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PROTOCOL FOR ASSESSING THE NATURAL ATTENUATION OF CHLORINATED ETHENES IN GROUND-WATER SYSTEMS

Francis H. Chapelle
U.S. Geological Survey
720 Gracern Rd., Suite 129
Columbia, SC 29210

ph: 803-750-6116
fax: 803-750-6181
email: Chapelle@USGS.gov

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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:

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

and

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

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.

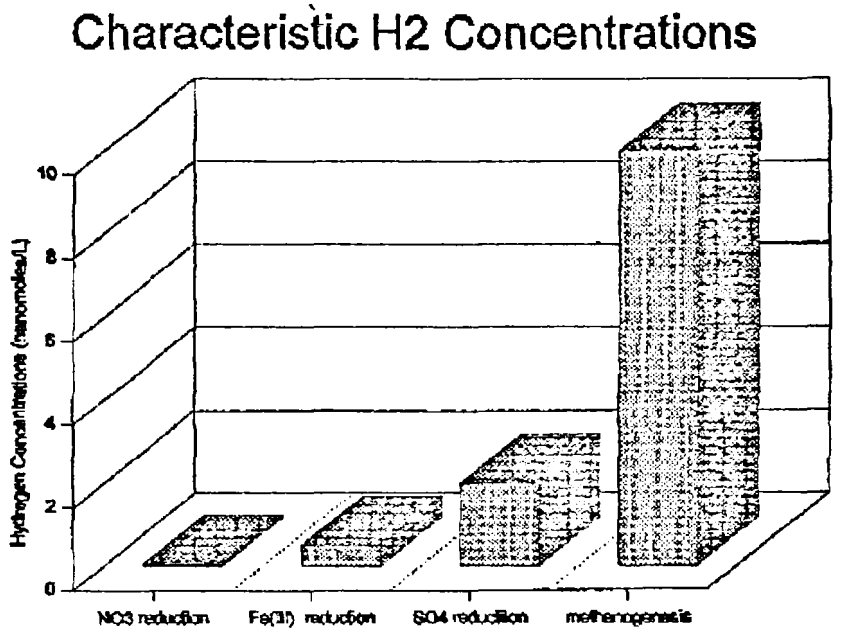

Figure 2.—*Hydrogen concentrations characteristic of different predominant redox processes in aquatic sediments and ground-water systems.*

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_{H_2} is the dimensionless Henry's Law coefficient for the distribution of H_2 between the gaseous and dissolved phases (H_{H_2} = 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