Understanding Chlorinated Hydrocarbon Behavior in Groundwater:

Investigation, Assessment and Limitations of Monitored Natural Attenuation

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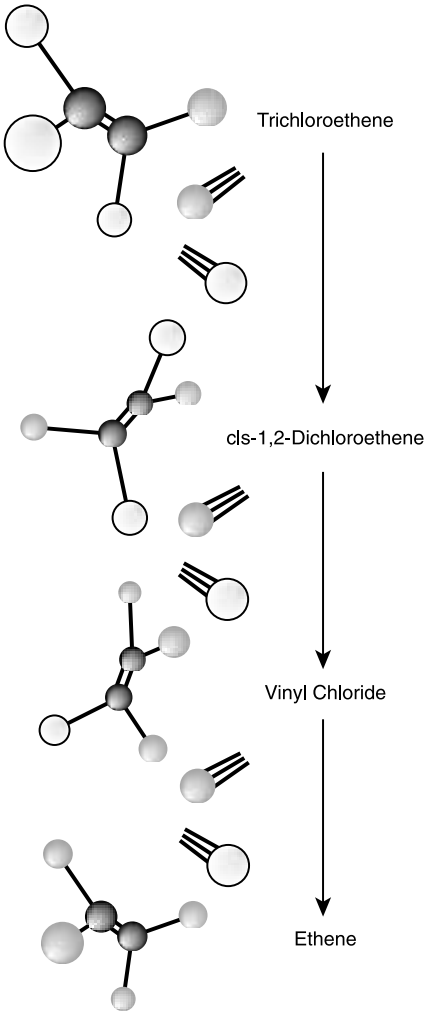

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Chapter 1

Purpose & Introduction

1.1 Purpose

This document is intended to provide guidance on characterizing and monitoring sites where monitored natural attenuation of chlorinated hydrocarbons is being considered as part of a cleanup remedy. All sites with chlorinated hydrocarbon contamination of soil or groundwater should identify the:

1. Degree and extent of contamination, including the presence of residual or mobile non-aqueous phase liquid (NAPL).
2. Geologic and hydrogeologic controls on contaminant migration.
3. Degradation patterns for contaminants and changes in geochemical species.
4. Factors driving degradation of the chlorinated contaminants and determine whether those factors will continue to function until cleanup standards are met.
5. Rate of mass loss of contaminants and estimate a cleanup time frame.
6. Long-term monitoring program that will be put in place to verify that cleanup goals will be met.
7. Contingency plan(s) if MNA fails or land use changes.

This guidance document is for responsible parties (RPs), consultants or other interested parties, and Department of Natural Resources (DNR) staff. This guidance should not be used as the sole reference for understanding or evaluating natural attenuation processes. Rather, it is to be used along with published references, state of the practice research and development, information from training courses and current journals. The material presented is based on available technical data and information and the knowledge and experience of the authors and the peer reviewers.

1.2 Introduction

Natural attenuation refers to any naturally occurring physical, chemical or biological process that degrades contaminants or limits their movement in the subsurface. Natural attenuation processes include dilution, dispersion, sorption, precipitation, volatilization, biotic and abiotic degradation and transformation. The processes that reduce mass of contaminants in the environment and are most effective and acceptable for meeting environmental standards and reducing risk to people and the environment are degradation (biotic and abiotic) and immobilization. However, it is often quite difficult to distinguish in the field the contributions from the various natural attenuation processes to the observed changes in contaminant concentration.

Monitored natural attenuation (MNA) has been termed a "knowledge-based remedy in which a proper engineering analysis informs the understanding, monitoring, predicting, and documenting of the natural processes, rather than manipulating them" (U.S. EPA, 2001). As such, MNA takes place only after a contaminated site has been investigated, site data analyzed, source control measures completed, and attenuation processes understood. MNA requires an adequate, long-term monitoring program that confirms that natural attenuation processes will protect public health, welfare and the environment until cleanup standards are met.

MNA has most commonly been applied to petroleum contaminants. Field and laboratory experience over the last two decades has established that benzene, toluene, ethylbenzene, and xylene (BETX) are likely to degrade in the natural environment under both aerobic and anaerobic conditions. Chlorinated hydrocarbons degrade through different pathways and under different conditions than petroleum. Understanding of chlorinated hydrocarbon degradation and confidence in long-term degradation is not as advanced as that of BETX degradation. The assumptions routinely employed with natural attenuation of petroleum cannot be applied to chlorinated hydrocarbons. For instance, groundwater screening levels from vapor intrusion models which were developed for petroleum compounds (e.g., the Johnson and Ettinger model) would typically be protective of the indoor air pathway for BETX but may not be protective of the indoor air pathway for chlorinated hydrocarbon contaminants.

Recent reviews of Monitored Natural Attenuation conducted by the National Research Council (2000) and EPA's Science Advisory Board (2001) have concluded that MNA may serve as an effective remedy for chlorinated contaminants at some limited number of contaminated groundwater sites. However, every contaminated site presents its own challenges and MNA should never be assumed to be effective. Chlorinated contaminants present unique challenges to determining their fate in the environment. Availability of a carbon source along with the proper geochemical and microbial conditions necessary for degradation determine whether chlorinated contaminants will degrade naturally. Effectiveness of MNA is based on fully defining the plume, documenting conditions for natural attenuation throughout the plume, and long-term monitoring data that documents natural attenuation processes will continue to be effective until standards are met.

Most sites contaminated with chlorinated hydrocarbons will require active remediation for source reduction and perhaps for plume control. MNA is more likely to be successful when used as one part of a comprehensive site cleanup, rather than as a sole remedy, at most chlorinated hydrocarbon sites.

This guidance specifically covers degradation and natural attenuation processes of chlorinated aliphatic hydrocarbons (CAH) which include chloroethenes, chloroethanes, and chloromethanes. The concepts of site investigation and monitoring can be applied to other recalcitrant compounds, such as chlorobenzenes, and MTBE, but degradation pathways and natural attenuation processes for these latter compounds are not addressed.

This guidance document reviews the criteria necessary to determine whether MNA may be a feasible remedial alternative at a site contaminated with chlorinated compounds. Topics reviewed include:

- contaminant source and type
- geologic/hydrogeologic setting
- site geochemistry and redox patterns
- patterns of contaminant degradation
- degradation rate determination
- long-term monitoring needs
- assessment and determination of effectiveness of natural attenuation processes
- regulatory structure of investigation, cleanup and closure

1.3 Applicability

This guidance is intended to help owners, consultants and regulators assess natural attenuation processes at sites contaminated with chlorinated aliphatic hydrocarbons and understand what role these processes may play in the cleanup of the site. This guidance does not address natural attenuation of chlorinated aromatic compounds (e.g., chlorobenzene), polyaromatic compounds (e.g., PCBs), MTBE, or other recalcitrant chemical compounds. However the basic concepts of site investigation and monitoring can be applied to any contaminant. When considering remedial alternatives, the capacity of natural attenuation processes to remediate contamination should be compared with other cleanup remedies and the best combination of alternatives chosen which result in a cost-effective and timely cleanup.

This guidance contains recommendations on assessing behavior and degradation of chlorinated hydrocarbons, monitoring groundwater and plume movement, assessing contaminant fate, etc. that are applicable to remedy selection regardless of whether MNA is part of the selected remedy. The information in this guidance may be particularly useful in supporting in-situ biological treatment of chlorinated hydrocarbons, such as in-situ bioremediation or bioaugmentation strategies.

Monitored natural attenuation is a remedy for environmental contamination in the same vein as engineered remedies (such as air sparging, pump and treat, soil venting). This guidance provides the framework for implementing a MNA remedy for chlorinated hydrocarbon contaminants. The framework for MNA does not apply to every contaminated site. Proper assessment of remedial options should produce an appropriate, cost effective remedy for the site. There are some contaminated sites where MNA can not be effectively assessed and where active remedies are either not effective or not practicable. Long-term monitoring of the environmental contamination may be an appropriate response at these sites after ascertaining that public health, welfare and the environment are protected. However, long-term monitoring by itself is NOT a remedy. In cases where monitoring alone is the only response available, long-term monitoring may need to continue until new remediation technologies are available to address the contamination or until environmental standards are met.

This guidance can be applied to assessment of chlorinated hydrocarbon plumes that emanate from municipal solid waste landfills. However, the regulatory requirements for landfills are not addressed in this guidance. Landfill regulations can be found in the NR 500 Administrative Code series.

The Wisconsin Administrative Code requirements governing the application of natural attenuation include ch. NR 140, Groundwater Quality and the NR 700 Series, Environmental Protection--Investigation and Remediation, Wis. Adm. Code. This guidance specifically references various sections of these codes.

1.4 Limitations

MNA will rarely serve as the sole remedy at a site. The vast majority of properties contaminated with chlorinated hydrocarbons will require active remediation to remove the source and possibly to control groundwater movement. **As a remedy, MNA is best used to address residual groundwater contamination after active remedies have removed the majority of the contamination.**

There are many sites where application of this guidance may be difficult or impossible. (For instance, sites with nearby public wells.) Those sites may not be candidates for the use of MNA as a remedy or may require additional remedial measures. Monitored natural attenuation should be assessed and applied as a remedial action with expected performance goals just like any other remedial action (e.g., soil venting, air sparging, in-situ oxidation). The applicability and limitations of MNA must be considered before MNA can be selected and implemented with any assurance of success. For instance, MNA is difficult to implement at a site with an undefined source area; or at a site with a poorly defined contaminant plume that cannot be adequately monitored; or a site where groundwater flow direction fluctuates significantly. A remedy selection process with specific cleanup objectives should be performed on all sites contaminated with chlorinated hydrocarbons to help ensure that the best, most cost-effective remedy is implemented for the given site.

1.5 Regulatory Review of Submittals

The NR 700 Wisconsin Administrative Code series is “self-implementing”. That is, responsible parties are expected to apply regulatory requirements found in the NR 700 series to cleanup of environmental contamination. Responsible parties are required to report contamination to the Department and submit reports detailing the progress of cleanup. Examples of standard submittals include site investigation work plans, site investigation reports, remedial action option reports, monitoring plans and reports, operation and maintenance plans and reports, closure reports, etc. The DNR, at its discretion, may choose to review these reports. Responsible parties and consultants can request that the Department review a submittal and provide written comments. However, the appropriate review fee (specified in NR 749) must accompany the request.

There are significant benefits to requesting Department review of submittals. Department review will help ensure that the cleanup complies with appropriate statutes and regulations and will provide technical input to the proposed actions. Department review is especially important during planning processes, such as the site investigation work plan, development of remedial action options and long-term monitoring programs. It is much more cost effective to determine if additional fieldwork or alternate remedial actions are needed during the planning process than after implementation of an inadequate plan. For example, the fee for Department review of a site investigation work plan is small ($500) compared to remobilization for additional site investigation (which can be several thousand dollars or more).

1.6 Disclaimer

This document is intended solely as guidance, and does not contain any mandatory requirements except where requirements found in statute or administrative rule are referenced. This guidance does not establish or affect legal rights or obligation, and is not finally determinative of any of the issues addressed. This guidance does not create any rights enforceable by any party in litigation with the State of Wisconsin or the Department of Natural Resources. Any regulatory decisions made by the Department of Natural Resources in any matter addressed by this guidance will be made by applying the governing statutes and administrative rules to the relevant facts.

This guidance is based on requirements found in chs. NR 140, 141, 708, 716, 720, 722, 724, and 726, Wis. Adm. Code; the Hazardous Substance Spill Law, s. 292.11, Wis. Stats., the Environmental Repair Statute, s. 292.31, Wis. Stats., and the Groundwater Law, s. 160.23 and 160.25, Wis. Stats.

1.7 Other Relevant Guidance Documents

When using this guidance, the following documents may be helpful. Using these documents is encouraged where appropriate.

- Close Out Guidance on the Use of Deed and Groundwater Use Restrictions and Deed Notices, PUBL-RR-606 http://www.dnr.state.wi.us/org/aw/rr/archives/pubs/RR606.pdf
- Interim Guidance on Natural Attenuation For Petroleum Releases, PUB-RR-614 http://www.dnr.state.wi.us/org/aw/rr/archives/pubs/RR614.pdf
- Department of Health and Family Services guidance on "Chemical Vapor Intrusion and Residential Indoor Air" http://www.dhfs.state.wi.us/eh/Air/pdf/VI_guide.pdf

DNR guidances may be obtained by:

A. Sending a request to: Public Information Requests, Bureau for Remediation and Redevelopment, Department of Natural Resources, P.O. Box 7921, Madison, WI 53707.
B. Calling the publication request line at (608)-264-6009.
C. Downloading the files from the internet at http://www.dnr.state.wi.us/org/aw/rr/archives/pub_index.html

1.8 Contact Person

Questions regarding this guidance should be directed to Theresa Evanson – RR/3, WDNR, P.O. Box 7921, Madison, WI 53707, phone number 608-266-0941, e-mail Theresa.Evanson@dnr.state.wi.us.

1.9 Guidance Revisions

This guidance will be updated as needed. Comments and concerns may be sent to "Guidance Revisions", Gary Edelstein - RR/3, WDNR, P.O. Box 7921, Madison, WI 53707, phone number 608-267-7563.

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Chapter 2

Laying the Basis for MNA: Chlorinated Hydrocarbon Behavior, Site Investigation and Monitoring Network

A conceptual model is a 3 dimensional understanding of the site history, contaminant source, soil and groundwater contamination, hydraulic properties of the groundwater flow system, distribution and fate of mobile, residual and dissolved contaminants and likely receptors. The conceptual model serves to guide the investigation, remediation and monitoring efforts used to deal with contamination. All data collected about a site is used to support and revise the site conceptual model, which then guides site remediation efforts. The conceptual model is the framework for the "prognosis" at the contaminated site and as such, is constantly evolving.

The conceptual model evolves as additional data is collected and assessed. Data used for developing the conceptual model should be quantitative as well as qualitative. Assessing natural attenuation mechanisms and determining whether those mechanisms can be relied on for plume control and protection of the environment and human health will, in most cases, require the use of predictive tools, such as statistical trends or fate and transport models. These predictive tools allow development of specific performance measures that, in turn, allow assessment of the conceptual model. For instance, data analysis from a site investigation can predict a certain capacity for natural attenuation in an aquifer. The long-term effectiveness of natural attenuation processes at the site is then borne out by results from long-term monitoring. Long-term monitoring results are then used to confirm the adequacy of the conceptual model as well as determine whether remedial goals are being met.

2.1 Overview of Chlorinated Hydrocarbon Behavior in the Subsurface

2.1.1 Physical behavior of chlorinated hydrocarbons

Understanding the physical behavior of chlorinated hydrocarbon in the subsurface will help guide site investigation strategies and define exposure pathways. Chlorinated hydrocarbons can enter the subsurface as a separate non-aqueous phase liquid (NAPL), in solution (e.g., dissolved in water), and/or as a vapor phase. It is important to determine how the chlorinated hydrocarbon has entered the subsurface (e.g., whether the release was on going, episodic, or a one-time event). This knowledge will guide the site investigation and subsequent remediation.

Chlorinated solvents have a density greater than water and the NAPL that forms is referred to as a dense non-aqueous liquid (DNAPL). An example of a DNAPL contaminant is perchloroethene (PCE) used in dry-cleaning clothing. DNAPL released to the environment can migrate through the soil where it coats soil particles and is held in soil and aquifer pores (referred to as residual NAPL[1]). Because it is denser than water, DNAPL that reaches the groundwater can move below the water table and, if enough DNAPL is released, move to great

[1] Residual NAPL (which can be either dense or light phase) is held in soil or aquifer material under capillary forces and will not flow under the force of gravity and will not drain into a well.

depths below the surface forming "pools" of free phase liquid on low permeability surfaces (referred to as "free" or "mobile" NAPL[2]). The residual and mobile DNAPL serve as long-term sources of groundwater contamination. Groundwater plumes emanating from DNAPL can exist throughout the vertical extent of the aquifer. However, small releases of DNAPL can remain in the unsaturated soils and never reach groundwater. Chlorinated solvents in soils are a source of vapor contamination that can migrate to enclosed spaces (such as basements) and serve as a source of contamination to shallow groundwater.

The ability of soils to hold DNAPL is dependent on the properties of the DNAPL and the subsurface media. The saturation of a DNAPL in soil (i.e., the volume fraction of pore space occupied by the liquid) is difficult to directly measure, but is dependent on interfacial tension between water and the DNAPL, the wettability of the media, capillary pressure, relative permeability of the formation, and the solubility, volatility, density, and viscosity of the NAPL. (Mercer & Cohen, 1990). The interaction of DNAPL and soils can lead to DNAPL spreading along the water table leading to significant contaminant mass at the soil - water table interface, even though DNAPL is denser than water. This happens because interfacial tension and capillary pressures cause a DNAPL pressure head to build up at the water table until the DNAPL is able to penetrate the water table.

Solvent mixtures that are less dense than water can contain chlorinated compounds. These are referred to as light non-aqueous phase liquids (LNAPL). For example, a petroleum solvent that contains a significant percentage (e.g., 25%) of trichloroethene (TCE) can have a density less than water. A release of LNAPL to the soil will tend to move through the soil, with significant amounts being held in the soil. If enough solvent mixture is released, the LNAPL will "float" on the water table and will tend to create a shallow groundwater plume near the source. Farther downgradient from the source, the dissolved contaminant plume may move to deeper levels in the subsurface due to infiltration of clean water above the plume, to hydraulic gradients, and/or to site stratigraphy.

Aqueous mixtures can also contain chlorinated hydrocarbons. As contaminated water, such as landfill leachate, enters the subsurface it moves through the soil or unsaturated zone and, if there is enough volume, enters the groundwater. Aqueous phase contaminants are less likely to cause significant vapor plumes in the soil (although in the example of landfills, significant vapor contaminants can originate from the source waste). The hydraulics of the flow system and the retardation characteristics of the contaminants will determine movement of dissolved phase contaminants in the groundwater.

Vapor migration within unsaturated soils and bedrock can be a source of shallow groundwater contamination in any direction from the original source area. Soil gas monitoring is useful in identifying these source zones. Mendoza and McAlary (1990) show that in sandy material a TCE vapor plume will spread rapidly by "molecular diffusion and possibly density driven advection. Phase transfer reactions will . . . significantly increase the size of the potential source of ground-water contamination". The relationship between contaminant concentrations in the soil-gas and concentrations in the groundwater is not straightforward and is strongly dependent on soil moisture content (McCarthy and Johnson, 1993). In addition, chlorinated compounds in shallow groundwater (even at concentrations that approach groundwater enforcement standards) can volatilize and present a threat of vapor intrusion to indoor air.

[2] Free or mobile NAPL occurs at saturations high enough to move under the force of gravity and will drain into a well.

Whether vapors will off-gas from a shallow groundwater plume is dependent on the depth of the capillary fringe and the amount of unsaturated pore space available for vapor migration. Depending upon site conditions, soil gas monitoring may be useful to identify shallow groundwater contaminant plumes.

Figures 1 and 2 illustrate the concepts of chlorinated compound movement in the subsurface.

Appendix A presents methods to assess DNAPL in the subsurface. All site investigations should assess the source(s) of the chlorinated compounds, including an estimate of the volume of contaminant in the source zone of the release. The source, history and location of the release, the characteristics of the release, the subsurface characteristics and the fate of the contaminants after the release will largely determine the subsurface distribution of the contaminants. The goal of a site investigation is to identify the subsurface distribution of contaminants, assess contaminant fate and transport and to lay the basis for selecting a remedy that will lead to the cleanup of the contamination.

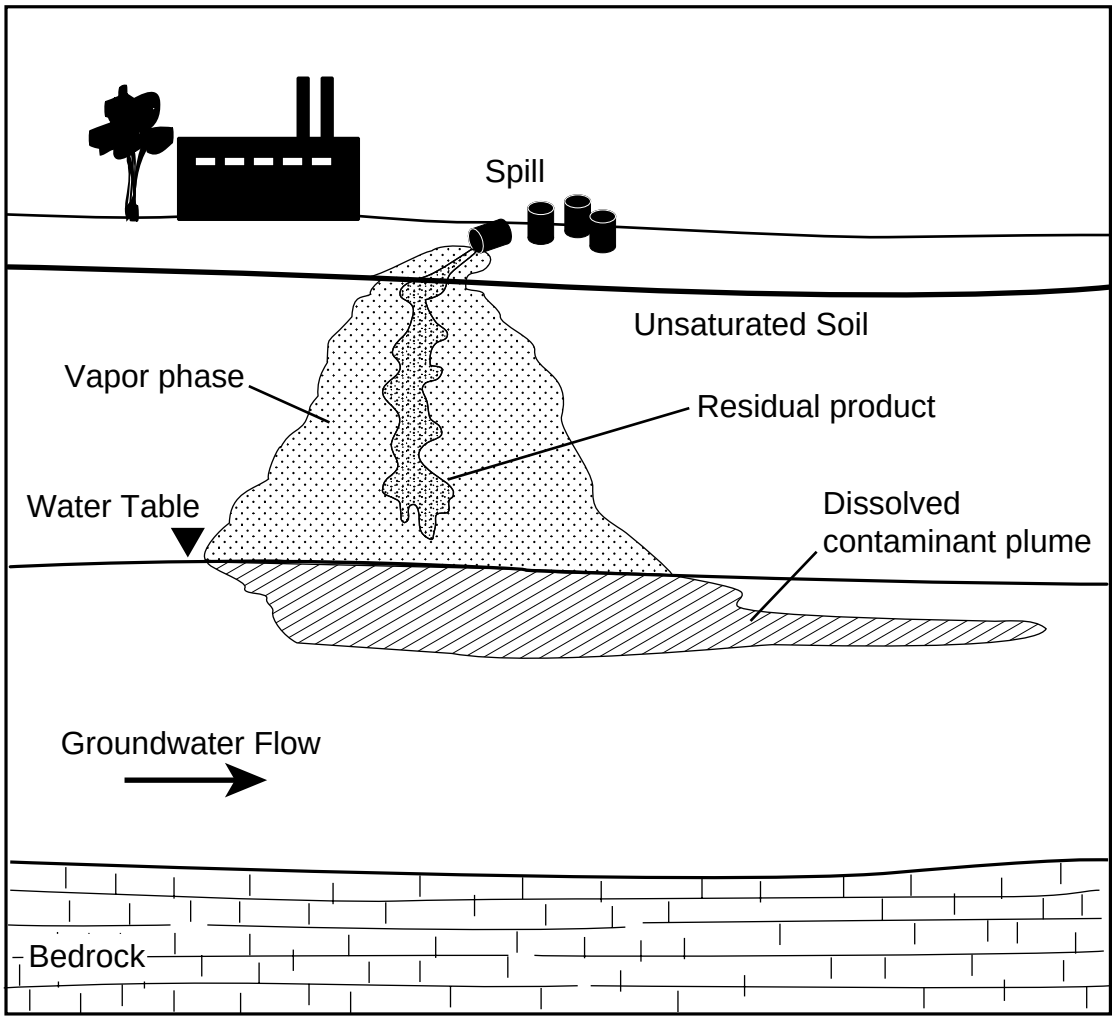

Figure 1. Release of a small volume of chlorinated solvent. The spill does not exceed the retention capacity of the soils. The residual product is entrained on the soil particles and DNAPL never reaches the water table. Primary sources of contamination to the groundwater are soil vapor migration and surface water infiltrating through the contamination. (Graphic after Schwille, 1988.)

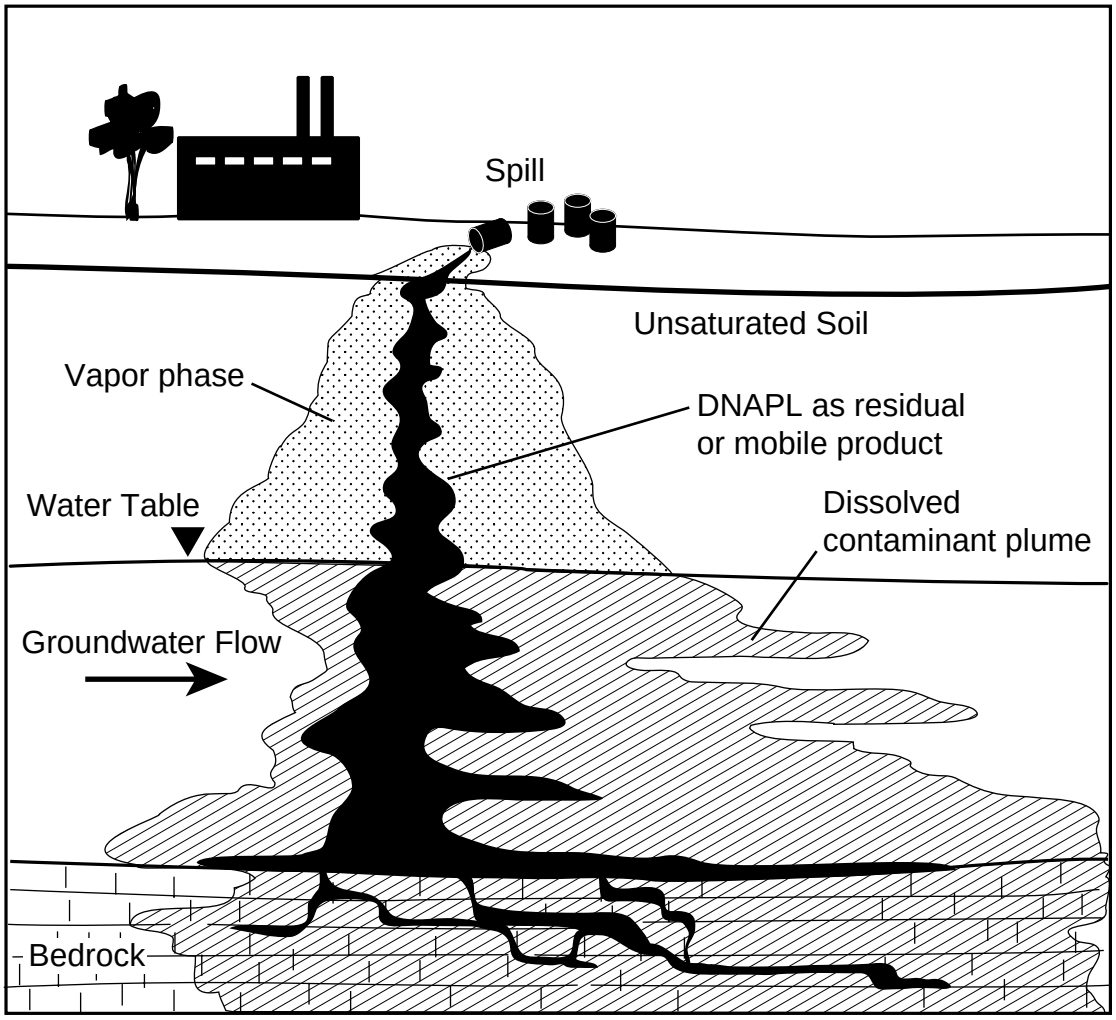

Figure 2. Release of a large volume of chlorinated solvent. The spill exceeds the retention capacity of the soils and underlying aquifer materials. The chlorinated solvent moves through the soil and groundwater as a DNAPL. In this illustration, the DNAPL forms “pools” along less permeable bedrock surfaces. (Graphic after Schwille, 1988).

2.1.2 Degradation processes affecting chlorinated hydrocarbons

When a chlorinated contaminant enters the subsurface, the contaminant will partition among four possible compartments: soil-air, soil-water, soil-matrix and NAPL (when the soil pores are saturated with solvent). Contaminant moving from these phases (but mainly the dissolved fraction) will subsequently contaminate groundwater. The contaminant concentration and mass in all the contaminant phases need to be understood to effectively and efficiently clean up the contamination. Natural attenuation processes occur in all media (with perhaps the exception of NAPL), but the most studied processes are those occurring in groundwater. Physical processes, including sorption on soil grains, volatilization, dilution in groundwater, etc. that serve to reduce contaminant concentration all play a part in natural attenuation processes. However, for purposes of cleaning up the environment and meeting regulatory goals, mass loss of chlorinated compounds from the subsurface occurs primarily through biotic and abiotic destruction. Site investigation should include monitoring and assessment for patterns of contaminant and geochemical changes that are indicative of these destructive processes. The primary naturally occurring degradative processes affecting CAHs include anaerobic and aerobic biotic processes and abiotic destruction. A short summary of the destructive processes are provided below. Appendix C addresses degradative mechanisms in more detail. Other references on this topic include Wiedemeier (1999); Wiedemeier (1998); U.S. EPA (2000).

2.1.2.1 Reductive dechlorination

The degradation of chlorinated compounds with 3 or 4 chlorine atoms are subject primarily to reductive dechlorination. Reductive dechlorination (a.k.a. halorespiration) is a microbially mediated process in which the chlorinated compound serves as an electron acceptor and a chlorine atom is removed sequentially from the core carbon molecule (e.g., ethene, ethane or methane). Reductive dechlorination occurs under strongly reducing conditions and requires carbon as a food source for the microbes. Less chlorinated compounds (those with 1 or 2 chlorine atoms) are also subject to reductive dechlorination but the degradation rates are usually slower than for the more highly chlorinated compounds. Complete reductive dechlorination produces ethene, ethane, or methane and CO_2.

Reductive dechlorination often results in partial dechlorination that can lead to accumulation of intermediates such as cis-DCE and vinyl chloride. Vinyl chloride is a known human carcinogen and, as such, has a groundwater enforcement standard that is 25 times lower than either PCE or TCE. The increased toxicity of the degradation product illustrates why it is critical to understand the subsurface processes affecting degradation and transport of chlorinated hydrocarbons. The selected remedy must adequately protect human health and result in the cleanup of parent contaminants and their breakdown products.

2.1.2.2 Oxidative destruction

CAHs serve as an electron donor (food source) when microbes oxidize the contaminants. Microbes have not been found to oxidize PCE. Oxidation can occur under both aerobic and anaerobic conditions, with oxygen (an aerobic process) or nitrate, iron, sulfate, methane (anaerobic processes) serving as the electron acceptor. The less chlorinated compounds, such as cis-DCE and vinyl chloride are subject to oxidation. Enhanced bioremediation systems can stimulate the oxidation of TCE, which occurs fortuitously (i.e., the microbe receives no benefit from the degradation). However, it is not likely that TCE is microbially oxidized under natural conditions.

2.1.2.3 Abiotic destruction

Abiotic degradation involves chemical reactions in soil and water that do not require the mediation of microbes. The primary naturally occurring abiotic processes are hydrolysis and elimination (a.k.a. dehydrohalogenation). Abiotic degradation is usually a slow process but plays an important role in some of the CAHs. 1,1,1-TCA can be transformed by both hydrolysis and elimination reactions while chloroethane and chloromethane can be transformed by hydrolysis. (See figures in Appendix C).

2.1.3 Chlorinated hydrocarbon movement in the subsurface

No single natural attenuation process controls contaminant movement in the subsurface. The combination of the physical setting and biological and non-biological subsurface processes affect contaminant movement. A review of plume formation, hydrogeologic settings, and transport processes involved in the movement of chlorinated hydrocarbons is beyond the scope of this guidance. Summaries of these topics can be found in NRC (2000) and Wiedemeier (1999). Non-destructive abiotic processes such as advection, dispersion, sorption, volatilization and dilution from recharge that affect contaminant movement are not reviewed here. However, the site investigation should define the hydrogeologic setting of the contaminated site and assess all the pertinent processes affecting chlorinated hydrocarbon movement. This information should then be incorporated into the site conceptual model and other tools used to assess the effectiveness of natural attenuation processes to control and remediate contaminants.

2.2 Site Investigation

A site investigation is planned with some understanding of the site geology, the source of the release and the likely physical, chemical, and biological processes affecting the chlorinated contaminants in the subsurface. Site investigation requirements are contained in NR 716, Wis. Adm. Code. Site specific considerations will always guide the site investigation. All contaminated sites must identify the horizontal and vertical degree and extent of environmental contamination.

Responsible parties and consultants must submit a site investigation work plan as required by NR 716.09. In order to receive review comments, responsible parties must request that the Department review a submitted site investigation work plan and pay the required fee (refer to NR 749). Department review of the work plan helps ensure that the NR 716 requirements are addressed and reduces the need for subsequent site investigation work. However, if a review is not requested or the fee not paid, responsible parties should not assume the work plan will not be reviewed. NR 716.09(3)(b) requires responsible parties to wait 60 days from the submittal of the work plan to begin the field investigation. If fieldwork must start before the 60-day review period, responsible parties should contact the Department for permission to proceed.

Because MNA is a “knowledge-based” remedy, it is critical that an adequate site investigation be conducted. Typically, MNA sites will require more thorough site investigation than sites where only active remedies are applied. Investigators need a better understanding of the variability in the subsurface (which controls physical, chemical and biological processes) combined with the expected natural degradation processes if they are to properly apply MNA as a remedy. Good data collection during the site investigation will improve the reliability of the site conceptual model and site analytical or numerical models. A single effort at site investigation

will rarely result in complete assessment of a contaminant source and groundwater plume. An iterative site investigation is recommended to successively delineate the source and plume.

The results of the site investigation should provide an initial understanding of the plume behavior, subsurface heterogeneity, likely attenuation processes, the 3-D extent of the plume, hydrogeological control, and an initial estimate of contaminant decay rates. These results will help the investigator determine where MNA may be a viable remedy and where and how to apply other remediation technologies to achieve site cleanup goals. In almost all cases where MNA is proposed, long-term monitoring to confirm plume behavior, attenuation processes, decay rates, and cleanup predictions will follow site investigation and interim remedial measures.

The following outlines the site-specific information that a site investigation should address in order to define the degree and extent of contamination and lay the basis for assessing natural attenuation processes. It is not a checklist of regulatory requirements -- see NR 716 for site investigation requirements. Additional information on many of these topics can be found in DNR publication RR-614, Interim Guidance on Natural Attenuation for Petroleum Releases.

Most site investigations will benefit from the use of rapid site characterization techniques. These techniques allow rapid definition of the physical and chemical characteristics of the contaminated site. Appendix B provides internet links to references for rapid site characterization technologies.

2.2.1 Identifying soil and groundwater contamination

The site investigation (SI) will involve a number of field activities at the contaminated site as well as gathering as much existing information about the site as possible. Usually a number of permanent monitoring wells (water table and piezometers) are installed during the SI. These wells may or may not subsequently be used during the long-term monitoring phase to assess MNA.

2.2.1.1 Degree & extent of contamination

1. *History of contaminant release*. This includes the volume, physical and chemical characteristics of the contaminants released and approximate date, location and condition (surface spill, underground leak, etc.) of the release. Site history includes the following: ownership and land use of the property; location of above and below ground structures (including utilities); and all other site specific information that will help identify potential impacts of the contaminant release and guide the site investigation (refer to NR 716.07).
2. *3-D understanding of the location and extent of contaminant source area(s).* The source area is usually the location of the original release. However, there are sites where the mass of contaminant has moved significant distances from the original release. The source area includes the soil[3] and saturated material[4] that contain free or residual phase product. Techniques that can help delineate source areas include: soil vapor surveys; carefully collected samples of soil and saturated material; and rapid site characterization techniques.

[3] Soil is defined in NR 700.03(58) as “unsaturated organic material, derived from vegetation and unsaturated, loose, incoherent rock material, of any origin, that rests on bedrock other than foundry sand, debris and any industrial waste”.
[4] Saturated material is any subsurface material that is saturated with groundwater.

3. *The potential for a continuing source release* (from pipes, tanks, and residual or mobile DNAPL). The source of contaminant release should be controlled to the extent possible. Pipes and tanks can be inspected and tested for leaks. Residual and mobile phase product in the subsurface provides a continuous source for vapor, soil and groundwater contamination. Mobile (free) phase product must be removed to the maximum extent practicable (NR 708.13). Soil gas surveys can be an excellent site investigation tool for identifying source areas as well as vapor pathways for indoor air exposure. EPA's standard operating procedure for collecting soil-gas samples can be found at http://www.ertresponse.com/sops/2042.pdf. EPA's SOP on water-level measurements (http://www.ertresponse.com/sops/2043.pdf) includes monitoring the headspace in monitoring wells to determine the presence of VOCs before lowering any depth-measuring device into the well. Because of mobility, monitoring vapor phase contamination may be a better indication of the source area than groundwater monitoring wells alone.
4. *Extent and type of soil and groundwater contamination*. The extent and type of contamination in soil and groundwater beyond the source area(s) must be identified. In addition, the characteristics of the soil and saturated material are critical in understanding the fate and transport of contaminants through the subsurface.

2.2.1.2 Hydrogeologic and geochemical framework

1. *Groundwater and soil contaminant and geochemical parameter distributions*. Data from the SI should be used to quantify the mass of contamination in the soil and saturated material. Redox conditions of the soil and groundwater should be determined. Soil gas samples can be used to screen for contaminant concentration, oxygen, carbon dioxide and the presence of methane in soil. Groundwater should be sampled and analyzed for contaminants, their degradation products, terminal electron acceptors and other parameters that identify conditions of plume development (refer to Table 1, Section 3.2).
2. *Regional hydrogeology including regional drinking water aquifers and confining units*. The contaminated site should be tied into the regional hydrogeologic setting to determine the overall risk the site poses to receptors and the likely paths of contaminant movement if contaminants enter the regional flow system.
3. *Site-specific hydrogeology* including:
    a. local drinking water aquifers
    b. location of private and public water supply wells & use of these wells
    c. lithology
    d. site stratigraphy, including identification of transmissive vs. non-transmissive units (i.e., site heterogeneity)
    e. grain size distribution
    f. hydraulic conductivity of each lithologic unit based on grain size, pump tests or monitoring well testing
    g. 3-D understanding of groundwater hydraulics (e.g., groundwater flow fields, horizontal & vertical hydraulic gradients, water table & potentiometric surface maps over several seasons.).
    h. preferential flow paths
    i. bedrock fracture frequency and orientation
    j. location and type of surface water bodies
    k. groundwater recharge & discharge areas

2.2.1.3 Define potential receptors and exposure pathways.

Potential receptors include: water supply wells; contaminant discharges to surface waters; and vapor migration to enclosed spaces. The site investigation should determine whether any

exposure pathway is "complete", that is an actual (versus potential) threat exists to human health or the environment. The remedy chosen for the site must address all completed exposure pathways.

1. *Water supply wells*. Identify all public water supply wells and high capacity wells within 1 mile[5] and private water supply wells within 1,200 feet of the contaminated site. Public water[6] supply and high capacity wells[7] induce groundwater gradients that can affect contaminant movement. In addition, many high capacity wells operate seasonally and can cause seasonal shifts in groundwater flow direction and/or gradient. Impacts to water supplies must be immediately reported to the well users and to the Department. Action (such as providing an alternative water supply) must be taken if any contaminant exceeds NR 140 enforcement standards (ES) at a private well or NR 809 Safe Drinking Water standards for community or municipal wells.
2. *Surface waters*. Identify all surface water bodies within a mile of the contaminated source area. Identify all surface water discharge locations and assess the affect of the surface water discharge on contaminant movement. If contaminated groundwater is discharging to surface water, the impact of the discharge must be evaluated. Staff in the Department's surface water quality program should be consulted to determine the impact of any discharge on surface water.
3. *Soil gas migration*. Vapor intrusion from chlorinated contaminants migrating through soils is a significant concern when buildings are located near source areas or located over shallow groundwater plumes. Chlorinated hydrocarbons do not readily degrade in the vadose zone and contaminants can travel significant distances through soils to enter buildings. EPA has developed draft guidance to assess the indoor air intrusion pathway. That guidance can be found at: http://www.epa.gov/epaoswer/hazwaste/ca/eis/vapor.htm. This guidance provides a work sheet to determine if indoor air may be a pathway of concern upon evaluation of data from soil gas and groundwater monitoring. As the draft EPA guidance makes clear, groundwater enforcement standards (ES) for chlorinated compounds (especially PCE, TCE and vinyl chloride) may not be protective of the indoor air pathway. The Wisconsin Division of Health has developed an indoor vapor intrusion guidance that can be downloaded from: http://www.dhfs.state.wi.us/eh/Air/pdf/VI_guide.pdf.

   If soil-gas sampling or groundwater concentrations below buildings indicate that contaminant vapors may be migrating into a structure, then passive or active venting of the structure may be necessary. Installing a venting system may be more cost-effective than opting for continued indoor air quality monitoring. An example of a venting system includes sub-slab depressurization that has proven effective in reducing radon gas levels in homes can be found at http://www.dhfs.state.wi.us/dph_beh/RadonProt/Radon/ActionsReduceRadn.htm.

Before MNA can be considered as a site remedy, it must be established that receptors are not currently affected or likely to be affected in the future. If receptors are affected by the contaminant then in almost all cases an active remedy (perhaps combined with MNA) will be

[5] Identifying public water supply wells within 1 mile of the contaminated site is recommended because of the persistence and ability of chlorinated contaminants to migrate long distances in groundwater.
[6] The definition of a public water supply well can be found in NR 812.07(80). The Department's database on drinking water systems and high capacity wells can be accessed at: http://www.dnr.state.wi.us/org/water/dwg/DWS.htm
[7] The definition of a high capacity well can be found in NR 812.07(51), (52) and (53).

necessary to remove or contain the contamination such that the receptor is adequately protected.

2.2.2 Predictions of contaminant fate & transport

For complicated sites with chlorinated contaminants (highly heterogeneous sites or sites exhibiting strong transient flow or sites with high contaminant levels) it is recommended that a fate and transport model be developed after the SI (National Research Council, 2000). A fate and transport model can be very useful in assessing alternative conceptual models for the site and for understanding complex flow or complex contaminant characteristics. A contaminant fate and transport model will benefit the assessment of a contaminated site by:

- predicting contaminant flow paths;
- assessing the expected extent of a contaminant plume;
- testing alternate hypothesis for plume movement and attenuation;
- aiding in placement of long-term monitoring wells;
- refining the site conceptual model;
- assessing the strength of the contaminant source;
- predicting contaminant concentrations in time and space along the plume;
- predicting plume life and estimating a time to cleanup using various remediation strategies;
- providing a baseline to compare results of long-term monitoring; and
- contingency planning. The model can assess active remedial options for containing or controlling the contaminant plume, if this is necessary.

The complexity of the fate and transport model will be determined by the complexity of the contaminated site. Models range from fairly simple, one dimensional screening models (e.g., Biochlor) to complex 3-D models. One source of models is EPA's Center for Subsurface Modeling Support: http://www.epa.gov/ada/csmos.html.

For less complicated sites, statistical, graphical, and mass budget analysis (as discussed in Chapter 3) may suffice for assessing site data. Whatever methods are used to assess data, the results should be verified by long-term monitoring.

2.2.3 Site investigation report

The goal of a site investigation is to identify the subsurface distribution of contaminants, assess contaminant fate and transport and to lay the basis for selecting a remedy that will lead to the cleanup of the contamination. Site investigation reports must be submitted to the Department. Department review with written comments can be requested if the request is accompanied by the appropriate review fee. A complete site investigation report should present all the site data in a manner that achieves the goals of the SI and includes all the requirements of NR 716.15. Site investigation reports for chlorinated contaminants where MNA is being considered as a remedy should include detailed assessment of the geology and hydrogeology of the site as well as mapping and identifying patterns of contaminant degradation and geochemical parameters. Site investigation reports for chlorinated contaminant sites may need to be more extensive than the minimum requirements of NR 716.15. The following points should be particularly emphasized in the site investigation report:

1. A description of the site conceptual model, summarizing the information the conceptual model is based upon.

2. A description of the source and estimate of the mass of contamination in the source zone. Identify areas of residual and/or free NAPL, if applicable.
3. Water table and piezometric surface maps with an assessment of change in groundwater flow direction, horizontal and vertical gradients, and velocity for each date of measurement.
4. Detailed geologic and hydrogeologic cross-sections with enough cross-sections to depict each soil boring and monitoring well at the site. At a minimum, cross-sections should be constructed along the center line of plume and perpendicular to the center line across the source area and across the dissolved plume, showing the following:
    i. screen length and depth
    ii. geology with groundwater flow paths indicated
    iii. contaminant concentrations at each well screen interval or boring and mapped isoconcentrations for each compound
5. Identify preferential flow paths for contaminant movement (in DNAPL, subsurface air and groundwater).
6. Preliminary assessment of natural attenuation processes occurring at the contaminated site using appropriate assessment tools.
7. If available, results of a fate and transport model to help evaluate the history and behavior of the groundwater plume and to predict future contaminant concentrations at specific monitoring points in the well network. If a fate and transport model has not been used for the site, the results of other assessments such as graphical analysis, decay rate calculations and mass budgets from the initial SI data can be used to make predictions of expected contaminant movement and concentrations in the future.

At the end of the site investigation, all the information necessary for screening a site to select a remedy should exist. Screening to determine whether MNA is a likely remedy requires knowledge of the plume behavior, assessment of contaminant degradation patterns, and assessment of the rate of contaminant degradation. Plume behavior can be assessed once a proper monitoring well network is in place. Data collected from the monitoring network is then used to assess degradation conditions throughout the plume and to extract degradation rates. These topics are dealt with in the following section and in Chapter 3.

2.3 Selecting and Evaluating Remedial Actions

Upon completion of a site investigation, and perhaps a feasibility study, a remedy selection process, as presented in NR 722, should be completed for every site contaminated with chlorinated hydrocarbons. Data collected during the SI should be used to identify, evaluate and select a final remedial action (or actions) that will result in a timely and cost-effective site cleanup. Initial screening of likely remedial technologies (required by NR 722.07(2)) should determine the range of options available for a specific site. These options are then evaluated for technical and economic feasibility (NR 722.07(4)). The technical feasibility of each option is evaluated considering long-term and short-term effectiveness, implementability, and restoration time frame. Economic feasibility is evaluated by estimating the costs associated with each remedial option and then comparing the costs to what can be technically achieved by each option.

The remedy (or remedies) selected must meet the criteria of NR 722.09, namely, environmental laws and standards for soils, groundwater, surface water and wetlands, air discharge, and solid and hazardous waste laws. The remedy evaluation and selection process must be documented in a Remedial Action Options Report (NR 722.13), which must be submitted to the Department.

Responsible parties and consultants are strongly encouraged to seek DNR review and comment on the RAOR to help ensure that the proposed cleanup complies with applicable laws and regulations.

Monitored natural attenuation may be one of the options evaluated during the remedy selection process. In most cases, MNA is appropriate only after implementation of a source control remedy and, perhaps, other remedies to reduce contaminant mass. Selection of MNA as part of the cleanup at a site will require establishing a long-term groundwater monitoring network and assessment of natural attenuation processes over time to determine the effectiveness of the remedy. These topics are addressed in the following sections of this guidance.

2.4 Long-term Monitoring Well Network

Site investigation is intended to characterize the degree and extent of contamination in the environment. Assessing the impact of natural attenuation processes on contaminant fate and transport requires site data beyond those collected during a typical site investigation. At most sites where MNA is the selected remedy, additional monitoring wells will be needed. Some monitoring wells from the SI may be useful while others could be abandoned. The long-term monitoring well network will allow detailed characterization of groundwater flow and geochemistry within the plume. **An adequate long-term groundwater monitoring network, along with properly collected samples, are the underpinnings for understanding the hydrogeologic system and lays the basis for assessing natural attenuation of the contaminants. Without this basis, it is difficult to assess natural attenuation processes and determine the effectiveness of MNA as a remedy.**

Properly placed and constructed permanent monitoring wells are one of the most important tools in assessing long-term natural processes. When installing a permanent well monitoring network designed to assess natural attenuation processes, monitoring wells should be:

- Placed to identify the primary flow paths of the chlorinated contaminants.
- Installed in transects (i.e., lines of wells) perpendicular to the groundwater flow path to track lateral and vertical movement of the plume over time.
- Screened so that groundwater samples are collected from the most contaminated portion of the plume.
- Spaced along the flow path so that natural attenuation processes can be assessed in relation to groundwater and contaminant movement with time.
- Placed downgradient of the plume to serve as sentinel wells.

In addition, other media (such as soil gas or surface water) may require monitoring during the remedial activities. An appropriate monitoring plan and monitoring locations should be developed for these media.

2.4.1 Identify primary contaminant flow paths

Heterogeneity is a fact of life when investigating geology at contaminated sites. **The question that should be asked is how to minimize the influence of heterogeneity at a contaminated site so that it may be possible to effectively monitor and adequately assess natural attenuation processes.** A site can be so heterogeneous that it is not possible to establish an adequate well monitoring network such that an appropriate natural attenuation assessment can be made. For these sites, other remediation techniques will need to be selected.

Studies have investigated site heterogeneity and variation in hydraulic conductivity over short vertical and horizontal distances (Hurt et al., 2001; Wilson et al., 1995). The frequency of subsurface sampling (both vertically and horizontally) should be chosen to reflect the expected heterogeneity. At some sites, significant variations in hydraulic conductivity and contaminant concentrations occur over horizontal distances of a few feet and vertical distances of much less than a foot. Conventional drilling techniques in which 1 to 2 feet of soil or saturated material are collected for every 5 vertical feet of drilling may miss the most permeable units that move contaminants the longest distances.

Collection of subsurface sampling data is crucial in identifying the primary flow path of contaminants. Without identifying the contaminant flow path(s), erroneous conclusions regarding the risk the site presents to receptors and the effectiveness of any chosen remedial technology can easily result. Investigation techniques, such as direct push methods, core samplers, geophysics, flow meters, etc. can be used to give a detailed picture of the variation in grain size and hydraulic conductivity of the subsurface. Direct push methods for determining hydraulic conductivity using short screen intervals (e.g., 6”) have been developed (Wilson et al. 1997). Other rapid site investigation techniques can identify changes in subsurface materials on a continuous basis as the drill rod is advanced.

If the contamination has entered fractured bedrock, the orientation of fracture zones and other factors controlling DNAPL or groundwater movement need to be identified. Special investigation techniques, including tracer tests, may help identify preferential flow patterns in these settings. Identifying and remediating DNAPL and contaminated groundwater in bedrock is an active area of research and is beyond the scope of this guidance.

2.4.2 Monitoring plume behavior

Groundwater flow within a given hydrologic system varies in response to such things as infiltrating rain fall/snow melt, pumping of nearby wells, elevation changes of nearby surface water bodies, and changes in land use. A monitoring well network needs to be extensive enough to detect vertical and horizontal movement of a plume due to shifting groundwater flow directions. This is especially important for sites located near hydrologic divides when seasonal effects can be pronounced. Without an adequate monitoring network, an investigator can interpret a contaminant plume that has shifted away (either horizontally or vertically) from a line of monitoring wells as a loss of contaminants due to natural attenuation. An adequate monitoring well network and proper interpretation of groundwater analyses should help an investigator avoid this pitfall.

2.4.2.1 Locating monitoring well transects

In order to separate hydrologic changes from biological changes in a plume and allow quantification of changes in contaminant mass over time, transects of monitoring wells should be installed perpendicular to the contaminant plume. A monitoring well transect is a line of wells placed perpendicular to the movement of the plume. Transects should be placed such that changes in plume movement can be intercepted and monitored vertically and horizontally. Complete delineation of the plume requires that wells be placed within the plume and in uncontaminated groundwater upgradient, side gradient, downgradient, and at depth beneath the plume. Figure 3 illustrates the concept of a monitoring well network aligned in transects. The most important locations for transects include:

- Upgradient of the source. These wells will assess the geochemistry of the groundwater entering the plume and any contaminants entering the plume from upgradient.
- Immediately downgradient of the source. These wells will be used to assess changes near the center of the plume and possibly any deep source areas (such as DNAPL). The spacing of wells along a transect should be determined by the expected width of the plume.
- One or more transects through the body of the plume, depending on the overall length of the plume.
- Near the edge of the plume. This transect should detect any expansion of the plume.
- Sentinel wells beyond the edge of the plume. These wells are placed between the plume and any downgradient receptor. These wells provide an "early warning" of expansion of the plume and possible increased risk to downgradient receptors.

The actual number of monitoring wells and piezometers used for long-term monitoring at a site will depend upon the variability in hydraulic gradients and direction of groundwater flow and how well characterized the plume is. Sites with uniform flow fields will require fewer monitoring points than sites with significant hydraulic variability.

2.4.2.2 Defining the plume vertically

Vertical monitoring of a plume usually requires installation of nested monitoring wells which include one water table well and one or more piezometers[8]. Standard piezometers are constructed with 5-foot well screens while water table wells are usually constructed with 10-foot screens. These lengths may or may not be appropriate for monitoring the vertical thickness of the plume or the geologic unit through which the plume moves. Wells should be screened to intersect the most permeable unit(s), because contaminants will move through these units fastest. Cho et al., 2000, discusses a technique for measuring vertical profiles of hydraulic conductivity. Screen lengths and depths of wells should be constructed so that the monitoring wells produce groundwater samples representative of the plume at that location. Wells should be placed so that the full vertical extent of the plume is defined. At least one piezometer in a well nest should extend into clean groundwater below the deepest extent of the plume. To prevent cross-contamination, it may be necessary to double case piezometers that extend through geologic confining layers or through highly contaminated zones.

2.4.2.3 Defining the plume horizontally

The velocity of the groundwater and distance to potential receptors should be one of the most important considerations when placing transects of monitoring wells along the plume. Horizontal spacing of transects along the contaminant plume allows the same volume of water to be sampled as the groundwater moves past the lines of monitoring wells. The spacing of the monitoring wells will control how frequently a given volume of groundwater can be sampled over time. For example, if monitoring wells are spaced equal to a distance that the groundwater is expected to flow in 1 – 2 years then groundwater samples should be collected every 1 – 2 years. (This is to avoid the incorrect conclusion that natural attenuation is effective at a well location when, in fact, the contaminants have simply migrated to a more downgradient location.) In very permeable formations it may be possible to place wells at distances that correspond to 3

[8] Piezometers in Wisconsin are monitoring wells *sealed below the water table* for determining the elevation of the potentiometric surface and/or collecting groundwater samples. Screen lengths of piezometers are to be 5 feet or less, by rule.

– 6 months of groundwater flow. Plumes in less permeable units may require well spacing at intervals that represents several years of groundwater movement.

Actual spacing of monitoring wells along the plume will depend upon site specific issues such as location of receptors, access to monitoring locations, variability in direction and velocity of groundwater flow, etc. The investigator must understand the relationship between the actual well spacing at the site and contaminant plume movement in order to assess the effectiveness of natural attenuation processes.

2.4.2.4 Sentinel wells

Monitoring well networks need to be robust enough to identify unforeseen changes in groundwater flow due to pumping nearby wells or changes in land use. Sentinel wells provide a way to identify these unforeseen circumstances. Sentinel wells should be placed downgradient and side gradient from the source where there is no expected impact. Sentinel wells should be located between the source and possible receptors such that an impact to a sentinel well will trigger contingency remedial efforts before a downgradient receptor is affected. If sentinel wells become contaminated, contingency plans should provide for a course of action to capture or control contaminants such that the contaminants do not move beyond the sentinel wells.

It is very important to properly locate and screen sentinel wells because these wells help determine whether the plume is expanding or is at steady state. The wells should be screened using geochemical signatures of the plume to define “treated groundwater” – that is, groundwater that has moved through the plume and still retains the geochemical signature (e.g., the geochemical “footprint”) of the plume but has no contaminants. Common “footprints” would be high ferrous iron, low sulfate, and high total inorganic carbon. Sentinel wells should be close enough to the edge of the plume to determine plume behavior within a fairly short period of time. For instance, if groundwater flows 20 feet per year and the sentinel wells are 200 feet from the plume, it will take at least 10 years of monitoring to determine if the plume is stable. (It will take longer if the contaminants are retarded along the flow path.) If the sentinel wells are placed 40 feet from the plume edge, stability can be determined within as little as 2 years, depending upon the retardation factor of the contaminants.

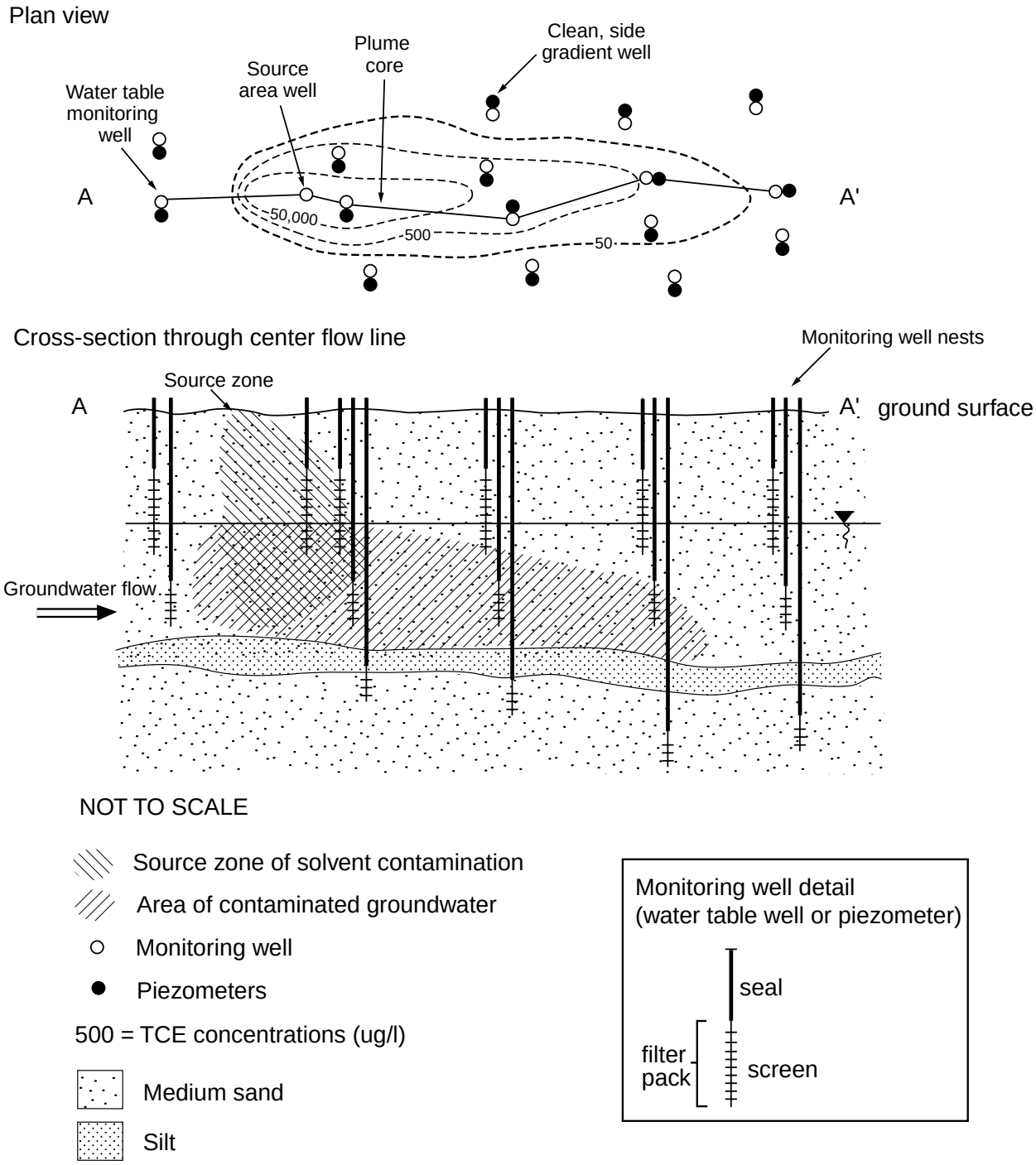

Figure 3. Schematic of groundwater monitoring network using transects of monitoring wells.

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Chapter 3

Tools to Assess Natural Attenuation of Chlorinated Hydrocarbons

The primary evidence for the effectiveness of MNA is loss of contaminant mass or decreasing mass flux across control planes in the plume. Loss of contaminant mass is often assessed indirectly through documenting decreases in contaminant concentration and concomitant changes in geochemistry. To effectively assess MNA, information is needed on decreasing contaminant concentrations; decay rates and their variation with changes in the hydrologic system; contaminant degradation patterns; extent to which natural process control plume movement; and an assessment of the likelihood that these processes will continue until cleanup standards are met. This chapter discusses conditions necessary for biodegradation of chlorinated compounds; assessing patterns of degradation; determining degradation rates; and data analysis necessary to show that MNA is effective as a remedy.

Not every contaminated site will need to use every tool presented here. There may be assessment methods not presented here that are appropriate for determining the effectiveness of MNA. The goal is to collect adequate site-specific data and evaluate the effectiveness of MNA, as outlined in Section 3.4.

3.1 Environmental Conditions Necessary for Degradation of Chlorinated Hydrocarbons

Chlorinated hydrocarbons can degrade under a variety of environmental conditions. The processes most important to MNA are reductive dechlorination (where the chlorinated compound serves as an electron acceptor) and oxidation (where the chlorinated compound serves as an electron donor). Environmental conditions that support natural attenuation processes for chlorinated compounds (particularly reductive dechlorination) include:

- Microorganisms capable of degrading the contaminants
- Oxidation-reduction (redox) capacity of the groundwater
- Sufficient electron donors (e.g., a carbon source)
- Absence of competing electron acceptors

3.1.1 Microorganisms capable of degrading contaminants

Natural degradation of contaminants relies on microorganisms that produce enzymes that degrade the contaminants. Usually microorganisms are benefited in some way by the degradation process (the organism gains energy to carry on life processes). Generally, if products of complete dechlorination are evident at a contaminated site, microcosm studies are not needed. There are situations where microcosm studies or gene assays (such as polymerase chain reaction analysis to identify the presence of specific microorganisms) are warranted. Such situations include the accumulation of intermediate dechlorination products or an inability to determine whether dechlorination is occurring.

To date *Dehalococcoides ethenogenes* is the only anaerobic microorganism that is known to completely dechlorinate chlorinated ethenes in the laboratory. Other species of *Dehalococcoides* working together with a group of microorganisms called a “consortium” can also dechlorinate chlorinated ethenes. Hendrickson et al., 2002, has shown that

Dehalococcoides species were found in 21 of 24 soil and groundwater samples contaminated with chlorinated ethenes collected in North America and Europe. At the sites where *Dehalococcoides* was not found, chlorinated degradation proceeded only to 1,2-DCE that then accumulated in the groundwater. This preliminary study indicates that there may be a strong link between the presence of a specific microorganism and the likelihood that natural reductive dechlorination will be successful at a given site. For sites where incomplete reductive dechlorination is occurring, bioaugmentation (the addition of bacterial cultures to the subsurface) may be an effective approach to remediating the site.

3.1.2 Oxidation-reduction (redox) capacity of groundwater

The oxidation state or redox condition of the aquifer determines the energetics of the microbial system and the likely degradation processes. It is very difficult to determine the oxidation state through direct measurement so geochemical processes are used to infer the redox conditions present. Groundwater redox conditions can indicate the likelihood of reductive dechlorination (and other attenuation processes) occurring, but aquifer redox condition cannot predict the extent to which reductive dechlorination will occur (Loffler et al., 1999). For instance, groundwater in a high oxidative state indicates that PCE will not dechlorinate. A low oxidative state (indicating reducing conditions) may indicate the potential to dechlorinate PCE, but it does not establish the degree or extent to which PCE will degrade.

The less chlorinated compounds (i.e., DCE and VC) can undergo direct oxidation under the right environmental conditions. This is discussed further in Appendix C. For example, vinyl chloride undergoes the following oxidation reaction:

$$C_2H_3Cl + 2\ NO_3^- + H^+ \rightarrow 2CO_2 + 2H_2O + Cl^- + N_2\ (g)$$

The most common method of assessing redox conditions in groundwater is through monitoring native terminal electron acceptors (TEA), such as oxygen, nitrate, manganese, iron, sulfate, and methane. Appendix D discusses redox characterization of groundwater in greater detail.

3.1.3 Availability of a carbon source (electron donors)

The main driving force that determines aquifer redox condition is the presence of a degradable carbon source. Because redox reactions must balance, the total mass of TEA used (including chlorinated compounds) is determined by the amount of carbon available for oxidation. The subsurface at some contaminated sites contain naturally occurring carbon (e.g., buried peat, petrolific rock) that can drive a system anaerobic and support reductive dechlorination. Most commonly, anthropogenic carbon (e.g., petroleum spills) provide a carbon source that drives the soil or groundwater system anaerobic. Without a carbon source, or when a carbon source becomes exhausted, reductive dechlorination will not occur and highly chlorinated compounds will not dechlorinate.

The “ultimate” electron donor is hydrogen (H_2). The generalized reductive dechlorination reaction can be written:

$$R\text{-}Cl_n + H_2 \rightarrow R\text{-}H\text{-}Cl_{n-1} + H^+ + Cl^-$$

Where: R = aliphatic group

Hydrogen is produced when one group of microorganisms break down simple carbon molecules and other microorganisms use H_2 as a direct electron donor. Hydrogen concentration in

groundwater serves as a measure of redox potential. The greater the H_2 concentration in groundwater, the more reduced the conditions. H_2 above 1 nM can support reductive dechlorination. Appendix D discusses H_2 concentrations at greater length.

When reductive dechlorination is the primary natural attenuation process at a site, investigators should attempt to identify the source and mass of carbon that is sustaining MNA, particularly if the carbon is anthropogenic (e.g., from a petroleum source). At these sites, it is difficult to predict the long-term viability of MNA if the source of the carbon is unknown. A common approach to limited subsurface carbon mass is to add a carbon source such as lactate, molasses, etc. Active in-situ bioremediation (ISB) remedies (such as carbon addition) can work with natural subsurface processes to enhance contaminant degradation.

3.1.4 Absence of competing electron acceptors

In reductive dechlorination, chlorinated contaminants serve as electron acceptors, which means that the native geochemical compounds (e.g., nitrate and ferric iron) become competitors in electron transfer processes that generate energy for microorganisms. Reductive dechlorination will not occur in the presence of oxygen, nitrate or readily reducible ferric iron. Sulfate-reducers and methanogens can reductively dechlorinate CAHs. An increase of ferrous iron, a decrease in sulfate and an increase in sulfide and methane usually accompany reductive dechlorination.

3.2 Assessing Patterns of Natural Attenuation in Groundwater

Natural attenuation processes can be deduced through studying the patterns of contaminant degradation and geochemical changes throughout the source area and plume. Patterns are likely to vary throughout a plume. Often the most strongly reducing conditions occur near the source zone and the plume encounters less reducing conditions as it moves downgradient. However, this pattern can be reversed. A chlorinated hydrocarbon plume may have little available carbon in the source zone and encounter a petroleum plume at some distance downgradient where geochemical conditions are strongly reducing. The degradation and geochemical patterns need to be assessed at each monitoring point to determine the likely degradation conditions at specific points in the aquifer. Then inferences can be drawn as to the likely conditions prevailing through various segments of the plume.

As chlorinated contaminants are degraded, the mechanisms controlling the degradation produce or consume materials resulting in geochemical signatures that are identifiable in groundwater. These geochemical signatures have been referred to as “footprints” or “geochemical footprints.” Changes in groundwater geochemistry along with loss of groundwater contaminants help establish a “cause and effect” relationship that is critical to documenting natural attenuation processes at a site. (NRC, 2000).

3.2.1 Geochemical footprints

The primary reason for assessing geochemical parameters is to establish the footprint of the plume (Wilson, 2002). Geochemical parameters help identify where the plume is and where it is not. With a proper monitoring well network, geochemical parameters can identify “treated” groundwater, that is, formerly contaminated groundwater that contains the geochemical signatures of degradative activity. Geochemical parameters also establish the likely degradative mechanisms occurring within the plume.

3.2.1.1 Evidence of specific natural attenuation mechanisms

Footprints of reductive dechlorination (i.e., PCE, TCE, and 1,1,1-TCA) show loss of the parent compound, production of daughter products, acid (H^+), CO_2, and Cl^- (refer to Appendix C). Reductive dechlorination is also associated with H_2 levels > 1 nM. Monitoring groundwater for these compounds and assessing changes in these compounds over time and distance within the plume aids greatly in determining microbial processes likely taking place within the plume. Table 1 summarizes the geochemical parameters most commonly monitored in groundwater at sites contaminated with chlorinated hydrocarbons.

The existence of the patterns of degradation (geochemical footprints) does not mean that natural attenuation processes control the contaminant plume. It only means that certain microbial processes are likely occurring in the groundwater. For example, incomplete degradation leads to accumulation of daughter products that may be more toxic than the parent compound. A plume of PCE that extends beyond the zone of high carbon content is likely to move with the groundwater flow. This is why proper monitoring over time along with a thorough understanding of a site's hydrogeology is critical to remediating chlorinated hydrocarbon contamination.

If the geochemical and redox environment indicates that reductive dechlorination is unlikely (i.e., oxygen and/or nitrate are present, ferrous iron and/or methane are absent, etc.), oxidative degradation of lower chlorinated compounds can still occur. Examples of geochemical footprints for oxidation of chlorinated hydrocarbons include loss of electron acceptors (such as nitrate) and production of alkalinity and Cl^-. Vinyl chloride, methylene chloride (dichloromethane) and methyl chloride (chloromethane) are degraded through oxidative or abiotic processes much more readily than through reductive dechlorination.

Table 1*
Geochemical Patterns Expected with Reductive Dechlorination

Analyte	Concentration in Source Zone or Change from Background	Explanation
Arsenic (As^{+3})	Increase over background	Mobilized under anaerobic conditions if As present. May exceed ES standards.
Chloride (Cl^-)	> 2x background	From dechlorination. Environmental factors may interfere (e.g., road salt). Initial contaminant concentrations may be too low to detect a significant increase in Cl^-.
Dissolved Oxygen (D.O.)	< 0.5 mg/l	Oxygen suppresses reductive dechlorination. Cis-DCE, 1,1-DCE, 1,1-DCA, VC, methylene chloride, and chloromethane may degrade aerobically.
Ethane	Present	Daughter product of reductive dechlorination of 1,1,1-TCA. Also produced from ethene.
Ethene	Present	Daughter product of reductive dechlorination of VC.
Ferrous Iron (Fe^{+2})	Increase over background	Reductive dechlorination may take place under iron reducing conditions. VC may be oxidized under these conditions.
Hydrogen (H_2)	> 1 nM	Reductive dechlorination possible. VC may accumulate.
Hydrogen (H_2)	< 1 nM	VC oxidized. Reductive dechlorination may not occur.
Manganese (Mn^{+2})	Increase over background	If present on soil surfaces, Mn serves as an electron donor. Reductive dechlorination may not take place under Mn reducing conditions.
Methane	Increase over background	Indicates the most reduced groundwater conditions. VC accumulates at methane >0.5 mg/l.
Nickel	Increase over background	Mobilized under anaerobic conditions if Ni present. May exceed ES standards.
Nitrate (NO_3^-)	< 1 mg/l	Presence of NO^{-3} suppresses reductive dechlorination. Methylene chloride, VC, other low chlorinated compounds may degrade in the presence of NO^{-3}.
Oxidation Reduction Potential (ORP) with Ag/AgCl electrode	<-100 mV <50 mV	Reductive dechlorination likely. Reductive dechlorination possible.
pH	5 < pH > 9	Optimal range for microbial activity.
Specific Conductance	Increase over background	General water quality parameter; helps determine that sample is collected from the same groundwater system.
Sulfate (SO_4^{-2})	Decrease compared to background	Reductive dechlorination may occur under SO_4^{-2} reducing conditions. However, high levels of SO_4^{-2} can inhibit reductive dechlorination.
Sulfide (S^{-2})	Increase over background	Reductive dechlorination may occur. S^{-2} may not be detected because of precipitation with Fe^{+2}.
Temperature		Affects microbial energetics. At cooler temps, dechlorination can proceed at lower H_2 levels.
Total Inorganic Carbon (TIC)	Increase over background	Measures CO_2 species produced by microbial metabolism. (See Appendix D)
Total Organic Carbon (TOC)	> 20 mg/l	Source of organic carbon necessary as driver for reductive dechlorination to proceed. Anthropogenic sources of carbon include BETX.

* Adapted from Wiedemeier, 1998.

3.2.1.2 Establish effectiveness of the groundwater monitoring networks.

Geochemical footprints can also be used to establish a hydrologic connection between source area and downgradient monitoring wells. If the geochemical footprint at a source well is similar at a downgradient well, then the downgradient well is in the flow path of the plume. If the geochemical footprints are significantly different, then the downgradient well is not in the contaminant flow path. This principle can be used to determine which downgradient wells are most useful for assessing natural attenuation. Assessment of natural attenuation decay rates should include only those wells that intersect the plume in order to draw proper conclusions about plume behavior. Particularly useful geochemical footprints for this purpose include chloride, methane, specific conductance, and total inorganic carbon[9] (Chapelle et al., 2002).

Ideally, sentinel wells near the downgradient edge of the plume should exhibit geochemical parameters (e.g., Cl^- from contaminant degradation) without the presence of the contaminant. This observation adds credence to the claim that the natural degradation processes have contained the plume and that the extent of the groundwater plume has been adequately defined.

3.2.2 Patterns of contaminant degradation

Appendix C discusses various degradative processes and the resulting biotic and abiotic degradation products. *Contaminant degradation patterns* can give clues as to the nature of the original release as well as to the microbial processes occurring at a site. Table 2 gives examples of contaminants found in groundwater, the likely source material and the likely degradation process.

Table 2*
Selected Contaminant Degradation Patterns

Contaminant Present	Likely Source Material	Degradation Process
cis-DCE>> trans-DCE + 1,1-DCE	PCE	Reductive dechlorination
trans-DCE>>cis-DCE	trans-DCE	None
1,1-DCE>>cis-DCE	1,1,1-TCA and PCE	Reductive dechlorination
1,1-DCE	1,1,1-TCA	Elimination
1,1-DCA	1,1,1-TCA	Reductive dechlorination

* Adapted from "Chlorinated Solvent Training, State Coalition for Remediation of Dry Cleaners (SCRD)" Tampa, FL, September 25 – 29, 2000.

Another approach to contaminant degradation patterns is to *calculate ratios* of daughter to parent compounds or ratios of selected geochemical analyte to contaminant concentration. Ratios can help reveal patterns not observable directly through concentration data. Wiedemeier et al., 1999, assessed chlorinated hydrocarbon plume behavior through ratios, including:

$$\frac{cis\,DCE}{total\,DCE} \qquad \frac{DCE+VC}{PCE+TCE} \qquad \frac{Total\,Solvent}{BTEX} \qquad \frac{Methane}{Total\,Solvent} \qquad \frac{\Delta Chloride}{Total\,Solvent} \qquad \frac{\Delta Chloride}{Methane}$$

[9] Total Inorganic Carbon (TIC) is the sum of carbon dioxide, carbonic acid, bicarbonate and carbonate. See section 4.3.3.4.

A problem with interpreting ratios is that the retardation factor (R) for the compound in the numerator is not the same as R for the compound in the denominator. Contaminants with a large R tend to "stay" at a location while contaminants with an $R \approx 1$ tend to "leave".

Contaminant degradation patterns can be assessed graphically. One example is the construction of isoconcentration maps of individual and total chlorinated compounds. Geochemical and *contaminant footprints* can be constructed from isoconcentration maps. These maps should be constructed and evaluated after each sampling round.

One of the most difficult issues in assessing MNA at chlorinated sites is that degradative processes may not be complete or may overlap. The expected reductive degradation pattern (for instance, PCE $\rightarrow$ TCE $\rightarrow$ DCE $\rightarrow$ VC $\rightarrow$ Ethene/Ethane) may not be observed. In some plumes, reductive dechlorination can stop after the formation of cis-DCE causing the accumulation of this contaminant. In other plumes, DCE and VC may not be detected because aerobic or anaerobic microbes oxidize them. Neither of these situations produces the expected end products of ethene/ethane. One way to distinguish these possible degradative scenarios is to monitor for hydrogen in the groundwater (Wilson, 2002). Chapter 4 and Appendix D discuss hydrogen monitoring.

3.3 Determining Natural Attenuation Rates

Unlike BETX, where benzene degradation can be tracked separately from toluene, ethylbenzene and xylene, degradation of chlorinated hydrocarbons are linked together. A decrease of a more chlorinated hydrocarbon (e.g., PCE) results in an increase in lesser chlorinated compounds (TCE, c-DCE). A temporary increase in less chlorinated intermediates may be expected without necessarily indicating plume expansion. However, this is complicated by the fact that the lesser chlorinated compounds are usually more soluble and hence more mobile in the environment. To establish a trend in the behavior of chlorinated hydrocarbons, a system of linear equations is needed to produce a coherent set of trends for contaminants. The constraints from the trends may need to be added to a fate and transport model to predict plume behavior and the likely effectiveness of MNA.

This section presents some simplified tools to establish linear trends. These tools should not be relied upon for assessment of complicated contaminated sites – e.g., sites with a large variability in flow direction. However, the tools can be appropriately used at less complicated sites (e.g., simple geology, no NAPL, straightforward hydrologic system) to assess if deviations in the observations are within acceptable bounds at contaminated sites during long-term monitoring. Major deviations should be noted and the reasons for the deviations explored.

Natural attenuation decay rates should be estimated for each monitoring well that intersects the plume through analysis of contaminant concentration data with time and distance. **For MNA to be an effective remedy, the decay rates of the source zone and the plume must indicate that contaminant concentrations will reach cleanup goals within a reasonable period of time**. Most methods for calculating decay rate constants assume that the plume is at steady state – which is that the plume has reached its maximum length and is expected to recede back toward the source. In addition, the decay rate in the plume should be faster than the decay rate in the source. If the decay rate in the plume is substantially SLOWER than the source decay rate, then the plume may be expanding, even if concentrations over time are decreasing at all the monitoring wells (Figure 4).

Figure 4 illustrates that as a plume of contaminated groundwater moves away from a source a peak concentration will move past a point, and after that time concentrations at that point will decrease even if the plume continues to expand. In most instances, monitoring wells are placed at a site some time after the contaminant release has occurred. The area of contaminated groundwater identified in the site investigation can be expected to decline due strictly to advection/dispersion processes even if degradation is not occurring. Monitoring over a relatively short period of time will, in most cases, disclose declining contaminant trends unless there is a continuing release. This is why properly placed sentinel wells and long-term monitoring are so important to MNA. Sentinel wells must be placed to intercept the plume if it is expanding. Monitoring must be conducted over a long enough period of time to assess the behavior of the entire plume and each contaminant within the plume. **The monitoring program must establish that the plume is not expanding and establish that the rates of degradation will allow cleanup goals to be realized within a reasonable period of time.**

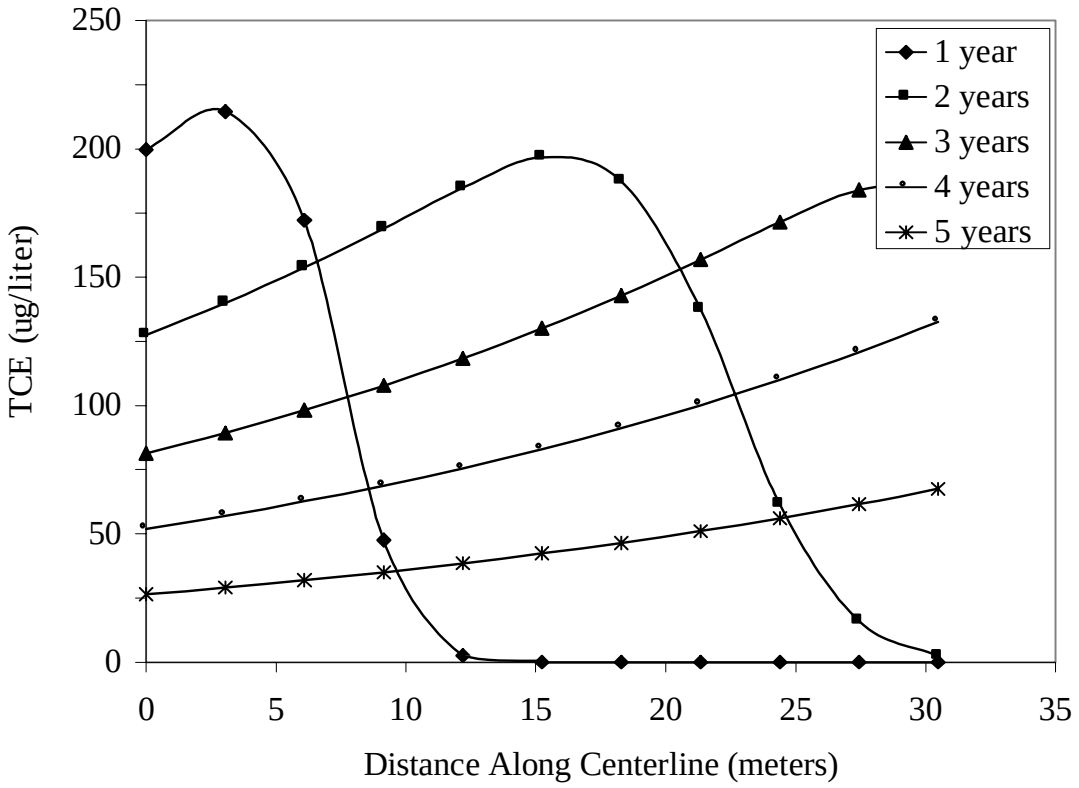


Figure 4. Illustration of an expanding plume. The concentrations decrease at specific distances along the plume while the plume as a whole migrates downgradient. No addition of contaminant at distance x = 0 is assumed.

3.3.1 Establishing steady state

A plume must reach steady state before MNA can effectively serve as a site remedy. At steady state, a plume has reached its maximum extent and the concentrations within the plume are constant. Decreasing concentrations occur in post-steady state plumes. Several methods to estimate whether a plume is at steady state are listed below. (Illustrations of some of these methods can be found in Interim Guidance on Natural Attenuation for Petroleum Releases at http://www.dnr.state.wi.us/org/aw/rr/archives/pubs/RR614.pdf.) These methods implicitly assume that the groundwater flow direction is invariant. When large shifts occur in groundwater flow direction, tests for plume stability using concentration data alone will not yield reliable results. Specifically, the non-parametric test should not be used when analysis of groundwater fluctuation reveals either large downward vertical gradients or a large shift in groundwater flow direction.

The EPA Science Advisory Board has stated that "there is no scientific research that establishes a reliable method for predicting whether a chlorinated solvent plume is stable or at steady state, without extensive monitoring of the plume over time" (US EPA, 2001). Therefore, while there are methods for estimating whether steady state has been achieved, for chlorinated hydrocarbons in particular, long-term monitoring is the most reliable method to establish that a plume is at steady state.

3.3.1.1 Plots of monitoring data

Monitor water table wells and piezometers within a groundwater plume and sentinel wells outside the plume to establish that the plume is not expanding and that contaminant concentrations within the plume are declining. Observed contaminant concentration vs. time for each well should be graphed using linear or semi log plots. Concentration vs. distance data should be graphed in a similar fashion. Data plots should be updated after each monitoring round. Visually inspect the data for trends. Concentration-distance plots can be constructed by plotting each time interval on a single graph to compare trend changes. If a change in trend is found, evaluate the change to determine what effect it may have on MNA. Slower decay rates may indicate an expanding plume, especially if found in downgradient wells. Analyze the range of decay rates that will result in meeting site cleanup goals and determine if the observed decay rates fall within the acceptable range.

3.3.1.2 Non-parametric statistics

Non-parametric statistics (such as the Mann-Kendall or Mann-Whitney tests) can help assess qualitatively (but not quantitatively) whether contaminant concentrations are decreasing at any given monitoring well. Non-parametric statistics CANNOT be used to estimate time to cleanup or determine decay rates. However, non-parametric tests may be useful to screen for declining concentration trends. Declining trends, along with clean sentinel wells (monitored over a significant period of time) may help establish whether the assumption that the plume is at steady state is conservative or not. Given a series of concentration data from a monitoring well, if we cannot conclude there is a declining trend from a non-parametric test, then the data is unlikely to provide useful information on degradation rates or fit a first order rate model. Wisconsin DNR speadsheets for the Mann-Kendall and Mann-Whitney tests can be found at http://www.dnr.state.wi.us/org/aw/rr/archives/pub_index.html#15.

Conclusions from Mann-Kendall, Mann-Whitney or other non-parametric tests must not be used alone as evidence of MNA at sites contaminated with chlorinated compounds. Conclusions from non-parametric statistical tests regarding plume stability are not statistically

robust. This problem is exacerbated when small data sets are analyzed. For the tests to be useful, the confidence level (1-α) is typically set lower than the 90% or 95% generally accepted by statisticians. With the low confidence level, we try to avoid the mistake of concluding that a data set with a truly increasing trend has no trend. Natural data variability can confound the tests. Estimating the coefficient of variation is recommended to address this problem. If the conclusion from a non-parametric test results in a declining trend, then a regression analysis should be conducted to assess decay rates. The changes of concentrations with time should also be assessed in light of changes in water table and groundwater flow direction. Hydrogeologic changes can be more important in explaining the observed decreases in contaminants than other presumed degradation processes. The Mann-Kendall test can not be used on data that exhibits seasonal variability.

3.3.1.3 Mass loss calculations

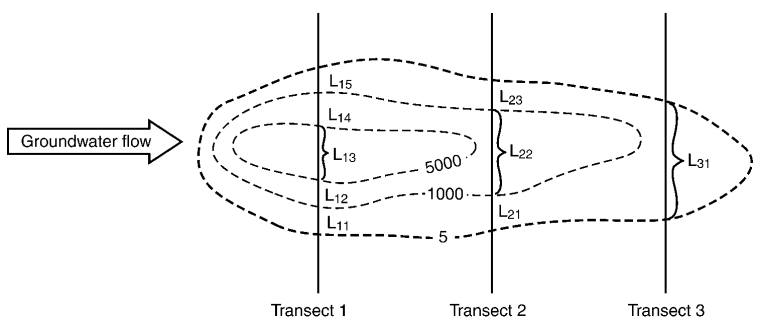
Mass flux or mass balances on the plume can help in assessing plume stability. Mass flux calculations involve contaminant or electron acceptor movement across plume transects while mass balance calculations usually assess changes in contaminant, geochemical and carbon mass within the plume over time. Mass flux calculations are subject to the same underlying assumptions that exist for the first order degradation rate constants, including a steady-state plume (see section 3.3.2). Examples of mass flux methods can be found in Wiedemeier et al. (1999), Weaver et al., (1997), Suarez and Rifai (2002). Examples of mass balance method can be found in National Research Council (2000).

Box 1 gives an example of a mass flux calculation through aquifer transects. Calculate mass flux of contaminants through each transect annually to determine the trend in mass changes along the plume over time.

Box 1
Mass Flux Estimate
(after Wiedemeier, 1999; and Suarez and Rifai, 2002)

1. Draw several transects (lines) perpendicular to the groundwater flow at various distances downgradient of the source. These serve as control planes. Transects of monitoring wells also serve as control planes.
2. Determine the distance between two consecutive contaminant contours crossing each transect.
3. Estimate the volume of water passing through each transect between two consecutive contours using the equation: $V_w = Lbvn$
   Where: V_w = water volume per unit time
   L = length of a perpendicular line connecting the isoconcentration contours
   b = thickness of the plume
   v = groundwater velocity
   n = porosity
4. Calculate the mass of water passing through the transect, $M_w = V_w\rho$
   Where: M_w = mass of water per unit time
   ρ = bulk density of water (62.5 lb/ft^3)
5. Estimate mass of contaminant crossing a transect: $M_c = M_wC_I$
   Where: M_c = mass of contaminant per unit time
   C_i = average concentration within the contour interval crossed by the transect
6. Calculate the contaminant mass for each consecutive contour line along the transect and add up the mass.
7. Compare the mass change at each transect over time

Plan View of TCE Plume (contours in ppb)



Key:
L_{11} = length of perpendicular line connecting isoconcentration contours.

Example: Transect 2: b = 10 feet; v = 100 ft/yr; n = 0.3

Transect Segment	Concentration	M_w (lb/yr)	M_c (lb/yr)
$L_{21} + L_{23}$ = 150 ft	5 – 1,000 ppb, $\bar{X}$ = 500 ppb	*2.81 x 10^6	**1.4 lb/yr
L_{22} = 200 ft	1000 ppb	3.75 x 10^6	3.75 lb/yr
		Total:	5.15 lb/yr = mass flux of contaminants for transect 2.

*M_w = (150 ft)(10 ft)(100ft/yr)(0.3)(62.5 lb/ft^3) = 2.81 x 10^6 lb/yr
**M_c = 2.81 x 10^6 lb/yr (.50 ppm) / 1 x 10^6 = 1.40 lb/yr

3.3.2 Estimating decay rates

First order decay models provide a parametric estimate of how fast degradation is occurring at given monitoring points. Almost all degradation constants quoted in the literature are first order degradation constants because calculation of first order rate constants is straightforward and collected data often appears to a fit first order decay model. The models use plots of logarithmically transformed concentration data over time to estimate degradation rates at specific monitoring points in the aquifer or along a primary groundwater flow line.

When adequate data exists, decay rates should be estimated. The approaches described in this section can be used to determine whether contaminant concentrations are decreasing. Spatial and temporal analysis of the data should indicate that the plume has stable boundaries. The following discusses the limitations of first order decay models. These limitations should be considered in context of the overall assessment of site remediation.

Extracting first order rate information from field data is prone to error due to uncertainties in monitoring well placement, variations in groundwater flow, and fluctuations in plume movement. Use of first order rate models assumes:

- a steady-state plume
- a uniform groundwater flow field
- contaminant concentration data are collected along the plume centerline
- a constant source strength with time (i.e., dissolution from the source is not a function of time)
- volatilization is negligible

If these assumptions are violated, then a first order decay model would likely result in erroneous degradation rates. McNab and Dooher (1998) presented a critique of steady state analytical techniques including those presented in this section. They concluded that an advancing plume could mimic a plume at steady state, particularly when few monitoring points are used. All decay rates must be verified in the field by monitoring to determine if contaminant loss reflects the calculated rates. In addition, there must be enough monitoring wells long the centerline of the plume to determine that the calculated rates aren't artifacts of dispersion.

First order rate models can be modified for plumes not at steady state by correcting contaminant concentrations for a "conservative" tracer, if one exists in the plume. A conservative tracer should have a retardation factor similar to the contaminant. This allows for correction of dilution/dispersion/adsorption losses. (See Wiedemeier et al., 1999, p. 342 for an example.) **However, a plume that has not reached steady state is not a candidate for a MNA remedy.** Another method for extracting rate constants is to use laboratory derived rate constants. However, laboratory derived rates are often faster (by an order of magnitude or more) than field measured rates.

If the conditions described above are met, the methods presented in this section can be relied upon to estimate decay rate constants for the source area and for wells within plume. Rate constants should be calculated using several methods and the results compared. Long-term monitoring data should be used to verify or modify the decay rates. If the rate constants vary with location along the plume, then that variation needs to be considered when predicting groundwater fate and transport for the site. The "goodness of fit" of the first order decay model with actual site data should be evaluated. In addition, sensitivity analysis should be conducted on the input data. Site specific data should always be used to determine decay rate constants.

Using literature values to estimate clean up time of a source area and plume is NOT acceptable. (For further information see references by Weidemeier, 1996; Weidemeier et al.,1999; Newell, 2002)

Several simple, public domain, 1-D models can be used to calculate first order decay rates. These include such models as Biochlor 2 (http://www.epa.gov/ada/csmos/models/biochlor.html); Natural Attenuation Software (http://www.cee.vt.edu/nas/); Bioscreen (http://www.epa.gov/ada/csmos/models/bioscrn.html), etc.

3.3.2.1 First order decay at a point in the plume (Temporal Analysis)

Plot either the natural log of the concentration data vs. time or prepare a semi-logarithm plot of concentration versus time for individual wells within the plume to determine the data trend and calculate a first order decay rate. First order decay is expressed as:

$$C(t) = C_o\, e^{-(kt)} = C_o\, 10^{-(k' t)}$$

where: $C(t)$ is the concentration (ug/l) at time t (day);
C_o is the initial concentration (ug/l);
k is the first-order decay rate (per day) at a well; and
$k' = k/[\ln(10)] = k/2.303$

For each well within the plume, the time to reach the cleanup goal for that well can be estimated from:

$$t_{cleanup} = \frac{\ln\left[\frac{C_{goal}}{C_{present}}\right]}{-k}$$

where: C_{goal} = groundwater cleanup standard (M/V)
$C_{present}$ = contaminant concentration in the latest sampling round (M/V)
k = first order degradation rate at the specific monitoring well (1/T)
$t_{cleanup}$ = time to reach the groundwater cleanup standard (T)

A simple test regarding whether a contaminant plume is expanding can be done through the comparison of the estimated $t_{cleanup}$ from monitoring wells located within the plume. When the estimated $t_{cleanup}$ at a downgradient well is <u>larger</u> than the $t_{cleanup}$ at an upgradient well, then the plume may be advancing. Note that a sentinel well can become contaminated even when decreasing concentrations are observed at upgradient monitoring wells.

3.3.2.2 First order decay along the plume centerline (Spatial Analysis)

Plot either the natural log of the concentration data vs. distance or prepare a semi-logarithm plot of concentration versus distance using data from wells located along the centerline of the plume. Determine the data trend and calculate a first order decay rate for the bulk plume using a procedure similar to that presented in section 3.3.2.2.

$$C(x) = C_o\, e^{-(k/v_c)x} = C_o\, 10^{-(k'/v_c)x}$$

Where: C(x) = concentration (ug/l) at a distance along the plume centerline
k is the first-order decay rate (per day) in the plume; and
k' = *k*/[ln(10)] = *k*/2.303
v_c = contaminant velocity in groundwater (L/T)
x = distance along plume centerline from the source (L)

To determine k, the slope of the line from the log-linear regression analysis of concentration along a plume path (at a particular time) must be multiplied by the contaminant velocity (v_c). The distance the contamination would travel downgradient from the source to reach cleanup standards (ES levels) can be calculated:

$$d_{ES} = \frac{\ln\left[\frac{C_{ES}}{C_{source}}\right]}{-k}(v_c)$$

Where: d_{ES} = distance to the point where the NR 140 enforcement standard (ES) is expected to be met (L)

A monitoring well placed at distance d_{ES} along the plume centerline would be expected to not exceed the ES for the particular contaminant. Estimating d_{ES} from time to time can provide a measure of whether the plume is expanding or not. When the d_{ES} estimated at the current time is larger than the d_{ES} estimated at a previous time, then the plume may be expanding.

3.3.2.3 First order decay in the source area (Temporal Analysis)

First order decay in the source area groundwater can be calculated by using concentration-time data from source wells. The calculation is performed in the same way as for individual wells in the plume (see section 3.3.2.1). The time to meet cleanup standards in the source zone can also be calculated.

These rates reflect decay rates for dissolved contaminants only. **If residual or free phase NAPL is present, this method cannot be used to estimate cleanup times in the source.** Free phase NAPL must be removed to the extent practical (in accordance with NR 708.13). Residual phase NAPL should be removed or treated to the extent practical. These phases represent the majority of the contaminant mass and natural attenuation processes are not particularly effective in reducing these phases.

3.3.2.4 Buscheck and Alcantar procedure (Spatial Analysis)

The Buscheck and Alcantar method relies on a first order decay model but attempts to extract the biodegradation rate in the analysis by accounting for advection and dispersion. To apply this method, the boundary condition assumes steady state – that is, for any particular well there is no change in concentration with time.

$$\lambda = \frac{v_c}{4\alpha_x}\left(\left[1 + 2\alpha_x\left(\frac{k}{v_x}\right)^2\right] - 1\right)$$

where: λ = first order decay rate (includes biologic and volatilization losses)

α_x = longitudinal dispersivity
v_c = retarded contaminant velocity in the x direction (L/T)
v_x = groundwater seepage velocity in the x direction (L/T)
k/v_x = slope of a line from the log-linear regression analysis of contaminant concentration versus distance along the plume flow path.

3.3.2.5 Decay rates using mass flux measurements (Spatial Analysis)

Bockelmann et al. present a method for determining first order decay rates from compound-specific mass flux calculations. The method requires knowledge of the average groundwater travel time (Δt) between the adjacent control planes (see Box 1).

$$M_{d_{cp2}} = M_{d_{cp1}} e^{-k\Delta t}$$

where: $M_{d_{ct1}}$ = near source (control plane 1) compound specific mass flux (M/T)
$M_{d_{cp2}}$ = downgradient from source (control plane 2) compound specific mass flux (M/T)
k = 1st order decay rate averaged between the control planes (1/T)
Δt = average travel time between the control planes (T)

$$k = -\ln\left(\frac{M_{d_{cp2}}}{M_{d_{cp1}}}\right)\frac{1}{\Delta t}$$

The same assumptions that apply to all first order decay models apply to decay calculated using the mass flux method. Mass flux methods assume the concentration associated with each sampling point is constant over the area represented by the sampling point. The greater the distance between monitoring wells (as well as the downgradient distance between the control planes), the greater the uncertainty of both the contaminant concentration (and hence mass) and the contaminant travel time.

3.4 Data Evaluation

Monitoring data should be evaluated in connection with the remediation goals at the contaminated site. **Site data should be reviewed after every sampling event.** Periodically (e.g., annually or biannually, but not less frequently than every 5 years), prepare reports using the tools in this Chapter or other methods to assess natural attenuation processes. Data evaluation should address the following topics. Examples of evaluation methods are also listed.

1. Demonstrate that the plume is stable and/or receding. After establishing an adequate monitoring network, monitoring of the 3-D plume should demonstrate that the plume has not migrated beyond the established vertical and horizontal limits determined in the site investigation. Assessment of plume behavior can include the following. Mass balances performed on the plume at set time periods (e.g., every 2 years) to determine that mass is decreasing within the plume. Compare up and downgradient contaminant concentrations. Assess fluctuations in groundwater flow direction and gradient. Does the groundwater

monitoring network continue to allow adequate assessment of the plume? Have groundwater flow direction or velocity changed significantly during the assessment period? If so, what are the ramifications for contaminant movement? Monitoring data should be displayed in tables for ready reference and comparison.

2. Demonstrate that receptors are protected. Confirm the direction and velocity of groundwater and contaminant movement to ensure changes in predicted movement have not occurred. Sentinel wells should remain free of contaminants. If directly threatened, receptors should be monitored on a frequency determined by the long-term monitoring plan. Confirm that other pathways for contaminant migration, such as vapor intrusion into structures, are protected.
3. Detect changes in environmental conditions supporting natural attenuation processes. Assessment of natural attenuation processes can include the following. Assess the groundwater geochemistry and determine whether monitoring well screens, particularly sentinel wells, are within the flow path of the groundwater plume. Estimate carbon mass remaining to support reductive dechlorination and determine whether conditions supporting contaminant degradation are likely to continue into the future. Construct isoconcentration maps of contaminants/geochemical parameters and draw conclusions regarding degradation processes. Assess changes in geochemical footprints compared with predicted degradation processes.
4. Detect new releases or new sources of contamination. Evaluate source area wells for increases in contaminant concentrations; assess contaminant and geochemical concentrations in the plume for unexpected changes that may signal new sources or releases of contaminants.
5. Determine if natural attenuation processes are performing as predicted. Recommended methods for this include the following. Assess contaminant and geochemical conditions in the source area and plume to determine that expected processes (such as reductive dechlorination) are occurring. Assess decay rates in the source and plume and determine expected time to cleanup. Construct trend analyses. Assess actual trends over time compared to predicted concentrations and previous trends. Determine degradation rates and compare to the rates predicted from the MNA original assessment.
6. Determine if projected cleanup targets (such as predicted half-life concentrations in wells) are being met. Revisit the original conceptual model and analytical model(s) used to assess MNA at the site and validate those models with more recent data. Determine whether the models continue to accurately reflect the site or whether changes in the models are needed.
7. Assess any unpredicted condition, such as the presence of new breakdown products (indicating a change in degradation processes) or a change in contaminant migration rate or direction. Determine how these changes affect predictions for site cleanup and possible impact to receptors. Reassess the conceptual site model and reevaluate site investigation and monitoring results.

Data evaluation should lead to conclusions as to whether the selected remedy is performing as expected; human health, welfare and the environment continue to be protected; the monitoring program is adequate to assess changes in plume configuration; etc. Monitoring reports should clearly state the results of the data assessment and the conclusions drawn by the investigator.

Chapter 4

Monitoring MNA Remedy

Monitoring is the heart of a monitored natural attenuation remedy. The monitoring program at a site must specify data quality objectives, goals of monitoring, monitoring wells to be included, the frequency of monitoring, the parameters to be monitored, sampling and analytical methodology, and the generation of monitoring reports. This chapter discusses the concepts that should be considered before establishing a monitoring program for MNA.

4.1 Data Quality Objectives (DQO)

All testing of environmental media requires attention to the sampling and analysis methods used to collect and analyze the media. When analyzing groundwater for contaminants and geochemical indicators, data quality considerations should include the following:

1. Precision of the sampling methodology and analysis. Precision refers to the reproducibility of the data. Precision is important in making comparisons between monitoring wells (such as comparing dissolved oxygen concentrations in upgradient and source zone groundwater) and between monitoring rounds.
2. Sensitivity of the sampling methodology and analysis. Sensitivity refers to the ability to detect a substance and to distinguish differences in concentration. Sensitivity is important in distinguishing uncontaminated groundwater from contaminated groundwater, for instance.
3. Representativeness of the sample. Representativeness expresses the degree to which data accurately and precisely represent actual groundwater conditions. Representativeness is dependent upon ensuring proper design of the sampling program, ensuring that proper sampling techniques are used, and that proper analytical procedures are followed.
4. Comparability of data. Data comparability refers to the extent to which measurement techniques between sampling points and sampling rounds provide the results that can be reliably compared.

The goals of the monitoring program will determine the level of precision and sensitivity needed for the geochemical indicators. For instance, while comparison of sample data to groundwater ES would require sample analysis at the part per billion (ppb) level, the analysis for H_2 must be sensitive to the part per trillion (ppt) level. This underscores a level of care beyond typical NR 140 sampling and handling when dissolved H_2 is analyzed. <u>Base the choice of sampling and analytical methodologies on the goals of the monitoring program</u>. Often, geochemical parameters are used in a more qualitative fashion to determine changes within the groundwater plume over time and/or compared to upgradient, uncontaminated groundwater. Therefore, there is no standard or “correct” concentration for geochemical parameters. For on-going, natural attenuation assessment, the monitoring philosophy should be “use whatever works”. This includes the use of field or laboratory methods that give an accurate representation of site conditions. If a round of geochemical data is to be used in a quantitative manner then select field or laboratory methods which will give data the highest known quality that is practical. Because many geochemical parameters are sensitive to redox conditions, field generated data will often produce better quality data than laboratory analysis. For instance, levels of dissolved oxygen, ORP, dissolved manganese, and ferrous iron rapidly change upon exposure to the

atmosphere. Field analytical methods for these compounds will likely produce data that is more representative of actual site conditions.

Several web resources are available to further define and clarify the data quality objective (DQO) process.

Crumbling, D.M. 2001. Clarifying DQO Terminology Usage to Support Modernization of Site Cleanup Practice (EPA/542/R-01/014) http://www.epa.gov/tio/download/char/dqo.pdf

Crumbling, D.M. 2001. Applying the Concept of Effective Data to Environmental Analyses for Contaminated Sites (EPA/542/R-01/013) http://www.epa.gov/tio/download/char/effective_data.pdf

Robbat, A., Jr. A Guideline for Dynamic Workplans & Field Analytics: The Keys to Cost-Effective Site Characterization and Cleanup (last modified, June 26, 2002) http://www.epa.gov/swertio1/download/char/dynwkpln.pdf

Guidance for the Data Quality Objectives Process for Hazardous Waste Sites (EPA/600/R-00/007) 2000. http://www.epa.gov/quality1/qs-docs/g4hw-final.pdf

4.2 Goals of Monitoring

Each site should establish specific goals to be achieved by monitoring. The list below contains goals expected at all sites. Specific sites may have additional goals beyond those listed here. Monitoring reports should contain information to show that the monitoring goals for the site are being met and assess whether the monitoring program is adequate to achieve the monitoring goals. At a minimum, the goals of monitoring should establish that:

1. *MNA is effectively protecting receptors*. The monitoring well network, frequency of monitoring, and, where necessary, monitoring nearby receptors, will help establish that existing receptors are protected. Monitoring schedules and well networks may need to be adjusted if new receptors are established (such as private water supply wells or high capacity irrigation wells) near the contaminant plume.
2. *Sentinel wells remain free of contamination.* Sentinel wells are the "early warning system" that a plume is expanding. Confirmation of contaminants reaching a sentinel well should trigger the implementation of a contingency plan to control contaminant movement.
3. *There have been no new sources or releases of contamination*. Monitoring wells should be located such that new spills or releases are detected quickly. This includes operating facilities as well as releases caused by hydrogeologic changes that mobilize previously unsaturated or immobile contaminants. New sources can result in contaminant "slugs" that move through the plume and may cause the plume to expand.
4. *The contaminant plume is stable and receding*. The acceptability of MNA is based on control of the contaminant plume in three dimensions. Monitoring well networks must be extensive enough to establish that the plume is contained within delineated boundaries. Changes in groundwater velocity, geochemical conditions, degradation patterns, groundwater use, etc. can cause a previously stable plume to advance.
5. *The remedy is performing as predicted to reduce contaminant concentrations*. Predictions of contaminant concentrations at specific points in time and space should be made during site investigation and remedy selection. These predictions reflect assumptions made in the site conceptual model. Monitoring will determine accuracy of the site conceptual model and

lead to refinement of that model. Assessing contaminant reductions over time will also determine whether the remedy is on track to meet site cleanup goals.

6. *Contaminant mass in the subsurface is being reduced*. Cleanup of the aquifer is based on contaminant mass loss through degradation. The monitoring well network and sampling program should be designed to allow assessment of contaminant mass in the subsurface and calculation of mass loss of all contaminants in the plume over time.
7. *The conditions necessary for MNA continue to be present at the site*. Degradation of chlorinated compounds relies on specific geochemical and redox conditions. Those conditions, such as carbon content or competing electron acceptors, can change over time. Even when contaminant concentrations are reducing as predicted, it cannot be assumed that natural attenuation conditions will continue into the future. Changes in geochemistry or redox conditions can result in plume migration beyond established boundaries and impact to receptors.
8. *Cleanup goals will be achieved within a reasonable period of time*. Monitoring should continue until it is established that cleanup standards will be met within a reasonable period of time. Interpretation of reasonable period of time will differ for each contaminated site, based on risk to receptors and existing and future land use. Predictions of achieving cleanup goals based on historical data are useful for assessing the conceptual model and for setting performance goals. Monitoring and data assessment should be structured to determine the likelihood that MNA will ultimately achieve cleanup standards. If it is determined that cleanup cannot be achieved by MNA alone within a reasonable period of time, then additional remedial efforts should supplement or replace MNA.

4.3 Site Specific Monitoring Considerations

The monitoring goals for a site will be achieved through implementing a site-specific monitoring plan. The basis for selecting monitoring wells, frequency of monitoring, and parameters to be monitored in a monitoring plan is built upon monitoring changes over time in the hydrologic, geochemical and contaminant environments at the site. The following discussion assumes that a monitoring well network has been established at the site, that the plume has been defined in 3 dimensions and that a basis for implementing MNA as a remedy has been established.

4.3.1 Hydrologic monitoring

Monitoring changes in site hydrology includes:

1. Water level monitoring. Water levels should be measured in all monitoring wells (regardless of whether an individual well is sampled) at least as often as water quality samples are collected at a site. Water table and piezometric maps should be constructed after every monitoring round. Assess contaminant levels versus groundwater elevation for plumes that are confined to the shallow water table zone to determine if water table fluctuations affect the observed contaminant concentrations. (See Guidance On Natural Attenuation For Petroleum Releases RR 614.zip file at http://www.dnr.state.wi.us/org/aw/rr/archives/pub_index.html#15 for a spreadsheet that compares the statistical significance of water table trends with trends in contaminant concentration.) For deeper plumes, assess changes in piezometric head on groundwater flow direction and vertical gradient.
2. Groundwater flow velocity and gradients. Using hydraulic conductivity values determined during the site investigation, determine groundwater flow direction, gradient and velocity after every monitoring round. These data should be assembled and visually represented on

a site groundwater flow map by groundwater flow vectors. Groundwater flow vectors indicate groundwater flow direction and travel distance over the time monitored. An example of this type of compilation can be found in Wilson et al., 2000.

3. Surface water – groundwater interaction. Where groundwater plumes are or may discharge to a surface water body (e.g., river, lake, wetland), the interface between the surface water and groundwater system should be monitored. This will likely require placing monitoring wells near the groundwater discharge area, perhaps even within a stream or lake bed. Monitor water elevation and water quality of the groundwater and surface water. Surface water quality near the discharge area, by it self, is not sufficient to establish whether contaminants are entering the surface water body. Groundwater gradients and contaminant levels in wells nearest the surface water discharge location should be used to determine contaminant loading to the surface water body.
4. Tracking land use changes that will affect site hydrology over time. This includes such things as installation of pumping wells that can influence the flow direction of the plume, development that affects surface water infiltration or discharge of groundwater.

4.3.2 Contaminant monitoring

The site investigation results will serve as a guide to determining which parameters to sample and analyze at a site. Contaminant monitoring should include all contaminants detected at the site, including all breakdown products expected from the parent compounds. Contaminant monitoring should also include compounds that may be mobilized due to redox conditions at the site. For instance, arsenic naturally occurs in most geologic media. Under reducing conditions, such as those associated with reductive dechlorination, arsenic can be reduced to become toxic and mobile in the environment. Other naturally occurring metals that may be mobilized under reducing conditions include manganese and nickel. Initial site investigation should include screening for these metals (As, Mn, and Ni). If levels above background occur in the plume, then routine monitoring should be conducted for these metals. Contaminants of concern should be analyzed using EPA Standard Methods for groundwater. See “Frequency of Monitoring” below for further information.

4.3.3 Geochemical monitoring

Chapelle et al. (2002) place geochemical parameters into 3 categories:

- those useful for assessing system redox status (e.g., dissolved oxygen, hydrogen, methane, sulfide, ORP, pH and temperature);
- those useful for assessing the potential for microbial metabolism of contaminants (e.g., oxygen, nitrate, sulfate, total organic carbon); and
- those that measure degradation processes (e.g., chloride, methane, ethene/ethane, specific conductance, total inorganic carbon).

Table 1 in Section 3.2 lists the standard geochemical parameters that should be considered for sampling and analyses at sites contaminated with chlorinated hydrocarbons. Selection of geochemical parameters for sampling and analysis is a site-specific decision. See section 4.3.4 and 4.3.5 for additional guidance on adjusting selected parameters and frequency for monitoring. *Information about sampling dissolved oxygen, nitrate, manganese, ferrous iron, sulfate, alkalinity, and ORP can be found in Wisconsin DNR, 1999*. Other geochemical parameters are discussed below.

4.3.3.1 Chloride

The degradation of CAH produces chloride (Cl^-) ion. Chloride is conservative in groundwater. That is, it tends to travel with the groundwater front and is not retained on aquifer surfaces nor does dissolved chloride enter into any significant chemical or biochemical reactions in natural water. Chloride can serve as a tracer to estimate groundwater flow velocity and direction and can aid in determining contaminant degradation rates. However, natural and anthropogenic sources of chloride can mask the Cl^- concentrations from CAH degradation. In Wisconsin, the most common source of Cl^- is road salt. All CAH contaminated sites should analyze background and plume concentrations of Cl^- to determine whether Cl^- is useful for interpreting degradation and plume movement at the site. If Cl^- is useful, then it should be included in the long-term monitoring program. Chloride analysis is usually performed in a laboratory using an EPA standard ion-chromatography method.

4.3.3.2 Hydrogen

Hydrogen is the "ultimate" electron donor in reductive dechlorination. A discussion of the role of hydrogen in reductive dechlorination can be found in Appendix D. Because hydrogen accumulates in groundwater only under very reduced environments, hydrogen levels are a good reflection of the redox conditions. However, it is difficult to achieve accurate and reproducible hydrogen measurements due to field sampling and handling challenges. A bubble strip method is used to measure hydrogen which requires that groundwater be pumped continuously at a rate of 500 ml/min for approximately 30 minutes. The type of pump used, pumping methods and rates, and the type of well casing affects measured levels of hydrogen (Vroblesky and Chapelle, 2002).

Because of these problems, Chapelle et al. (2002) recommend that hydrogen be measured when redox processes cannot be interpreted from other monitoring parameters. Chapelle gives the example of a TCE plume with decreasing TCE concentrations, minor accumulation of cis-DCE downgradient and no detectable vinyl chloride. This situation can be interpreted two ways – as weak dechlorination activity or as strong degradation. If the dechlorination is weak, the TCE is loss is due to dispersion and dilution with some conversion to cis-DCE and the cis-DCE is not converted to VC. If the dechlorination is strong, the TCE loss is due to dechlorination and the cis-DCE is transformed to carbon dioxide without producing VC. Hydrogen concentrations in the aquifer can distinguish between these two scenarios. Hydrogen concentrations greater than 1 nM support, but don't prove, the second interpretation.

There is no EPA Standard Method for measuring hydrogen. McInnes and Kampbell (2000) discuss two methods of hydrogen sampling. Hydrogen concentrations can be measured in the field (preferred) or laboratory with a gas chromatograph using a reducing gas detector (Kampbell and Chapelle, 2002).

4.3.3.3 Methane, ethene, ethane

Methane in groundwater is characteristic of strong reducing conditions, such as those that support reductive dechlorination. Ethene is a result of the complete dechlorination of PCE and TCE. Under strongly reducing conditions, ethene can be further reduced to ethane. Ethane is also the reductive dechlorination end product of 1,1,1-TCA. These three parameters are critical in supporting the efficacy of reductive dechlorination at a sites contaminated with chlorinated hydrocarbons and should be included in routine sampling.

Like hydrogen, methane, ethene and ethane are dissolved gases. Sampling methodology should ensure that the groundwater does not contact the atmosphere, leading to the loss of the

dissolved gas in the sample. For all three analytes, groundwater samples are preserved with sulfuric acid and capped with airtight sepa. Samples can be shipped to a laboratory for analysis by gas chromatography (Kampbell and Chapelle, 2002).

4.3.3.4 Sulfide

Sulfide (S^{-2}) is formed when sulfate is reduced. Sulfate reduction may indicate that redox conditions are conducive to reductive dechlorination. Sulfide will generally be found in groundwater with less than 1 ppm dissolved oxygen and low ferrous iron. Sulfide is easily lost from groundwater samples through volatilization or oxidation. Therefore, sulfide analysis should be performed in the field using colorimetric analysis and a field spectrophotometer. Because of interfering geochemical reactions for sulfide, it is more common to monitor the loss of sulfate (SO_4^{-2}) at a CAH contaminated site.

4.3.3.5 Total organic carbon

Biodegradable carbon is the engine that drives reductive dechlorination. Wiedemeier et al. (1998) found that total organic carbon (TOC) should be greater than 20 mg/l to support reductive dechlorination. EPA Standard Methods for total organic carbon 9060 or 415 should be used for analysis. TOC should be routinely sampled and analyzed.

4.3.3.6 Total inorganic carbon

Carbon dioxide is the end product of microbial degradation of organic compounds and is therefore a measure of the biological activity within an aquifer. Alkalinity has traditionally been used as a measure of carbon dioxide, but alkalinity can be misleading due to reactions of carbonate minerals and the effect of high concentrations of titrable organic acids in groundwater. The change in total inorganic carbon in groundwater has been found to be a better measure of carbon dioxide. Chapelle et al (2002) have found that TIC can be one of the most useful footprints of the contaminant plume. TIC can be measured directly during TOC analysis or TIC can be calculated from the measurement of alkalinity, pH, and dissolved carbon dioxide. The methods for calculating TIC can be found in Appendix D, taken from Chapelle et al. (2002) at http://www.epa.gov/ada/download/reports/epa_600_r02_002.pdf.

4.3.4 Adjusting monitoring parameters during long-term monitoring

Once baseline geochemistry and contaminant concentrations are established for all monitoring wells, adjustments can be made in parameters and wells routinely monitored. It may be that some wells will be monitored less frequently than others or that a select list of parameters will be routinely monitored while a full suite of parameters is performed at all the wells only infrequently. Requests to adjust the monitoring program should be based on the stability of the plume and the data needs to adequately assess the plume over time. These data needs are discussed more fully under frequency of monitoring.

4.3.5 Frequency of monitoring

Quarterly monitoring is usually employed during the site investigation to establish seasonal changes in groundwater flow direction and velocity as well as define contaminant and geochemical concentrations and variation with seasonal fluctuations. Once the hydrologic, contaminant, and geochemical variation for the site is determined (usually two to three years of quarterly monitoring), monitoring frequency can be reassessed. Decisions on monitoring frequency should consider the following criteria.

a. Threat to receptors. Estimated time for contaminants to reach nearby receptors is one of the primary considerations in monitoring frequency. Longer flow time between the edge of the plume and the receptor support reduced monitoring frequency.
b. Variability in the groundwater flow regime. Significant seasonal changes in groundwater elevation, flow direction or gradient support the need for more frequent monitoring. Monitoring data should capture the variability in plume movement. Assess the existing quarterly data by selectively removing data points – if the data were assessed using semi-annual or annual data points, what would the results yield? Decisions on monitoring frequency and monitoring dates should be based on how apparent degradation rates or data trends are likely to change with reduced monitoring data.
c. Lag time in contaminant movement. The "lag time" of contaminant movement from source areas to downgradient wells is a consideration in monitoring frequency. For shallow contamination affected by seasonal water table fluctuation an increasing concentration in near source wells may not appear for several months in downgradient wells. Seasonal concentration peaks across the site may occur in different months of the year, necessitating more frequent monitoring.
d. Plume stability. The stability of plume configuration and concentration and the likelihood of temporal or spatial changes are primary determinants of monitoring frequency. Decreased monitoring frequency can be considered when it is established that a plume is at "steady state". At steady state a plume should be stable spatially while concentrations are steady. If these conditions cannot be documented, then long term quarterly monitoring may be necessary.
e. Apparent degradation rate of contaminants. Monitoring frequency should reflect the half-life of the contaminants being monitored. Frequent monitoring is more important for contaminants that degrade quickly than for slowly degrading contaminants.
f. Significant changes in monitoring results. Significant increases in contaminants, contamination of previously uncontaminated wells, etc. should trigger reassessment of monitoring frequency.
g. Land use changes. Installation of high capacity wells near the contaminated site or other external factors that may change the horizontal or vertical groundwater gradients will result in more frequent monitoring to define the effects on groundwater flow and contaminant movement. This situation may also require additional well installation.

Reports assessing MNA and estimating the effectiveness of MNA to achieve cleanup standards at the site should be produced on a frequency commensurate with the monitoring frequency, but no less often than every 5 years (see Reporting Requirements below).

4.3.6 Length of long-term monitoring

How long to continue long-term monitoring is a function of:

- contaminant source decay
- plume decay
- contaminant and groundwater velocity
- fluctuation of contaminant movement over time
- potential receptors
- confidence in the characterization and predictability of the flow system and contaminant movement
- natural attenuation capacity of the soils and aquifer (i.e., the available mass of electron donors and acceptors to maintain degradation processes until standards are met).

- ability to verify cleanup assumptions and models through empirical monitoring data
- ability to eventually meet cleanup standards.

Sites with chlorinated contaminants will usually perform 2 to 3 years of quarterly monitoring for initial characterization of MNA. Once variation in the groundwater system is understood frequency of monitoring can be reduced as discussed in section 4.3.5. Long-term monitoring at reduced frequency may last many years depending upon site-specific conditions. In general, contaminant levels in groundwater should approach or attain NR 140 enforcement standards before monitoring ceases.

4.4 Assessment of Monitoring Goals

After each monitoring round the water quality data should be evaluated to determine if the goals of monitoring are being achieved. The evaluation will include an analysis of:

- Protection of receptors. Are receptors free of contamination? Are there any new threats to receptors?
- Plume behavior. Has the plume remained within the boundaries delineated during the site investigation? Has the groundwater flow direction or velocity changed such that changes in the vertical or horizontal movement of the plume may occur?
- Contaminant levels. Are the contaminant levels declining or remaining constant? Have contaminant levels increased, indicating a new release or mobilization of contaminants? Are contaminant levels being met at specific wells as predicted by site models? How has contaminant mass changed from previous monitoring periods?
- Geochemical changes. Have geochemical footprints changed, indicating a change in the contaminant plume? Do geochemical data indicate appropriate conditions for continued degradation of contaminants?
- Effectiveness of natural attenuation as a remedy. Do conditions at the site continue to support predicted natural attenuation processes? Are expected patterns of contaminant degradation found? Do contaminant levels reflect predicted degradation rates?
- Progress made toward achieving cleanup goals. Do data continue to reflect estimated cleanup time frames?

Monitoring results must be submitted to the Department after each sampling event in accordance with NR 724.17(3). Data analysis, using the techniques and tools described in Chapter 3 or other methods, should be performed at regular intervals determined by the site monitoring plan. Assessment of long-term monitoring data, analysis and conclusions should be submitted to the Department periodically in long-term monitoring reports, but not less frequently than every 5 years.

4.5 Decision Criteria if Monitoring Goals are not met

After assessing data from each sampling round, a decision should be made on whether MNA continues to be an adequate remedy or whether additional remedial actions are necessary. Additional remedial actions can range from increasing frequency of monitoring to installing additional monitoring wells to implementing an alternative remedy. The following criteria should be considered in determining whether additional remedial action is necessary.

4.5.1 Increasing contaminant concentrations

Increased contaminant concentrations in the source area may indicate a new release or may result from a temporary hydrologic condition, such as increased leaching due to a rainfall event. Contaminant concentrations increasing in the plume may be a temporary anomaly or may indicate that assumptions in the conceptual site model are flawed. Concentration increases at the leading edge of the plume may indicate an expanding plume. The cause of an increasing contaminant trend must be assessed before an adequate response can be taken. Decisions on taking additional action will include the locations where increasing trends are detected, the threat to receptors, and the amount of time available for an alternative response given the risks posed by the site. Responses to increasing contaminant trend may include:

- Increased frequency of monitoring until decreasing trends are once again established.
- Limited site investigation to determine the causes for increasing trends, such as a soil vapor investigation or using direct push technologies to collect soil and groundwater samples.
- Selection of another groundwater remedy, particularly if trends indicate the groundwater plume is expanding horizontally or vertically. This will usually trigger implementation of the contingency plan (see section 4.6).

4.5.2 Contaminants detected outside of previously established contaminant boundaries

Contaminant migration in vapors, soil, or groundwater beyond the contaminant boundaries established by the site investigation will trigger additional response actions. At a minimum, the new detection of contaminants should be confirmed by additional sampling. If the contamination is confirmed at a location beyond the original contaminant boundaries, then the site conceptual model and site remedy must be reassessed and appropriate action taken to halt expansion of the contamination, including implementation of the contingency plan.

4.5.3 Contaminants are not decreasing at the rate predicted

Compare data trends and contaminant concentration against those predicted from site models conducted at the end of the site investigation. If concentrations are not decreasing at the predicted rates or incomplete degradation is occurring, then the conceptual site model should be revisited and analytical models of the site reassessed. Additional source control or other measures may be necessary to meet clean up goals. In addition, the monitoring plan should be revisited. Monitoring frequency, monitoring parameters and selection of monitoring points should be reassessed. Additional monitoring wells or piezometers may also be necessary.

4.5.4 Changes in land use that affect MNA remedy

Land use changes, particularly the development of nearby municipal, agricultural, or private wells may affect the choice of MNA as a remedy for the site. Other changes, such as an upgradient contaminant release, may adversely affect MNA processes. Any change near the plume or source that could affect the stability of the plume, the location of receptors, etc. will trigger a reassessment of MNA as an effective remedy.

4.6 Contingency Plan

It is recommended that sites with MNA remedies develop a contingency remedy in the event that MNA does not prove to be effective or fails to protect human health, welfare and the environment. The contingency plan should be tiered to respond to various scenarios of changed conditions at a site. Examples include:

- Contingency if contaminant concentrations increase within the plume: adjustments will be made to the monitoring plan such as increased monitoring frequency or additional parameters.
- Contingency if contaminants are found in previously uncontaminated side gradient wells: additional wells will be installed to monitor changes in groundwater flow direction. Results of this effort may trigger additional action, depending on location of threatened receptors, the possibility of plume expansion, etc.
- Contingency if contaminants are found to not be degrading at rates that protect receptors: install an alternative remedy to reduce contaminant mass to levels where rates of natural attenuation processes will be protective.
- Contingency if receptors are contaminated: a series of additional responses would likely be triggered, including directly addressing the impact to human health and the environment, installing additional active remedies to control contaminant movement, undertaking additional site investigation to reassess the conceptual site model and identifing sources of contamination and pathways of contaminant movement.

The active contingency remedies should, at a minimum, be designed to contain the contaminants such that the contaminants do not move beyond the boundaries established by the site investigation. The contingency plan should address all possible pathways at the given site that could impact a receptor. Initial engineering designs for alternative remedies should exist at the time the MNA remedy is implemented, if the contamination poses a threat to nearby receptors. This will help ensure that the contingency plan can be implemented quickly if the MNA remedy fails.

4.7 Long-term Monitoring Plan and Reporting Requirements

NR 724.17 addresses long-term monitoring requirements. The specific requirements of a long-term monitoring plan are addressed in the rule. The monitoring plan should also include the issues discussed in this Chapter, namely:

- Data quality plan
- Statement of the goals of monitoring
- Site specific monitoring program, including frequency of monitoring
- Methods of data assessment
- Decision criteria for making adjustments to the long-term monitoring program

Submit monitoring data to the Department after each sampling event. An in-depth report assessing the progress of the MNA remedy should be submitted on a frequency determined by the Department, but not less frequently than every 5 years. The monitoring report should include all the requirements of NR 724.17 and comply with the approved monitoring plan.

Chapter 5

Regulatory Requirements

5.1 Certain Regulatory Considerations

The NR 700 Wisconsin Administrative Code series applies to all cleanups performed in the State of Wisconsin. Most sites contaminated with chlorinated hydrocarbons will particularly be affected by:

- NR 706 – Hazardous substance discharge notification and source confirmation requirements
- NR 708 – Immediate and interim actions
- NR 714 – Public information and participation
- NR 716 – Site investigations
- NR 720 – Soil cleanup standards
- NR 722 – Standards for selecting remedial actions
- NR 724 – Remedial and interim action design, implementation, operation, maintenance and monitoring requirements
- NR 726 – Case closure
- NR 749 – Fees for providing assistance; remediation and redevelopment program

This chapter is not a comprehensive review of these regulations, but instead emphasizes certain aspects of these codes with respect to MNA of chlorinated hydrocarbons. The previous chapters in this guidance discuss the application of aspects of NR 708, 716, 722 and 724 to sites contaminated with chlorinated compounds. The following discusses aspects of NR 714 and 720. Section 5.2 discusses aspects of NR 726 and 749 as they apply to closure of sites with chlorinated hydrocarbon contamination.

5.1.1 NR 714 – Public information and participation

The National Research Council (2000) found in its review of natural attenuation for groundwater remediation that there were potential community concerns about the use of MNA and concluded that "community involvement should be a critical component of decisions regarding natural attenuation" (p. 48). The report goes on to recommend three key principles of community involvement:

1. Involve the community early
2. Provide the community with influence in the decision-making process
3. Build a working relationship with the community

Chapter NR 714, Public Information and Participation, lays the basis for developing and implementing a public participation program at contaminated sites. NR 714.07 applies to all environmental cleanup sites in the State. In addition to NR 714 requirements, NR 726 has a public notification requirement at closure for sites with groundwater contamination that affects neighboring properties. The NR 726 requirements are discussed in section 5.2.1.4

> NR 714.07(1) Evaluation of the need for public participation. The need and level of a public participation program shall be assessed by the responsible party and be based

upon known or potential threats, public concern, and the need to collect additional information from the public or other considerations.

NR 714.07(2) Notification. If the Department or responsible party determine that public participation regarding the specific site is necessary, the responsible party must notify the public (through various means) of the description of the contamination, actions to mitigate the contamination, and a contact person to obtain more information.

NR 714.07(3) Posting of signs. Department-issued signs must be posted at a facility in the locations stated in the code.

NR 714.07(4) Requests for site or facility-specific information. Any interested person may make a written request to the Department for information about a specific site or facility and receive from the Department copies of Department approvals or rejections of specific plans submitted by the responsible party.

NR 714.07(6) Additional public participation options are listed that the responsible party or the Department may use to inform the public of actions on the contaminated site, including contacting government officials and interested individuals; contacting mass media; holding public meetings; distributing literature; establishing an information clearinghouse; etc.

5.1.2 NR 720 – Soil cleanup standards

While this guidance emphasizes MNA as it pertains to groundwater, any remedial plan must also address soil contamination that remains on site above applicable soil standards. NR 720 lays out the procedures for establishing generic and site-specific residual contaminant levels (RCLs). Soil above generic or site-specific RCLs must either be cleaned up to the numerical standards or a soil performance standard must be established for the soil. The Department has issued guidance on calculating RCLs as well as the criteria for establishing soil performance standards. See the following links:

Determining residual contaminant levels using the EPA soil screening level web site, 01/2002
http://www.dnr.state.wi.us/org/aw/rr/archives/pubs/RR682.pdf

Application of Soil Performance Standard Guidance, 10/2001
http://www.dnr.state.wi.us/org/aw/rr/archives/pubs/RR676.pdf

Interim guidance on the use of leaching tests for unsaturated contaminated soils to determine groundwater contamination potential, 3/1997.
http://www.dnr.state.wi.us/org/aw/rr/archives/pubs/RR523.pdf

Interim guidance on soil performance standards, 3/1997.
http://www.dnr.state.wi.us/org/aw/rr/archives/pubs/RR528.pdf

5.2 Case Closure when using MNA for Chlorinated Compounds

The discussion below summarizes closure criteria that apply to MNA, which must be met before closure can be granted under NR 726. It is not a checklist of closure criteria. Closure checklists are discussed in section 5.3.

5.2.1 Case closure criteria

5.2.1.1 Source control and interim actions completed

NR 726.05(2)(b)1 a. – f. states the requirements for source control that must be taken before case closure can be sought. NR 726 source control requirement includes, but is not limited to, the following sources: existing tanks, pipes, barrels, containers that may discharge hazardous substances, and free product. The goal for source control is that the source of the contamination will be removed, contained or controlled to prevent to the extent practicable new discharges to groundwater and to protect public health, safety and welfare. There are some situations where source control will be very difficult to achieve. Sources that cannot be removed, contained or controlled in accordance with administrative rules may not meet the criteria for closure. For instance, free product must be removed in accordance with criteria found in NR 708.13. Free product DNAPL identification and removal from the subsurface is difficult and may not be possible in some cases. **Sites where the source cannot be removed, effectively contained or controlled to the extent practicable may not qualify for closure under NR 726.** When practical efforts to remove, contain or control a source have been expended and releases to groundwater above NR 140 enforcement standards continue, on-going monitoring may be more appropriate than site closure.

Site closure reports must document the actions taken to remove, contain or control the source and the impacts of any remaining source contamination on soil, groundwater, surface water, or other contaminated media.

5.2.1.2 Demonstrated effectiveness of natural attenuation

NR 726.05(2)(b)1.f. and 2. state the requirements for demonstrating the effectiveness of natural attenuation at a site. The closure report must show that natural attenuation processes will:

- Reduce the concentration and mass of a substance and its breakdown products in groundwater to adequately protect public health and the environment. The site investigation, remedy implementation and subsequent long-term monitoring should result in evidence that demonstrates contaminant mass, as well as concentration, are declining for all contaminants of concern, including break-down products. To demonstrate the effectiveness of natural attenuation processes, it should be shown that:
  - the mass of contaminants is decreasing in the groundwater plume;
  - all contaminants degrade to innocuous products or are immobilized;
  - contaminant decay rates will achieve standards within a reasonable period of time;
  - the long-term efficacy of contaminant decay processes can be relied on;
  - the plume has achieved steady state;
  - concentrations are declining within the plume and source;
  - sentinel wells have and will remain clean over time;
  - there are no current or future pathways of exposure;
  - human health, welfare and the environment will be protected in the future until groundwater cleanup standards are met.

- Prevent groundwater from migrating beyond boundaries of the property or properties that will be listed on the GIS Registry of Closed Remediation Sites. At a minimum, the contaminant plume margin must be demonstrated to be stable over time while contaminant concentrations within the plume are declining. Monitoring must be conducted for a long enough period of time to determine:
  - Contaminant decay rates;
  - Variations in contaminant flow and velocity; and
  - Contaminants will not present threats to receptors in the future.

- Bring groundwater into compliance with ch. NR 140 groundwater quality standards within a reasonable period of time, considering the criteria in NR 722.07. Data must verify that cleanup standards are met or will be met within a reasonable period of time. Because conditions that stimulate degradation of chlorinated contaminants can and do change with time, **before closure can be granted long-term monitoring must demonstrate that contaminants are degrading at predicted rates and that the conditions of degradation will be maintained until NR 140 groundwater quality standards are met**. Demonstrating that MNA conditions will be maintained until standards are met can include such things as:
  - Estimates of contaminant mass remaining in the subsurface
  - Estimates of carbon mass available to continue reductive dechlorination processes
  - Estimates of electron acceptor mass available for oxidative processes
  - Mass balances on the contaminant and electron acceptors/donors over the time frame expected for cleanup.

  In addition, future land use changes that could affect MNA must be assessed. Such land use changes include the addition of water supply wells, increased pumping of nearby wells, construction activities that would change surface infiltration patterns, etc. If land use changes occur that could affect MNA, the effects on the remedy should be determined by appropriate monitoring of the plume.

5.2.1.3 Meeting standards within a reasonable period of time

NR 726.05(b)(2) requires that natural attenuation bring groundwater into compliance with NR 140 groundwater quality standards within a reasonable period of time. Reasonable period of time is determined in relation to the criteria of NR 722.07(4). The remedy selection process allows a comparison of various cleanup options using technical and economic criteria to judge the overall “best” cleanup approach. The chosen remedial option may be a series of treatment technologies (a “treatment train”) that includes MNA as one aspect of the overall cleanup. The standard of a “reasonable period of time” is met by the cleanup options that will protect human health and the environment and meet cleanup standards in the most practical and economically effective way.

5.2.1.4 Notification of contamination to third-party landowners

NR 726 Appendix A contains the required text of a letter sent to third-party landowners whose property has groundwater contamination that exceeds NR 140 enforcement standards at the time of closure. The Department will not review a closure request for 30 days after the letter is sent so that the affected property owner may provide any technical information that indicates the closure should not be granted. The information must be submitted in writing to the Department within 30 days of mailing the letter in order to be considered before the closure decision is made.

5.2.2 Institutional controls

Institutional controls are required where contamination remains on a property or properties at the time that closure is sought from the Department. Institutional controls must be maintained for the duration that the contamination remains at the site. When it can be documented that the applicable standards have been met, the responsible party may request that the property be removed from the GIS Registry of closed remediation sites and (if applicable) that a deed affidavit be issued for filing stating that the conditions of a deed restriction are no longer in force.

5.2.2.1 GIS registry of closed remediation sites

If contaminants above NR 140 enforcement standards remain in groundwater or contaminants above a generic or site specific RCL remain in soils at the time of closure, the property or properties on which these exceedances occur must be placed on the Department's GIS Registry of Closed Remediation Sites. NR 726.05(2) and (3) specifies case closure submittal requirements for placement of a site on the GIS registry. Closure requests for placement of sites on the GIS registry must be accompanied by the appropriate review fees, which are found in NR 749.

5.2.2.2 Deed restrictions on properties with contaminated soil and/or groundwater

Deed restrictions are required if there are conditions that must be maintained post-closure to ensure the continued effectiveness of the remedy until groundwater and/or soil standards are met. Processes laid out in NR 720 determine applicable soil standards. Contaminated soils that exceed generic or site-specific residual contaminant levels (RCLs) for the groundwater or direct contact pathways **will** require a deed restriction **if** a condition (such as an impermeable cap) is required to protect the specific pathway. In most cases, sites with deed restrictions will also be listed on the GIS Registry. The exception to this is the case where soil standards meet industrial RCLs at closure of an industrial facility. In this case, a deed restriction is required but listing on the GIS registry for contaminated soils is not required.

Conditions requiring deed restrictions are found in NR 726.05(8). Examples of required deed restrictions include:

- remediation of a property classified as industrial to industrial residual contaminant levels;
- buildings or structural impediments have prevented complete investigation of a contaminated site;
- a cap or other structure must be maintained to protect groundwater; and
- a cap or other structure must be maintained to protect people from direct contact with contamination.

NR 726.05(8)(c) allows deed restrictions or deed notices to be placed on properties as a condition of case closure under other circumstances not listed elsewhere in the administrative code. An example of a deed restriction under this provision would be a closure granted with land use restrictions that must be complied with in order to maintain conditions that stimulate degradation of chlorinated contaminants. Such land use restrictions would remain in effect until it is demonstrated that cleanup standards are met. Further information can be found in the Department's institutional control guidance at http://www.dnr.state.wi.us/org/aw/rr/archives/pubs/RR606.pdf.

5.2.3 Case closure report and checklists

Chapter NR 726, Case Closure, addresses the requirements for obtaining case closure. The Department has developed checklists to aid in submitting a closure request. These include:

WDNR Case Summary and Close Out Form
http://www.dnr.state.wi.us/org/aw/rr/archives/pubs/4400-202.pdf

Checklist of Documents for GIS Registry Packet
http://www.dnr.state.wi.us/org/aw/rr/archives/pubs/RR688.pdf

The case summary and close out form (Wisconsin DNR Form 4400-202) and accompanying closure request fee (found in NR 749) are required to be submitted with all closure requests. The GIS Registry packet and registry fee is required if any NR 140 groundwater ES or NR 720 soil RCL is exceeded.

The closure request should document all the elements required in NR 726 and the specific topics discussed in this guidance regarding chlorinated hydrocarbon remediation and show that that the requirements of closure have been met at the site. The closure report should address:

1. Site conceptual model. All assumptions about the site including geology, hydrology, contaminant type, movement, pathways of exposure, extent of contamination, processes affecting contaminant fate and transport, etc.
2. Summarize the site investigation to show that all site investigation requirements were met. Include data summary tables of all data collected at the site, maps, figures, etc.
3. Discuss all interim and remedial actions taken at the site and the relationship of those actions to natural attenuation processes and long-term monitoring results. Establish that adequate source control measures have been taken such that NR 140 groundwater standards will be met within a reasonable period of time.
4. Summarize analytical or numerical models used in assessing site data. Discuss model predictions and monitoring efforts to verify model predictions.
5. Discuss evidence for natural attenuation processes occurring at the site, rates of contaminant decay, evidence that degradation rates will continue into the future, and predictions of when NR 140 groundwater standards will be met. Establish consistency of degradation processes over time in the source and throughout the plume. Include all tables, figures and graphs necessary to support data analysis.
6. Summarize all monitoring data and discuss analysis of monitoring data. Assess data quality and validity and biases imposed by fluctuations in the hydrologic system at the site. Discuss observed plume behavior and 3-dimensional fluctuations in plume movement. Discuss the adequacy of the monitoring network to describe the degree and extent of the plume and discuss likely behavior of the plume in the future. Discuss the length of time of monitoring has taken place in relation to the distance groundwater has moved during that same time period.
7. Discuss future land use at the site and the possibility of new receptors or land use changes. Address whether the changes will affect the on-going degradation processes that have been established at the site. Discuss institutional controls and their effectiveness into the future.
8. Summarize public participation and notification efforts undertaken at the site.

9. Discuss when NR 140 standards are likely to be met and land use restrictions or other actions necessary to ensure public health, welfare and the environment will be protected until standards are met.

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Appendix A

Assessment of Dense Non-Aqueous Phase Liquids (DNAPL)

Identifying the sources of a chlorinated hydrocarbon plume is critical to the conceptual site model and to effective remediation of the plume. However, identifying the source(s) of a chlorinated groundwater plume can present a complicated problem. For instance, a leaking municipal landfill may provide a continuous source of dissolved chlorinated compounds leaching to groundwater. Non-dissolved sources of chlorinated compounds include dense non-aqueous phase liquids (DNAPL) and occasionally, light non-aqueous phase liquids (LNAPL). DNAPL indicates the presence of undissolved (non-aqueous) product that is denser than water in the subsurface (e.g., pure TCE has a density of 1.46). A mixture of organic compounds can also be lighter than water (LNAPL) and "float" on the groundwater table but still contain chlorinated compounds such as PCE and TCE. Of these scenarios (dissolved source, LNAPL, DNAPL), DNAPL is usually the most difficult to characterize as well as remediate.

Remediation of DNAPL is beyond the scope of this guidance. However, methods exist and new methods are being developed for identifying the likely presence of DNAPL in the subsurface and estimating DNAPL mass in the subsurface. Investigating the history of contaminant release is the first step to determining the likely presence of DNAPL. DNAPL is more likely to be present where bulk solvents were used, transported or disposed, including entities such as electronics, defense, chemical, rail, automotive, boat, shoe, food processing, textile, and dry cleaners. (Doherty, 2001)

DNAPL can occur as a:

- residual phase where the DNAPL either coats soil surfaces or is held in soil pore space by capillary pressure.
- mobile phase, accumulating in pools of solvent that can move by gravity.

These phases can be difficult to identify because of the heterogeneity of the soil and bedrock systems, the circuitous paths that a DNAPL may travel as it traverses through the subsurface, the great depths that DNAPL can penetrate in the subsurface, and the characteristics of the DNAPL itself. Mobile DNAPL can move horizontally along bedding planes and contacts between more permeable and less permeable geologic units. Gravity, more often than hydraulic head in the groundwater, controls DNAPL movement. Therefore, if the presence of DNAPL (especially mobile DNAPL) is suspected, a thorough understanding of site geology and product constituents are needed before likely locations and pathways of DNAPL movement can be identified.

Methods to identify DNAPL in the subsurface

U.S. EPA discusses the difficulties of identifying residual and free phase DNAPL in "Development of a Data Evaluation/Decision Support System for Remediation of Subsurface Contamination" (EPA/600/R-01/044, http://www.epa.gov/ahaazvuc/pubs/reports.html). Direct identification of residual DNAPL requires 1) that samples be collected from the DNAPL zone, which is usually problematic and 2) that an accurate estimation of sorption coefficients be made so that partitioning calculations reflect the maximum concentration expected to be adsorbed onto soils. Studies at the Borden site in Canada (U.S. EPA, 2001a) showed residual saturation of soil after a PCE release was dependent upon grain size distribution, the presence of mobile

NAPL, and the rate of the release. Assuming samples can be collected within the residual or free phase DNAPL zone, there are methods available to identify the presence of DNAPL (see Kram et al., 2001):

1. Analyze soil, water, or headspace vapor from drill cuttings or samples for the contaminant of concern. Partitioning theory can be applied to determine the likelihood of a separate DNAPL phase.
2. Add Sudan IV or Oil Red O dye to soil samples. These dyes turn red in the presence of NAPL.
3. Samples taken below the water table can be shaken and observed for the presence of NAPL.
4. Expose samples to UV light and observe for fluorescence.

Other DNAPL identification methods:

1. Soil gas surveys in the vadose source zone.
2. Estimating the presence of DNAPL from aqueous concentrations in monitoring wells. Rules of thumb (e.g., 1% or 10% of saturated aqueous concentration, adjusted for mole percent of the compound in the NAPL) can be applied. However, concentrations less than this do not preclude the possibility of NAPL.
3. Flexible liner underground technologies everting (FLUTe) uses a coated membrane liner inserted into a borehole that changes color in the presence of DNAPL. The membrane is placed in the borehole and then withdrawn. Stains on the membrane indicate the location of DNAPL. This technology can be used in vadose zone, below the water table and in porous media or bedrock.
4. A number of remote sensing techniques used in conjunction with cone penetrometers. See Kram et al., 2001 for more details on these techniques.

Methods to estimate mass of DNAPL in the subsurface

All methods to estimate mass of DNAPL in the subsurface are subject to the constraints of sampling methodology and subsurface characteristics. A short discussion of three methods: aqueous concentrations, direct soil measurements, and partitioning interwell tracer tests, are discussed below.

Aqueous Concentration Ratios

All methods using aqueous concentrations to estimate DNAPL mass depend on borings and monitoring wells being placed to intercept the highest aqueous concentrations in the plume. In addition, the aqueous interaction of a multi-component DNAPL is important in the aqueous models.

Devlin and Barbaro (2001) use the concepts of Raoult's law and ratios of dissolved components to estimate mass of NAPL remaining in the subsurface. This method has the advantage of using existing concentration vs. time data from groundwater monitoring wells near a NAPL source and pure phase solubility of NAPL components to estimate NAPL mass. The method also requires:

a. knowledge of the molar composition of the NAPL and that the NAPL consist of at least 2 components (so that a ratio can be established);
b. knowledge of the cross-sectional area of the NAPL in the aquifer;
c. the aquifer be composed of porous media;

d. the source be primarily residual NAPL (the method has not been assessed in situations where a pool of NAPL exists or where a "skin" has developed on the NAPL);
e. the assumption of equilibrium partitioning between NAPL and groundwater be valid; and
f. established cross-sectional monitoring of the groundwater plume, near the NAPL.

U.S EPA developed 2 models to estimate NAPL mass based on aqueous concentrations. The first, a 1-D model was used to estimate a point source location and mass while the second, a 3-D formulation was used to model a continuous NAPL source. The use and limitations of these models are discussed in U.S. EPA (2001a).

Soil Chemical Analyses

Mariner, Jin and Jackson (1997) have developed an algorithm to estimate the NAPL saturation of porous media, given soil sampling results. The algorithm is based on partitioning and phase equilibrium. With it, we can estimate the distribution of a NAPL among the different phases that are in the soil-air, soil-water, soil-matrix, and a separate NAPL phase. NAPL saturation is defined as the fraction of the pore space occupied by NAPL. One hundred percent NAPL saturation means that all the available pore space is occupied by the NAPL. The algorithm's key concept revolves around the idea of the soil-saturation-limit concentration – which, under phase equilibrium, is the maximum concentration of contaminant that the soil can "hold" in its pores and matrix without NAPL existing as a separate phase. The C_{sat} (or the soil-saturation limit) is estimated and then compared to available soil data. The nearer the soil data is to the C_{sat} concentration, the more likely we can expect a separate NAPL phase to exist.

Mariner et al.'s screening model to calculate NAPL saturation, NAPLANAL, can be downloaded free from www.napl.net. The algorithm can be used to predict whether NAPL is expected in the subsurface when soil data (in wet-weight concentrations) are available. To relate soil concentrations to geology, it is best to collect core samples of source areas and then to analyze the soil and saturated material for contaminant concentrations. Because NAPL usually follows preferential pathways through the subsurface, a significant number of soil borings are usually needed to identify areas of residual NAPL and to better estimate the NAPL volume.

Partitioning interwell tracer test (PITT)

In a partitioning interwell tracer test (PITT), several tracers are injected into the subsurface, migrate through the suspected DNAPL zone under a forced flow system, and are collected at extraction wells. The different partitioning characteristics of the tracers are used to estimate the mass of DNAPL in the subsurface. At least one tracer is non-reactive with the DNAPL, while other tracers react (and are therefore retarded in their flow) through the DNAPL. The arrival times and concentration of the tracers at the extraction well are used to estimate the mass of the DNAPL. There are many drawbacks to PITT tests (the location of the DNAPL zone must be known, natural organic content must be low, lithology can cause random movement of the tracers, the geologic media must be fairly permeable, flow paths must be established to capture the tracers, etc.). However PITTs allow mass estimates and can be very useful in designing a remedial action. In addition, PITTs can be used to follow the progress of a remedy. (See Mariner et al., 1999; Deeds, Pope & McKinney, 1999; Dwarakanath, Deeds & Pope, 1999; and Nelson et al., 1999.)

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Appendix B

Web-Based Resources Useful in Planning a Rapid Characterization of a Contaminated Site

"Rapid site assessment," "accelerated site characterization," and "expedited site characterization" are a few catch phrases to describe less-than-conventional techniques developed and implemented for the purpose of investigating contaminated sites more efficiently by utilizing a dynamic work plan that allows adjustments based on on-site analysis and real-time decision making. The investigation involves the use of on-site mobile laboratories and direct-push technologies to characterize soil and ground water contamination, assess cleanup options, and install temporary monitoring wells. Listed here are a number of websites where investigators can learn more about implementing protocols that have proven effective in past rapid site assessments. Summaries from the websites are included so that readers can focus on the websites that may be more useful for their specific purpose. Each of the websites may have links to several other websites that may have additional information on the subject of rapid site assessment.

Background on Rapid Characterization

http://clu-in.org/triad/

EPA's Technology Innovation Office (TIO) has recently assembled a web site focused on improved site characterization and faster cleanups through the integration of systematic planning, dynamic work plans, and real-time measurement technologies to achieve more cost-effective hazardous waste site cleanup strategies.

http://www.epa.gov/tio/pubichar.htm

U.S. EPA's Technology Innovation Office is promoting more effective strategies for characterizing and monitoring hazardous waste sites. In particular, the wide-spread adoption of a new paradigm which uses an integrated triad of systematic planning, dynamic work plans, and on-site analysis for data collection and technical decision-making at hazardous waste sites is recommended.

http://clu-in.com/goto.cfm?link=%2Fproducts%2Fmoreinfo%2Fdynwkpln%2Ehtm&id=73

"Dynamic workplan" is the term used to describe a hazardous waste site characterization approach that incorporates several key elements: systematic planning, conceptual site model, selected analytical methods/equipment, and adaptive sampling strategy.

http://www.anl.gov/ER/ESC.html

Argonne National Laboratory (ANL) expedited site characterization methodology called QUICKSITE. QUICKSITE$_{(SM)}$ is an iterative, integrated process using careful analysis of existing data, multiple complementary characterization methods, and on-site decision making to optimize site investigations.

http://apps.em.doe.gov/ost/pubs/itsrs/itsr77.pdf

Innovative Technology Summary Report: Expedited Site Characterization. Expedited Site Characterization (ESC) has been developed, demonstrated, and deployed as a new

time-saving, cost-effective approach for hazardous waste site investigations. ESC is an alternative approach that effectively shortens the length of the assessment period and may significantly reduce costs at many sites. It is not a specific technology or system but is a methodology for most effectively conducting a site characterization.

Field Lab Requirements

http://clu-in.org/download/char/dynwkpln.pdf

The document is aimed at helping federal and state regulators, siteowners and their consulting engineers, and remediation companies understand what is involved in constructing and carrying out a dynamic workplan. The purpose of the document is to illustrate the many factors that should be considered in incorporating field analytical instrumentation and methods into an adaptive sampling and analysis program for expediting the site investigation process. This dynamic process should result in a faster, better, and hopefully cheaper site characterization and cleanup.

http://www.clu-in.org/programs/scmt/Verarea.htm

Technology verification reports from EPA's Technology Innovation Office (TIO) including: field portable gas chromatographs/mass spectrophotometers, portable x-ray fluorescence analyzer, PCB analysis, well head monitoring for VOCs, soil gas sampling methodologies.

http://www.frtr.gov/site/analysismatrix.html

Federal Remediation Technologies Roundtable (FRTR) field sample analysis tools, explained and rated by detection limits, applicable media, selectivity, turn around time and ability to produce quantitative results.

Investigation Techniques

http://fate.clu-in.org

Field Analytic Technologies Encyclopedia (FATE). This online encyclopedia is intended to provide information about technologies that can be used in the field to characterize contaminated soil and ground water, monitor the progress of remedial efforts, and in some cases, for confirmation sampling and analysis for site close out. The site also contains training modules on the use of each field technology and the process of planning for field based site characterization.

http://www.epa.gov/swerust1/pubs/sam.htm

Expedited Site Assessment Tools For Underground Storage Tank Sites: A Guide for Regulators**.** (EPA 510-B-97-001). March 1997.

http://www.sp.uconn.edu/~hydrogeo/deprept.htm

UCONN_DEP Expedited Site Assessment Reports On-Line. Recommended Guidelines for Multilevel Sampling of Soil and Ground Water in Conducting Expedited Site Investigations at Underground Storage Tank Sites in Connecticut, March 12,1997

http://www.astm.org/cgi-bin/SoftCart.exe/DATABASE.CART/PAGES/D6235.htm?L+mystore+gatz5037+959192570

D6235-98a, Standard Practice for Expedited Site Characterization of Vadose Zone and Ground Water Contamination at Hazardous Waste Contaminated Sites.

http://www.astm.org/cgi-bin/SoftCart.exe/STORE/filtrexx40.cgi?U+mystore+knne6594+-L+E1912+/usr6/htdocs/astm.org/DATABASE.CART/PAGES/E1912.htm

ASTM Standards on Assessment and Remediation of Petroleum Release Sites including*: E 1912, Guide for Accelerated Site Characterization for Confirmed or Suspected Petroleum Releases* -offers a practical method for quickly and cost-effectively characterizing a site.

http://www.epareachit.org/index3.html

EPA REACH IT is a system designed to search, view, download, and print information about innovative remediation and characterization.

http://www.frtr.gov/site/samplematrix.html

FRTR Field sampling and collection techniques explained and rated by media, depth, cost and technology status.

http://www.cmst.org/vendor/

DOE Vendor Database for Environmental Applications. This site is devoted to chemical and physical property measurements of environmental samples and includes characterization, monitoring, and sensor technology.

http://www.brownfieldstsc.org

Assessing Contractor Capabilities for Streamlined Site Investigations, Office of Solid Waste and Emergency Response, United States Environmental Protection Agency, EPA 542-R-00-001, January 2000. Includes links to database listings of new technologies, how they are used, if they have been demonstrated and proven effective and reliable, where they are most effective, their performance specifications, etc.

http://www.em.doe.gov/define

Department of Energy (DOE) Preferred Alternatives Matrix, including characterization and site remediation.

Site Review

http://www.epa.gov/ordntrnt/ORD/WebPubs/projsum/600sr98020.pdf

An evaluation of rapid site-assessment techniques for plume delineation and subsurface site characterization was carried out using cone penetrometer and ambient temperature headspace (ATH) analysis techniques. A decision framework was developed to guide the user in data collection, data reduction, data interpretation, and decision making efforts to evaluate the nature and potential extent of intrinsic plume bioattenuation taking place under a given set of site conditions.

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Appendix C

Destruction Mechanisms for Chlorinated and Selected Recalcitrant Compounds

Chlorinated compounds are generally considered recalcitrant to degradation. This is due primarily to the oxidative state of the molecules. The higher the number of chlorine substitutes on the hydrocarbon molecule, the more oxidized the compound. The oxidation state of the compound determines the range of chemical and biological transformations that the compound is likely to undergo (Vogel, 1994). For instance, perchloroethene (PCE) is already a highly oxidized molecule that will not naturally undergo further oxidation in groundwater, but can be reduced under the proper geochemical conditions. Vinyl chloride, with only one chlorine atom substitution, is subject to oxidation using oxygen and ferric iron as electron acceptors (Bradley & Chapelle, 1997).

It is often difficult or impossible to determine in the field the exact mechanisms functioning to transform the chlorinated compound. (Stoichemetrically balanced reactions for degradation of chlorinated compounds can be found in Wiedemeier et al., 1998.) However, an understanding of the geochemical environment and the patterns of contaminant degradation are essential to discerning the likely degradative processes at a site. Knowledge of the degradative mechanisms will help the investigator determine the effectiveness of a natural attenuation remedy, the need for supplemental remediation, and craft a long-term monitoring program.

Destructive mechanisms can be divided into biotic and abiotic processes.

Biotic

All degradative mechanisms involve the transfer of electrons to or from the contaminant molecule. Microorganisms often mediate this transfer of electrons. Oxidative state of the environment as well as the contaminant determines the direction of the electron transfer and whether a particular transfer is likely to occur. Biodegradation of chlorinated compounds in groundwater occurs via three basic mechanisms:

- As a primary growth substrate (i.e., microorganisms use the contaminant as food for energy and growth)
- As an electron acceptor (i.e., microorganism “breathes” the contaminant)
- Through cometabolism (i.e., the contaminant is fortuitously degraded without producing energy for the microorganism)

Microbial degradation requirements include: electron donors (availability of a carbon source), electron acceptors (e.g., oxygen, nitrate, iron (III), manganese (IV), sulfate, carbon dioxide), essential nutrients, and proper environmental conditions (proper range of pH, temperature, salinity, redox potential).

<u>Primary Growth Substrate</u>

The fewer the substituted chlorine atoms on a hydrocarbon molecule, the more likely it is that microbes can use the contaminant directly as a growth substrate (electron donor). When the contaminant serves as a primary growth substrate, microorganisms use oxygen (aerobic) or minerals (anaerobic -- such as nitrate, iron, sulfate, and carbon), as electron acceptors.

Aerobic Biodegradation

Of the chlorinated ethenes, vinyl chloride is the most susceptible to aerobic oxidation under natural groundwater conditions. While laboratory studies have shown TCE may degrade oxidatively, there is no field evidence supporting this. Cis-1,2-dichloroethene (cis-DCE), and 1,2-dichloroethane (1,2-DCA) may be subject to aerobic biodegradation. Chloroethane tends to hydrolyze (an abiotic reaction) preferentially over aerobic or anaerobic biodegradation. Vinyl chloride rapidly degrades aerobically, particularly in comparison to reductive dechlorination (Wiedemeier et al., 1998; Vogel, 1994). Chloromethane (CM) and dichloromethane (DCM) are degraded aerobically (Leisinger, 1994). Chlorobenzene and polychlorinated benzene (up to tetrachlorobenzene) are degraded aerobically, similar to benzene (Wiedemeier et al., 1998).

Anaerobic Biodegradation

Areas of high organic carbon (anthropogenic or natural in origin) in groundwater often have depleted oxygen levels. In these cases, compounds such as nitrate, iron (III), manganese (IV), sulfate and carbon dioxide can serve as electron acceptors while the contaminant is anaerobically oxidized. Anaerobic degradation of petroleum hydrocarbons is well established. However, there is little evidence for transformation of chlorinated compounds through anaerobic oxidation (Wiedemeier et al., 1998). Bradley and Chapelle (1996) demonstrated that microbes can oxidize vinyl chloride using ferric iron as an electron acceptor. The same investigators (Bradley and Chapelle, 1997) showed that 1,2-DCE and vinyl chloride were oxidized under Fe(III) and methanogenic conditions. It has been shown that 1,2-DCE can be anaerobically oxidized under Mn(IV) reducing conditions (Bradley et al., 1998). DCM and CM can serve as sole sources of carbon for microbial consortia under anaerobic conditions ranging from nitrate to methanogenic conditions (Yu, 2000).

<u>Electron Acceptor (Reductive Dechlorination)</u>

Highly oxidized molecules (such at PCE, TCE, TCA) can serve as electron acceptors for microbes when another carbon source is available as a primary growth substrate. A number of environmental conditions must exist for reductive dechlorination to take place:

1. The presence of a primary growth substrate, such as fuel hydrocarbons, low molecular weight organic compounds (e.g., lactate, acetate, glucose, etc.), fatty acids, landfill leachate, etc.
2. The presence of highly chlorinated contaminants. The fewer the chlorine atoms on a molecule, the less effective reductive dechlorination will be. While vinyl chloride will reductively dechlorinate to ethene, it is a slow process compared to aerobic oxidation of vinyl chloride.
3. Highly reduced (anaerobic) conditions are necessary. Reductive dechlorination will not take place under denitrifying conditions (e.g., nitrate must be absent). The process is most effective under sulfate reducing or methanogenic conditions. Vinyl chloride will only undergo reductive dechlorination under methanogenic conditions.
4. Microorganisms capable of dechlorination must be present. Intermediates, such as cis-DCE can accumulate because the existing microorganisms cannot produce the appropriate enzymes to continue the dechlorination process (Ellis, 2000).

Contaminated groundwater undergoing reductive dechlorination typically reflects the following changes (Wiedemeier et al., 1998):

- Ethene is produced as the end product of reductive dechlorination
- Methane is usually present
- Ferrous iron is usually present
- Oxygen and nitrate are absent
- Hydrogen concentrations are > 1 uM

Figures C-2 through C-5 illustrate the common degradation pathways and include products expected from reductive dechlorination of carbon tetrachloride, 1,1,1- trichloroethane (TCA), tetrachloroethane (PCA), and tetrachloroethene (PCE).

Reductive dechlorination conserves the organic carbon. That is, the sum of the molar concentrations of compounds in a dechlorination sequence should not change as one compound is dechlorinated to form another compound (Wilson, 2001). For instance, the sum of the molar concentrations of PCE, TCE, cis-DCE, vinyl chloride, and ethene should remain constant during the dechlorination process, even as the molar concentrations of individual compounds change (See Box C-1). However, the complexity of site hydrogeology (e.g., different retardation factors for different compounds) coupled with microbial kinetics and other degradative processes (such as the anaerobic oxidation of cis-DCE and vinyl chloride or abiotic conversion of chloroethane) may obscure this relationship. At some sites, intermediates of dechlorination will accumulate while at other sites, dechlorination intermediates may not be found. Both of these situations can be the result of kinetic limitations of the degradative process, can be due to the mix of degradative processes, can be the result of the monitoring system, or due to other site-specific circumstances.

Box C-1

Converting mass of daughter product to equivalent parent compound

1. Convert aqueous concentrations to moles

Compound	Molecular weight (g/mole)	Example concentration (ug/L)*	Molar Concentration (umole/L)
TCE	131.5	7411	56.4
1,2-DCE	97.	9117	94
VC	62.5	998	16
Ethene	28	480	17
		Sum:	183.4 uM equivalent TCE

Conversion: $\frac{ug/L}{ug/umole} = umole/L = uM$

2. Sum the total molar concentrations. If reductive dechlorination is the sole degradative process, then the ethene molecule is conserved and each molecule of DCE, VC and ethene represents a molecule of TCE degraded.
3. The molar ratios of the compounds can be used to assess degradative processes, and molar concentrations across the plume can be used to assess mass loss.

* Data from the St. Joseph, MI site

Cometabolism

Cometabolism is a fortuitous process in which a microorganism receives no benefit from the degradation of a compound. Typically, the microorganism produces an enzyme in response to some other environmental stimulus and that enzyme is able to also degrade the target contaminant. The most common example, aerobic cometabolism, rarely occurs naturally, but can form the basis of an engineered remedy.

In aerobic cometabolism, oxygenase enzymes (such as methane monooxygenase, toluene monooxygenase, etc.) are produced when microorganisms degrade compounds such as BETX, methane, propane, etc. under aerobic conditions. These enzymes are non-specific and are able to also degrade TCE and other chlorinated compounds (with the exception of PCE). (Wiedemeier et al., 1998)

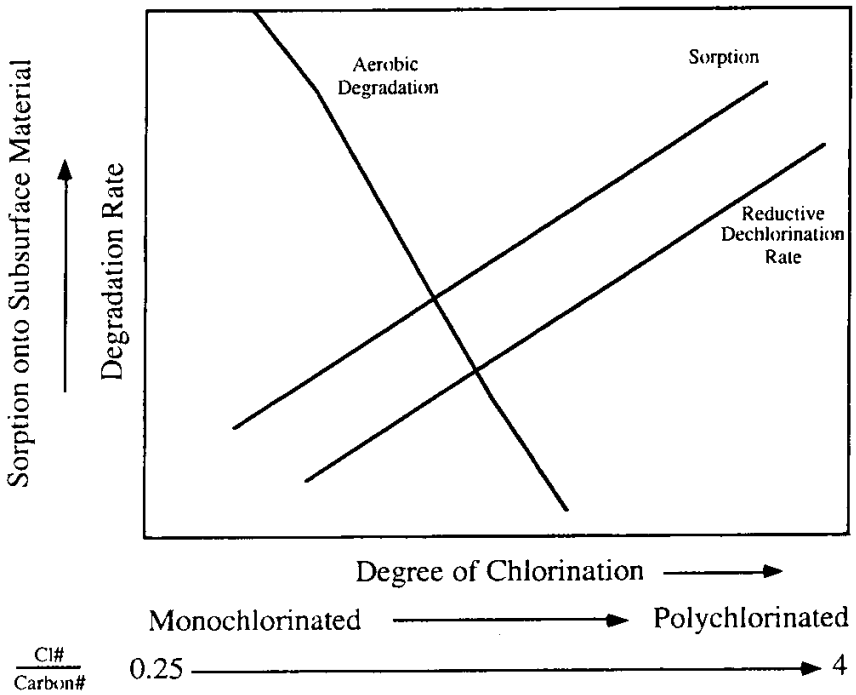
Abiotic

The most common abiotic reactions are hydrolysis [the halogen is replaced by with a hydroxyl (OH^-) group] and dehydrohalogenation (an elimination reaction that removes a halogen and a hydrogen from adjacent carbon atoms in an alkane and produces an alkene). Substitution and abiotic oxidation reactions also occur. Abiotic degradation primarily affects chlorinated and brominated methanes and ethanes. The kinetics of abiotic reactions varies greatly with each contaminant such that intermediates tend to accumulate. Often, biotic processes (which change pH and redox potential) are necessary to stimulate abiotic reactions. (Wiedemeier et al., 1998; Van Eekert, 1998).

The most well documented abiotic degradation reactions involve carbon tetrachloride, chloroform, chloromethane, trichloroethane (TCA), and chloroethane. McCarty (1997) states that TCA is abiotically converted under almost all likely groundwater conditions. The products of this abiotic transformation are acetic acid (approximately 80%) with the remaining 20 percent converting to 1,1-DCE. Chloroethane readily hydrolyzes to ethanol with a half-life of approximately 44 days (Wiedemeier et al., 1998). Temperature plays a significant role in biotic and abiotic reaction rates. For polychlorinated ethanes and methanes, abiotic half-lives are likely to be on the order of hundreds to thousands of years at ambient groundwater temperatures, while monochlorinated compounds have much lower half-lives (Wiedemeier et al., 1998).

Figure C-1

Relationship between degree of chlorination and aerobic degradation, reductive dechlorination and sorption.



(From Vogel, 1993)

Kinetics of Degradation for Chlorinated Compounds

Research on biodegradation of chlorinated compounds has yielded a wide range of degradation rates. Typically, degradation rates obtained in laboratory studies are faster (often by an order of magnitude) than rates obtained in the field. Suarez and Rifai (1999) summarized biodegradation rates from 138 laboratory and field studies of chlorinated compound degradation under aerobic and anaerobic conditions. Suarez and Rifai's (1999) estimated a median half-life (in days) based on studies where degradation occurred and then categorized the biodegradability of specific chlorinated compounds based on the recalcitrant rate (i.e., the percentage of studies where the compound was found not to degrade).

Table 1 (after Suarez and Rifai, 1999) summarizes the median half-life and recalcitrant rate for specific compounds according to degradation process. Table 1 points out that the efficiency of degradation varies greatly between pathways. Even for compounds like vinyl chloride, which will degrade under almost all redox conditions, kinetic limitations can lead to its accumulation in certain settings. Under the most favorable degradative conditions (reductive dechlorination), PCE was recalcitrant in 14% of the studies. This underscores the importance of determining the

effectiveness of degradation of contaminants on a site-specific basis and the rate limiting process for achieving clean up standards.

Table C-1

Biodegradability of Selected Chlorinated Hydrocarbons[1]

Contaminant	All Studies	Degradative Process			
		Aerobic Oxidation	Cometabolism	Reductive Dechlorination	Anaerobic Oxidation
Carbon Tetrachloride		(2)			
Half-life (days)	14			9	
% recalcitrance[4]	0%			0%	
TCA					
Half-life (days)	68	NC[3]	53	24	
% recalcitrance	30%	73%	20%	16%	
DCA (all isomers)					
Half-life (days)	990		15	1260	
% recalcitrance	8%		0%	0%	
PCE					
Half-life (days)	80	NC		32	
% recalcitrance	28%	60%		14%	
TCE					
Half-life (days)	151	NC	3	201	
% recalcitrance	14%	55%	0%	9%	
DCE (all isomers)					
Half-life (days)	173		2	234	
% recalcitrance	5%		15%	0%	
Vinyl Chloride					
Half-life (days)	14	8	0.462	80	58
% recalcitrance	0%	0%	0%	0%	0%

[1] After: Suarez & Raifai (1999)
[2] Blanks = insufficient data or data does not exist
[3] NC = not calculable
[4] % recalcitrance = percent of studies they reviewed showing no degradation under the conditions noted. Suarez & Raifai use the following scale:

%Recalcitrance	Biodegradability
<10%	Almost always
10 –25%	Frequently
25-50%	Sometimes
50-75%	Barely
>75%	Almost never

Other Recalcitrant Contaminants

There are many other environmental contaminants that tend to persist in the environment. Emphasis is placed on chlorinated methanes, ethanes and ethenes because they are common contaminants and found in many geologic environments. A short summary of the degradation of ethlene dibromide (EDB) and methyl *tertiary*-butyl ether (MTBE) follows.

Ethlene Dibromide (EDB)

The largest volumetric use of ethlene dibromide (1,2-dibromoethane) or EDB was as a lead scavenger in gasoline mixtures (especially aviation fuel). Other uses of EDB included: as a soil and grain fumigant insecticide and nematicide, as a solvent for resins, gums and waxes, and as a chemical intermediate in the synthesis of dyes and pharmaceuticals (HSDB, 2002)). The use of EDB on agricultural products was phased out by March 1984 (Weintraub et al., 1986) and its use as an anti-knock agent in gasoline was phased out with the advent of unleaded fuels.

The fate of EDB in soil and groundwater is quite variable. The most common environmental destructive mechanisms, volatilization and photodegradation, do not play a significant role in subsurface. EDB will abiotically hydrolyze in groundwater and soil pore water. It is estimated that at a groundwater temperature of approximately 10 – 15 ºC, the hydrolysis half-life of EDB is approximately 5 years (Weintraub et al.,1986). Biotically, EDB resembles the degradation pattern of 1,2-dichloroethane. It has been shown in laboratory studies that EDB will degrade both aerobically (Pignatello, 1986 and 1987) and anaerobically under reductive dehalogenation conditions (Bouwer and McCarty, 1985). However, Weintraub (1986) found that while sludges could dehalogenate EDB under methanogenic conditions, Florida soils could not. EDB has been shown to persist for decades (HSDB, 2002) in soils, indicating that EDB may be sequestered in soil micropores and/or that the environmental and microbial requirements for its degradation are not favorable.

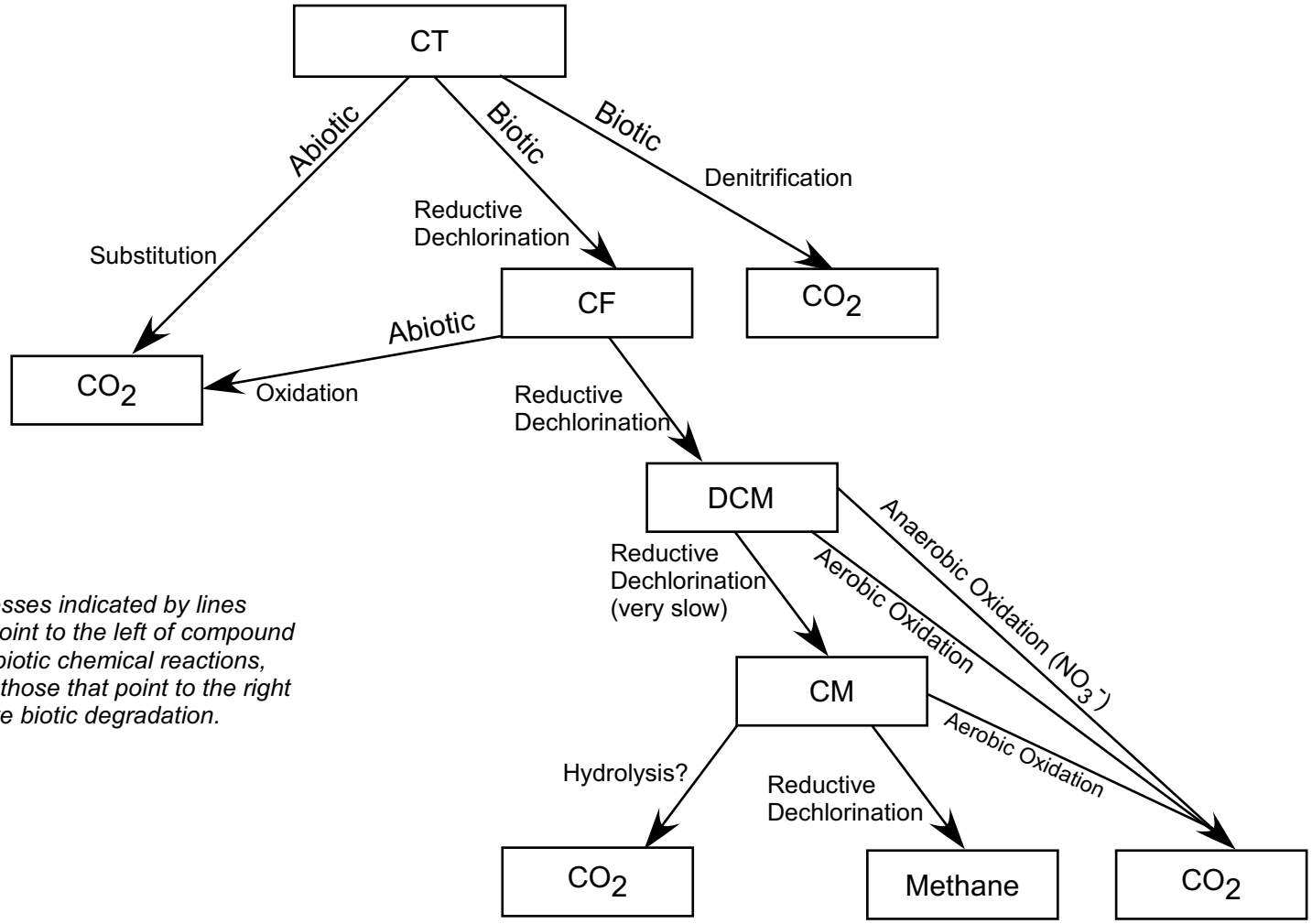
Methyl *tertiary*-butyl ether (MTBE) and other gasoline additives

Methyl *tertiary*-butyl ether (MTBE), other ethers (ethyl *tertiary*-butyl ether, ETBE and *tert*-amyl methyl ether, TAME) and alcohols (*tert*-butyl alcohol, TBA) are oxygenates added to gasoline to improve combustion efficiency. MTBE was initially added to gasoline in the late 1970s to replace lead. Because of the widespread use of MTBE, it has become a common contaminant at underground storage tank sites. MTBE is highly soluble in water and very mobile in soil and groundwater, resulting in contaminant plumes that can extend significant distances.

The most common environmental degradation pathway for MTBE is atmospheric photooxidation (Church, 1997). In aqueous systems, MTBE, because of its ether bond, tends to be unreactive. A number of studies have shown that adapted microbial consortia can aerobically degrade MTBE to TBA and subsequently degrade TBA to CO_2 (Fayolle et al., 2001). Even so, MTBE tends to have a long half-life (2 years or more) in the subsurface. Laboratory studies have not been able to establish anaerobic biodegradative mechanisms for MTBE. However, Wilson et al. (2000) has shown field evidence of natural attenuation of MTBE under methanogenic conditions. Several studies indicate that MTBE degrades only after benzene, toluene, ethylbenzene and xylene (BTEX) are gone from the plume (Wilson et al., 2000; Fayolle et al., 2001).

Figure C-2

Common Degradation Pathways for Chlorinated Methanes



Processes indicated by lines that point to the left of compound are abiotic chemical reactions, while those that point to the right involve biotic degradation.

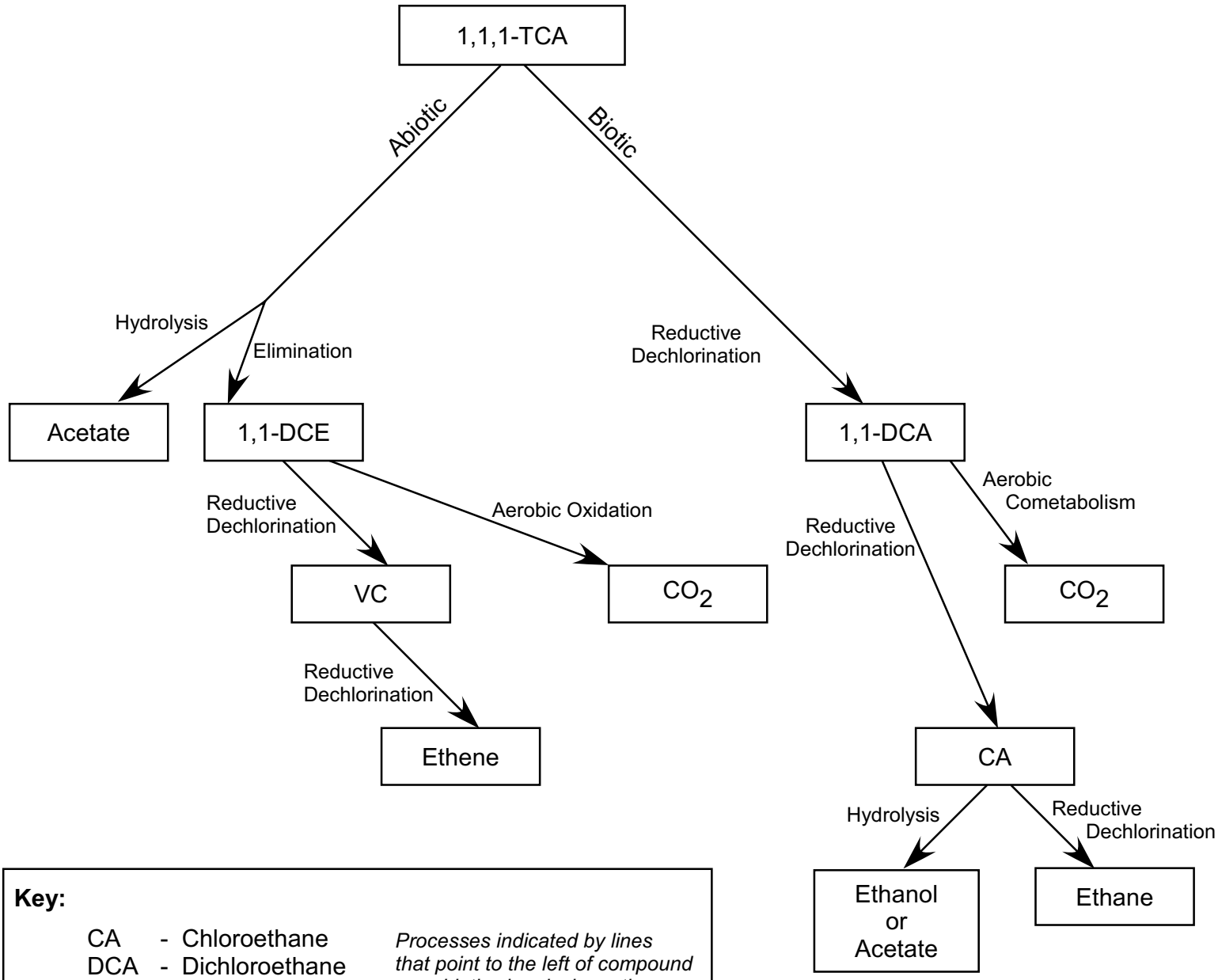
Key:

CF - Chloroform (Trichloromethane)
CM - Chloromethane (Methyl Chloride)
CT - Carbon Tetrachloride (Perchloromethane / Tetrachloromethane)
DCM - Methylene Chloride (Dichloromethane). Note that methylene chloride is a common lab solvent.

References: *Leisinger et al.* [1994]; *US EPA* [1998]; *Van Eekert et al.* [1998]; *Weidemeyer* [1999]; *Yu and Smith* [2000]

Figure C-3

Common Degradation Pathways for Chlorinated Ethanes (*1 of 2*)



Key:

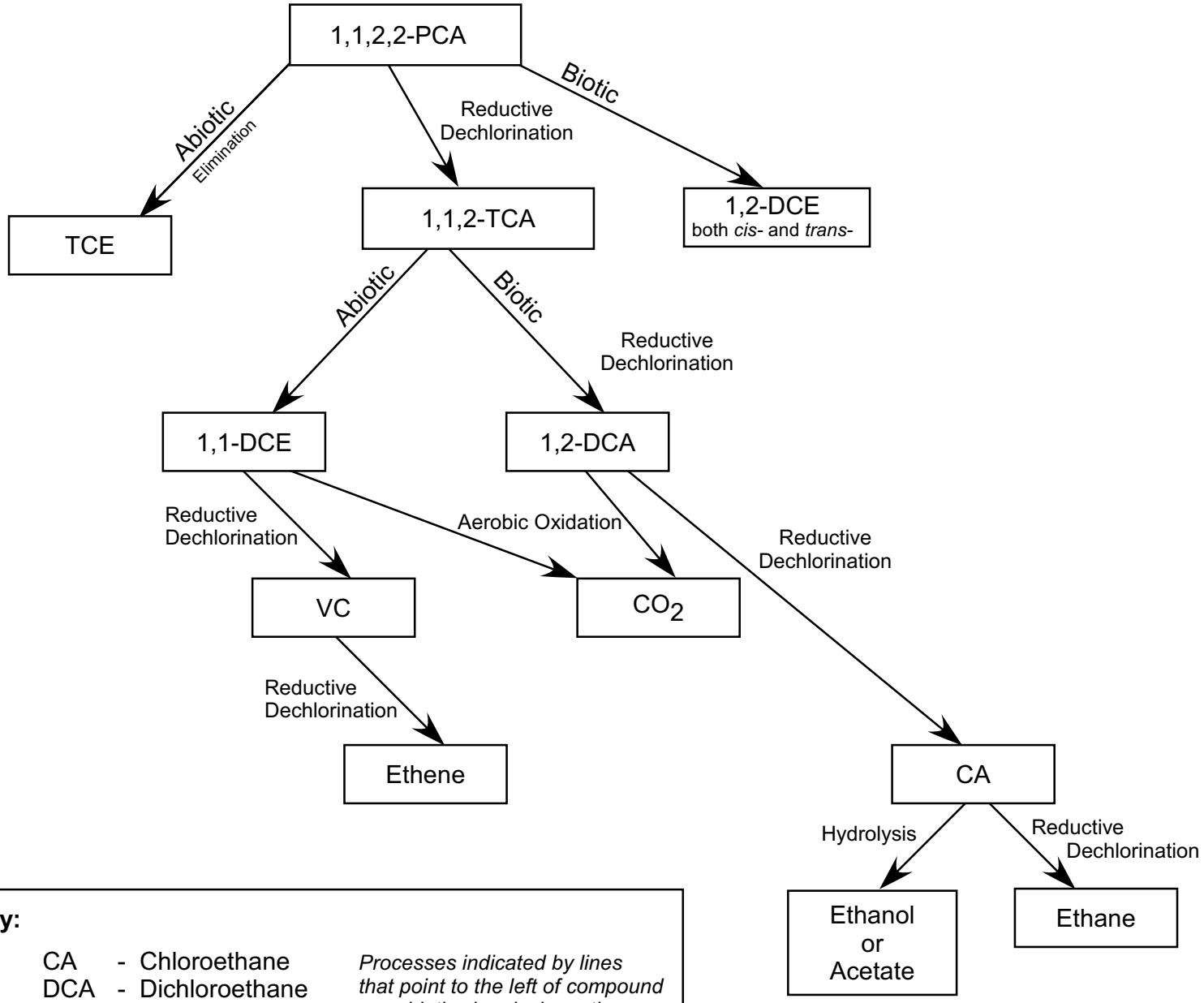
CA - Chloroethane
DCA - Dichloroethane
DCE - Dichloroethene
TCA - Trichloroethane
VC - Vinyl Chloride

Processes indicated by lines that point to the left of compound are abiotic chemical reactions, while those that point to the right involve biotic degradation.

Reference: *US EPA* [1998]

Figure C-4

Common Degradation Pathways for Chlorinated Ethanes (*2 of 2*)



Key:

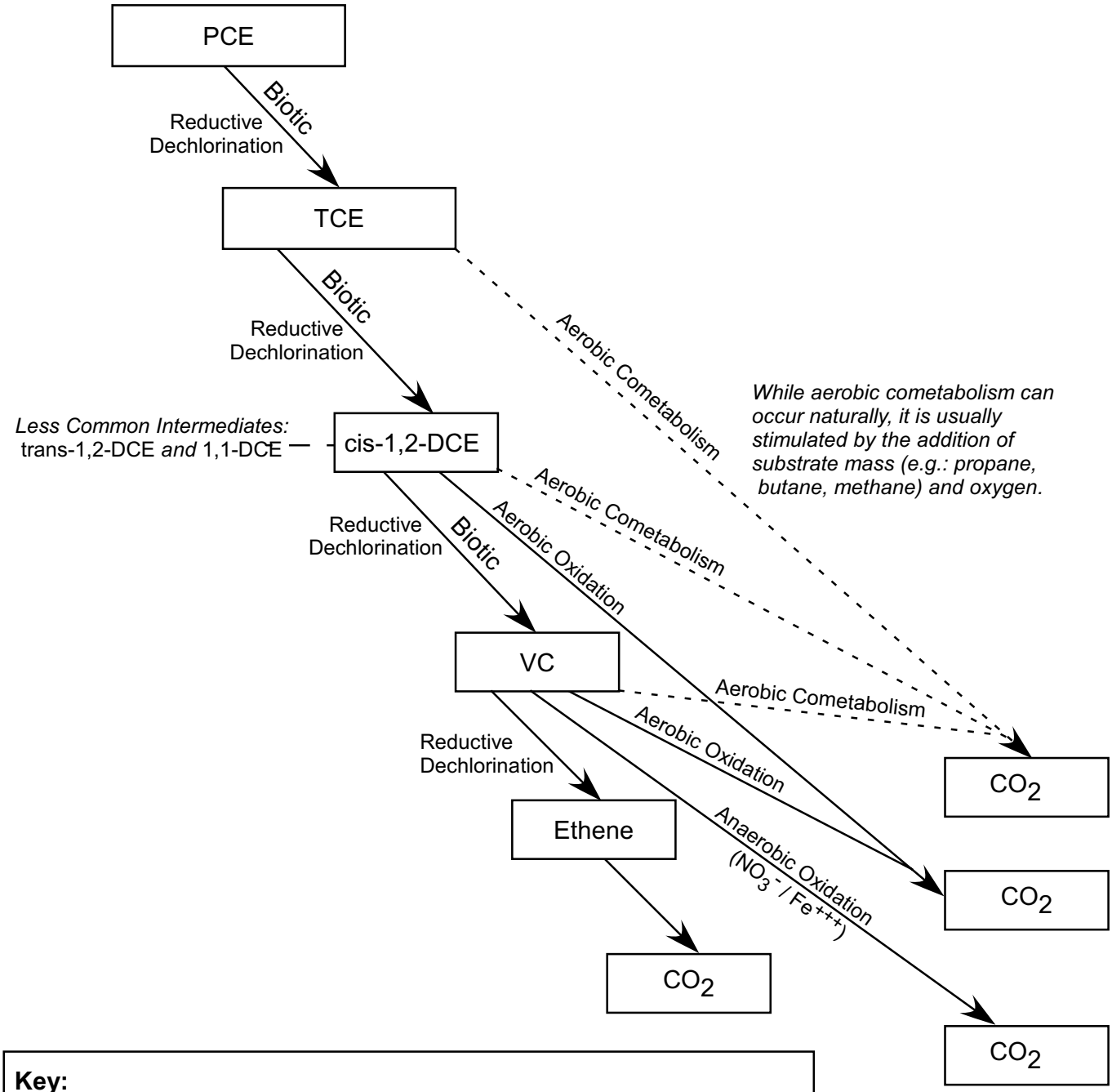
CA	-	Chloroethane
DCA	-	Dichloroethane
DCE	-	Dichloroethene
PCA	-	Tetrachloroethane
TCA	-	Trichloroethane
TCE	-	Trichloroethene
VC	-	Vinyl Chloride

Processes indicated by lines that point to the left of compound are abiotic chemical reactions, while those that point to the right involve biotic degradation.

Reference: *US EPA* [1998]
Lorah and Olsen [1999]
Chen et al. [1996]

Figure C-5

Common Degradation Pathways for Chlorinated Ethenes



Key:

DCE - Dichloroethene
PCE - Tetrachloroethene
TCE - Trichloroethane
VC - Vinyl Chloride

Processes indicated by lines that point to the left of compound are abiotic chemical reactions, while those that point to the right involve biotic degradation.

Reference: *US EPA* [1998; 2001]

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Appendix D

Redox Characterization of Groundwater for Natural Attenuation of Chlorinated Compounds

The oxidation-reduction (redox) state of an aquifer is critical in determining the degradation reaction that contaminants are likely to undergo. Oxidation-reduction refers to reactions in which electrons are removed from one species (the reductant which is oxidized) and added to another (the oxidant which is reduced). Complete chemical reactions require that oxidation and reduction be balanced. The biologically mediated degradation of contaminants consumes oxidized compounds and produces reduced compounds.

The redox state of an aquifer can be determined by measuring redox potential (ORP) in the field with an electrode. However, ORP has poor reproducibility and, by itself, is often unreliable for determining subsurface redox conditions. More reliable methods include measuring changes in terminal electron acceptors (TEA), measuring molecular hydrogen concentrations and determining the energetics of assumed reactions in the system. (Riis, 2000). Any of these methods can be used to determine the footprint of redox zones at a contaminated site. The redox zone(s) footprint can then be compared to the spatial patterns of contaminant degradation found at the site to determine the natural attenuation conditions and the likely natural attenuation processes at various locations on the contaminated site.

Much of the information found below is based on an EPA workshop held in 2000. The report titled, Workshop on Monitoring Oxidation-Reduction Processes for Ground-water Restoration (EPA 600-R02-002) can be found at: http://www.epa.gov/ada/pubs/reports.html .

D.1 TEAs and other parameters as indicators of aquifer redox condition

Specific geochemical parameters change in response to microbial metabolism of carbon. The changes in these geochemical parameters (or terminal electron acceptors) include disappearance of consumed electron acceptors (oxygen, nitrate, and sulfate) and production of reduced species (ferrous iron, manganese (II), hydrogen sulfide, and methane). The energy received as microbes metabolize carbon determines the order in which the terminal electron acceptors (TEA) are used:

oxygen > nitrate > manganese > iron > sulfate > carbon

Microbial degradation of chlorinated compound(s) may occur under any of these redox conditions depending upon which contaminants are present (see Appendix C). For instance, vinyl chloride is used as a food source (oxidizes) quickly in the presence of oxygen (aerobic). Vinyl chloride and cis-DCE can be oxidized anaerobically with nitrate and iron as the electron acceptors. Reductive dechlorination (in which the chlorinated compound serves as an electron acceptor) typically requires a redox state at least as anaerobic as sulfate reduction.

Chapelle et al. (2002) point out that assessing and interpreting terminal electron acceptors at a contaminated site is problematic. Reduced products of TEAs, such as ferrous iron, sulfide, and methane are transported downgradient through advection, making delineation of a given redox "zone" difficult. The location of redox zones can shift areally and temporally due to recharge, changes in dissolved oxygen input, organic matter availability, changing hydraulic gradients and

other factors. Monitoring wells screened across different redox zones make interpretation of redox zones very difficult. Investigators should try to define a "predominant" TEA process within defined areas of the groundwater plume.

The following is a discussion of TEAs and other parameters for determining redox conditions and analytical approaches to their measurement.

1. Dissolved Oxygen (DO). DO is a principal control on redox processes in groundwater, including the movement and fate of organic and metal contaminants. DO levels are controlled by recharge, microbial respiration, biodegradation of organic materials, and reactive mineral surfaces. (Wilkin and Ptacek, 2002)

   DO can be analyzed in the field with an oxygen probe, however a colorimetric field test kit is recommended. If an oxygen probe is used, flow through cell or overflow cell methods should be used. Methods selected should be sensitive to DO concentrations between 0 and 10 ppm. Oxygen probes and the indigo carmine colorimetric method are sensitive to 1 ppm DO. The rhodazine D colorimetric method is sensitive to DO levels less than 1 ppm. Accurate DO measurements require the use of purging, sampling, and analytical techniques that do not introduce air to the water column or sample. Assess DO before and after purging a well and use the lowest DO reading obtained as being representative of the groundwater conditions. In some cases, purging may not be necessary to obtain accurate DO measurements; however this should be confirmed by comparing non-purged and purged DO readings. Use consistent sampling and analytical methodologies on all monitoring wells to ensure comparability of the data.

2. Nitrogen species. Nitrogen exists most commonly in groundwater as nitrate (NO_3^-), nitrite (NO_2^-), and ammonium ion (NH_4^+). Nitrate serves as a TEA through the processes of denitrification and nitrate reduction. Denitrification occurs when nitrate (NO_3^-) is converted to nitrogen (N_2). Nitrate reduction is the process of converting nitrate (NO_3^-) to nitrite (NO_2^-) to ammoniim (NH_4^+). In redox reactions, denitrification is favored over nitrate reduction because microorganisms generate more energy through denitrification. Nitrate reduction will occur as conditions become more reducing (Snoeyink and Jenkins, 1980).

   While field methods exist, laboratory methods should be used to measure nitrogen species, primarily because the lab methods are less expensive. It is acceptable to use nitrate+nitrite as a measure of nitrate because nitrite makes up a small percentage of total nitrogen at the vast majority of sites. Nitrate specific analysis is also acceptable. However, if nitrate-only samples are not preserved, it is important that the samples be analyzed within 48 hours. Otherwise, bacterial action will convert the nitrate and bias the sample.

3. Iron species. In groundwater, iron exists in the following forms: dissolved ferrous (Fe^{+2}), dissolved ferric (Fe^{+3}), colloidal particles of ferrous or ferric iron, and with complexed organic or inorganic ligands (Wilkin and Ptacek, 2002). For the purposes of assessing groundwater redox conditions, dissolved ferrous iron is the species of most interest. Ferrous iron should be field analyzed using a colorimetric method as soon after sample collection as possible. Ferrous iron is oxidized to ferric iron through bacterial action and through physical processes that are a function of pH and the partial pressure of oxygen. At near neutral pH, ferrous iron rapidly converts to the ferric form, even under low partial pressures of oxygen.

4. Sulfur species. Dissolves sulfur occurs in groundwater primarily as sulfate (SO_4^{-2}) and sulfide (S^{-2}). Intermediate oxidation states of sulfur can be found in groundwater, but they are usually of low concentration. Sulfate is most easily measured in a laboratory using ion chromatography. The main interference with sulfate analysis is groundwater high in dissolved organic carbon (where sulfate-respiring bacteria will reduce the sulfate in the sample) and groundwater high in ferrous iron (where sulfate can be incorporated into the precipitated ferric hydroxide). (Wilkin and Ptacek, 2002).

   Sulfide will generally be found in groundwater with less than 1 ppm dissolved oxygen and low ferrous iron. Sulfide is easily lost from groundwater samples through volatilization or oxidation. Therefore, sulfide analysis should be performed in the field using colorimetric analysis and a field spectrophotometer.

5. Oxidation-Reduction Potential (ORP). Typically, ORP is the measurement obtained when a platinum electrode paired with a Ag/AgCl reference electrode is inserted in a flow-through cell. The E_h measurement of the sample can be obtained by correcting the potential reading to the Standard Hydrogen Electrode (SHE). E_h can be calculated by measuring the ORP of the sample and of a standard solution (where the E_h of the standard is known (Wilkin and Ptacek, 2002):

$$E_h = \text{ORP (mV)} - \text{ORP}_{\text{reference solution}} \text{ (mV)} + E_{h\ \text{reference solution}} \text{ (mV)}$$

   The E_h obtained does not correspond to calculated E_h values using aqueous redox pairs. This is because the groundwater is typically not at equilibrium. The ORP (or, corrected E_h) reading reflects many chemical reactions within the groundwater, so it is not possible to associate the ORP reading with a specific chemical condition in the groundwater. It is best to use the ORP or E_h value as a general guide to interpreting the other redox data at the site.

6. Methane. Methane, ethane and ethene are often collected and analyzed together. As dissolved gasses, methane, ethane and ethene can be easily lost from groundwater samples. Therefore sampling handling is critical to accurate results. The sample is collected in airtight bottles and preserved with diluted sulfuric acid. Analysis is performed by gas chromatography.

7. Total Inorganic Carbon (TIC). The end point of biodegradation is the production of carbon dioxide (CO_2). Dissolved CO_2 reflects the plume of contaminated groundwater and can be one of the most useful geochemical "footprints" (Chapelle et al., 2002). Alkalinity (the measure of the acid neutralizing capacity of a water sample) has been used as a surrogate measure of microbially produced CO_2. But alkalinity can provide a biased estimate of microbially produced CO_2 because contaminant plumes can contain high levels of titrable acids and the CO_2 produced can react with carbonate minerals. A better measure of dissolved CO_2 from degradative processes is the increase of total inorganic carbon over background groundwater.

   TIC is measured on an unfiltered groundwater (to avoid the loss of CO_2 to the atmosphere) and is usually equivalent to dissolved inorganic carbon. TIC can be measured in the laboratory by purging the TIC from an acidified sample and then measuring the CO_2 by infrared absorption. Alkalinity, pH, and free carbon dioxide can be measured in the field and TIC can be calculated. Chapelle et al, 2002, gives two methods for calculating TIC, depending on the pH of the groundwater sample (see Box D-1).

Box D-1

Calculating TIC

(Taken from Chapelle, Wilson, and Ludwig, 2002)

Method 1: Calculate TIC from the sum of measured alkalinity and measured free CO_2
Dissolved inorganic carbon is the sum of dissolved carbon dioxide, carbonic acid, bicarbonate, and carbonate. For convenience we will express the sum of dissolved carbon dioxide and carbonic acid as carbonic acid [$H_2CO_3^*$].

$$[TIC] = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{-2}]$$

Alkalinity is conventionally determined as the amount of acid required to titrate water to a colorimetric end point near pH 4.8. It is conventionally expressed as the amount of $CaCO_3$ that would be consumed by that amount of acid. The meq/liter of acid required is the alkalinity in mg/liter of $CaCO_3$ divided by 50.

$$\text{Alkalinity as } [H^+] \text{ consumed} = [HCO_3^-] + 2[CO_3^{-2}]$$

Each 100 mg/liter of $CaCO_3$ alkalinity accepts 2 meq/liter of H^+.

$$CaCO_3 \text{ alkalinity (mg/liter)}/50 = 0.5\,[HCO_3^-] + [CO_3^{-2}]$$

Free carbon dioxide is calculated from the amount of base needed to convert all the $H_2CO_3^*$ and HCO_3^- to CO_3^{-2}. It is usually expressed in mg/liter of CO_2.

Free carbon dioxide as [H^+] provided = 0.5 [HCO_3^-] + [$H_2CO_3^*$]
Each 44 mg/liter of CO_2 provides 2 meq/liter of H^+
Free Carbon Dioxide (meq/liter)/22 = 0.5 [HCO_3^-] + [$H_2CO_3^*$]
$CaCO_3$ alkalinity/50 + free CO_2/22 = [$H_2CO_3^*$] + [HCO_3^-] + [CO_3^{-2}] = TIC
TIC (mg Carbon/liter) = 12 ($CaCO_3$ alkalinity/50 + free CO_2/22)

Method 2: Calculation of TIC from Alkalinity and pH
This method should only be applied to waters with pH > 6.5 and easily measureable $CaCO_3$ alkalinity.

$$[TIC] = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{-2}]$$

The calculation proceeds in three steps:

(1) Calculate [HCO_3^-] from measured alkalinity and pH
(2) Then calculate [$H_2CO_3^*$] and [CO_3^{-2}] from the pH, the [HCO_3^-] as calculated previously, and the governing pKa.
(3) Then add the calculated [$H_2CO_3^*$] + [HCO_3^-] + [CO_3^{-2}] and multiply by 12,000 to convert to TIC (mg C/liter).

Alkalinity is conventionally determined as the amount of acid required to titrate water to a colorimetric end point near pH 4.8. It is conventionally expressed as the amount of $CaCO_3$ that would be consumed by that amount of acid. The meq/liter of acid required is the alkalinity in mg/liter of $CaCO_3$ divided by 50.

$$CaCO_3 \text{ alkalinity as } [H^+] \text{ consumed} = [HCO_3^-] + 2[CO_3^{-2}]$$
$$CaCO_3 \text{ alkalinity (mg/liter)}/50 = [HCO_3^-] + 2[CO_3^{-2}]$$

Calculation of [HCO_3^-]:

The ratio of = [HCO_3^-] and [CO_3^{-2}] can be predicted from the pKa of [HCO_3^-] and the pH.
The pKa of [HCO_3^-] to [CO_3^{-2}] and [H^+] is 10.49 at 10°C.
In other words: ([H^+][CO_3^{-2}]/ [HCO_3^-]) = $10^{-10.49}$ and [CO_3^{-2}] = [HCO_3^-]/$10^{(10.49-pH)}$
Substituting [HCO_3^-]/$10^{(10.49-pH)}$ for [CO_3^{-2}] in equation (1) yeilds

$$CaCO_3 \text{ alkalinity (mg/liter)}/50 = [HCO_3^-] + 2([HCO_3^-]/10^{(10.49-pH)})$$

Solving for [HCO_3^-] yields:

$$[HCO_3^-] = (\text{mg/liter } CaCO_3/50)\left(\frac{10^{(10.49-pH)}}{2+10^{(10.49-pH)}}\right)$$

Box D-1
(continued)

Calculation of $[CO_3^{-2}]$

Again the pKa of $[HCO_3^-]$ to $[CO_3^{-2}]$ and $[HCO_3^-]$ is 10.49 at 10°C.
In other words: $([H^+][CO_3^{-2}]/ [HCO_3^-]) = 10^{-10.49}$ and $[CO_3^{-2}] = [HCO_3^-] \bullet (10^{(-10.49-pH)})$

Calculation of $[H_2CO_3^*]$

The pKa of $[H_2CO_3^*]$ to $[HCO_3^-]$ and $[H^+]$ is 6.42 at 10°C.
In other words: $([H^+][HCO_3^-]/[H_2CO_3^*] = 10^{-6.42}$ and $[H_2CO_3^*] = [HCO_3^-]/ 10^{-6.42 + pH}$

*Definition of pH: $[H^+] = 10^{-pH}$

D.2 Molecular Hydrogen Concentrations

Molecular hydrogen (H_2) is the most important electron donor for reductive dechlorination (Wiedemeyer et al., 1999). Hydrogen is produced as carbon (such as ethanol, lactate, acetate, succinate, propionate, etc.) is fermented. Fermentation is an anaerobic process where the carbon source serves as both the oxidized and reduced species, producing hydrogen to balance the electron transfer. Once produced, other microbes (such as methanogens) utilize the hydrogen. The more oxidized the system, the more efficiently hydrogen is used. Hydrogen concentrations are very low under denitrifying conditions while H_2 accumulates under methanogenic conditions.

A generalized microbial redox reaction where hydrogen is the electron donor and the chlorinated contaminant is the electron acceptor (C—Cl represents a carbon – chloride bond in a chlorinated contaminant) can be represented by:

$$H_2 + C—Cl \rightarrow C—H + H^+ + Cl^-$$

Wiedemeyer et al. (1999) present the following table of expected hydrogen concentrations for given TEA processes.

Table D-1

Range of Hydrogen Concentration for a Given Terminal Electron Acceptor Process

Terminal Electron Accepting Process	Dissolved Hydrogen gas (H_2) Concentration[1]		
	nM	atm[2]	ug/l
Denitrification	<0.1	$<1.3 \times 10^{-7}$	$<0.2 \times 10^{-3}$
Iron (III) reduction	0.2 – 0.8	$0.26 – 1.0 \times 10^{-6}$	$0.4 – 1.6 \times 10^{-3}$
Sulfate reduction	1 – 4	$1.3 – 5.0 \times 10^{-6}$	$2.0 – 8.0 \times 10^{-3}$
Methanogenesis	5 – 20	$63 – 250 \times 10^{-6}$	$10 – 40 \times 10^{-3}$

[1] Expected concentration at 20 °C
[2] Measured in gas phase in equilibrium with water containing dissolved hydrogen.

Reductive dechlorination typically requires sulfate reducing conditions, so it can be expected that H_2 > 1 nM is necessary for reductive dechlorination to take place. Methanogenesis occurs only when fermentation also occurs. Therefore, the presence of methane in groundwater

indicates that hydrogen is being generated and reductive dechlorination processes are likely to occur.

Temperature plays an important role in hydrogen production and utilization. Table D-1 reflects expected hydrogen concentrations at 20 °C. At lower temperatures, reductive dechlorination may proceed at lower partial pressures of H_2. Jakobsen (1998) showed that at 8 °C "methanogenesis and sulfate reduction could bring the H_2 concentration down to about half of the value found at 20 °C". Average groundwater temperature in Wisconsin is approximately 13 °C (Karklins, 1996). At 13 °C, one could expect that sulfate reduction (& therefore reductive dechlorination) might proceed at $H_2 > 0.4$ nM. Actual H_2 concentrations at which reductive dechlorination may take place is highly site specific and is determined by the energetics of the aquifer system.

The oxidation of H_2 in groundwater is almost instantaneous; therefore H_2 concentrations are more likely than TEAs to represent an equilibrium reaction. In addition, because of its reactivity, H_2 is not transported in groundwater and it's presence is indicative of redox conditions at the location and time of sampling (Jakobsen, 1998).

Accurately determining H_2 concentration requires experience and an understanding non-microbial sources of H_2. Hydrogen concentrations should be used in conjunction with measurement of TEA and oxidation-reduction potential (ORP or E_h) to accurately assess likely aquifer redox reactions.

Hydrogen is collected in the field using the "bubble stripping" method originally developed by Chapelle and modified by McInnes and Kampbell. The sample is collected in a 20 mL nitrogen bubble inside a 250 glass sample vessel. A 2 mL aliquot of the bubble is removed and analyzed for hydrogen using gas chromatography with a reduction gas analyzer (McInnes and Kampbell, 2000).

D.3 Energetics of Aquifer System

The concept of sequential use of TEA assumes competitive inhibition – that is, that microbial metabolism will deplete oxygen, then nitrate, then available iron, etc. resulting in definable zones of individual TEA within an aquifer. In reality, iron and sulfate reduction and methanogenesis may intermingle within a given portion of a contaminated plume. It is often difficult to determine the electron acceptor process that dominates at any given location within the aquifer. Calculating the energy available to the microbial community based on TEA concentrations can help an investigator determine likely subsurface processes and determine whether reductive dechlorination can be expected. This may be particularly useful where PCE/TCE concentrations are declining but DCE/vinyl chloride/ethene are very low or absent. Under these circumstances, an investigator may not know whether reductive dechlorination is proceeding and the daughter products are quickly depleted or no degradation is taking place and the PCE/TCE is simply diluting along the flow path.

The actual TEA process in any given portion of a plume is determined by the energy available to the microorganisms and the microbial consortia existing in the aquifer. Jakobsen (1998) and others have shown how calculating energy yields using Gibbs energy of reaction can help an investigator determine an energy threshold value below which it is probable that a given reaction occurs. These calculations, by themselves, do not define which reactions occur or whether the reactions occur in the subsurface. Other supporting data, particularly water

chemistry, are necessary to support decisions regarding the likelihood of reductive dechlorination.

For further information on calculation of energetics of contaminant degradation in aquifer systems, refer to Jakobsen (1998), Richmond et al., (2001) and Wiedemeier et al., (1998).

Table D-2

Field and Laboratory Methods for Redox Parameters

Parameter	Field Method	Laboratory Method
Dissolved Oxygen (DO)	1. Colorimetric methods recommended. Indigo carmine – high range; Rhodazine D – low range. 2. Oxygen electrode in a flow-through or overflow cell.	Laboratory analysis not recommended.
Oxidation-Reduction Potential (ORP)	Combination platinum electrode with a Ag/AgCl reference electrode.	Laboratory analysis not recommended.
Nitrate (NO_3^-)	Field analysis not recommended. 60 – 100 ml glass or plastic container with preservative added.	1. Ion Chromatography recommended. Cool 4°C, holding time 48 hr. 2. Nitrate + Nitrite. Preserve with H_2SO_4, to pH<2, cool 4°C, 28 day holding time.
Ferrous Iron (Fe^{+2})	Colorimetric analysis with a field spectrophotometer recommended.	Laboratory analysis not recommended.
Manganese	Colorimetric analysis with a field spectrophotometer recommended.	Laboratory analysis not recommended.
Sulfate (SO_4^{-2})	Field analysis not recommended. 50 – 100 ml glass or plastic container.	Ion Chromatography preferred. Cool 4°C; 28 day holding time.
Sulfide (S^{-2})	Colorimetric analysis with a field spectrophotometer recommended.	Laboratory analysis not recommended.
Methane, ethane, ethene	Collect air tight bottles preserved with dilute H_2SO_4 and ship to lab.	Headspace analysis by gas chromatography with flame ionization detector (GC/FID).
Hydrogen (H_2)	Bubble stripping method to collect sample. Field lab analysis recommended. Use gas chromatography with reducing gas detector	Ship samples to lab and analyze using a gas chromatography with reducing gas detector.
Total Organic Carbon (TOC	Collect sample without headspace and store sample in amber bottle with TFE lined cap.	Cool 4°C and analyze immediately or preserve in field with H_3PO_4 or H_2SO_4 to pH < 2. Compustion-infrared method recommended.
Total Inorganic Carbon (TIC)	Determine alkalinity (endpoint titration to pH 4.5) and pH. For water with pH < 6.5, also use a colorimetric field kit for free carbon dioxide. Calculate TIC from the sum of carbonate and bicarbonate alkalinity plus free CO_2.	Ship samples to lab in a sealed container without headspace and without preservative. Purge TIC from acidified sample and measure CO_2 by infrared absorption. [Note: TIC is determined from the TOC sample.]
Chloride	Field analysis not recommended. 25 – 100 ml in glass or plastic container.	Ion chromatography recommended. Cool 4°C; 28 day holding time.
pH	Electrode in a flow through or overflow cell.	Laboratory analysis not recommended.
Temperature	Thermometer in a flow through or overflow cell.	Laboratory analysis not possible.
Specific conductance	Electrode in a flow through cell or an overflow cell.	Laboratory analysis not recommended.

* Ref: Chapelle et al., 2002; Wilkin and Ptacek, 2002; Karklins, 1996.

Appendix E

Physical / Chemical Properties and Uses of Chlorinated Hydrocarbons

Introduction

Chlorinated hydrocarbons have been widely used in industry for a variety of purposes. The density of the chlorinated hydrocarbons is greater than that of water, therefore, the undissolved phase in the subsurface is referred to as DNAPL. It is notoriously difficult to locate chlorinated hydrocarbons as DNAPLs in the subsurface, and therefore, difficult to remove this source of significant groundwater contamination. The health effects of many of these compounds can be reviewed at the EPA's Integrated Risk Information System (IRIS) site (http://www.epa.gov/iris/index.html) or the Agency for Toxic Substances and Disease Registry (ATSDR) site (http://www.atsdr.cdc.gov/toxfaq.html). The information at the ATSDR site is easier to read and understand than at the IRIS site. Another source used for the information below is Toxnet (http://toxnet.nlm.nih.gov/) which is a cluster of databases with information on hazardous chemicals, toxicology, and related areas.

Uses and Human Health Effects of Chlorinated Aliphatic Hydrocarbons

Methylene chloride is produced industrially in the U.S. by two methods. The older and currently less used method involves a direct reaction of excess methane with chlorine at high temperatures. The predominant method involves the reaction of methyl chloride with chlorine. This reaction is usually carried out thermally in the gas phase, but may be carried out at low temperatures and high pressure in the liquid phase. Methylene chloride is used as a solvent in paint removers, for cellulose acetate; degreasing and cleaning fluids; as solvent in food processing. In the past it was used in insecticides, but is no longer found in any pesticide formulation. Methylene chloride is rapidly absorbed through the alveoli of the lungs into the systemic circulation. It is also absorbed from the gastrointestinal tract, and dermal exposure results in absorption but at a slower rate than via the other routes of exposure. The ES for methylene chloride is 5 ug/L.

Chloroform is now used primarily in the manufacture of HCFC-22, monochlorodifluoromethane, a refrigerant and as a raw material for polytetrafluoroethylene plastics. Chloroform is also used as a solvent for fats, oils, rubber, alkaloids, waxes, resins; as cleansing agent; in fire extinguishers to lower the freezing temp of carbon tetrachloride; and in the rubber industry. Today, chloroform is prepared exclusively and on a massive scale by the chlorination of methane and/or monochloromethane (Toxnet, 2002). The groundwater enforcement standard for chloroform is 6 ug/L. Chloroform is readily absorbed into the body through dermal, inhalation, and ingestion pathways. Chloroform is metabolized in cells, forming phosgene as an intermediate. The reaction of phosgene with tissue proteins is associated with cell damage and death. Chloroform has been shown to be carcinogenic to rats and mice, but evidence of human carcinogenicity is inadequate. The ES for chloroform is 6 ug/l.

Carbon tetrachloride is readily absorbed into body tissues and when oxidatively transformed, produces phosgene as an intermediate. When anaerobically transformed, chloroform and dichlorocarbene are intermediates. The major uses of carbon tetrachloride (as a refrigerant, in metal degreasing, as an agricultural fumigant, chlorinating organic compounds, production of

semiconductors, and as a solvent) have been canceled due to oncogenicity and its toxic effect on liver and kidneys. The ES for groundwater is 5 ug/L.

1,2-Dichloroethane (1,2-DCA) This compound is a raw material for polychlorinated vinyl (PVC) and, therefore it is manufactured in large quantities. 1,2-DCA is also used as a degreaser and a component in cleaning agents, pesticides, adhesives, paints, and varnishes. It is made by the chlorination of boiling ethylene in the presence of metallocomplex catalysts. 1,2-DCA has a high chlorine content, which makes it expensive to incinerate. Its density is 1.2454. The ES for 1,2-dichloroethane in groundwater is 5 ug/L. 1,2-DCA is listed in the EPA's Toxic Release Inventory and is considered a mutagen and a possible carcinogen.

1,1,1-Trichloroethane (1,1,1-TCA) is used as a degreaser and is similar to trichloroethylene. It has a significantly higher threshold limit value (TLV) than trichloroethylene, is more stable at higher temperatures, and results in lower losses to the atmosphere. However, 1,1,1-TCA has a high ozone depletion potential (0.15). Its potential to deplete ozone is less than the chlorofluorocarbons but 1,1,1-TCA is used to a much larger extent with more losses to the atmosphere and, therefore, its damage to the ozone layer could be quite significant. Because of this, use of 1,1,1-TCA is being eliminated for all but chemical intermediate feedstocks (HSIA, 1994). The ES for 1,1,1-trichloroethane in groundwater is 200 ug/L.

1,1,2-Trichloroethane is used as a feedstock for making 1,1-dichloroethene and as a solvent. The ES for 1,1,2-trichloroethane in groundwater is 5 ug/L. However, it is not commonly found in drinking water. It has been detected in some wells at fairly small concentrations (31 ppb) (ATSDR, 1999). It is more commonly found in air and industrial wastewater. There is little information about the effects of exposure to 1,1,2-TCA for humans. Animals exposed to high doses suffer liver cancer and die at very high exposures.

Vinyl chloride is a gas with a boiling point of -13.4° C. It is used in the manufacture of polyvinyl chloride (PVC) which is used to make a variety of plastic products such as pipe, coatings for wire and cable, and upholstery. Vinyl chloride is also a product of the degradation of many of the other chlorinated hydrocarbons. It has been found in at least 496 NPL sites (ATSDR, 1997). The ES for vinyl chloride in groundwater is 0.2 ug/L. The State MCL for drinking water is 2 ug/l. Vinyl chloride is classified as a human carcinogen.

1,1-Dichloroethylene is often the number one derived organic chemical manufactured annually and is made in excess of 10 billion lb/yr (Chenier, 1992). Dichloroethylene is used to produce vinyl chloride, PCE, methyl chloroform plus other industrial chemicals. The ES for 1,1-dichloroethylene is 7 ug/L in drinking water.

Cis-1,2-Dichloroethylene has been found in at least 146 of the 1,430 National Priority List sites (Superfund) identified by the EPA (ATSDR, 1997). It is used in the manufacturing of solvents and often occurs in mixtures with its isomer, trans-1,2-dichloroethylene. The ES for cis-1,2-dichloroethylene in groundwater is 70 m g/L. The EPA has found that cis-1,2-DCE is not classifiable as a human carcinogen. However, exposure to cis-1,2-DCE has been shown to cause decreased numbers of red blood cells in animals and affect the liver.

Trans-1,2-Dichloroethylene has also been found in at least 563 NPL sites (ATSDR, 1997). Animals exposed to trans-1,2-DCE have suffered damage to their lungs and liver. At very high levels, the animals had damage to their hearts. No EPA classification exists for the carcinogeneity of trans-1,2-DCE. The ES for trans-1,2-dichloroethylene in groundwater is

100 ug/L.

Trichloroethylene (TCE) is used primarily as a chemical feedstock intermediate in production of the refrigerant hydrofluorocarbon (54%) and as a metal cleaner/degreasing solvent (42%) (HSIA, 2001). TCE is also an ingredient in typewriter correction fluids, paint removers/strippers, adhesives, spot removers, and rug-cleaning fluids. Before it was banned for health reasons, TCE was used in foods, beverages (decaffeination of coffee), pet foods, pharmaceuticals, and cosmetics. TCE is produced from either acetylene or ethylene. Beginning with acetylene, the acetylene is chlorinated to tetrachloroethane and dehydrohalogenated to produce TCE. With ethylene as the feedstock, the ethylene is chlorinated to form dichloroethylene which is chlorinated to form a mix of PCE and TCE. TCE has an aqueous solubility of about 1100 mg/L which can result in groundwater concentrations exceeding the ES of 5 ug/L quite easily. The density of TCE is 1.46 g/cm^3. TCE is considered as an intermediate between a probable and possible human carcinogen. Its effects on reproductive/developmental functions are not conclusive.

Tetrachloroethylene or perchloroethylene (PCE) is used mainly as a chemical intermediate (50%) for aerosols and refrigerants and in dry cleaning and textile processing (25%). It is also important in automotive aerosols (10%) and as an industrial metal degreaser (10%) (HSIA, 1998). It is a significant groundwater contaminant because the groundwater enforcment standard is 5 ug/L. With an aqueous solubility of about 200 mg/L, any separate phase PCE in the subsurface in contact with groundwater is likely to result in exceeding the drinking water standard. Disposal practices in the past such as using unlined trenches or ponds have resulted in substantial contamination of soils and aquifers. The density of PCE is 1.62 g/cm^3.

[Significant portions of the text of this appendix have been taken from http://www.ces.clemson.edu/ees/lee/napl/ci_hydrocarbons.htm. Modifications have been made to the original to include additional discussion of chemicals and to reference Wisconsin groundwater standards.]

References

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Table E-1
Chemical and Physical Properties of Chlorinated Hydrocarbons

Chemical	Molecular Weight[a] (g/mole) (MW)	Density[a] (g/mL) (ρ)	Solubility[b] (mg/L) (S)	Vapor Pressure (atm) (VP)	Henry's Law Constant[b] (dimensionless) (H')	Henry's Law Constant[b] (atm-m^3/mol) (HLC)	Koc[b] (L/kg)
Vinyl chloride	62.5	0.9106	2.76E+03	1.19E+00	1.11E+00	2.70E-02	1.86E+01
Methylene Chloride (Dichloromethane)	85	1.3266	1.30E+04	3.35E-01	8.98E-02	2.19E-03	1.17E+01
Trans-1,2-Dichloro ethylene	96.9	1.2565	6.30E+03	6.10E-01	3.85E-01	9.38E-03	5.25E+01
Cis-1,2-Dichloro ethylene	96.9	1.2837	3.50E+03	1.47E-01	1.67E-01	4.08E-03	3.55E+01
1,1-Dichloro ethylene	96.9	1.213	2.25E+03	6.06E-01	1.07E+00	2.61E-02	5.89E+01
1,1-Dichloro ethane	99	1.1757	5.06E+3	2.87E-01	2.30E-01	5.62E-03	3.16E+01
1,2-Dichloro ethane	99	1.2454	8.52E+03	8.42E-02	4.01E-02	9.79E-04	1.74E+01
Chloroform	119.4	1.4832	7.92E+03	2.43E-01	1.50E-01	3.67E-03	3.98E+01
Trichloro ethylene	131.4	1.4642	1.10E+03	8.62E-02	4.22E-01	1.03E-02	1.66E+02
1,1,2-Trichloro ethane	133.4	1.4397	4.42E+03	3.02E-02	3.74E-02	9.13E-04	5.01E+01
1,1,1-Trichloro ethane	133.4	1.3390	1.33E+03	1.71E-01	7.05E-01	1.72E-02	1.10E+02
Carbon Tetrachloride	153.8	1.5940	7.93E+02	1.56E-01	1.25E+00	3.04E-02	1.74E+02
Tetrachloro-ethylene	165.8	1.6227	2.00E+02	2.22E-02	7.54E-01	1.84E-02	1.55E+02

a=CRC (2001); b=U.S. EPA Soil Screening Guidance (1996)

Note: Vapor pressures in this table are calculated from the following relationship:

$$HLC\ (atm\text{-}m^3/mol) = \frac{(VP)(MW)}{(S)}$$

Where:
HLC = Henry's Law Constant (atm-m^3/mol)
VP = vapor pressure (atm)
MW = molecular weight (g/mole)
S = solubility (mg/l)

H' = Henry's Law Constant (dimensionless) = HLC x 41