GUIDELINES

NATURAL ATTENUATION OF CHLORINATED SOLVENTS IN GROUND WATER

MINNESOTA POLLUTION CONTROL AGENCY
SITE REMEDIATION SECTION

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EXECUTIVE SUMMARY

This document provides guidance on the selection of natural attenuation as a remedy for chlorinated solvents in ground water at sites regulated under the Minnesota Environmental Response and Liability Act (MERLA), including the Minnesota Superfund and Voluntary Investigation and Cleanup (VIC) Programs. It is part of the Risk-Based Site Evaluation Manual that outlines the process for making decisions at sites on the basis of risk to human health and the environment. Specifically, this document describes a phased process of site evaluation that begins with a screening procedure for natural attenuation. For sites with positive screening results, additional site characterization, verification, and implementation steps are required. These steps are intended to support the selection of a natural attenuation remedy.

The document emphasizes the subtle though important distinction between intrinsic biodegradation of contaminants in ground water and the process of selecting natural attenuation as a remedy for a particular site. As defined in this document, natural attenuation is "the demonstration that intrinsic degradation will reduce the concentrations of the contaminants before they pose unacceptable levels of risk to human health or the environment, or exceed ground water criteria at established points of compliance". Therefore, it is critical that 1) a natural attenuation remedy not be confused with a "no action" alternative, and 2) a natural attenuation remedy be clearly demonstrated on a site-by-site basis.

The screening phase involves sampling monitoring wells at background locations and within the plume. Samples are analyzed for a range of specific organic and inorganic analytes that, in addition to field measurements, indicate whether the oxidation/reduction status of the ground water is favorable to the biodegradation of the contaminants and their breakdown products. Preliminary modeling, including assumed degradation rates, provides a rapid assessment of whether natural attenuation is a potential remedy for the site.

The second phase consists of a detailed site characterization that is analogous to a feasibility study. It involves refining site specific degradation rates, obtaining hydrogeologic and lithologic data, defining plumes and exposure pathways, and determining distances to receptors of the ground water. Contour maps of contaminant concentrations, electron acceptors, and ground water elevations are developed. Fate-and-transport modeling refines predictions about the fate of contaminants over time. It may also include an evaluation of whether non-biological degradation of chlorinated solvents is occurring.

Implementation of the remedy includes the placement of "sentinel" wells between the plume edge and exposure points, establishing a long term sampling plan, and drawing up contingency plans in the event of unforeseen plume expansion.

The guidance includes technical discussions where needed, cites references in support of major concepts, and provides some biodegradation rate data helpful in the screening stages of the remedy.

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Natural Attenuation of Chlorinated Solvents in Ground Water

Interest in natural attenuation as a remedy for contaminated ground water is growing for a number of reasons. First, if natural attenuation can be adopted as a remedy, considerable savings in both effort and money are possible (though not guaranteed); second, contaminants may be destroyed in place to other compounds which are often harmless, rather than simply transferring them to another location or medium; and third, elaborate and intrusive engineered systems may not be needed for site remediation.

Potential disadvantages of a natural attenuation remedy may include a longer time that is required for ground water remediation, the need for a more detailed site investigation and characterization, long-term institutional controls, and long term monitoring costs and responsibilities. In addition, metabolic intermediates or breakdown products generated through biodegradation of the original contaminant may pose a greater health risk than the parent compound (49).

Apart from recognizing that contaminants can intrinsically degrade in ground water, caution must be exercised in selecting natural attenuation as a *remedy*. This summary outlines the major considerations for assessing natural attenuation as a remedy for chlorinated solvents such as perchloroethylene (PCE), trichloroethylene (TCE), dichloroethylene (DCE), and vinyl chloride (VC) in ground water. The reader is urged to consult other excellent resources on natural attenuation (1, 27, 42, 50, 59, 60).

What is a natural attenuation remedy?

Some aquifers have an intrinsic capacity for the biological degradation, abiotic degradation, adsorption, volatilization, and dispersion of contaminants in ground water. However, as a *remedy,* natural attenuation is the demonstration that this intrinsic capacity *will reduce the concentrations of contaminants and their metabolic intermediates or toxic breakdown products before they pose unacceptable levels of risk to human health or the environment or exceed ground water criteria at established points of regulatory compliance.*

Three key points regarding this remedy are emphasized below:

- **It is important that natural attenuation not be confused with or perceived as a "no action alternative".**

  Although the adoption of natural attenuation as a remedy can eliminate the need for an "engineered" or intrusive approach to remediation, modeling and extensive sampling are needed to adequately demonstrate that natural attenuation is sufficient to eliminate the risk of exposure to contaminants. Monitored natural attenuation must not be assumed as appropriate for a site and is not simply a "default" remedy if other remedies are found unacceptable (52).

- **Natural attenuation must be clearly demonstrated on a site-by site basis.**

  Demonstration of natural attenuation as a remedy is more than providing evidence that contaminants are breaking down or diluting. Rates of degradation and contaminant transport vary depending on location, and site conditions may be simple or complex. The effort required to demonstrate that natural attenuation is adequate as a remedy will depend on the complexity of the site and the desired degree of certainty in its efficacy. However, the burden of proof for a natural attenuation remedy rests with the party proposing it as a remedy. Site specific data and convincing arguments are expected in support of a natural attenuation remedy. As for any other remedy, monitored natural attenuation must meet all relevant remedy selection criteria and be protective of human health and the environment.

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- **Sources of contamination to ground water must be addressed.**

  Selection of natural attenuation as a remedy for ground water contamination does not imply that it is not necessary to remediate or remove sources of contamination to ground water when it is feasible (52). In general, sources of contamination in vadose soils should be addressed as per the Minnesota soil to ground water leaching guidance document (37).

Demonstrating that natural attenuation is a remedy can be broken down into three phases: screening, verification, and implementation.

The ***screening phase*** allows a rapid and inexpensive evaluation of whether biological degradation of the contaminants is occurring in the ground water. It is not meant to supplant a remedial investigation for the site or an evaluation of plume stability. However, a proper screening evaluation can prevent large expenditures of resources on sites where natural attenuation is not a promising remedial alternative. Currently, screening criteria for non-biological degradation of chlorinated solvents do not exist.

If results from the screening study are favorable, more detailed information is collected during the ***verification phase***. This involves establishing contaminant concentration trends, establishing contaminant degradation rates, conducting fate and transport modeling, refining an understanding of subsurface lithology, and collecting risk receptor information. This information is integrated into a convincing argument that natural attenuation is an effective remedy. Much of this information may already be available depending on the status of a site investigation.

Implementation of the remedy involves devising a long-term ground water monitoring plan to monitor the effectiveness of the remedy. Monitoring ground water at "sentinel wells" verifies that the plume is not expanding and that natural attenuation is performing as expected.

1.0 SCREENING FOR NATURAL ATTENUATION.

1. Establish that ground water conditions are favorable for the biological degradation of contaminants.

Locations:

Screening for natural attenuation can be a one-time sampling event. Ideally, samples are taken from locations 1) in the area of highest concentration; 2) downgradient from probable dense non-aqueous phase liquids (DNAPL); and 3) from an upgradient location representative of background conditions. An unimpacted down gradient location should be evaluated on the basis of geochemistry as well as the absence of contamination, and may not be available at many sites; in some cases, sidegradient wells may provide the best background locations, and site conditions may require modification of these locations. However, a background location is essential to allow a comparison of the geochemistry of uncontaminated ground water with that of the contaminant plume. A total of six monitoring wells or push probe points that are representative of these locations are sufficient. (For specifics on sampling procedures, see Attachment 1 or consult the EPA guidance document (49) on sampling procedures.) If possible, collect samples vertically within the plume, since ground water conditions may change with depth.

Push probe sampling techniques are very helpful in identifying the lateral and vertical extent of the plume and the locations of highest contaminant concentration. However, a study of field investigation techniques conducted by the Minnesota Pollution Control Agency (39) shows that Eh and concentrations of redox sensitive analytes including dissolved oxygen, nitrate, reduced iron and reduced manganese can differ significantly from samples

collected from established monitoring wells, implying that caution should be used when interpreting redox conditions from push probe ground water samples.

Samples:

Table 1 lists the analytes that are important in natural attenuation studies. Oxygen, pH, Eh, conductivity, and temperature are determined in the field, preferably through a low-flow cell designed for this purpose. Downhole probes are also acceptable. Other analytes, including reduced iron, reduced manganese, sulfate, sulfide, chloride, and nitrate can be measured using field test kits. Contaminants are analyzed in the laboratory through standard Environmental Protection Agency (EPA) methods. Appropriately preserved samples are sent to the laboratory for measurement of the dissolved gases methane, ethene, or ethane. Laboratory analysis is now available for preserved hydrogen gas samples (See Attachment 1, Section D).

Screening analysis:

The purpose of screening is to establish the potential for contaminant biodegradation in the ground water. Monoaromatic compounds (for example, benzene, ethylbenzene, toluene, and xylenes (BTEX)) biologically degrade readily under aerobic conditions. However, the biological degradation of highly chlorinated solvents occurs most efficiently under strictly anaerobic (chemically reducing) conditions that favor the microbial consortia capable of *reductive dehalogenation*. PCE, for example, though strictly non-biodegradable under aerobic conditions, can be microbially transformed to TCE, *cis*-dichloroethylene (cDCE), vinyl chloride (VC), and ethene in a highly reducing ground water environment. The difference is due to how bacteria metabolize these distinct groups of chemicals: various microbes use BTEX and similar compounds as a source of energy, while "breathing" an electron acceptor like oxygen; microbes that degrade chlorinated solvents use organic carbon (or BTEX compounds) for energy, while "breathing" the chlorinated compound as an electron acceptor. The aerobic biodegradation of BTEX or naturally occurring dissolved organic carbon can drive a ground water system anaerobic because oxygen is consumed in the ground water by the microbes faster than it can be replenished. Therefore, the biodegradation of BTEX compounds (though themselves contaminants) can lead to the conditions that favor the reductive dechlorination of chlorinated compounds.

A detailed discussion of the microbial degradation of BTEX and chlorinated compounds is beyond the scope of this document. However, in general, the less chlorinated the compound, the more amenable it is to aerobic biodegradation. Thus, TCE can degrade anaerobically or sometimes aerobically; vinyl chloride will biodegrade under aerobic conditions as well as under highly reducing conditions (56).

Other studies have shown that vinyl chloride and cDCE can biodegrade under iron reducing conditions (11, 12) and that cDCE can undergo anaerobic oxidation under manganese reducing conditions (13), a process that will not result in the formation of vinyl chloride. For more detailed information on the biodegradation of contaminants, several excellent reviews are available (8, 33, 48, 56).

While it has been demonstrated that chlorinated ethenes can abiotically degrade in the ground water (23, 35), it is currently not possible to easily screen for whether non-biological degradation is occurring at a site. Non-biological degradation of chlorinated solvents is dicussed later in this document.

Three methods are available to determine the oxidation/reduction (redox) status of ground water. The traditional approach is to measure the oxidation-reduction potential (ORP) of ground water with a platinum electrode. ORP is typically referenced to the standard hydrogen electrode (Eh) by correcting for temperature and the reference (for example, calomel) electrode. The manufacturer of the ORP electrode must be consulted in order to make the proper correction. Although ORP measurements indicate the approximate reducing potential of the system, they are often misleading due to the wide range of values that correspond to a particular oxidation/reduction condition (Figure 2). While convenient, the ORP is unsuitable as the sole indicator of the reducing status of ground water.

A more reliable approach to screening for possible biological degradation involves determining the *terminal electron acceptor* of the ground water system. Figure 1 shows the relationship between the geochemistry of ground water and its reducing potential. The redox status of the ground water, in turn, is indicative of the type of microbial metabolism that is dominant in the ground water. Oxygen utilizing organisms, for example, link their metabolism to the reduction of oxygen to water; iron reducing bacteria link iron III to their metabolism and produce iron II; sulfate reducing bacteria produce sulfide; and methanogenic organisms produce methane. Measuring these analytes in ground water helps reveal the relative capacity of the microbes that are present in that environment to biodegrade particular contaminants.

The third method involves measuring dissolved hydrogen in ground water. Hydrogen is produced through the fermentation of organic compounds in ground water, and is often referred to as the "metabolic currency" of anaerobic metabolism; the concentration of hydrogen in ground water corresponds to the predominant *in situ* microbial process. Thus, concentrations of dissolved hydrogen in ground water can determine the microbially catalyzed redox reactions in anaerobic groundwater that appear in Figure 1 (15, 18, 32). It is reported that concentrations of hydrogen below 0.1 nanomolar (nM) indicate nitrate reducing conditions; concentrations in the range of 0.2-0.8 nM indicates iron III as the terminal electron acceptor. Sulfate reduction is characterized by hydrogen concentrations in the range of 1-4 nM, and methanogenesis, which occurs under the most highly reducing conditions, corresponds to a hydrogen concentration from 5 to 15 nM (18, 32). However, there is evidence that in cold ground water (common in Minnesota), the hydrogen concentrations corresponding to these redox conditions may be somewhat lower (28).

The advantage to measuring hydrogen in ground water is that, unlike nitrate, sulfate, or reduced iron, hydrogen is very transient in ground water. It is possible, for example, for reduced iron, reduced manganese, and methane to migrate downgradient from the zone where it is formed, potentially confusing the assessment of redox conditions at a downgradient monitoring well. The transient nature of hydrogen prevents its migration to a downgradient location. This allows a more refined assessment of redox conditions at a particular location. Section E in Attachment 1 outlines the recommended field procedure for sampling hydrogen in ground water. Figure 6 depicts the apparatus used in the sampling procedure. For more detailed information, consult the papers by Chapelle et. al (20) and Lovley et. al. (32).

Screening for chlorinated ethylenes

Table 1 (from 50, 60) lists the analytes important to an evaluation of the biological degradation potential of chlorinated solvents (primarily for *chlorinated ethylenes* such as PCE and TCE). "Points" are awarded for favorable reducing conditions in ground water or the presence of metabolic byproducts of contaminants. For example, the presence of cDCE (at approximately a 5:1 or greater ratio to the *trans*- isomer of DCE) or VC demonstrates that TCE biodegradation is occurring in the ground water. Elevated concentrations of chloride ion over background levels is evidence that the parent chlorinated compound is being dehalogenated.

Compare the sampling results to the criteria in Table 1. If the numerical "score" from Table 1 is below 15, pursuing natural attenuation as a remedy for a site contaminated with chlorinated ethylenes is probably unwarranted, at least as a sole remedy.

Total points	Interpretation
0-5	Inadequate evidence for biodegradation
6-14	Limited evidence for biodegradation
15-20	Adequate evidence for biodegradation

>20 Strong evidence for the biodegradation of chlorinated solvents.

These numerical criteria should be applied cautiously for the following reasons:

a. The criteria in Table 1 are most suitable for the evaluation of chlorinated ethylenes. It may not be as useful to screen for the attenuation potential of other chlorinated compounds. Other contaminants such as methylene chloride or chlorobenzene, for example, can biodegrade under aerobic conditions; trichloroethane can abiotically degrade *via* hydrolysis to acetate or via dehydrodehalogenation to 1,1-dichloroethene. Thus, the demonstration of the redox conditions known to favor the dehalogenation of chlorinated ethylenes may not particularly *favor* the biodegradation of other chlorinated chemicals.

b. Numerical scoring results do not show that natural attenuation is a suitable remedy for the site. Table 1 was designed to highlight parameters that are particularly useful to a screening evaluation. The numerical score should be evaluated in context with the other screening items, but must not be used as the sole criteria in evaluating natural attenuation as a site remedy. The presence of metabolic intermediates or breakdown products, while indicating contaminant biodegradation, does not indicate the rate at which the degradation is occurring. As discussed in Section 3 below, the kinetics of degradation are an important factor in demonstrating a natural attenuation remedy for chlorinated contaminants. **The final evaluation of and justification for a natural attenuation remedy should not rely on the numerical scores derived from Table 1**.

c. Strongly reducing conditions alone do not guarantee that microorganisms capable of contaminant degradation are present or that dehalogenation is occurring. Highly reducing conditions are necessary for the presence of the microbial consortia needed to biologically dehalogenate chlorinated ethylenes such as TCE and PCE, but are not unequivocal evidence that the microbes responsible for that biodegradation are actually present. Conversely, there is evidence that significant degradation of cDCE and VC is possible under iron or manganese reducing conditions.

d. The screening results do not indicate the potential for non-biological degradation of chlorinated ethenes. Chlorinated ethenes can break down non-biologically in the presence of the iron-bearing minerals magnetite (30, 22) and iron sulfide (16, 17, 30). Unfortunately, no reliable screening indicators can demonstrate that abiotic degradation is occurring in the ground water at a site. The potential for abiotic degradation is discussed in more detail in the verification section.

Screening for contaminants other than chlorinated ethylenes

Screening for the degradation of chlorinated solvents other than chlorinated ethylenes or ethanes requires an adaptation of this approach based on an understanding of the degradation pathway for that individual chemical. If carbon tetrachloride is the contaminant of concern, for example, sampling for VC or cDCE is pointless, since these are not breakdown products of carbon tetrachloride. The presence of chloroform and high chloride concentrations, however, would suggest the breakdown of carbon tetrachloride in the ground water. Similarly, in screening for the biodegradation of pentachlorophenol, the formation of tetra- or trichlorophenols or anisoles would constitute evidence of the breakdown of this compound. Effective screening requires knowledge of a) the conditions that favor the abiotic or biotic degradation of that compound, and b) the metabolic intermediates or breakdown products resulting from the degradation of the parent contaminant. The degradation of some compounds, such as the pesticide alachlor, can result in many by-products of degradation. Clearly, a detailed discussion of the biodegradation of every potential chlorinated contaminant is beyond the scope of this document. Fortunately, there is a great deal of technical literature available for this purpose. The following is a suggested approach to screening for contaminants other than chlorinated ethylenes or ethanes:

- **Consult the technical literature**. Find out what is known about the biotic and abiotic degradation pathways for the contaminant in question. Note any degradation intermediates or breakdown products.
- **Note the environmental conditions that favor the degradation of the contaminant**. Are the conditions aerobic or anaerobic? If the conditions that most favor the biodegradation of a compound are aerobic, adhering to the redox-sensitive criteria in Table 1 will be misleading.
- **Does degradation of the contaminant rely on the presence or biodegradation of some other compound?** The biodegradation of certain compounds may occur through *cometabolism*: the contaminant will biologically decompose, but only when another compound is present. An example of this is the aerobic biodegradation of TCE, which requires the presence of a metabolic energy source such as methane, toluene, or phenol.

A list of analytes (geochemical and contaminant) would then be developed on a site-specific basis to screen for the natural attenuation of other contaminants based on an adequate understanding of the degradation pathways of that contaminant. Although such a list would lack a scoring assessment, further work on a natural attenuation remedy might be justified if metabolic intermediates were found and favorable conditions existed for the contaminant's biodegradation.

2. Gather site-specific ground water data to estimate flow characteristics.

To estimate ground water velocity and the movement of contaminants in ground water, site specific hydraulic conductivity (K) and hydraulic gradient (i) data are needed. Porosity (n) and dispersivity values are normally estimated based on literature values. Total organic carbon data is needed to determine the retardation of contaminants (Appendix A) along the ground water flow path; a conservative estimate is a fraction of 0.001. Assumptions may lead to simplistic, though useful, estimates to screen the site. More sophisticated analysis of ground water flow and contaminant transport can be done in the verification stages.

3. Estimate the spatial extent and concentrations of the plume, compliance boundaries, exposure points, and contaminant source areas.

This information is critical in determining the effectiveness of natural attenuation at the site. Locate the source of the contamination and estimate the distance along the ground water flow path from the source area to the leading edge of the plume. Also, measure the distance along a flow path to any downgradient receptors or compliance boundaries (consult the ground water guidance document (36) for additional information on regulatory compliance issues).

4. Estimate the rate of contaminant degradation.

If historical sampling data is available for the site, an estimate of the site-specific rates may be possible. See Section 3.0 and Appendices A and B for details on analysis.

If contaminant biodegradation is occurring in ground water at the site, literature estimates of the biodegradation rate can be assumed for screening purposes (26, 63). Use high and low estimates to vary the results of modeling.

It is important to distinguish an estimate of the *rate* of biodegradation from the mere observation of biodegradation. The biodegradation of a contaminant at some unknown rate does not necessarily mean that natural attenuation is an appropriate remedy; the question is *whether contaminant biodegradation is proceeding at a rate fast enough to eliminate the exposure risk to receptors.*

Exercise caution in adopting literature based biodegradation rates. Many rates found in the literature were obtained under conditions very unlike those found in aquifers. For example, TCE degradation rates can be found that were obtained from microcosm studies of TCE in sewage sludge, which is clearly inapplicable to ground water conditions. Select rates that were obtained under conditions that mimic the site ground water environment

as closely as possible. References that support the choices for biodegradation rate assumptions should accompany the screening results.

5. Estimate the rate of contaminant migration and compare it to the estimated rate of contaminant attenuation.

The objective of this step is to combine the information gathered in steps 1-5 and estimate the effect that natural attenuation is having on the contaminant plume. A number of models are available. The BIOSCREEN and BIOCHLOR models developed by Ground Water Services, Inc. and the Air Force Center for Environmental Excellence (41, 43) are non-proprietary, analytic models that are ideally suited to screening evaluations. The advantage of using a *screening* model over a more complex one is that a screening model can give a rapid assessment of the potential for natural attenuation at a site given limited time and data. It can also help identify where additional sampling points or monitoring wells should be located. By incorporating values for dispersion, adsorption, biodegradation, information about the source area, and plume measurements, the model calculates the distance that the ground water contamination is likely to migrate over a given time interval under those conditions.

Model the plume assuming that no degradation or attenuation is occurring, and then compare these results to those obtained when reasonable degradation factors are considered in the model.

6. Determine whether the predicted rate of natural attenuation meets screening criteria.

After modeling the contaminant transport:

1. does the screening effort suggest that the plume has moved a distance that is less than what would be expected if no contaminant degradation were occurring, based on the time since contaminant release and what is known about the ground water velocity and estimated contaminant retardation?
2. does the screening model indicate that it is possible that the contaminants are attenuating at a rate so that ground water applicable or relevant and appropriate requirements (ARARs) will be met at the established point of compliance?

If the answers to these questions are yes, a more detailed analysis (Section 2) in support of this remedy is required. If these conditions are not met, further analysis described in the following sections is certainly an option. However, consideration other remedial or containment alternatives for the site is strongly recommended.

2.0 DETAILED SITE CHARACTERIZATION: REFINEMENT OF THE SITE CONCEPTUAL MODEL.

A detailed site characterization is required to demonstrate the effectiveness of a natural attenuation remedy for chlorinated solvents. This is analogous to a feasibility study for other traditional remedies, and is meant to fill in "data gaps" and refine predictions of the future extent of the plume and contaminant concentrations. Detailed site characterization may include:

- locating contaminant source areas and the likelihood of NAPL (21);
- a complete analysis of exposure pathways for the contaminants. This should include ecological exposure pathways (for example, ground water migration to surface water) and projections of future aquifer use;
- additional hydrogeological information that defines the lateral or leading edges of the plume. This may include the identification of transmissive and non-transmissive units, grain size distribution, refinement of effective porosity values, and identification of preferential flow paths for ground water (40). Sampling of ground water over discrete, vertical intervals can yield valuable information about changes in redox

conditions with depth and identify possible downward migration of contaminants to lower aquifers or below the screened interval of a single monitoring well;

- collecting total organic carbon (f_{oc}) data for saturated soils and ground water, if not already collected in the screening phase;
- defining impacts from other contamination sources, including elevated concentrations of metals that may inhibit microbial activity (50); and
- refined estimates of site specific biodegradation rates (*See Section 3.2*)
- additional monitoring wells or push probe points.

During this phase of remedy analysis, a work plan should identify data gaps. Much of this information may already be available from previous investigations at the site.

The importance of a vertical sampling in ground water is illustrated in Table 2. Aquifers frequently demonstrate stratification in redox status, exhibiting aerobic conditions in the top few feet and becoming anaerobic with depth. Sampling at one depth can therefore yield misleading information depending on where the monitoring well is screened. For example, if the sample is collected only in the aerobic zone, it would appear that no degradation is occurring when in fact the potential for degradation may actually be greater with depth. Knowledge of this stratification is important in refining the extent of natural attenuation as a remedy.

The additional site characterization (either through analysis of data collected in previous studies or by collecting additional data) refines the three-dimensional conceptual model for the site. This can involve constructing contour maps for contaminants including degradation products (for example, cDCE) and electron acceptors (oxygen, nitrate, iron III, manganese IV, sulfate), and constructing potentiometric water table maps.

Additional refinements should include calculations such as sorption and retardation estimates (Appendix A), NAPL/water/soil partitioning calculations (if appropriate), and refined ground water velocity calculations.

3.0 RATE ANALYSIS: ESTIMATES OF SITE-SPECIFIC ATTENUATION KINETICS

3.1 Decreasing trends in contaminant concentrations: source decay terms

Decreasing contaminant concentrations with respect to the need for a response action or a remedy is discussed in the Groundwater Guidance document (36). Observations that ground water contaminant concentrations are decreasing with time are extremely valuable additions to an argument that natural attenuation is an effective remedy at a site.

However, as a single line of evidence, a few observations of decreasing contaminant concentrations does not constitute proof that natural attenuation is an adequate remedy for the site. There are several reasons for this. Concentrations may decrease, for example, for a few sampling rounds only to rebound to initial concentrations. Extended dry seasons that affect recharge to the aquifer may lower the water table. This may temporarily reduce ground water contact with source contaminant material, resulting in lower contaminant concentrations downgradient until the water table rises. Different sampling protocols or poor quality assurance/quality control (QA/QC) in sampling might also result in varying analytical results. These examples demonstrate the need for a thorough evaluation of changes in ground water contaminant concentration. Although a review of statistical methods is beyond the scope of this document, claims that concentrations are falling in ground water due to natural attenuation processes should be supported statistically. The empirical observation that solvent concentrations are falling should be supported with geochemistry data and modeling consistent with this guidance to demonstrate that natural attenuation is an important process affecting contaminants at the site.

Figure 4 shows data from a monitoring well that is downgradient of the source area of a ground water plume, where the sum of concentrations of all chlorinated solvents have decreased over four years of monitoring. The slope of the regression, 1.5×10^{-3} day^{-1}, corresponds to a source half-life of approximately 1.3 years[1]. Upper and lower bounds of confidence for the regression are useful in modeling efforts that can incorporate source decay terms. Similar analysis of other monitoring wells will give a range of source decay terms.

Approximation of the source half-life[2] may be valuable in approximating the time to cleanup, long-term monitoring plans, or meeting regulatory criteria for the site. However, extrapolations from regressions should be done cautiously and accompanied by modeling different possible scenarios and long term monitoring verification. For example, if the ground water environment is iron reducing, iron III may be depleted over time leading to a shift in terminal electron acceptor (30). This may in turn result in changes in the rate of contaminant biodegradation and the size of the plume.

3.2 Groundwater attenuation rates and degradation rate (lambda) calculations

Contaminant degradation is the primary factor contributing to a stable contaminant plume (15). Without it, adsorption (which retards contaminant velocity) and dilution alone are unlikely to yield a stable plume (i.e., one that is not expanding). Estimates of contaminant degradation rates can be derived through monitoring conservative tracers in the ground water (48, 58) or microcosm studies (61), although the rates derived from microcosm studies frequently overestimate *in situ* degradation rates (7, 61).

An alternative approach is to use regression techniques to determine site specific rates from available field data (48, 57). One method described by Buscheck and Alcantar (15) is summarized in Appendix A. Note that whereas Figure 3 shows data from an individual well in the evaluation of source decay, Figure 4 shows a regression of the logarithm of contaminant concentration with distance from the source area along the approximate centerline of the plume. In Figure 5, the slope of the log-linear regression, -0.0016 ft^{-1}, when multiplied by the ground water velocity of 124 ft yr^{-1}, gives an overall attenuation rate (k) of -0.2 yr^{-1}, or a half-life of approximately 3.5 years.

The biodegradation rate, λ, is estimated from the overall attenuation rate with estimates of the retardation constant (for details on this derivation, see Appendix A, Equation 3) and dispersion values along the plume axis. Using the site data for Figure 4 yields a λ of 0.12 yr^{-1} or approximately 60 percent of the overall attenuation rate, k, that includes attenuation due to adsorption and dilution. The biodegradation rate of 0.12 yr^{-1} is relatively low compared to many values found in the literature, which can range from 1.2 to 1.8 for microcosm studies or other field data (61). Thus, an initial natural attenuation screening that used degradation rates found in the literature might have easily overestimated biodegradation and therefore the effect of natural attenuation on this contaminant plume.

A similar approach involves an *in situ* tracer analysis. Whereas the method of Buscheck and Alcantar (15) used a regression of contaminant concentrations from multiple wells along the axis of the plume, the method of Wiedemeier *et al*. (58) allows an estimation of the biodegradation rate by accounting for the effects of a dilution on a conservative tracer (for a detailed discussion, see Appendix B). The technique relies on the assumption that the conservative tracer (usually Cl^-) is non-biodegradable and is only affected by dilution. Any change in the concentration of chloride is used to correct for the change in concentration of the contaminant

[1] Half-life = (0.693)/(degradation rate). In this case, (0.693/0.0015)*365 days/year = 1.3 per year.

[2] The source half-life is an estimate of how rapidly the contamination source is being depleted, and may reflect source removal efforts at a site. It is distinct from the contaminant biodegradation rate discussed in Section 3.2, which is an estimate of how rapidly the contaminant is biologically degrading in ground water.

caused by dilution[3]. Attenuation of the contaminant in excess of attenuation of chloride is therefore assumed attributable to biodegradation. This allows a degradation rate estimate within discreet segments of the contaminant plume, and may reveal degradation rates that differ between the source area and downgradient portions of the plume. It is a more empirical measure of the effect of attenuation, as opposed to the requirement for calculations of retardation constants, contaminant velocity, and estimates of dispersion used in Buschek and Alcantar's method.

Degradation rates derived through any of these methods are approximate. Non-linear sorption/desorption of the contaminants may affect the calculation of λ if the contaminant velocity term, Vc, is calculated assuming linear sorption with organic carbon. Also, without knowing the mass entering the system from a source, a "true" biodegradation rate cannot be measured. Additional assumptions are that the contaminant plume is "stable", lateral dispersion is negligible, and monitoring well locations are positioned along the axis of ground water and contaminant flow.

Changes in the direction of ground water flow and the averaging of contaminant concentrations across well screens of varying lengths may lead to distorted maps of contaminant plumes (29). These distortions may result in overestimates of contaminant attenuation rates, a possibility that requires careful consideration in the verification process and long term monitioring for natural attenuation remedies. However Ravi *et al*. (46) demonstrated at one site the validity of attenuation rates estimated through these techniques.

These limitations highlight the need for a comparison of degradation estimates measured through different means. Comparisons of the degradation rates found through the regression-by-distance method (15), a conservative tracer method (58), and literature values (26), or data from other sites (57, 63) will yield a range of reasonable rates. The goal is to achieve realistic and defensible estimates of the site-specific degradation rate for modeling purposes.

3.3 Calculation of a natural attenuation capacity term

The concept of "natural attenuation capacity" as a quantifiable term (19) is particularly useful in the analysis of other remedial options for a site (Appendix C). The capacity term depends on the site-specific biodegradation rate, assumptions of dispersion, and measurements of ground water velocity. The inherent uncertainties in these terms gives a range of values for the natural attenuation capacity of the site ground water that is helpful in making decisions about whether it is appropriate to view natural attenuation as an effective remedy.

The analysis is valuable in deciding the role of natural attenuation in a treatment train of remedies for the site. Frequently, the effects of natural attenuation on chlorinated solvents are insufficient to serve as the sole remedy for the site. The biodegradation rate may be very low or the distance to a compliance point may be shorter than the distance required for complete remediation through intrinsic contaminant destruction. While the effects of natural attenuation may be *insufficient* as a *sole* remedy, they are not *insignificant* in terms of site remediation. Thus, quantifying the natural attenuation capacity of the ground water "can be integrated with engineered methods to achieve overall site remediation" such as source removal or pumpout systems (19), and can be helpful in the process of evaluating other site remedies.

Balancing the contribution of natural attenuation against the benefits of feasible engineered remedial options is basically a cost-effectiveness consideration. For example, reducing the ground water velocity through pumping near the source area in a system with a very large capacity for contaminant attenuation may

[3] Other sources of chloride to ground water, such as road salt, may affect this analysis.

achieve remediation goals without the much larger costs associated with a complete ground water containment system. On the other hand, more costly engineered remedies are more defensible when the aquifer sediments have a low capacity for contaminant attenuation. The equations in Appendix C show that a reduction in the source contaminant concentration, a decrease in ground water velocity, an increase in the biodegradation rate, or any combination of the three has the effect of raising the natural attenuation capacity of the system. Remedial efforts should balance these considerations in a way that achieves contaminant reduction to the Minnesota ground water Health Risk Limit at the compliance point.

Engineered remedies may have a negative effect on natural attenuation processes (44) that should be considered by understanding the contribution of natural attenuation at a site. Chemical oxidation or air sparging, for example, will tend to increase dissolved oxygen and the oxidation/reduction potential in ground water, diminishing the intrinsic benefit of natural attenuation (22). Many "active" remedies, such as thermal treatment, damage the ability of the bacteria in the aquifer to degrade solvents, and may make solvent plumes larger. The evaluation of an engineered remedy in terms of how it will impact the naturally occurring remediation and the capacity of natural attenuation adds valuable perspective to the real cost/benefit of remedial actions.

The potential benefits associated with understanding the site specific biodegradation rate and the overall capacity for natural attenuation highlights the need to include these measurements and estimates early in the site investigation process. Apart from the possibility that natural attenuation may serve as the sole remedy, it is more likely that understanding these intrinsic properties in ground water can lead to more a cost-effective, iterative approach to planning the scale of ground water and soil remediation efforts. The recommendation for including natural attenuation sampling early in the site investigation (38) reflects the potential benefits of these characterization efforts.

4.0 Abiotic Degradation.

Until recently, non-biological contributions to natural attenuation remedies were largely ignored. While it was recognized that trichloroethane was abiotically transformed to 1,1-dichloroethene, for example, and that zero valent iron was highly effective in the dehalogenation of chlorinated solvents, naturally occurring or intrinsic abiotic reactions involving chlorinated ethenes were deemed insignificant in comparison to biological degradation.

Recent studies have demonstrated that chlorinated ethenes PCE, TCE, DCE, and vinyl chloride can break down non-biologically in contact with the minerals magnetite and pyrite (31, 16, 17; for a review, see 24, 34) Similarly, carbon tetrachloride was dechlorinated to chloroform in the presence of FeOOH (goethite) (2). Ferrey et al. (23) found that cis-DCE and 1,1-DCE were abiotically degraded in ground water at the Twin Cities Army Ammunition Plant. The rates of DCE degradation were similar to rates reported for the biologically-mediated degradation of these compounds (-0.2 to -0.4 per year), indicating that abiotic degradation is playing a substantial role in the reclamation of the aquifer. These studies and others demonstrate that in some instances abiotic mechanisms may be more important than biological degradation in the natural attenuation of chlorinated ethylenes in ground water.

The abiotic reactions involving chlorinated ethylenes at the TCAAP site (55) and the Baytown site (unpublished data) are occurring under geochemical conditions that are unfavorable to biological reductive dehalogenation of chlorinated ethenes. Therefore, the screening system (Table 1), which was designed to determine whether the redox status of ground water favors biological reductive dehalogenation, cannot predict abiotic degradation. Some studies (17, 31) have shown that acetylene is generated in the abiotic degradation of TCE, PCE, and DCE. However, acetylene has not always been observed in ground water where abiotic degradation is occurring. A more detailed site analysis is needed to verify abiotic degradation of chlorinated aliphatics in ground water.

The rate of contaminant degradation due to biological reductive dehalogenation should be internally consistent with the geochemistry of the ground water. For example, if ground water redox is poised at nitrate reducing conditions, chlorinated ethene concentrations should decrease as a function of distance due primarily to dilution. A calculated first order rate of decay that is in excess of the effect of dilution may indicate that the contaminants are degrading abiotically in the ground water. Ground water modeling may therefore be a reasonable screening tool for abiotic natural attenuation.

Verification of abiotic breakdown of contaminants requires 1) a demonstration that magnetite or pyrite is present in the ground water sediment, and 2) a laboratory microcosm study that confirms abiotic degradation of the contaminants in the sediment. Sampling the ground water sediment can normally be accomplished with a push-probe drilling rig fitted with a core designed to retrieve soil. Analysis of the sediment for magnetite and pyrite can be done at a mineralogical laboratory.

A microcosm study unequivocally demonstrates contaminant breakdown, either biologically or non-biologically. Microcosms are set up under conditions similar to the ground water environment with the contaminant of interest added to each. One half of the microcosms are heat killed to stop biological activity. If contaminants are degrading non-biologically due to iron-containing minerals, the rate of contaminant degradation measured over several months in the heat-killed microcosms would be similar to the rate of decay observed in the living microcosms. For more detail on microcosm construction and sampling, see references 23, 61, and 62.

5.0 MODELING: SIMULATING NATURAL ATTENUATION

Incorporating the site conceptual model and site-specific rate calculations to simulate the effect of natural attenuation on contaminants.

Site-specific fate and transport modeling that includes degradation rates helps predict contaminant migration and attenuation over time. The modeling performed in the screening evaluation (1.0 Screening for Natural Attenuation, Item 5) provides a convenient point to decide whether more resources should be committed to pursuing this remedy alternative. Computer modeling that incorporates the data gathered in Section 3 of this guidance can be used to generate projections of the long-term fate of the plume. Measurements of ground water velocity, sorption, estimates of the mass of contaminant at the source, and degradation rates used in refined fate and transport modeling helps estimate the distance that ground water contaminants are likely to migrate.

In its broadest sense, modeling a site consists of a conceptual model, site data, simulations, and interpretation of results. Each of these elements is critical for an adequate representation (modeling) of the site. Sufficient characterization data must be available to represent the existing plume: if, for example, the plume extent is unknown or underestimated, then the computer model cannot represent the site no matter what other information or features the model contains.

The conceptual model is developed from the analyst's understanding of the site, and includes features such as number of distinct aquifers, ground water flow directions, recharge and discharge zones, the source and type of contaminants, and knowledge of contaminant degradation pathways. In addition to these factors, the conceptual model should address the required dimensionality of the effort (e.g., one, two, or three dimensions). One- or two- dimensional models are applicable to certain problems, depending on the data collected at the site and the objectives of the modeling. Three-dimensional model applications are warranted only where extensive data collection has delineated the contaminant distribution at various locations around a site and across the aquifers involved. Clearly, if modeling is intended to predict the effect of natural attenuation, all of these factors must be considered. When modeling is attempted without careful attention to these factors, the results are based on false assumptions and accurate predictions will not be possible, regardless of the sophistication of the

computer model used. In general, the assumptions underlying the computer code used for simulating the site must match the conceptual model and qualitative understanding of the site.

It is important to identify and address any discrepancies between the capabilities of a given computer modeling program and the site conceptual model (53). One-dimensional models are useful for modelling the plume centerline, two-dimensional models are applicable to plumes that uniformly fill a single aquifer. If more than one aquifer is contaminated, or the plumes have a three-dimensional character, a three-dimensional model is required.

The frequent application of analytical transport models to predict the long term fate of ground water contaminants is a good illustration of this point. Analytical models, such as BIOSCREEN, are mathematical solutions to the ground water transport equation. Although they are easy to use, application of these models is limited because ground water flow is greatly simplified, requiring assumptions of homogenous aquifer properties and one-dimensional, steady ground water flow. These assumptions mean that analytical solutions to the transport equation do not account for things such as heterogeneous aquifers, drawdowns due to pumping wells, discharge to surface water bodies, or ground water flow divides. Further, in these models, advective transport of the contaminant is allowed to occur in only one dimension and transport in other dimensions is due solely to dispersion. Boundary condition specifications are necessary for developing analytical solutions, and generally deal with the source of contaminants and the treatment of the down gradient end of the domain. These are features that should be matched to site conditions. A plume discharging into a water body, for example, behaves differently than a plume flowing in an unbounded domain.

Numerical models remove many of the restrictions of analytical solutions, but may introduce other errors due to approximations necessary to their development. Numerical models are characterized by a grid placed over the simulation domain. The necessary compromises between grid spacing and computation time can lead to errors associated with grid spacing and the location of boundaries. For example, wide grid spacing can cause numerical dispersion of the plume, making the modeled plume more diffuse than the actual plume. The grid spacing may also contribute to mass balance errors. Mass balance in model solutions is of particular importance because the equations that govern ground water flow and contaminant transport are mass balance equations. *Thus, a minimum requirement for a correct numerical model application is that mass is conserved in the model output. Although mass balance errors attributable to numerical or grid spacing problems may be unavoidable, the modeler should minimize and clearly report them.*

Boundary conditions in numerical models must be carefully specified. Hydrologic boundaries correspond to features of the hydrologic system that are generally larger than the site scale. For example, a stream and river network may roughly define controlling water levels on a regional scale. Flow at a contaminated site lying in the watershed is influenced by these boundaries, but for reasons of practicality the model boundaries may be drawn at arbitrary locations around the site. When this is done, it is important that pumpage or other stresses not impact the boundaries specified in the model, and that this is documented. When modeled stresses do impact boundaries, the model cannot correctly represent the site.

Models usually require more data than is available from site investigations. First, geologic heterogeneity is not typically captured in its complete detail. Measurements are generally made on a coarser scale than existing heterogeneity. While complete elucidation of heterogeneity is generally not possible, a reasonable effort of delineating the main features of the aquifer is necessary.

Second, models contain parameter values that are almost never measured in the field but are required for modeling purposes. The most common examples of unmeasured parameters are the aquifer porosity and dispersivity. Input of such parameters is typically handled in two ways: as a best estimate and/or as a model calibration parameter. Estimation equations have been developed for dispersivities based on published field

studies. Literature values of porosity are often used. These can provide a starting point for calibration or they can be viewed as best estimates.

Input parameter values generally form the starting point for model calibration. Calibration is the process whereby the input parameters are adjusted so that the model matches field observations. Since there are multiple uncertainties in model inputs, calibration is needed to bring the model to a point of representing the aquifer and contaminant plume. First, models are calibrated to observed water levels. Drawdowns during aquifer tests can be used for calibrating model values as can other observed water levels. Second, the transport model should be calibrated to match the observed contaminant concentrations. This process starts with historical ground water contaminant concentrations. Using the site-specific estimates of biodegradation rate, ground water velocity, and retardation/sorption, the modeling should roughly predict current conditions. A poor correlation indicates the need to re-evaluate the quantitative terms discussed in Section 3, or may indicate that heterogeneity in the ground water system require more sophisticated modeling.

The required accuracy of the modeling depends to some degree on the relative location of the receptors to the plume. If the compliance boundary is at some distance from the leading edge of the plume, the adequacy of natural attenuation as a remedy may be demonstrated from a model application that is based on parameter values that represent "worst case" transport scenarios (for example, high end estimates of ground water velocity and contaminant half-life and a low end estimate of retardation). However, the modeling must reflect an understanding of site conditions, the contaminant distribution, and transport/transformation processes. This may demonstrate the effectiveness of natural attenuation as a remedy within certain bounds, or it may show that natural attenuation is clearly inappropriate for the site. The modeling documentation must show how the site conceptual model was devloped, why the particular model was selected, calibration strategy and results, the model predictions and interpretation, and the results of the worst-case simulations.

Reporting the modeling results:

The modeling report must include the following, preferably as a separate section in the report (an example can be found by consulting reference 53, 54):

- A clear statement of the modeling objectives;
- A description of the conceptual model of the site;
- Selection criteria for the particular model (60);
- Discussion of the discrepancies between the site and the computer code conceptual models;
- Justification for each input value, the source of the information, and whether input data was actually measured or assumed;
- A desription of the calibration strategy and calibration results;
- **A clear interpretation of the results, a discussion of how varying input parameters might affect any conclusions drawn from the modeling study (sensitivity analyses), and how the modeling objectives are achieved;**
- A discussion of the limitations of the modeling results (4).

6.0 IMPLEMENTATION.

Verification sampling (Section 2) provides historical data for an indirect demonstration of the natural attenuation processes at the site and the rate of contaminant reduction. The conceptual model development shows that the site-specific hydrogeology, transport, and fate issues are understood; the fate and transport modeling provides an affirmation of the potential for contamination reduction within the reasonable timeframe established for the site. These steps provide the arguments needed to show that natural attenuation is an acceptable remedy for the site. Implementation of the remedy involves the following steps:

Develop a long term monitoring and sampling plan:

It is important that predictions of the effectiveness of natural attenuation be verified through periodic monitoring. Monitoring wells include those that are placed to detect whether the nature of the plume is changing; and "sentinel" monitoring wells strategically placed to detect migration of contaminants outside the predicted area of containment.

Detection of contaminant in the sentinel wells should trigger actions to address plume expansion. The possibility of changes in ground water flow direction and the averaging of contaminant concentrations across well screens (29) should be considered in developing monitoring plans. For guidance on where to place sentinel wells, consult the discussion in the Minnesota Ground Water Guidance Document (36) pertaining to compliance boundaries and risk receptors. Multiple sentinel wells are recommended, and should evaluate both the horizontal and vertical aspects of the plume by spanning the depth of the aquifer.

Ideally, at least one monitoring well should be placed in an upgradient background location, one in the area of the source, one in the dissolved portion of the plume, and one in the periphery of the plume. The refined site conceptual model *(2.0, Site Characterization and Refinement of the Site Conceptual Model, above*) can help determine the best placement of these wells.

Develop contingency plans:

A monitored natural attenuation remedy may be implemented as the sole remedy for the site or as one part of a set of remedies. Contingencies should be made in the event that natural attenuation does not perform as expected, or if changes at a site result in modification of existing conditions. A reassessment of degradation rates and the overall natural attenuation capacity may be needed, or an alternative remedy may be implemented to halt the plume expansion. Changes in the existing use of the site would clearly warrant a reassessment of natural attenuation as a remedy for the site.

The net effect of a contingency plan may be to increase the natural attenuation capacity of the system (See Section 3.3). Plans for slowing the rate of contaminant transport in ground water through the strategic placement of pumpout wells, for example, can be drawn up as a contingency measure. Actions to further reduce the mass of contaminants leaving the source area may be another contingency approach.

Sampling:

Monitoring wells within the plume should be sampled for all contaminants and contaminant breakdown products, dissolved oxygen, nitrate, reduced iron, sulfate, and methane. Sentinel wells should be sampled for all contaminants, contaminant breakdown products, and dissolved oxygen.

Semi-annual sampling is recommended for at least two years following the decision to implement natural attenuation. This will establish a data trend that will serve as a baseline for future comparisons as well as verify

plume stability. Annual sampling is recommended after two years or at intervals deemed appropriate by Minnesota Pollution Control Agency staff.

Compliance:

The intent of this document is to provide the technical guidance for demonstrating that natural attenuation is a promising remedy for ground water contaminants. The monitoring and sampling described above is required to confirm that contaminants are attenuating in ground water in a manner that is consistent with modeling projections. However, these remedy verification efforts are distinct from and in no way replace the regulatory compliance requirements for the site: *a natural attenuation remedy must meet the same regulatory criteria or compliance boundaries as any other remedy*. Thus, consideration of the ground water regulatory compliance boundaries can influence the placement of sentinel wells used in the technology verification efforts (described above). *The appearance of contaminants in the sentinel wells will trigger deployment of contingency plans prior to contaminants reaching the ground water regulatory compliance points*.

While specific compliance criteria are established on a site-by-site basis, natural attenuation remedies are expected to meet the compliance criteria described in the Minnesota Ground Water Guidance Document (36) and is generally expected to prevent the migration of contaminants into previously unaffected portions of the aquifer. However, more importantly, if contaminants are expected to move downgradient above the Minnesota Health Risk Limits (HRLs) prior to stabilization and eventual recession, then a variance to Minn. Rule 7060 is required. Please refer to the Minnesota Ground Water Guidance document for details regarding compliance issues for ground water.

APPENDIX A: SITE SPECIFIC BIODEGRADATION RATE CALCULATIONS

I. Trend Line Analysis*

(*From*: Buscheck and Alcantar. 1995. Regression techniques and analytical solutions to demonstrate intrinsic bioremediation. *In*: Intrinsic Bioremediation, Hinchee, R.E., J.T. Wilson, and D.C. Downey, Eds. Batelle Press, Columbus, OH. pp. 109-116.)

Contaminant data from at least three monitoring wells situated along a transect parallel to ground water flow are required, as close to the centerline of the plume as possible. The overall attenuation rate, *k*, includes effects due to dilution, retardation, and degradation of the contaminant in ground water, and can be estimated from the relationship:

$$C_x = C_o e^{-k(x/Vx)} \qquad \text{Equation 1}$$

where

C_x = concentration of contaminant at x distance from the source;
C_o = concentration at the source;
V_x = ground water velocity and x/V_x is the residence time for contamination to move distance x;
k = overall attenuation rate.

Plotting the natural log of the contaminant concentration versus the distance from the source yields a line of slope $-k/V_x$.

The site specific biodegradation rate, λ, is estimated by accounting for the effects of dispersion and adsorption by the following steady-state solution to a one dimensional transport equation***:

$$\lambda = (V_c/4\alpha_x)\{(1+2\alpha_x[k/V_x])^2-1\} \qquad \text{Equation 2}$$

where

α= the scale-dependent aquifer dispersivity, an estimate of dispersion (approximately 5% of total distance x)**;
k/V_x= slope from the regression in Equation 1;
V_c= contaminant transport velocity.

V_c can be estimated by V_x/R_f, where R_f is the retardation factor for the compound of interest in the ground water:

$$R_f = 1+[(K_{oc})(f_{oc})(\rho)/n] \qquad \text{Equation 3}$$

where

K_{oc} = organic carbon partitioning coefficient for the contaminant;
n = porosity (assumed to be 0.3)
ρ = aquifer sediment density (assumed to be 1.7 to 2.0, depending on the soil composition;
f_{oc} = fraction of organic carbon in ground water sediments, conservatively assumed at 0.001. Samples for measuring organic carbon should come from samples on site in the plume or in its path.

(The value assumed for porosity should be consistent with the value chosen for soil density. For example, if the soil density is 2.0 g cm^{-1}, the corresponding porosity (assuming that the density of quartz is 2.7 g cm^{-1}) is 0.26.)

* A *major* assumption in using this method is that the plume is at steady-state. If the plume is expanding, then this technique will grossly overestimate the biodegradation rate of contaminants. Thus, it is important that this assumption be stated along with the results of this analysis. If natural attenuation is pursued at a site, *the long-term monitoring of ground water should verify that the plume is stable and that the estimation of λ calculated via this method is appropriate.*

** Equation 2 can be rearranged as:

$$\frac{\lambda}{k} = \frac{1}{R}\left[1 + \alpha x\left(\frac{k}{vx}\right)\right]$$

where $\frac{Vc}{Vx} = \frac{1}{R}$

shows that an overestimation of dispersivity (α) leads to an overestimation of the decay rate, λ. Although assumptions of α are necessary for modeling, reasonable values for α must be used.

*** One limitation of the method is that it may underestimate the biodegradation rate for breakdown products, such as cDCE, because they are not only decomposing but also being *formed* due to the biodegradation of the parent compound such as TCE.

II. Well-to-Well Analysis

(*From*: Wiedemeier, T.H., M.A. Swanson, J.T. Wilson, D.H. Kampbell, R.N. Miller, and J.E. Hansen. 1996. Approximation of biodegradation rate constants for monoaromatic hydrocarbons (BTEX) in ground water. Ground Water Monitoring and Remediation. Summer, 1996: 186-194.)

This method, similar to the method of Buscheck and Alcantar described in Appendix A, relies on a steady-state solution to a one dimensional transport equation to estimate a biodegradation rate constant.

Solving for the overall attenuation rate k in the relationship

$$C_x = C_o e^{-k(x/Vx)} \qquad \text{Equation 1}$$

gives

$$-\frac{\ln\left[\frac{Cx}{Co}\right]}{t} = k, \qquad \text{Equation 2}$$

where $t = (\frac{x}{v_x})$.

The *in situ* biodegradation rate is estimated by correcting for the effect of dilution with a conservative tracer in the ground water, such as chloride:

$$Cx_{(corrected)} = Cx\left[\frac{Cl^-_o}{Cl^-_x}\right] \qquad \text{Equation 3}$$

Where

Cl^-_o = chloride concentration at the upgradient location, and

Cl^-_x = chloride concentration at the downgradient well.

Replacing the Cx term in Equation 2 with the $Cx_{(corrected)}$ from Equation 3 yields an estimate of the biodegradation rate in the ground water between the two wells.

APPENDIX B: SITE SPECIFIC NATURAL ATTENUATION CAPACITY CALCULATIONS

The natural attenuation capacity of ground water is defined as the sum of dispersion, advection, biodegradation, and sorption on contaminants (16) according to the solute-transport equation:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - \frac{\rho_b K_d}{n}\frac{\partial C}{\partial x} - \lambda C . \qquad \text{Equation 1}$$

Assuming that the plume is at steady state, $\frac{\partial C}{\partial t} = 0$ and the sorption term, $\frac{\rho_b K_d}{n}$, becomes negligible. Equation 1 is then reduced to:

$$D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - \lambda C = 0 \qquad \text{Equation 2}$$

At x=0, $C = C_0$, and Equation 2 has the solution:

$$C(x) = C_0 e^{-\left[\frac{-v+\sqrt{v^2+4D\lambda}}{2D}\right]x} \qquad \text{Equation 3}$$

Where

$C(x)$ = the contaminant concentration at distance x;

C_0 = the contaminant concentration at x=0;

D = the coefficient of hydrodynamic dispersion, proportional to the ground water velocity and the scale-dependent aquifer dispersivity, α, where $D = v(\alpha)$;

λ = the site specific contaminant biodegradation rate;

x = distance from the source; and

v = ground water velocity.

The exponential term

$$-\left[\frac{-v+\sqrt{v^2+4D\lambda}}{2D}\right] \qquad \text{Equation 4}$$

in Equation 3 quantifies "the contaminant-lowering capacity of an aquifer per meter of flowpath". Note that Equation 4 is an estimate of the total effect of natural attenuation on a contaminant that incorporates the effect of biodegradation on the contaminant. From Equations 3 and 4, the natural attenuation capacity is affected primarily by the ground water velocity, the initial concentration of contaminant in the source area, and the site-specific biodegradation rate. Reducing the ground water velocity will increase the system's capacity to effectively deal with the contaminants in ground water within a specified distance. Similarly, knowing the intrinsic capacity of the aquifer to attenuate a contaminant can indicate how much to reduce the contaminant concentration at the source to reach a given concentration x feet downgradient.

The calculation of natural attenuation capacity is clearly prone to unavoidable uncertainty in the estimates of ground water velocity and biodegradation rate. Therefore, any estimate of attenuation capacity should include a range of estimates that acknowledge the uncertainty associated with ground water flow velocity, biodegradation rate, and dispersion. Varying the estimates of biodegradation rate and ground water velocity can establish realistic boundaries for the capacity of a system to attenuate contaminants.

Table 1: Analytical Parameters and Weighting for Screening

Analyte	Concentration in Most Contaminated Zone	Interpretation/Comments	Points
Oxygen[a]	<.5 mg/L	Tolerated; suppresses reductive dechlorination at higher concentrations	3
Oxygen[a]	>1 mg/L	Vinyl chloride may be oxidized aerobically, but reductive dechlorination will not occur	-3
Nitrate[a]	<1 mg/L	May compete with reductive pathway at higher concentrations	2
Manganese (II)	>1 mg/L	Anaerobic oxidation of cDCE possible	2
Iron (II)	>1 mg/L	Reductive pathway possible; anaerobic oxidation of vinyl chloride to CO2 possible	3
Sulfate[a]	<20 mg/L	May compete with reductive pathway at higher concentrations	2
Sulfide[a]	>1 mg/L	Reductive pathway possible	3
Methane[a]	>.01 mg/L	Ultimate reductive breakdown product	2
	>1	Vinyl chloride accumulates	3
	<1	Vinyl chloride oxidizes	
Oxidation reduction potential[a]	<50 mV against Ag/AgCl	Reductive pathway possible	<50 mV = 1 <-100 mV = 2
pH[a]	5<pH<9	Tolerated range for reductive pathway	
DOC	>20 mg/L	Carbon and energy source; drives dechlorination; can be natural or anthropogenic	2
Temperature[a]	>20^{o}C	At T>20^{o}OC, chemical process can be accelerated[(†)]	1
Carbon dioxide	>2x background	Ultimate oxidative breakdown product	1
Alkalinity	>2x background	Results from interaction of carbon dioxide with aquifer minerals	1
Chloride[a]	>2x background	Product of organic chlorine ; compare chloride in plume to background conditions	2
Hydrogen	>1 nM	Reductive pathway possible; vinyl chloride may accumulate	3
	<1 nM	Vinyl chloride oxidized	
Volatile fatty acids	>0.1 mg/L	Intermediates resulting from biodegradation of aromatic compounds; carbon and energy source	2
BTEX[a]	>0.1 mg/L	Carbon and energy source; drives dechlorination	2
Perchloroethene[a]		Material released	0
Trichloroethene[a]		Material released	0
		Product of perchloroethene dehalogenation	2[b]
Dichloroethene[a]		Material released	0
		Product of trichloroethene biodegradation; if amount of *cis*-1,2-dichloroethene is greater than 80% of total dichloroethene, it is likely a product of trichloroethene or perchloroethylene dehalogenation.	2[b]
Vinyl chloride[a]		Material released	0
		Product of dichloroethene biodegradation	2[b]
Ethene/Ethane	<0.1 mg/L	Product of vinyl chloride dehalogenation	>0.01 mg/L=2
			>0.1 = 3
Chloroethane[a]		Product of vinyl chloride biodegradation under reducing conditions	2
1,1,1-Trichloroethane[a]		Material released	0
1,1-dichloroethene[a]		Product of trichloroethene degradation or abiotic degradation of	

[a] Required analysis.
[b] Points awarded only if it can be shown that the compound is a breakdown product (i.e., not a constituent of the source of NAPL)

(*Modified from: Wiedemeier, T.H., J.T. Wilson, D.H. Kampbell, R.N. Miller, and J.E. Hansen. 1996*).

[(†)] Temperature may have limited utility for assessing biodegradation potential. While some have found that the biodegradation rate of some chlorinated compounds is temperature dependent, others (9) found that the degradation of toluene is not dependent on temperature. Temperature may have a larger affect on abiotic degradation processes such as the degradation of 1,1,1-trichloroethane to 1,1-dichloroethylene.

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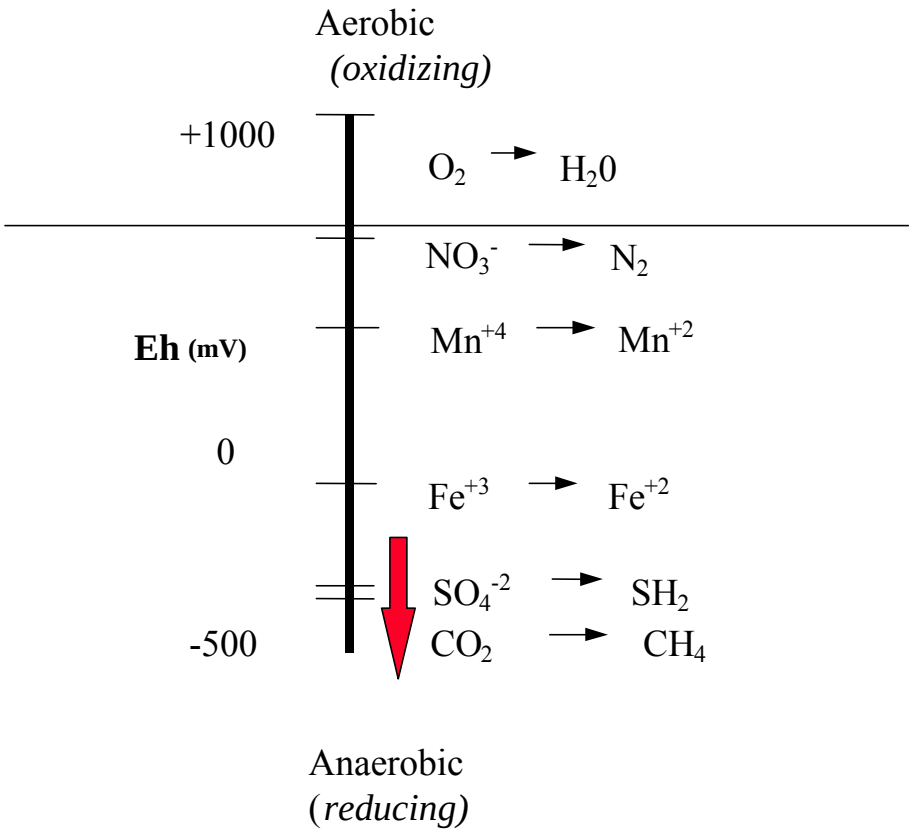
Table 2: Ground water geochemistry versus depth in regional unconsolidated and bedrock aquifers.

Analyte	Upper Unconsolidated	Middle Unconsolidated	Lower Unconsolidated	Bedrock Aquifer
Oxygen	9.5	0.8	0.2	0.2
NO_3^-	2.6	<0.1	<0.1	<0.1
Mn^{+2}	0.13	1.12	1.3	0.67
Fe^{+2}	<0.1	<0.1	<0.1	1.8
SO_4^{-2}	28	3.3	4.6	6.8
CH_4	Non-detect	0.06	0.02	0.01
Eh *	118	-60	-119	-243

* Readings in millivolts.
All concentrations are in mg/L.
(*From Brandon,et al., 1998*)

Figure 1: Geochemistry of ground water as an indication of oxidation/reduction status



(*Modified from Bouwer, 1993.)*

The redox status determines the predominant electron acceptor in the ground water. This figure relates the geochemical half-reactions to the corresponding redox potential in millivolts. The arrow shows the range of conditions that are most favorable to the biological dechlorination of chlorinated solvents such as PCE or TCE, indicating that the efficiency of contaminant degradation is highest under methanogenic or sulfidogenic ground water conditions.

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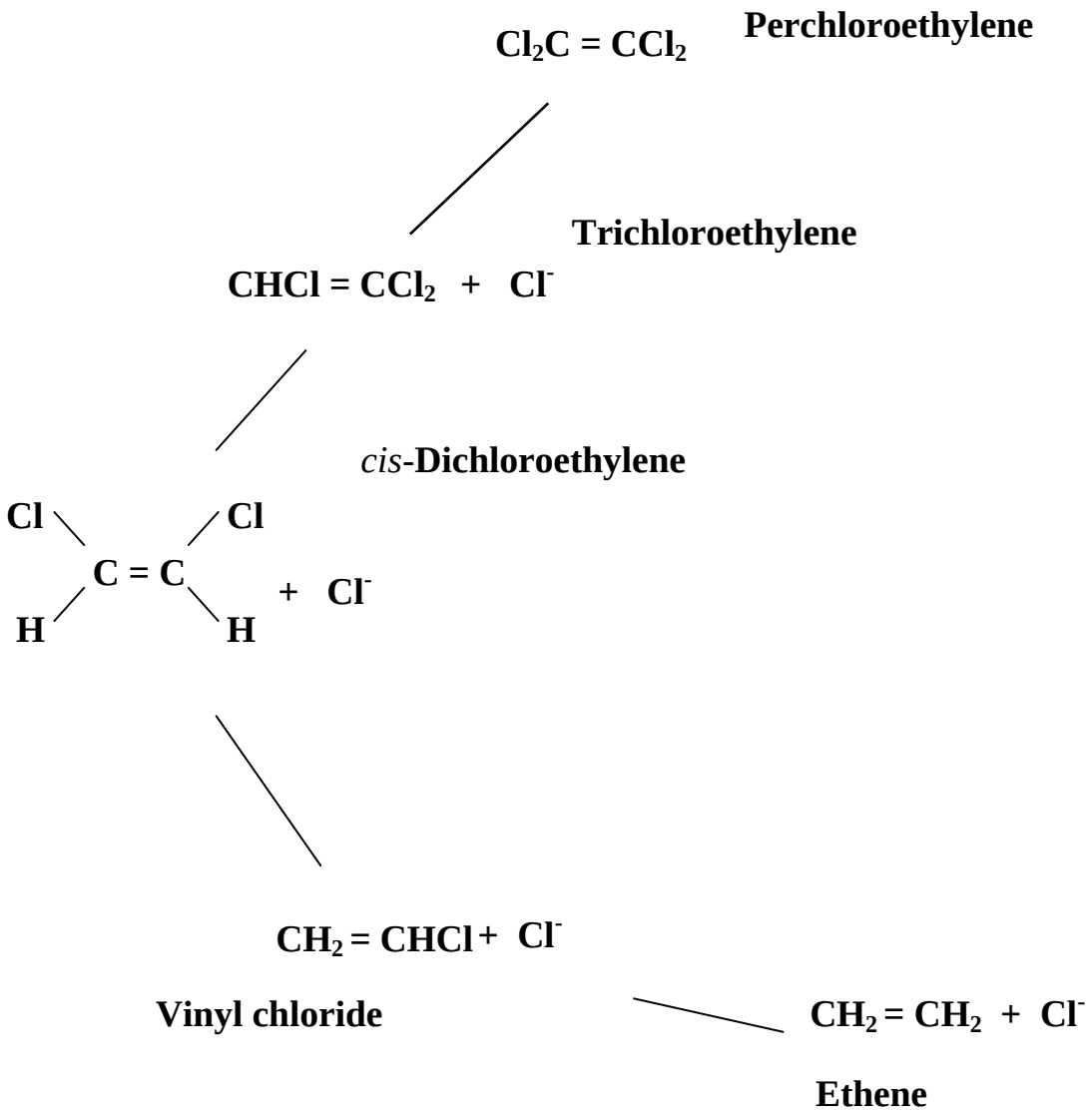
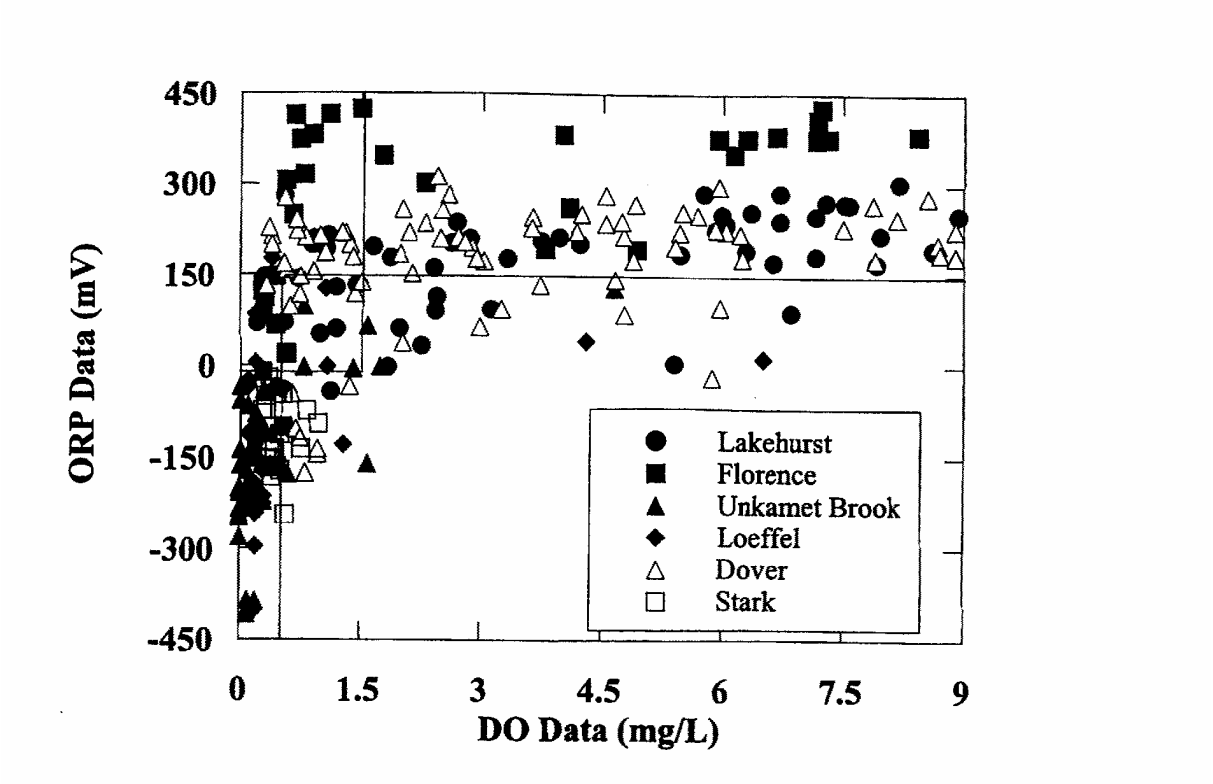
Figure 2: Biological reductive dechlorination pathway for chlorinated ethenes.



The biological reductive dehalogenation of the highly chlorinated solvent PCE producing TCE, cDCE, and VC as metabolic intermediates; vinyl chloride, in turn, is often reduced to the non-toxic compound ethene. The process is favored under sulfate reducing or methanogenic conditions in ground water. However, under manganese or iron reducing conditions, cDCE and VC may also biologically decompose without the formation of ethene.

Figure 3: Eh versus dissolved oxygen levels in ground water from six sites.



(*From Harkness, et al., 1998*)

The large variability between measurements of Eh and corresponding oxygen concentrations shows that although Eh may be useful for rough estimates of redox status, it is not suitable to accurately identify those conditions required for reductive dehalogenation of chlorinated ethylenes. Measurements of oxygen, nitrate, reduced manganese, reduced iron, sulfate, and methane are therefore necessary to clearly establish the redox potential of the ground water.

Figure 4: Contaminant concentration versus time from a single monitoring well.

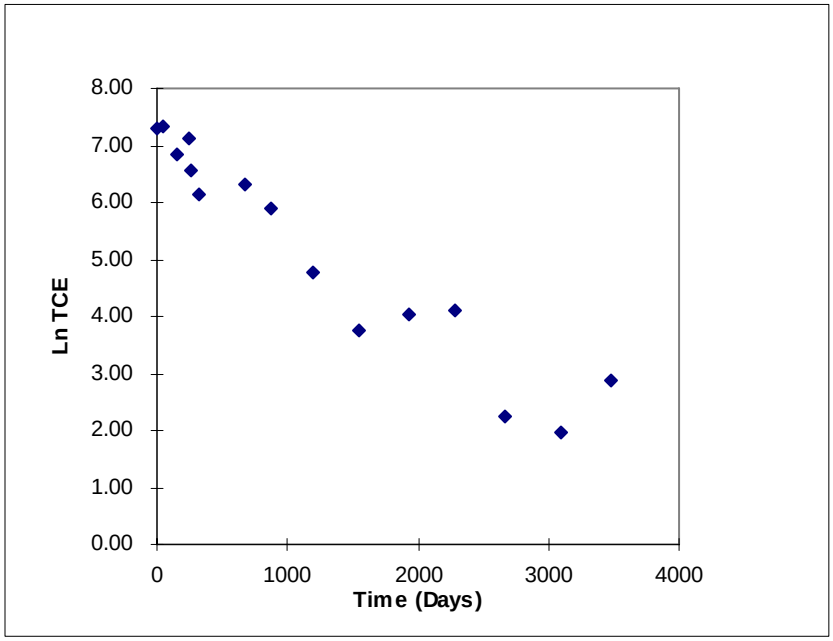
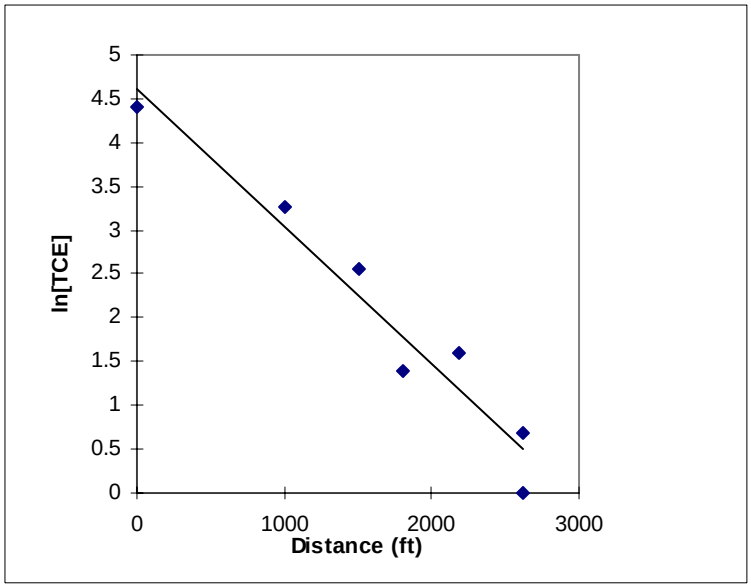


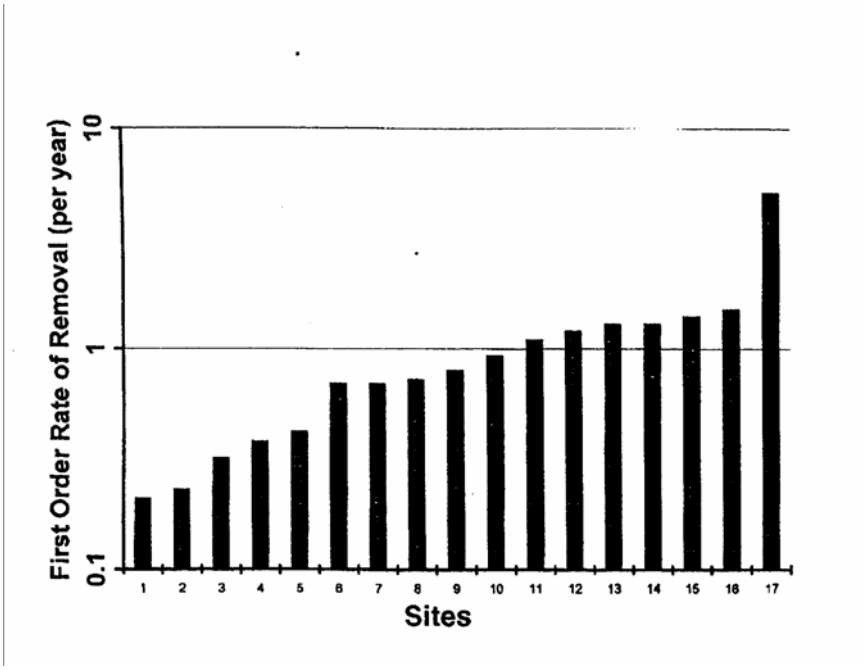
Figure 3 shows the natural logarithm of TCE concentrations plotted against time from a single monitoring well downgradient of the contaminant source area. The slope of the linear regression (*y = -0.0015x + 7.0*) yields an estimate of the rate of source decay of 0.0015 day^{-1}. Upper and lower bounds to the estimate can be determined statistically by setting 95% confidence intervals to the regression; analysis of multiple monitoring wells can refine the rate estimates that are useful in refined modeling efforts. (Note, however, that concentrations of breakdown products such as dichloroethylene or vinyl chloride may be increasing at the same location.)

Figure 5: Contaminant concentration versus distance



Log transformed concentration data at time *t* from wells situated along the centerline of contaminant plume is plotted against distance. The slope of the regression, *k*, includes effects due to dilution, retardation, volatilization, and degradation of the contaminant in ground water. In this example, k= -0.0016 ft^{-1}. Extraction of the biodegradation rate constant, λ, is discussed in Appendix A.

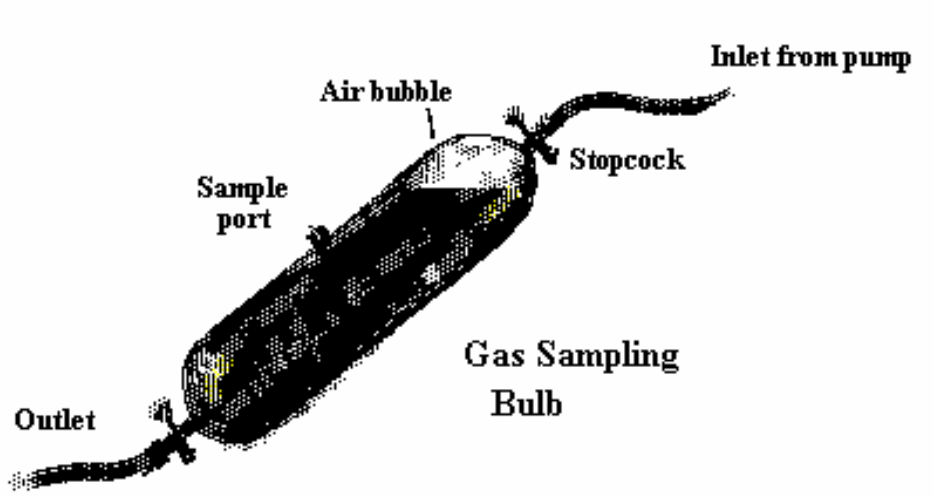
Figure 6: Typical TCE biodegradation rates in ground water



(From Wilson, J.T., D.H. Kampbell, and J.W. Weaver. 1996)

This figure illustrates that the first order biodegradation rate, or λ, varies widely depending on redox conditions prevailing in the ground water. A conservative biodegradation rate, in the range of 0.2 yr^{-1}, may be assumed for site screening purposes if the ground water geochemical environment favors the biodegradation of TCE and if TCE breakdown products are present. Published field degradation rates such as this can be helpful for placing site-specific degradation rate constants in a realistic context prior to refined modeling efforts.

Figure 6: Apparatus for sampling dissolved hydrogen in ground water.



The gas sampling apparatus for dissolved hydrogen consists of inlet and outlet ports fitted with stopcocks. The gas bubble (approx. 40-50 cc) is allowed to equilibrate with the ground water, which flows into the cell from the top and past the bubble at approximately 200-400 ml min^{-1}. Following an equilibration time of 30 minutes, a 10cc sample of gas is withdrawn with a gas-tight syringe from the sample port that is fitted with a septum. The sample can then either be analyzed immediately on a field hydrogen analyzer or injected into a sample container designed specifically for the preservation of hydrogen gas samples and sent to a laboratory for analysis.

ATTACHMENT 1: WORKPLAN CHECKLIST FOR NATURAL ATTENUATION

The following list itemizes the work needed to demonstrate that natural attenuation is a remedy for chlorinated solvents. Items are grouped by those required for an initial screening and those required for a detailed demonstration that natural attenuation is an acceptable remedy for the site.

Tasks that are considered essential for each phase of the evaluation are preceded by a shaded box; those that are optional (but may be necessary at a later stage in the investigation) are preceded by an open box. The collection of data beyond the required minimum may be attractive due to mobilization costs, time factors, or other site specific considerations.

Natural attenuation work plans or reports submitted to the MPCA for review should address each of theitems included below or the reasons why individual tasks or analyses were either inappropriate or not feasible.

Detailed discussion of the purpose of these tasks can be found in U.S. EPA's *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater* prepared in cooperation with the Air Force Center for Environmental Excellence (AFCEE), Technology Transfer Division (50).

A. Screening Tasks

1. Well/Groundwater locations and samples:

- ■ 1 background, upgradient from suspected source area
- ■ 1 background, side-gradient to plume or source area
- ■ 1 in source area
- ■ 2 within area of dissolved portion of contaminant plume
- ■ 1 downgradient of "toe" of plume

Sample number and frequency:

- ■ One round of sampling for each well

2. Geochemical Data:

Field*:

- ■ Oxygen (Field test kit and/or probe)
- ■ Temperature
- ■ Eh (oxidation/reduction potential)
- ■ pH
- ■ Reduced iron (FeII)
- ■ Reduced manganese (MnII)
- □ Carbon dioxide (CO_2)
- □ Hydrogen (From PVC wells only, using non-electrical pumps. For a detailed discussion of this method, see references 20, 32.)
- □ Conductivity
- □ Sulfide

Laboratory:

- ■ Nitrate (NO_3^{-2})
- ■ Sulfate (SO_4^{-2})
- ■ Sulfide (H_2S) (sulfide can oxidize during holding times)

- ■ Methane (CH_4)
- ■ Chloride (Cl^-)
- ■ Total organic carbon
- □ Alkalinity (See reference 47 for interpretation)

Contaminant ‡

- ■ Tetrachloroethylene (PCE)
- ■ Trichloroethylene (TCE)
- ■ Trichloroethane (TCA)
- ■ Dichloroethane (DCA)
- ■ Chloroethane
- ■ Dichloroethylene (DCE)
  (*cis*-1,2-dichloroethylene; *trans*-1,2-dichloroethylene; 1,1-dichloroethylene)
- ■ Vinyl chloride (VC)
- ■ Benzene, toluene, xylene, ethylbenzene (BTEX)
- ■ Ethene/Ethane
- □ Soil contaminant data, by depth in source area

(See Sections D and E below or Table 2.1 in the *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater* (50) for a compilation of analysis and sample preservation methods)

3. Aquifer data:

- ■ Hydraulic conductivity
- ■ Hydraulic gradient
- ■ Porosity estimate
- ■ Summary of local geologic features (aquitards, aquifer types, etc.)
- □ Vertical data on geochemistry
- □ Risk analysis of downgradient receptors
- □ Regulatory point of compliance
- □ Water table fluctuations
- □ Aquifer sediment total organic carbon

4. Biodegradation rate:

- ■ Assumed conservative biodegradation rate from literature (25, 63).
- □ Laboratory microcosm study (61, 62).
- □ Site specific estimate using conservative groundwater tracers (58).
- □ Site specific estimate using regression analysis (15)

5. Calculations:

- ■ Groundwater velocity estimate using hydraulic conductivity and hydraulic gradient data.
- ■ Comparison of electron acceptor and chloride concentrations to background samples.
- ■ Retardation/sorption estimate for contaminants.

6. Screening/Modeling

- ■ "Score" site data as per the AFCEE Protocol (Table 1) (50, 59).†
- □ Screening model, using "worst case" and "best case" scenarios of biodegradation rate, dilution, source mass, and groundwater velocity terms (41, 43)**

- □ Refined fate and transport modeling (provided that the necessary data has been collected to support this level of analysis. (3, 4, 5, 6, 9, 45)

.

** Field measurements can be made with a combination of probes and commercially available field test kits. Field analytical measurements using these kits must supported with quality control measures. This may include duplicate samples, occasional duplicate laboratory analysis for certain analytes (such as sulfate), standard samples of varying concentrations, field blanks, and rinseate controls. When not addressed in site-specific standard operating procedures, approval from regulatory QA/QC personnel is recommended prior to proceeding with field testing. This should include agreement on the level of data quality that these measurements will represent in subsequent analysis and decisions. Redox measurementsfrom samples collected from monitoring wells may differ from those collected from push probe samples (39).*

*** These screening procedures are intended to provide a basis for deciding whether contaminant attenuation is occurring and whether further sampling and analysis of this remedy is worthwhile. Though not required, running a screening model prior to verification efforts is strongly encouraged. This work can minimize the cost and effort at sites where contaminant attenuation is unlikely to occur at rates necessary for a natural attenuation remedy.*

‡ *This list is applicable to ground water contaminated with chlorinated aliphatic compounds. Obviously, the list should be modified to reflect site-specific contaminants and possible metabolic intermediates of biodegradation. Subsequent sampling may reveal the presence of contaminants (or their reductive metabolites) not detected in the screening phase.*

† *Most applicable for chlorinated ethylene contaminants.*

B. Verification

1. Wells/Groundwater samples:

(From the screening phase)

- ■ 1 background, upgradient from suspected source area.
- ■ 1 background, side-gradient to plume or source area.
- ■ 1 in source area.
- ■ 2 within area of dissolved portion of contaminant plume.
- ■ 1 downgradient of "toe" of plume.
- ■ Additional monitoring wells based on a Site specific analysis of data needs. (This might include definition of the downgradient extent of the plume; well nests to determine the vertical distribution of contaminants and electron acceptors; estimation of dense, non-aqueous phase liquids (DNAPL) extent; contouring of groundwater electron acceptors, etc.)

Sample number and frequency:

For each well:

- ■ a) Four rounds of groundwater samples, approximately 6 months apart,

  Or

  b) Based on the groundwater velocity term, determine the time needed for groundwater to travel the length of the plume. Sampling should occur at a minimum of four times within this "residence" time of groundwater flow according to the general rule:

{Plume length (ft)]/Groundwater velocity (ft/year)}/ 4 = time between samples

The size and complexity of the site - as well as inconsistent sampling results - may warrant more frequent monitoring. Verification sampling is intended to provide data to refine predictions of natural attenuation and allow adequate analysis and modeling of the site. It is distinct from sampling required in the long term monitoring events.

2. Geochemical Data:

Field:

- ■ O_2
- ■ Temperature
- ■ Eh (oxidation/reduction potential)
- ■ pH
- ■ FeII
- ■ MnII
- □ Hydrogen (from PVC wells only)
- ■ Conductivity
- □ CO_2
- □ Sulfide

Laboratory:

- ■ NO_3^{-2}
- ■ SO_4^{-2}
- ■ H_2S (can during holding times.)
- ■ CH_4
- ■ Cl^-
- ■ Total organic carbon

□ Estimate of Fe(III) available in aquifer sediments (30)
□ Alkalinity (See reference 47 for interpretation)

Contaminants[‡]

■ PCE
■ TCE
■ TCA
■ DCA
■ Chloroethane
■ DCE (*cis*-DCE ; *trans*-DCE; 1,1-DCE)
■ VC
■ BTEX
■ Ethene/Ethane
□ Acetylene*

[‡] *This list is applicable to ground water contaminated with chlorinated aliphatic compounds. Obviously, the list should be modified to reflect site-specific contaminants and possible metabolic intermediates of biodegradation. Subsequent sampling may reveal the presence of contaminants (or their reductive metabolites) not detected in the screening phase.*

Other contaminant information:

■ Estimate of DNAPL or LNAPL extent
■ Estimate of source area boundaries
■ Estimate of mass released in the source area based on historical data

Saturated/Unsaturated Soil:

■ Soil contaminant data, by depth in source area
□ Soil total organic carbon
(may also be required to evaluate the potential leaching to groundwater)
■ Contaminant Kd or Koc values from literature (37, 51)
(required to calculate retardation constant for contaminants; may also be required to evaluate potential leaching to groundwater)
■ Soil density
■ Soil/sediment porosity
□ Magnetite and pyrite concentrations in saturated sediment*

3. Aquifer data

■ Summary and analysis of local geologic features that may include: confining units; aquifer types; drinking water aquifers; analysis of boring logs; hydrogeologic section maps.
■ Depth of aquifer
■ Lithology
□ Vertical data on geochemistry and contaminant concentrations[†]
■ Risk analysis of downgradient receptors, including ecological receptors and future exposure points
■ Regulatory point of compliance
■ Advection and dispersivity assumptions
■ Potentiometric water table maps
■ Isopleth maps of intermediate metabolic products
■ Isopleth maps of electron acceptors
■ Isopleth maps of contaminants

□ Isopleth maps of above subjects by depth, if warranted

□ Identification of zones of high transmissivity and preferential flow paths through boring log analysis, cone penetrometer studies, or downhole flowmeter (40)†

† *Strongly recommended.*

4. Contaminant degradation potential:

■ Field measurement of degradation using tracers.
Or

■ Using data from at least three monitoring wells (preferably four or five), an analysis using regression analysis (15).

□ Laboratory microcosm study (61)**.

5. Calculations:

■ Retardation coefficient

■ NAPL/water partitioning constants

■ Site specific biodegradation rate, using well-to-well analysis or Buscheck and Alcantar's steady-state solution to a one dimensional transport equation (15).

■ Refined estimates of groundwater velocity and direction based on additional data

■ Natural attenuation capacity estimate (19).

6. Modeling and Analysis:

■ Refined fate and transport modeling.

□ Soil leaching modeling for source area. (37) (This will assist in determining the flux of contaminants to groundwater to evaluate source removal options and in assessments of the natural attenuation capacity for the site)

■ Refined three-dimensional conceptual model for the site (21).

■ Evaluate source removal effect on attenuation processes (19, 37).

■ Conduct additional sampling and analysis to fill data gaps, if needed.

□ Evaluate "active" remedies to augment natural attenuation (19).

■ Compile "weight of evidence" arguments; solicit regulatory approval for a natural attenuation remedy.

C. Long term monitoring plan

1. Wells/Groundwater samples:

■ Monitoring wells from verification phase (modified if necessary after modeling and development of refined conceptual model

■ Sentinel well locations, based on analysis and modeling results

Sample number and frequency:

■ Semi-annually during the first year

□ Annual sampling after one year if stable results from first year.

Monitoring wells (in area of plume):

■ Contaminants of concern

■ O_2

■ NO_3^{-2}

■ FeII

- ■ MnII
- ■ SO_4^{-2}
- ■ CH_4
- ■ Water level
- ■ Other analytes of regulatory concern

Sentinel or compliance monitoring wells (downgradient of plume):

- ■ Contaminants of concern
- □ Electron acceptors (including oxygen, nitrate, sulfate, reduced iron, reduced manganese, and methane)

2. Other:

- ■ Contingency plans for unexpected plume expansion.

** to demonstrate the potential for abiotic attenuation reactions.*
*** required to demonstrate abiotic attenuation reactions.*

D. Sampling Recommendations.

The following is a compilation of the analytical methods for a natural attenuation evaluation and recommendations for sample collection procedures. The reader is also urged to consult the MPCA Risk-Based Site Characterization and Sampling Guidance (38). The types of samples and the methods of collection may vary depending on site-specific considerations. Thus, individual work plans for sampling should be approved before proceeding with sampling.

Table 1.

Analyte/parameter	Method[1]	Sampling comments and recommendations
Reduced iron (Fe^{+2})	Field test kit[2]	--
Reduced manganese (Mn^{+2})	Field test kit	--
Oxygen	Field test kit O_2 Probe[3]	-- Use in flow cell apparatus.
Eh	Eh Probe	Use in flow cell apparatus.
pH	pH Probe Litmus paper	Use in flow cell apparatus.
Conductivity	Conductivity probe	Use in flow cell apparatus.
Temperature	Thermocouple or thermometer	Use in flow cell apparatus.
Carbon dioxide	Field test kit	--
Sulfide	Field test kit	--
Methane	Laboratory analysis	40 ml serum bottle with crimp cap. Preserve sample with 5 drops of 50% H_2SO_4[4]
Dissolved organic carbon	EPA lab method 9060	40 ml serum bottle with crimp cap. Preserve sample with 5 drops of 50% H_2SO_4[5]
Alkalinity	Field test kit	--
	EPA lab method 310	Screw-cap plastic bottle, no preservative necessary.
Sulfate	Field test kit	--
	EPA lab method 9035; 9036	Screw-cap plastic bottle, no preservative necessary; store at 4C.
Chloride	Field test kit	--
	EPA lab method 9250; 9251	Screw-cap plastic bottle, no preservative necessary

Nitrate	Field test kit	--
	EPA lab method 352	250 ml Screw-cap plastic bottle, preserve with 5 drops H_2SO_4
Hydrogen	Field hydrogen analyzer	Sample collected via dissolved gas flow cell as per reference (32) [6]
BTEX	EPA lab methods 465E; 8021B	40 ml VOA bottles, preserved with HCl
Chlorinated VOCs	EPA lab methods 465E; 8021; 8260	40 ml VOA bottles preserved with HCl

1. Laboratory methods may vary depending on the individual laboratory standard operating procedures. Consult lab personnel to ensure that sample collection is consistent with laboratory analytical standard procedures.

2. a) Several commercially available and reliable test kits are available. Ensure that the range of the test kit analysis is consistent with the expected range sampled.
   b) Provision for QA/QC requirements should be included in using field test kits. As for any other sampling protocol, sample blanks, duplicate sample analysis, and duplicate laboratory analysis are appropriate in gathering data. Check with quality assurance personnel to verify QA/QC sampling and the frequency of duplicates. Generally, one in ten samples should be run in duplicate.

3. All probes and electronic instruments must be calibrated as per the manufacturers' instructions on a daily basis prior to making measurements.

4. Preservative is added to reduce the pH so that any methane is not degraded biologically; the vials need to be sealed tightly to eliminate volatilization to the atmosphere

5. Preservative is added to reduce the pH so that organic carbon is not biologically degraded.

6. Samples for hydrogen analysis can be collected only from PVC wells and cannot be collected using any electrical pump. Use a peristaltic or some form of pneumatic pump. Some analytical laboratories now offer hydrogen analysis on preserved hydrogen gas samples collected in the field.

E. Recommended Field Sampling Procedure.

1. After well purging, record pH, temperature, Eh, and conductivity readings using a low flow cell apparatus and appropriate probes until readings are stable.
2. Fill (4) HCl preserved volatile organic analysis (VOA) vials for BTEX and solvent analysis.
3. Fill (2) 250 ml plastic screw cap bottles. Add H_2SO_4 to one and label this one as "preserved" for the analysis of ammonia and nitrates.
4. Completely fill (2) 40 ml serum crimp vials for the analysis of ethane, ethene, and methane; add a few drops of H_2SO_4 and immediately seal with crimp cap.
5. Perform all field test kit analyses (this may include iron II, manganese II, sulfate, sulfide, nitrate, and chloride)
6. Hydrogen sampling (*Modified from reference 50*):

   Note: Ground water samples for hydrogen analysis must be collected from a PVC monitoring wells with non-electrical pumps, such as a peristaltic pump or a positive displacement pneumatic pump. Steel risers or electrically driven pumps will hydrolyze water resulting in artificially high hydrogen concentrations in the sample. Wells must be at least 2 months old prior to sampling for hydrogen.

   a. Position the intake hose of the pump at the depth of the screened interval.

   b. Attach a glass 250 ml gas sampling bulb to the outflow end of the hose and adjust the flow rate to 200-400 ml/min. Holding the outlet end of the tube upright, nearly fill the sampling bulb with water, allowing a bubble of approximately 40 cc to remain in the bulb. Invert the sampling bulb at 45 degrees so that the incoming stream of water, entering the vessel from the top, flows past the bubble before exiting the bulb at the lower end (see Figure 6).

   c. Allow 30 minutes for the gas bubble to equilibrate with the hydrogen concentration in the ground water.

   d. Using a gas-tight syringe, remove 10cc of gas from the sampling bulb via the sampling septum on the side of the sampling bulb. Close the valve on the syringe.

   e. If using a sampling container specifically designed for the preservation of hydrogen samples, inject the amount of gas specified by the laboratory into the sampling container and preserve as per the laboratory's instructions. Otherwise, analyze on a field hydrogen chromatograph. Duplicate samples are recommended.

   Please consult references 20, 31, and 50 for additional information on hydrogen sampling protocol and analysis.

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