text{grad } K/\theta$$

where v is average seepage velocity (ft/d), grad is the hydraulic gradient (dimensionless), K is the hydraulic conductivity (ft/d), and θ is average porosity (dimensionless).

Step 3--Measure concentrations of redox-sensitive parameters (Table 1), major anions and cations (Table 2), and contaminants (Table 3) in ground water from the site.

Step 4--Using the results of step 3, apply the logic of Figure 1 to deduce the distribution of ambient redox processes at the site. In addition, use these data to document contaminant concentration changes as ground-water flows downgradient, and concentration changes of chloride as ground-water flows downgradient.

Step 5--Categorize the site according to the following characteristics:

1. **Type 1 aquifer**--methanogenic conditions at contaminant source area, grading to Fe(III)-reducing conditions immediately downgradient of the source area, and finally grading to oxic conditions further downgradient.

2. **Type 2 aquifer**--Sulfate-reducing or Fe(III) reducing conditions at contaminant source area, grading to oxic conditions downgradient.

3. **Type 3 aquifer**--Oxic conditions at contaminant source area grading to Fe(III)-reducing, sulfate-reducing, or methanogenic conditions downgradient.

4. **Type 4 aquifer**--Uniformly oxic conditions in contaminant source area and downgradient areas.

Step 6--Interpret potential for natural attenuation according to the following general guidelines

- **Type 1 aquifer**--rapid and efficient reductive dechlorination at the source area followed by oxidation of DCE and VC downgradient of the source area. High potential for natural attenuation, with first-order biodegradation rate constants on the order of 10^{-2} to 10^{-4} d^{-1}.

- **Type 2 aquifer**--reductive dechlorination at source area followed by oxidation of DCE and VC downgradient of source area. PCE and TCE transported to oxic zone will cease rapid degradation. Moderate potential for natural attenuation. First-order biodegradation rate constants on the order of 10^{-3} to 10^{-5} d^{-1}.

- **Type 3 aquifer**--No reductive dechlorination at source area, some dechlorination downgradient. Moderate to Low potential for natural attenuation.

- **Type 4 aquifer**--No reducive dechlorination. TCE and TCE stable in solution. First-order rate constants less than 10^{-6} d^{-1}.

An example of how this methodology can be used is given in Appendix III.

Appendix I.--Analysis of dissolved methane concentrations.

In the laboratory, 30-ml septated serum vials should be capped and sealed. These vials will be used to collect water samples for methane analysis. In the field, a 250-ml gas-sampling bulb equipped with a single septum should be attached to the discharge pipe of the well, and purged at a rate between 500 and 1000 mls/min to eliminate all air and bubbles. After the bulb has been purged for 2-3 minutes, a needle and 10-ml glass syringe is used to withdraw 5 mls of water from the gas-sampling bulb. This water is then injected into a sealed 30-ml septated serum vial, and the vial returned to the laboratory for analysis. In the laboratory, an aliquot of the *gas headspace* (not the water) is analyzed by gas chromatography with flame ionization detection for methane. The amount of methane in the headspace is then normalized for the volume of water added (5 mls), the volume of the headspace (25 mls) and the Henry's Law partition coefficient, and results reported as mg methane per liter of water.

Appendix II.--Analysis of dissolved hydrogen concentrations.

Ground-Water Hydrogen Concentrations.

Sampling Method. The concentration of H_2 dissolved in the ground water will be estimated using the "bubble strip" method. Place the intake hose of a peristaltic pump down the sampling well. Position the intake at the depth of the screened interval. Attach a glass, water-sampling bulb to the outflow end of the hose. Turn on the pump and adjust the flow rate to about 500 to 700 mL/min. Briefly hold the outlet end of the sampling bulb in the upright position to remove any gas bubbles from the bulb. Place the bulb in a horizontal position and inject 20 mL of hydrogen-free N_2 gas. Allow the N_2 bubble to come into equilibrium with the flowing ground water. This equilibration process takes approximately 20 minutes. After 20 minutes remove 3-5 mL of the gas bubble using a 10 mL glass syringe with attached mini-inert valve. Close the valve to seal the sample. Wait an additional 5 minutes and remove another 3-5 mL from the N_2 bubble. Close the valve to seal the sample. Analyze both samples on the hydrogen detector. If the H_2 concentrations of the duplicate samples are not similar it may be necessary to take a third gas sample in the same manner.

Analytical Method. Using the "bubble strip" method, the headspace H_2 concentration is determined by gas chromatography. A schematic of the hydrogen detection gas chromatograph is given in figure 2. In GC analysis a gaseous sample is injected into the stream of a carrier gas. In this case N_2 is the carrier. The sample is transported by the carrier through a separation column where the components of the sample are separated based on variations in their efficiency of transport through the column matrix. The column we use is packed with CarboSieve II which separates chemical species primarily on the basis of molecular size. The separated components elute from the column and pass through a heated bed of HgO where the reduced gases (primarily H_2 and CO) are oxidized and Hg vapor is released. The concentration of Hg vapor released is directly proportional to the concentration of reduced gases present in the sample and is detected by means of an ultraviolet photometer.

The concentration of H_2 dissolved in the ground water can be estimated from the headspace concentration as follows:

1) Prepare a calibration curve for H_2 using a 100 ppm Scotty II standard gas

mixture. We can convert ppm (by volume) units to molar units by using the Ideal Gas Law as follows:

$$PV = nRT$$

Rearrange to give:

$$\frac{n}{V} = \frac{P}{RT}$$

where n is the quantity of gas in moles, V is the volume the gas occupies in Liters, P is the partial pressure of the gas in atm, T is the temperature in °K, and R is the gas constant (R = 0.08205 atm L mole^{-1} °K^{-1}. Thus the concentration of a pure gas at atmospheric pressure and room temperature is 40.9 mmoles/L. For a 100 ppm standard (ie. 100 μL/L), the H_2 concentration in molar units is:

$$(40.9\,mmoles\ /L_{H_2})(10^{-4}L_{H_2}/L_{gas})(10^{6}nmoles\ /mmole\ ) = 4090\ nmoles\ /L_{gas}$$

Using this as a stock create a calibration curve and calculate the linear regression which describes this response curve.

2) Load the sample N_2 gas collected from the sampling bulb into the sample loop. Close the sample loop outlet valve and presurize the loop. Inject the sample.

3) Calculate the dissolved H_2 concentration from the headspace H_2 concentration (concentration of H_2 in gaseous sample) using the following relationship:

$$C_w = \frac{C_h}{H_{H_2}}$$

where C_w is the dissolved H_2 concentration in nmoles/L, C_h is the headspace H_2 concentration in nmoles/L, and H_{H2} is the dimensionless Henry's Law coefficient for the distribution of H_2 between the gaseous and dissolved phases (H_{H2} = 50.4).

If you prefer to work with gas concentration units of ppm (ie. μL/L), then the dissolved H_2 concentration (nmoles/L) can be calculated from the headspace concentration (ppm) by multiplying by 0.8 as indicated in the following equation:

$$C_w = \frac{C_h(40.9 nmoles\ L^{-1} ppm^{-1})}{H_{H_2}}$$

$$C_w = C_h(0.8 nmoles\ L^{-1} ppm^{-1})$$

where C_w is the dissolved H_2 concentration in nmoles/L; C_h is the headspace H_2 concentration in ppm; 40.9 nmoles L^{-1} ppm^{-1} is a conversion factor for converting ppm into nmoles/L; and H_{H_2} is the Henry's Law coefficient for the distribution of H_2 between the gaseous and dissolved phases (H_{H_2} = 50.4).

4) Identify the predominant terminal electron accepting process based on the following characteristic ranges:

Iron Reduction	0.2 - 0.8 nM
Sulfate Reduction	1 - 4 nM
Methanogenesis	5 - 25 nM

Appendix III.--Example of assessing natural attenuation of chlorinated ethenes.

Identifying Redox Conditions that Favor the Natural Attenuation of Chlorinated Ethenes in Contaminated Ground-Water Systems

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Introduction

In the last several years, it has been demonstrated that petroleum hydrocarbons biodegrade in virtually all ground-water systems (1), and that natural attenuation can greatly reduce the transport of contaminants away from particular hydrocarbon spills (2,3). These results have raised the prospect that chlorinated ethenes--perchloroethene (PCE), trichlorothene (TCE), dichloroethenes (DCEs), and vinyl chloride (VC)--will prove similarly amenable to natural attenuation processes. However, the microbial processes leading to biodegradation of chlorinated ethenes can be much different from those of petroleum hydrocarbons. Petroleum hydrocarbons universally serve as *electron donors* (that is, as an energy source) in microbial metabolism. In contrast, chlorinated ethenes, in addition to serving as electron donors, can function as *electron acceptors* (that is, they are reduced via reductive dechlorination), or can be fortuitously degraded by various cometabolic processes. Because of this diversity, it is not surprising that the efficiency of chlorinated ethene natural attenuation varies widely amoung ground-water systems.

Under anoxic conditions, chlorinated ethenes are subject to reductive dechlorination according to the sequence:

$$\text{PCE} \Rightarrow \text{TCE} + \text{Cl} \Rightarrow \text{DCE} + 2\text{Cl} \Rightarrow \text{VC} + 3\text{Cl} \Rightarrow \text{ethylene} + 4\text{Cl} \quad (1)$$

However, the *efficiency* of dechlorination appears to differ for methanogenic, sulfate-reducing, Fe(III)-reducing, or nitrate-reducing conditions. Dechlorination of PCE and TCE to DCE is favored under mildly reducing conditions such as nitrate- or Fe(III)-reduction (4) whereas the transformation of DCE to VC, or the transformation from VC to ethylene seems to require the more strongly reducing conditions of methanogenesis (5,6,7). Further complicating this picture is the fact that lightly chlorinated ethenes such as VC can be oxidized under oxic (8) or

Fe(III)-reducing conditions (9), and by various cometabolic degradation processes (10).

It is clear, therefore, that an accurate delineation of redox conditions is central to evaluating the potential for the natural attenuation of chlorinated ethenes in ground-water systems. The purpose of this paper is to summarize a methodology for identifying the zonation of redox conditions in the field. This methodology can serve as an *a priori* screening tool for identifying ground-water systems where redox conditions will favor natural attenuation of chlorinated ethenes. Conversely, this methodology can identify systems where natural attenuation of chlorinated ethenes is not favored, and other remediation technologies should be considered.

Methodology for Determining Redox Processes in Ground-Water Systems

Platinum electrode Eh measurement historically has been the most widely used method for determining redox conditions in ground-water systems. While Eh measurements can accurately distinguish oxic from anoxic ground water, they can not distinguish between different anoxic processes such as nitrate reduction, Fe(III) reduction, sulfate reduction, or methanogenesis. One reason for this is that many redox species, such as hydrogen sulfide (H_2S) or methane (CH_4), are not electroactive on platinum electrode surfaces (11). Because distinguishing between these processes is critical to evaluating the natural attenuation of chlorinated ethenes, it is clear that Eh measurements alone cannot provide the needed information.

A different methodology, which is based on microbial physiology, has recently been introduced for delineating redox processes (12, 13, 14) . This method relies on three lines of evidence: (1) the consumption of electron acceptors, (2) the production of metabolic endproducts, and (3) measuring concentrations of transient intermediate products. Molecular hydrogen (H_2), the most ubiquitous intermediate product of anaerobic microbial metabolism, has proven to be especially useful in this context. Different electron-accepting processes have characteristic H_2-utilizing efficiencies. Nitrate reduction, the most energetically favorable anoxic process, maintains H_2 concentrations below 0.1 nanomoles per liter (nM). Fe(III) reduction maintains H_2 concentrations between 0.2 and 0.8 nM, whereas for sulfate reduction the characteristic range is between 1 and 4 nM. Methanogenesis, the least energetically favorable anoxic process is characterized by H_2 in

the 5 to15 nM range.

Patterns of electron-acceptor consumption, final product accumulation, and H_2 concentrations can be combined in order to logically identify redox processes (13). For example, if sulfate concentrations are observed to decrease along an aquifer flowpath, if sulfide concentrations are observed to increase, and if H_2 concentrations are in the 1 to 4 nM range characteristic of sulfate reduction, it may be concluded with a high level of confidence that sulfate reduction is the predominant redox process. If all three possible indicators (electron acceptor consumption, endproduct production, and H_2 concentrations) indicate the same redox process, a high degree of confidence in the delineation is warranted. Conversely, if only one indicator is available, or if there are conflicting lines of evidence, proportionally less confidence in the redox delineation is warranted.

Measuring Hydrogen Concentrations in Ground Water

With the exception of dissolved hydrogen (H_2), all of the redox-sensitive parameters (dissolved oxygen, nitrate, nitrite, ferrous iron (Fe^{2+}), hydrogen sulfide, sulfate, and methane) needed to assess redox processes are made routinely in ground-water chemistry investigations. Hydrogen concentrations in ground water can be made using a gas-stripping procedure (13). A standard gas-sampling bulb is attached to a stream of water produced from a well and purged for several minutes (~500 ml/min) to eliminate all gas bubbles. Next, 20 ml of nitrogen, made H_2-free by passing through a hopcalite column is introduced to the bulb through a septum. As water continues to purge the bulb, H_2 and other slightly soluble gases partition to the headspace and asymptotically approach equilibrium with the dissolved phase. After 20 to 25 minutes, equilibrium is achieved and the gas bubble is sampled using a syringe. A duplicate sample is taken five minutes later. H_2 is then measured by gas chromatography with reduction gas detection. Concentrations of aqueous H_2 are then calculated from H_2 solubility data. For fresh water in equilibrium with a gas phase at one atmosphere pressure, 1.0 parts per million H_2 in the gas phase corresponds to 0.8 nM of dissolved H_2.

An Example of Redox Zone Delineation Related to the Natural Attenuation of Chlorinated Ethenes, Cecil Field, Florida

An example of how redox processes can be delineated, and how this delineation affects assessment of natural attenuation of chlorinated ethenes, was performed by the U.S. Geological Survey in cooperation with the U.S. Navy at Site 8, Naval Air Station (NAS) Cecil Field. Site 8 was a fire-training area used to train Navy personnel in fire-fighting procedures (fig. 1). Over the operational life of Site 8, a variety of petroleum products and chlorinated solvents seeped to the underlying ground-water system.

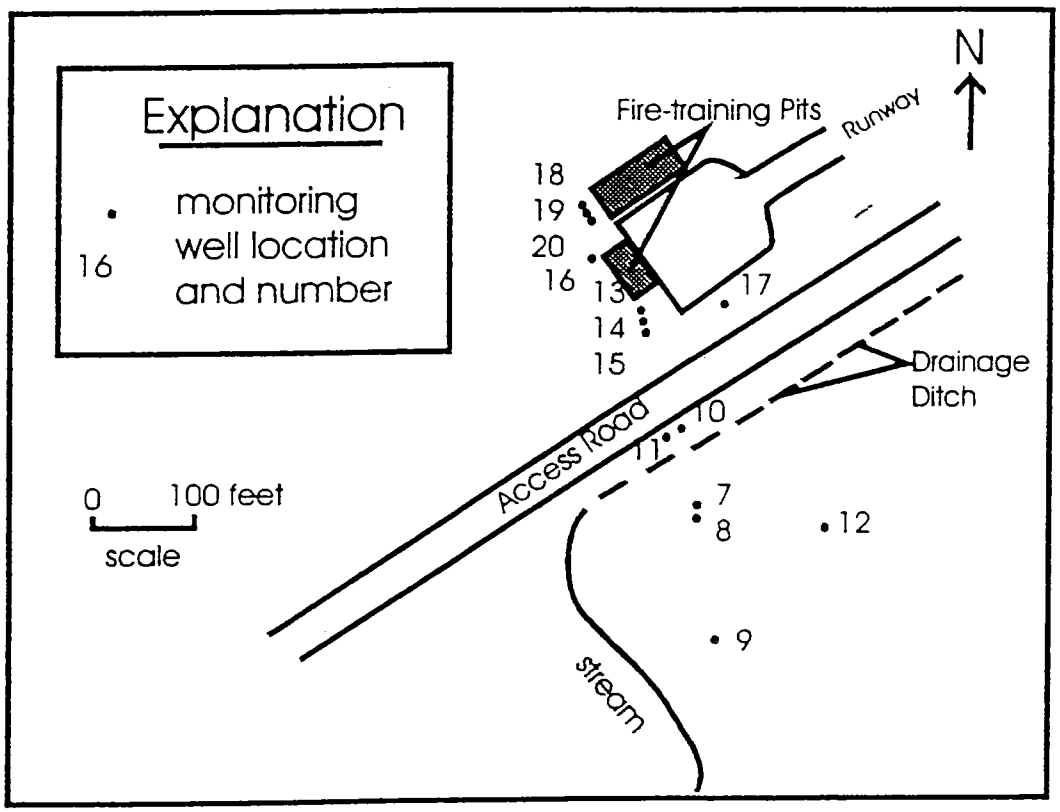

Figure 1.--Map showing location of fire training pits and monitoring wells, Site 8, NAS Cecil Field, Florida.

Changes in the concentrations of redox-sensitive constituents along the flowpath of the shallow aquifer system are shown in Figure 2. Ground water at the site is oxic upgradient of the fire pits

but becomes anoxic downgradient of the fire pits (Fig. 2A). Once the water becomes anoxic, concentrations of methane begin to rise, peaking at about 7 mg/L 200 feet downgradient (Fig. 2A) and indicating the presence of methanogenic conditions. Between 170 and 400 feet downgradient, concentrations of sulfate decrease, and concentrations of H_2S increase (Fig.2B) indicating active sulfate reduction. Concentrations of dissolved Fe^{2+} remain below 1 mg/L until about 400 feet along the flowpath, and then increase to about 2.5 mg/L indicating active Fe(III) reduction. The H_2 concentrations are consistent with the redox zonation indicated by the other redox-sensitive parameters (Fig. 2C). H_2 concentrations in the range characteristic of methanogenesis are observed in ground-water near the fire training pits where high methane concentrations are present.

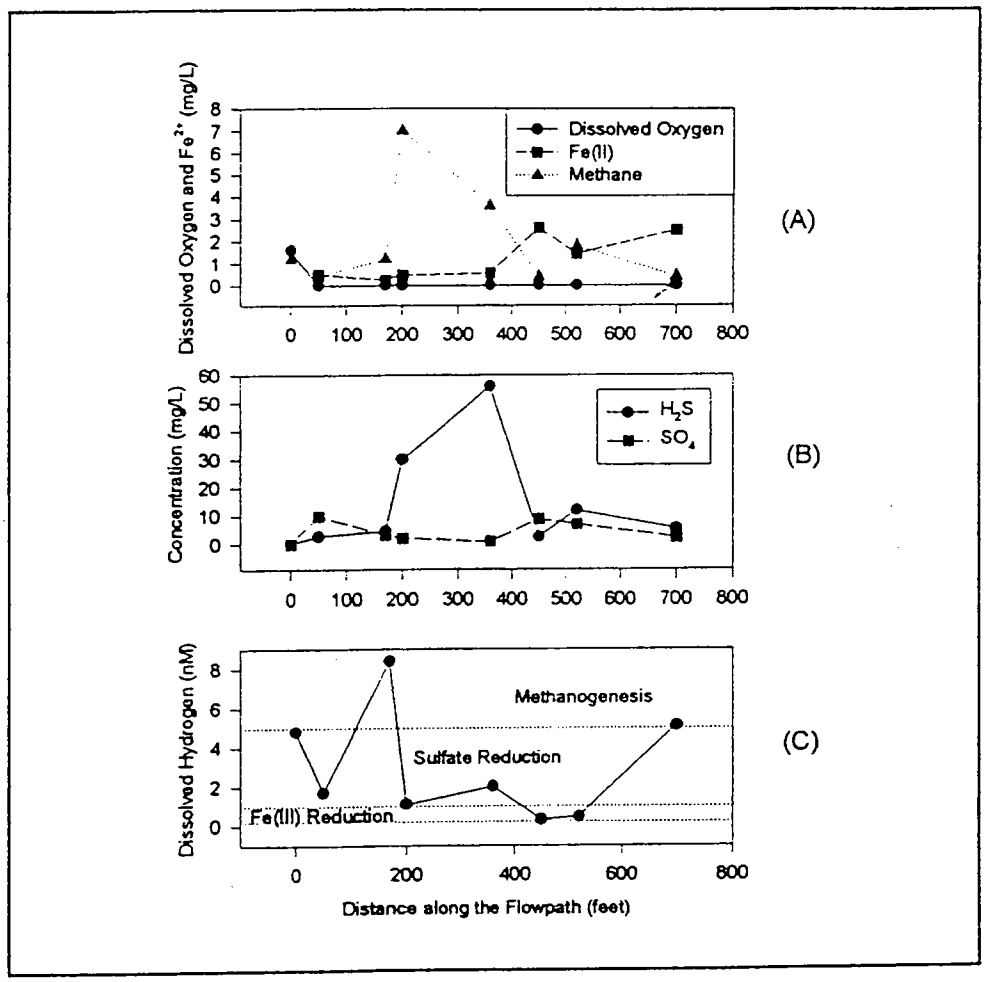

Figure 2.--Concentration changes of redox-sensitive parameters along ground-water flowpaths in the shallow aquifer, Site 8, NAS Cecil Field, Florida.

Between 200 and 170 feet downgradient where sulfate concentrations decline and sulfide concentrations increase, H_2 concentrations are in the 1-4 nM range characteristic of sulfate reduction. Finally, between 400 and 500 feet downgradient, where concentrations of Fe^{2+} increase, H_2 concentrations are in the 0.2 to 0.8 nM range characteristic of Fe(III) reduction.

A cross section showing the interpretation of these data, and which includes wells screened deeper in the flow system, is given in Figure 3. A methanogenic zone is present near the contaminant source, surrounded by sulfate-reducing and Fe(III)-reducing zones further downgradient. This redox zonation suggests that the natural attenuation of chlorinated ethenes will be rapid and efficient at this site. Near the contaminant source, methanogenic and sulfate-reducing zones favor dechlorination of PCE, TCE, and DCE. In the downgradient Fe(III)-reducing zone, anoxic oxidation of vinyl chloride to CO_2 can occur (Fig. 3).

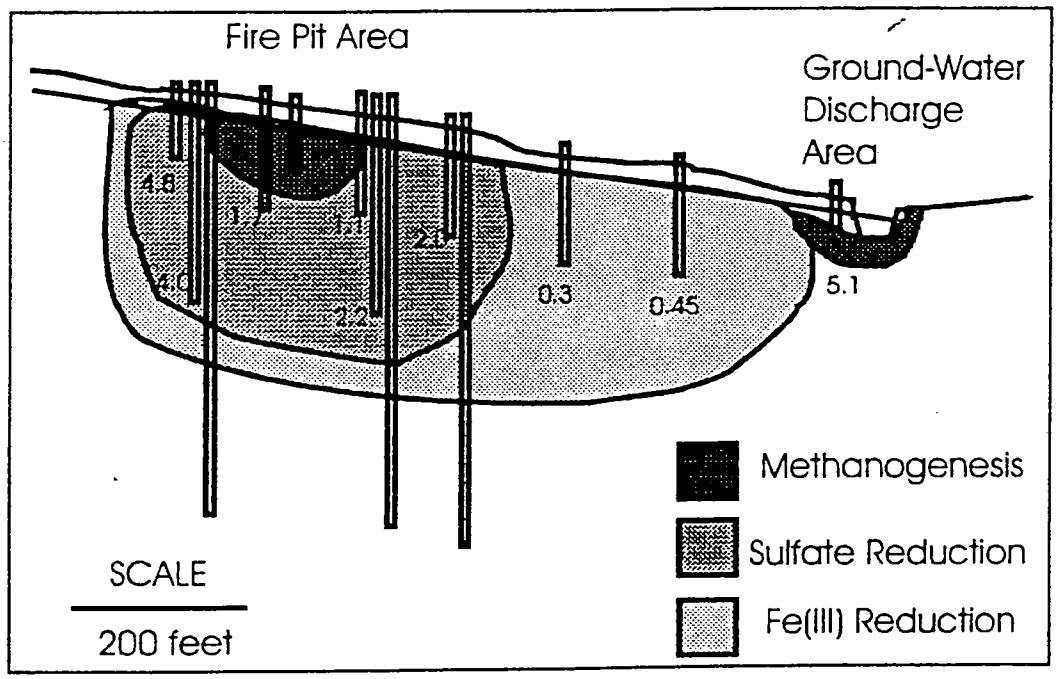

Figure 3.--Concentrations of dissolved hydrogen (nM) and the zonation of predominant redox processes, Site 8, NAS Cecil Field, Florida.

These biodegradation processes, which can be postulated solely on the basis of the observed redox zonation, are consistent with the observed behavior of chlorinated ethenes at this site (Fig. 4A). PCE, TCE, and VC are present in ground water near the fire-training pits, but drop below detectable levels along the flowpath. In fact, natural attenuation of chlorinated ethenes at this site has been so efficient that the best water-chemistry record of the original contamination is probably the elevated concentrations of dissolved inorganic carbon (Fig. 4B) and dissolved chloride (Fig. 4C) observed in downgradient ground water that currently lacks measurable chlorinated ethene contamination. These patterns suggest that most of the chlorinated ethenes have been completely transformed to CO_2 and chloride by the cumulative effects of reductive dehalogenation in the methanogenic and sulfate-reducing zones, and oxidative processes in the downgradient Fe(III)-reducing and oxic zones.

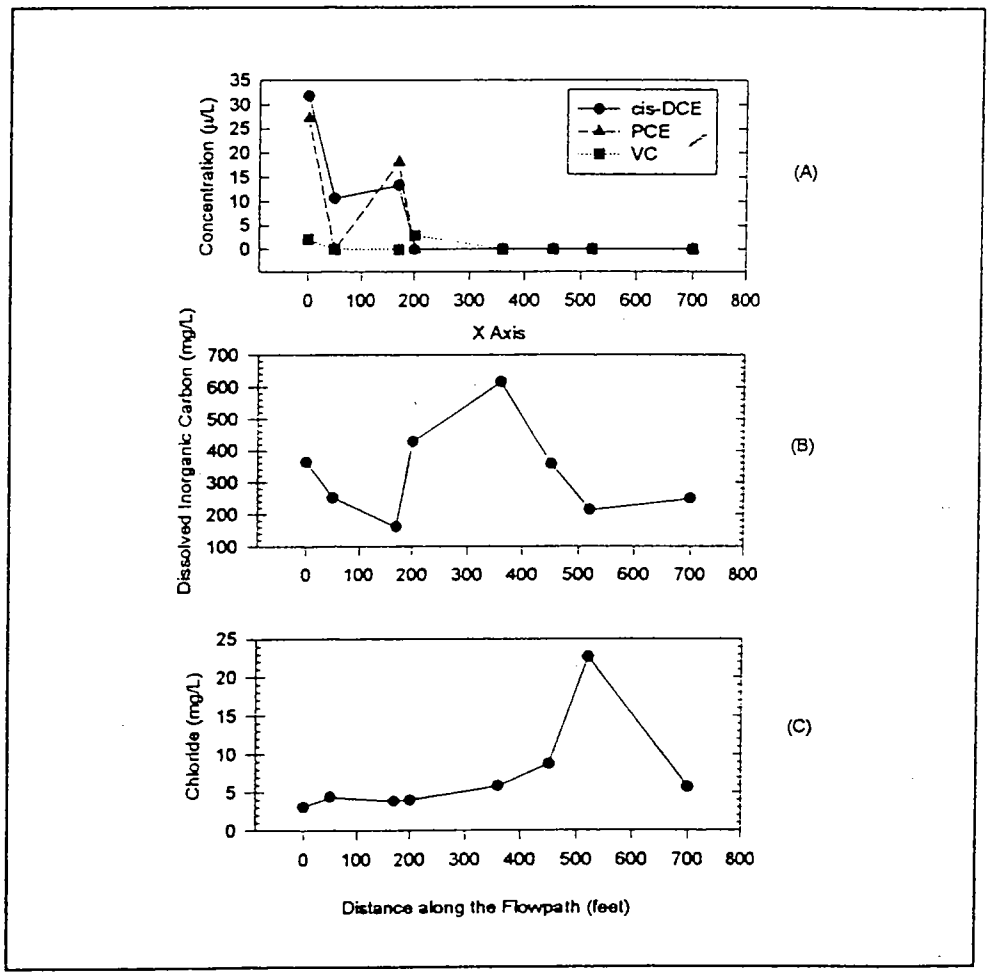

Figure 4.--Concentration changes of chloride, dissolved inorganic carbon, and chlorinated ethenes along ground-water flowpaths.

Conclusions

An understanding of ambient redox conditions is a powerful tool for assessing the efficiency of natural attenuation of chlorinated ethenes. The methodology for assessing redox conditions involves tracking (1) the disappearance of electron acceptors, (2) the appearance of endproducts, and (3) concentrations of H_2. Using this information, it is possible to logically deduce redox zonation at particular sites, and assess the confidence that is appropriate for the delineation. This methodology was demonstrated for a site at Cecil Field, Florida. The progression from methanogenic $\Rightarrow$ sulfate reduction $\Rightarrow$ Fe(III) reduction $\Rightarrow$ oxygen reduction has efficiently decreased concentrations of chlorinated ethenes indicating that natural attenuation is a viable remedial option at this site.

References

1. Hinchee, R.E., J.A. Kittel, and H.J. Reisinger (eds.). 1995. *Applied Bioremediation of Petroleum Hydrocarbons*. Battelle Press, Columbus, OH.

2. Weidemeyer, T.H., D.C. Downey, J.T. Wilson, D.H. Kampbell, R.N. Miller, and J.E. Hansen. 1995. Technical protocol for implementing the intrinsic remediation with long-term monitoring option for natural attenuation of dissolved-phase fuel contamination in ground water. United States Air Force Center for Environmental Excellence; Brooks Air Force Base; San Antonio, Texas, p.129.

3. Chapelle, F.H., J.M. Landmeyer, and P.M. Bradley. 1996. Assessment of intrinsic bioremediation of jet fuel contamination in a shallow aquifer, Beaufort, South Carolina. U.S. Geological Survey Water Resources Investigations Report 95-4262, 30 p.

4. Vogel, T.M., C.S. Criddle, and P.L. McCarty. 1987. Transformations of halogenated aliphatic compounds. Environmental Science and Technology 21:721-736.

5. Friedman, D.L., and J.M. Gossett. 1989. Biological reductive dechlorination of tetrachloroethylene and trichloroethylene to ethylene under methanogenic conditions. Applied and Environmental Microbiology 55:2144-2151.

6. DeBrunin, W.P., M.J.J. Kotterman, M.A. Posthumus, G. Schraa, and A.J.B. Zehnder. 1992. Complete biological reductive transformation of tetrachloroethene to ethane. Applied and Environmental Microbiology 58:1996-2000.

7. DiStefano, T.D., J.M. Gossett, and S.H. Zinder.1991. Reductive dechlorination of high concentrations of tetrachloroethene to ethene by an anaerobic enrichment culture

in the absence of methanogenesis. Applied and Environmental Microbiology 57:2287-2292.

8. Davis, J.W. and C.L. Carpenter. 1990. Aerobic biodegradation of vinyl chloride in groundwater samples. Applied and Environmental Microbiology 56:3878-3880.

9. Bradley, P.M. and F.H. Chapelle. 1996. Anaerobic mineralization of vinyl chloride in Fe(III) reducing aquifer sediments. Environmental Science & Technology 40: 2084-2086.

10. McCarty, P.L. and L. Semprini. 1994. Groundwater treatment for chlorinated solvents. in *Handbook of Bioremediation*, Lewis Publishers, Boca Raton, p. 87-116.

11. Stumm, W. and J.J. Morgan. 1981. *Aquatic Chemistry;* John Wiley & Sons: New York, p. 780.

12. Lovley , D.R. and S. Goodwin. 1988. Hydrogen concentrations as an indicator of the predominant terminal electron-accepting reaction in aquatic sediments. Geochemica et Cosmochimica Acta, 52: 2993-3003.

13. Chapelle, F.H., P.B. McMahon, N.M. Dubrovsky, R.F. Fujii, E.T. Oaksford, and D.A. Vroblesky. 1995. Deducing the distribution of terminal electron-accepting processes in hydrologically diverse groundwater systems. Water Resources Research 31:359-371.

14. Lovley, D.R., F.H. Chapelle, and J.C. Woodward. 1994. Use of dissolved H_2 concentrations to determine distribution of microbially catalyzed redox reactions in anoxic groundwater. Environmental Science and Technology, 28:1255-1210.