New Jersey Department of Environmental Protection

Site Remediation Program

Monitored Natural Attenuation Technical Guidance

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1 INTENDED USE OF GUIDANCE DOCUMENT

This technical guidance is designed to help the person responsible for conducting remediation to comply with the State of New Jersey Department of Environmental Protection (NJDEP or Department) requirements established by the Technical Requirements for Site Remediation (Technical Rules), N.J.A.C. 7:26E. This guidance will be used by many different people involved in the remediation of a contaminated site, including: Licensed Site Remediation Professionals (LSRPs), Non-LSRP environmental consultants and other environmental professionals. Therefore, the generic term "investigator" will be used to refer to any person that uses this guidance to remediate a contaminated site on behalf of a remediating party, including the remediating party itself.

The procedures for a person to vary from the technical requirements in regulation are outlined in the Technical Rules at N.J.A.C. 7:26E-1.7. Variances from a technical requirement or departure from guidance must be documented and adequately supported with data or other information. In applying technical guidance, the Department recognizes that professional judgment may result in a range of interpretations on the application of the guidance to site conditions.

This guidance supersedes all previous Department guidance issued on this topic and was prepared with stakeholder input. The committee consists of:

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2 PURPOSE

This guidance is being developed due to changes to the way contaminated sites are remediated in New Jersey pursuant to the Site Remediation Reform Act (SRRA) N.J.S.A. 58:10C-1 et seq. The Department rules under which this document will be implemented are the Administrative Requirements for the Remediation of Contaminated Sites (ARRCS) Rules, N.J.A.C. 7:26C, the Industrial Site Recovery Act (ISRA) Rules, N.J.A.C. 7:26B, the Underground Storage of Hazardous Substances (UST) Rules, N.J.A.C. 7:14B, and the Technical Rules. N.J.A.C. 7:26E

This technical guidance document was developed to provide detailed technical information on the use of monitored natural attenuation (MNA) as a remedial action for a contaminated ground water site in New Jersey. The term MNA refers to the reliance on natural attenuation processes to achieve the applicable ground water remediation standard. Natural attenuation processes include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in ground water. These processes include biodegradation, dispersion, dilution, sorption, volatilization, and chemical or biological stabilization, transformation, or destruction of contaminants. At sites with organic compound contamination, MNA is most effective where the natural processes permanently degrade or destroy contaminants. For inorganics, MNA is most effective where immobilization or radioactive decay is demonstrated to be occurring.

MNA is most appropriate when used in conjunction with other remedial measures or as a follow up to an active remedial action. Approaches to evaluate and implement MNA as a remedial strategy for ground water are outlined in this technical guidance document. The objective of the evaluation process is to demonstrate that MNA will result in a reduction in the concentration of ground water contaminants until they meet the Remediation Standards at N.J.A.C. 7:26D.

This technical guidance document does not address enhanced MNA. Other agencies such as the Interstate Technology and Regulatory Council (ITRC) have developed guidance documents to address enhanced MNA (ITRC, 2008). The focus of this document is on the MNA of ground water, and it does not address natural attenuation in soil.

The Department has requirements (N.J.A.C. 7:26E) for the evaluation of receptors, light non-aqueous phase liquid (LNAPL) and immediate environmental concerns (IECs). Please consult Department rules and guidance on these issues prior to evaluating the applicability of MNA for a given site.

3 DOCUMENT OVERVIEW

The scope of this document is to address MNA of ground water for organic compounds, particularly petroleum hydrocarbons and chlorinated solvents, inorganics and radionuclides. Numerous references are listed for additional information, and excerpts from selected references are provided in the Appendices.

Decisions to utilize MNA are supported by site-specific data and analysis. This guidance involves the use of a conceptual site model (CSM) based on a site characterization that focuses on MNA as a remedy. An understanding of the distribution of the ground water contaminants and the site hydrogeological data are critical elements of the site characterization. The technical guidance outlines a line of evidence approach used to evaluate whether MNA is an acceptable remedial action. The primary line of evidence evaluates contaminant spatial distribution and decreasing concentration trends over time. The secondary line of evidence evaluates geochemical conditions to ensure they are supportive of natural attenuation. The tertiary line of evidence involves microbiological and isotopic studies that can be used as additional lines of evidence to confirm natural attenuation.

A long term monitoring (LTM) plan is necessary to evaluate the effectiveness of the MNA ground water remedy. If, during the long term monitoring program, MNA is determined to no longer represent a protective remedy, the investigator must evaluate an alternative remedy (N.J.A.C. 7:26E-6.3(e)3ii). The MNA remedy involves the issuance of a Department Remedial Action Permit for Ground Water (RAP-GW); (N.J.A.C. 7:26C-7). A Classification Exception Area (CEA) is to be established prior to obtaining the permit (N.J.A.C. 7:9C-1.6).

4 APPLICABILITY OF MONITORED NATURAL ATTENUATION

For an MNA remedy to be appropriate, it must be protective of public health and safety, and of the environment. At sites with organic compound contamination, MNA is most effective where natural processes permanently degrade or destroy the contaminants. For inorganics, MNA is most effective where immobilization or radioactive decay is demonstrated to be occurring. As discussed below, this Section also addresses technical impracticability and conditions precluding MNA.

This technical guidance document assumes that the investigator evaluating MNA has complied with all applicable regulatory requirements and followed applicable technical guidance documents, including but not limited to Preliminary Assessment/Site Investigation (PA/SI), and Remedial Investigation (RI) requirements for Soil and Ground Water, and the evaluation of receptors.

4.1 Monitored Natural Attenuation Role in Remedial Actions

This section focuses on MNA as a potential component of a site's remedial strategy. Over the years, as scientific knowledge and understanding of MNA processes have increased, so too has the use of MNA in remedial actions. Remedial actions must be protective of public health and safety and of the environment, and meet site-specific remedial objectives. MNA can be evaluated along with other remedial approaches and technologies to assess if it is an appropriate component of a site remedy. In order to implement a MNA remedy, adequate site characterization data and analysis are needed to demonstrate that natural attenuation is occurring MNA needs to be implemented within the context of a RAP-GW, which is discussed in Section 7 of this technical guidance.

Consistent with United States Environmental Protection Agency (USEPA) guidance, MNA is most appropriate when used in conjunction with other remedial measures or as a follow up to an active remedial action. MNA should not be considered a default remedy, and MNA is not appropriate for every site (USEPA, 1999). MNA may be appropriate as a sole ground water remedy if no source is present and site conditions indicate that natural attenuation alone would meet the remediation objectives.

Source control and long term performance monitoring are fundamental components of any MNA remedy. Following source control measures, MNA could be used in conjunction with or without other active remedial measures, depending on whether MNA alone is sufficient to achieve remediation objectives. Often, a phased remedial strategy is undertaken by implementing source control measures during initial remediation stages and collecting additional data to determine the most appropriate ground water remedy. Because lingering sources may unacceptably extend timeframes for all remediation strategies, including MNA, it is appropriate to target source areas during initial remediation stages, and subsequently collect additional data to design the most effective long term ground water remedy.

The evaluation of MNA as a remedial alternative will follow the Department's remedy selection process, as indicated in N.J.A.C. 7:26E-5 et al. Critical factors to be evaluated when considering MNA include: (1) whether the contaminants are likely to be effectively addressed by natural attenuation processes (e.g., degraded if organic contaminants, immobilized or decayed if inorganic contaminants), (2) the ground water plume's potential for migration, and (3) the potential for unacceptable risks to human health or the environment. Since some natural attenuation processes may create degradation products that are more mobile and/or more toxic than the parent contaminants, the presence of such degradation products must be assessed. N.J.A.C. 7:9C and N.J.A.C. 7:26E require the remediation of all contaminants, which would be inclusive of degradation products that exceed GWQS.

If land use changes would influence the effectiveness of MNA, the MNA evaluation must address this issue, not only in the remedy selection process, but also within the context of the Remedial Action Protectiveness/Biennial Certification – Ground Water documentation (N.J.A.C. 7:26E-8.7(a)1ii). Land use changes might affect ground water use, contaminant pathways, or geochemistry necessary for the continued effectiveness of MNA.

Comparative advantages and disadvantages of MNA as a remediation strategy should also be deliberated in the remedial evaluation process. For example, potential advantages of MNA include reduced waste generation, reduced energy use, and, in some cases, reduced lifecycle costs. Potential disadvantages include increased remediation timeframes relative to active remedies, and loss in long term effectiveness of MNA associated with changes in hydrologic and geochemical conditions over time.

4.1.1 Source Control

Source control is a fundamental component of any MNA remedy (USEPA, 1999). Source control measures typically include removal, treatment, or containment. Contaminants in soil and ground water that are not adequately addressed by source controls may complicate a successful MNA long term cleanup strategy. Residual contamination in soil could continue to leach into ground water and might exceed the rate at which natural processes can attenuate the ground water contamination. Contamination in the saturated zone that is not addressed by source control measures could result in contaminant releases exceeding the natural attenuation capacity of the system to control the contaminants. Equally important, uncontrolled and lingering sources pose a potential threat to downgradient receptors. Thus, compliance with the Soil Remediation Standards Impact to Ground Water pathway should be demonstrated prior to implementation of a MNA remedy.

4.1.2 Technical Impracticability

Selecting MNA as a remedy does not imply that active remediation is infeasible or technically impracticable from an engineering standpoint. Consistent with federal guidance, MNA is not a direct or presumptive outcome of a technical impracticability determination. A determination of technical impracticability indicates that the cleanup levels and objectives that would otherwise be required cannot practicably be attained using available remediation technologies (USEPA, 1999). Additional information is contained in the Department's Technical Impracticability Guidance Document.

4.2 Conditions That Generally Preclude Monitored Natural Attenuation as a Sole Ground Water Remedy

Conditions that generally preclude the application of MNA as a sole remedy for ground water contamination include the following:

Expanding Ground Water Plume: An expanding ground water plume indicates that contaminant release exceeds the natural attenuation capacity of the system to control the contaminants. (e.g., N.J.A.C. 7:26E-6.3(e)1i(4))

Effective Monitoring Limitations: Complex hydrogeologic systems such as fractured bedrock or karst formations present difficulties for the monitoring of contaminant migration and natural attenuation processes. Such conditions potentially constrain the adequate monitoring of a natural attenuation remedy to ensure, with a high degree of confidence, that potential receptors will not be impacted. In addition, the effectiveness of natural attenuation processes in bedrock (particularly crystalline rock) has not been established sufficiently. As noted by the Wisconsin Department of Natural Resources guidance on natural attenuation (Wisconsin, 2003), attenuation processes such as sorption, cation exchange, biodegradation and hydrolysis are not as effective in fractured bedrock environments.

Receptors Impacted (N.J.S.A. 58:10C**):** Contamination has impacted human and/or ecological receptors (e.g., potable wells, surface water, vapor intrusion to indoor air, utilities). Further information on addressing impacted receptors is available in the Department's Vapor Intrusion, Immediate Environmental Concern (IEC), and Receptor Evaluation Technical Guidance documents. Where vapor intrusion or potable well impacts exist, but mitigation measures or remedial systems are in place, MNA may be considered as a supplemental component of the site remedy.

Imminent Threat to Receptors: When the travel time of contaminants to a potential receptor, as estimated through calculation of the ground water seepage velocity (Section 7), represents an imminent threat to receptors, additional justification is necessary to demonstrate the viability of MNA as a protective remedy. For example, MNA may be considered if a calibrated flow and solute transport model demonstrates that the travel time to the receptor does not represent an imminent threat. As applicable, such justification would be especially important when the contaminant plume is located within a wellhead protection area established by the Department.

Free and/or Residual Product: Natural remediation of free and/or residual product will not be allowed (N.J.A.C. 7:26E-6.1(d)). The person responsible for conducting the remediation must obtain the Department's written approval when treatment or removal of free product or residual product is not practicable.

5 SITE CHARACTERIZATION

The Department's SI/RI/RA Ground Water Technical Guidance Document outlines the nature and scope of investigations typically required to ensure for effective site characterization. Essential to the evaluation of a monitored natural attenuation remedy is an understanding of contaminant hydrogeology and site geochemistry. This may include development of a conceptual site model (CSM) that is commensurate in detail to the level of site complexity. Basic aquifer matrix and hydraulic characteristics should be measured or estimated to evaluate contaminant transport over time, and the three dimensional distribution of contamination in the saturated zone needs to be understood in terms of extent and total mass, to provide a baseline for long term monitoring.

Finally, factors that may influence mass loading to the plume or the orientation of plume migration (e.g., seasonal variation in recharge and water level, irrigation or supply well pumping) should be acknowledged, as necessary, to allow for design of a monitoring program that is sensitive to these considerations.

5.1 Conceptual Site Model for Monitored Natural Attenuation

A CSM is a written and graphical representation of the physical, chemical and biological processes that control the transport, migration and interaction of chemicals of concern through environmental media associated with an Area of Concern (AOC) or an entire remediation site (Site).

An understanding of the nature and magnitude of ground water contamination and specific pathway information should be incorporated into the development of an overall CSM for the site and/or AOC, as described in the Department's Conceptual Site Model Technical Guidance Document. This guidance provides a description of the basic components that should be included into the development of a CSM for a site or AOC. To develop a CSM for a site where MNA is proposed, data should be acquired to characterize site and background conditions, as well as natural processes that would influence contaminant fate and transport. In these cases, the CSM should form the basis for selecting and developing model applications for evaluating transport processes, reaction mechanisms, attenuation capacity within the aquifer, and the sensitivity of attenuation processes to changes in site conditions Some or all of the information highlighted below typically forms the basis for development of a complete CSM for sites where MNA is proposed as the remedy:

Organics

- concentration and distribution of contaminants, degradation products, and ground water geochemical parameters (e.g., electron acceptors including dissolved oxygen, nitrate, sulfate, and iron (III); chloride, pH, alkalinity, oxidation-reduction potential)
- microcosm studies demonstrating the occurrence of biodegradation
- sorption and retardation calculations
- stable isotopic evidences for degradation of contaminants (e.g., Appendix B)
- mass flux calculations (e.g., Appendix C)

Inorganics

- data needed to determine contaminant sorption onto aquifer materials (collection of aquifer cores and ground water samples from the same zone and analysis of contaminant concentrations both in the aquifer solids and the ground water)
- ground water chemistry, aquifer solids composition, chemical speciation data to determine attenuation mechanisms
- data to assess the attenuation capacity of the aquifer (example: colloidal matter, organic carbon content, total dissolved solids (TDS))
- data to determine the contaminant immobilization and long term stability
- rates of radioactive decay
- mass flux calculations (e.g., Appendix C)

5.2 Aquifer Characteristics

Detailed characterization of aquifer characteristics such as hydraulic conductivity, hydraulic gradient, and porosity of the aquifer materials is very important for the evaluation of MNA as a viable remedy for ground water remediation at a site. Aquifer characterization data represent basic inputs to the estimation of seepage velocity (Section 7.1) and support the forecasting (modeling) of plume behavior over time. These data are also essential to the evaluation of mass flux and mass discharge (Section 6.1.4), which can help explain whether the contaminant plume is stable, expanding or contracting (Section 6.1.1), and determine how much mass removal from the source would allow MNA to be utilized as a viable remedial option. Performance of field or laboratory tests to obtain aquifer characterization data, or presentation of typical data ranges, are described in a range of standard references, including Dominico and Schwartz (1990) and Fetter (2001). Appendix D contains a summary discussion of important aquifer characteristics and provides a wide range of additional references to support the investigator.

5.3 Contaminant Spatial and Temporal Distribution

Initial monitoring to support MNA should include the collection of data horizontally and vertically over time, such that the nature and distribution of the contaminant source areas and the ground water plume are understood. In general, robust characterization efforts are needed to support an evaluation of MNA and the frequency of monitoring events during the early stage of site characterization are generally higher than those associated with LTM.

As outlined in Section 6.1, a minimum of eight rounds will typically be needed to demonstrate the applicability of MNA. Of these eight rounds, four consecutive quarterly ground water monitoring events are necessary to evaluate spatial and temporal distribution. Selection of the monthly period within which sampling is performed should reflect observed variability in site conditions. If adequate data to define seasonal variation in contaminant concentrations, geochemical parameters and water levels (ground water flow patterns) are not available, monitoring of these parameters should be performed to determine the short-term variation, and to verify that data collected from any new monitoring points are consistent with the site CSM.

5.3.1 Evaluation of Seasonal Trends

It is important to understand the impact of seasonal variations of recharge on contaminant concentrations and plume behavior. In general, four consecutive quarterly ground water level and contaminant monitoring events are used to capture potential seasonal variations in plume dimensions and possibly flow direction. Investigators should consider the use of available tools, such as dedicated water-level loggers, to determine if significant, naturally occurring water-level fluctuations occur throughout the year or in response to specific climatic changes. This will help not only identify significant changes in hydrologic conditions, but also to schedule contaminant or geochemical monitoring during these events (e.g., snow melt, breakup of river ice, seasonal changes in ground water orientation or gradient due to changes in recharge, pumping, etc.). Additional information concerning timing of quarterly sampling may be found in Wiedemeier, et al., 2005.

Environmental monitoring data often exhibit seasonality, and seasonal influences represent one factor that accounts for changes in contaminant concentrations or geochemistry over time (US Army Corps of Engineers, USACE, 2008). Seasonality is a predictable, periodic increase or decrease that occurs within a time period or cycle, such as one year. The key to identifying such trends is the repetition of the same pattern for each cycle. Identifying seasonality or other repetitive trends (i.e., persistent cyclic variations) is necessary before long term increasing or decreasing temporal trends can be evaluated in environmental data. To identify these, the investigator should visually inspect plots of data across time for seasonal or repetitive trends. The investigator should explain identified seasonal trends with respect to site history, geology, chemistry, and professional judgment.

The presence of seasonal variability in ground water concentration time series data can make discerning trends difficult. This is because it contributes short-term variation, caused by water-level fluctuations and other seasonal effects, which appear as background noise in conventional trend analyses such as Mann-Kendall. If the source of the seasonal effect can be identified, one way to minimize the effect is to normalize the concentration data to the source variable. For example, if ground water concentrations are shown to be correlated with water levels in monitoring wells, they could be “normalized” by dividing concentrations by water levels (Helsel and Hirsch, 2002). As discussed in Section 6.1.3, the Seasonal Kendall test is a modification of the Mann–Kendall test that addresses this short-term seasonal variability and allows evaluation of overall trends (see also Appendix E).

Certain seasonal conditions may be observed routinely in source zone monitoring wells screened across the water table, and these conditions should not necessarily be considered anomalous (see Table 1 below). For example, increases in constituent concentrations during the dry season, or decreases during the wet season, are typically the result of changes in sample dilution due to changes in the saturated thickness of the aquifer across the well screen. Similarly, a decrease in concentration during a drought period likely represents the dropping of the water table below a "smear zone" of residual contamination. On the other hand, there are seasonal conditions that may warrant further investigation in source zone water table monitoring wells, including abnormally high constituent concentrations during the wet season (which could be associated with potential new sources or the result of entrained LNAPL release). It should be noted that the scenarios described above will be less evident in downgradient monitoring wells, depending on the distance of those wells from the source zone, as discussed in Sections 5.3.2 and 5.3.3. Anomalous seasonal variation of constituent concentrations in downgradient wells may be the result of shifts in the orientation of ground water flow due to seasonal variations in recharge, coupled with aquifer heterogeneity and anisotropy (e.g., Rivett and Feenstra, 2005), and/or seasonal pumping.

Table 1
Possible Causes of Seasonal Conditions Observed
at Source Zone Water Table Monitoring Wells

Observed Condition	Dry Season	Wet Season
High Concentration	Low well screen dilution	Potential new source Water table rises into/above zone of residual contamination
Low Concentration	Water table falls below "smear zone" of residual contamination	High well screen dilution

5.3.2 Defining Plume Geometry

The placement of monitoring wells and the frequency of sampling should yield data to allow for detection of significant changes in plume configuration and definition of trends in contaminant concentrations over time. Seasonal changes and/or anisotropy (common in most natural aquifer systems) can cause ground water flow directions to change by 10^o – 40^o. This, in turn, may lead to misinterpretation of plume attenuation at fixed longitudinal points. For example, (as illustrated in Figure 1) a decreasing trend in concentrations at a downgradient monitoring well may be attributed solely to natural attenuation when, in fact, the decreasing trend is related to a temporal shift of the plume from its core to fringe. Pumping tests or other hydrologic testing methods may be used to evaluate anisotropy (ASTM D5850 – 95, 2006).

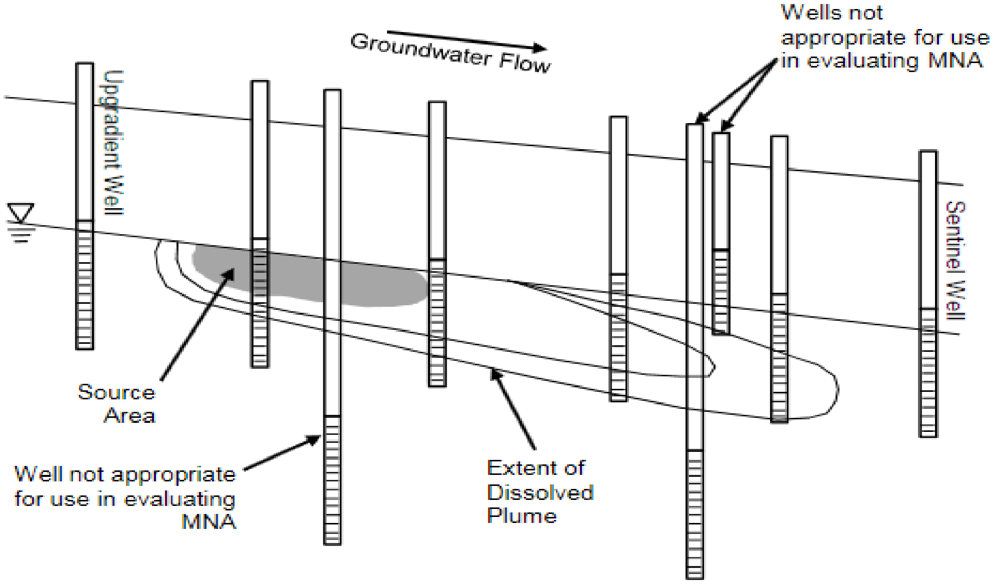
Initial characterization should reflect the understanding that contaminant plumes are dynamic, three-dimensional entities, and effective monitoring of natural attenuation processes involves a three-dimensional network design and clearly defined performance criteria (Wiedemeier et al., 2005). The ground water monitoring well network for most sites will typically include an upgradient well, at least one transect of wells screened within the longitudinal axis of the plume, and one transect screened within the transverse axis of the plume (Missouri DNR, 2007). This monitoring well array facilitates contaminant mass flux baseline conditions (see Section 6.1.4) and can be useful for targeting source zones and quantifying future natural attenuation.

It is important to note that diffusion from low permeability zones within an aquifer (also referred to as "back diffusion") can sustain contaminant release from a source zone. In general, the older a release, the more likely it is that back diffusion is the source for contaminant concentrations at the head of a persistent plume (Sale et. al, 2008; Chapman and Parker, 2005). The placement of monitoring wells should address the potential for this condition.

The locations and screened intervals of monitoring wells should be based on site stratigraphy and plume behavior as revealed during site characterization. It is not uncommon for discrete lenses to retain and/or convey significant contamination within a larger water-bearing unit, and this phenomenon should be considered as part of the CSM and MNA remedial design. This requires an understanding of the three-dimensional relationship between contaminants and stratigraphy to ensure that monitoring wells are screened in the appropriate hydrogeologic unit, and that plume monitoring wells define the path of contaminated ground water flow. Even in a relatively homogeneous sandy aquifer, the core of the plume may occur in thin discrete zones. For this reason, identification of the plume core may not be accomplished with conventional monitoring well networks. In many cases, field screening tools (e.g., membrane interface probe) or vertical profiling using direct-push sampling (e.g., hydropunch or Waterloo sampler) may be necessary

Figure 1

Generalized Monitoring Well Network



to identify the appropriate monitoring zones. Although it may not be appropriate for every site, the USEPA's TRIAD approach (ITRC 2003) is one way to rapidly collect detailed spatial site characterization data to support MNA remedies. In general, saturated screen lengths of 5 feet to 10 feet are recommended to help mitigate the dilution of water samples from potential vertical mixing of contaminated and uncontaminated ground water. Screening a larger area of the saturated zone may result in averaging of contaminant concentrations and hydraulic properties, yielding misleading data.

The appropriate location, depth and construction of wells can play a critical role in understanding flow regimes and plume distribution. For example, in settings where vertical flow components are important, errors can be made if water levels from monitoring wells or piezometers screened at different depths are plotted incorrectly.

5.3.3 Identification of Hydraulic Perturbations

As stated earlier, seasonal ground water table fluctuations or recharge events, anisotropy, and geologic heterogeneity can make it difficult to properly characterize contaminant distributions. Appropriate characterization of plume dimensions can be further complicated by perturbations attributable to natural and/or anthropogenic factors that influence hydrogeologic conditions at a site. These can be due to nearby ground water recovery systems, earthwork/soil disturbance projects, stormwater modifications proximal to a site, and surface waters (i.e., streams, lakes, etc.). The location, recovery rates, operational periods, and construction of pumping wells proximal to the sites should be researched prior to conducting field sampling events. Similarly, the stage/elevation of nearby surface waters (which could represent ground water recharge or discharge zones) should be understood. Highly variable ground water monitoring data due to perturbations often leads to exceedingly long, expensive, and inappropriate site characterization. Investigators should therefore be cognizant of sources of perturbations and, if persistent phenomena, consider modification of the monitoring well network to account for these influences.

Investigators should monitor ground water levels frequently enough to detect and characterize the sensitivity of ground water flow regimes to perturbations. In some cases, such as in tidally influenced areas, weekly or even continuous water level measurements may be needed (N.J.A.C. 7:26E-3.7(e)3iii; Serfes, 1991; California EPA, 1995).

Recent analysis of a large ground water dataset evaluated the relative importance of different types of variability due to perturbations, natural attenuation processes, aquifer and well characteristics, sample collection and handling, and laboratory analysis (McHugh et al., 2011). The research indicated that ground water quality variability is higher in wells screened in more permeable soils and wells screened close to the water table surface. Additionally, the effects of perturbations were generally more appropriately characterized when the density of monitoring points was increased rather than the frequency of monitoring increased.

6 LINES OF EVIDENCE

Demonstrating the applicability of MNA is commonly approached in three stages, where information that is more detailed is generally collected at each stage to provide added levels of confidence that MNA represents a viable remedy. These three stages of data evaluation are commonly referred to as “primary”, “secondary” and “tertiary” lines of evidence (Table 2). The primary line of evidence includes evaluating plume behavior and contaminant trends that ***directly*** demonstrate natural attenuation. The secondary line of evidence consists of geochemical data that ***indirectly*** indicate that natural attenuation processes are occurring at the site (i.e., contributing processes). The tertiary line of evidence involves microbiological and isotopic studies that can be used as additional lines of evidence to confirm natural attenuation. In some cases, these latter studies in and of themselves can be as compelling as evidence derived from geochemical assessment.

Table 2
Lines of Evidence

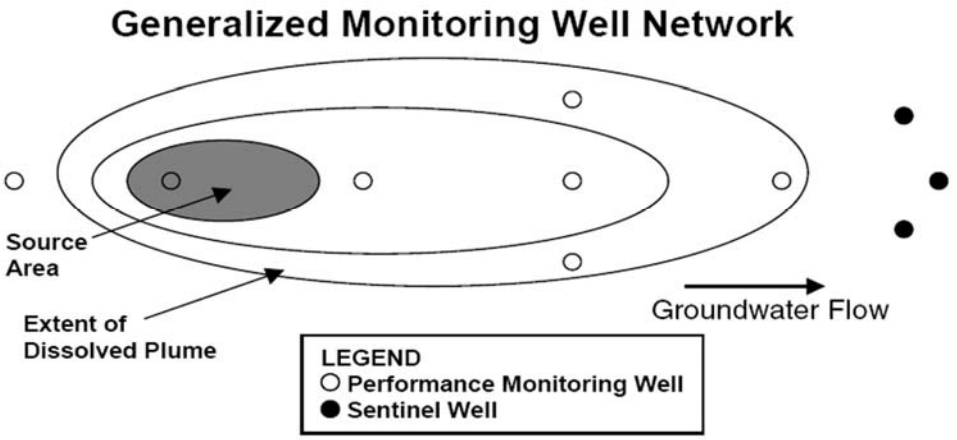
Primary Line of Evidence	Plume Behavior - stable or shrinking plume Contaminant Trends - decreasing levels
Secondary Line of Evidence	Geochemical Conditions
Tertiary Line of Evidence	Microbiological and Isotopic Studies

6.1 Primary Line of Evidence - Evaluation of Contaminant Plume Characteristics

MNA effectiveness is determined principally by decreasing contaminant concentrations with time in conjunction with a stable or receding ground water plume. The ability to measure such behavior is based on the establishment of a monitoring array during the site investigation, remedial investigation, or source remediation phase that characterizes the COCs both laterally and vertically. Ideally, monitoring well placement reflects the results of high resolution screening level analysis (for example, the use of vapor surveys or membrane interface probe (MIP) testing) to maximize the representativeness and usability of the data analysis performed during the monitoring phase (USEPA, 2001). The array will vary based on site specific considerations, including the complexity of site lithology, hydrogeology, geochemistry, and the spatial and temporal distribution of source loading, but a typical scenario is illustrated in the Figure 2 below, and consists of performance monitoring wells (e.g., up-gradient, source, plume longitudinal, plume transverse, plume fringe) and sentinel wells. In simple cases (e.g., limited UST release, effective source remediation and/or relatively homogenous lithology), the array may consist only of an upgradient, source, and downgradient plume fringe/sentinel well.

It is important to distinguish between the monitoring requirements necessary for plume characterization (e.g., to establish plume geometry and validate projections of plume behavior over time) and those necessary to ensure for the protection of receptors. This concept is embodied in the suggested monitoring frequency schedules provided in Section 7.

Figure 2



Source: Missouri DNR 2007, and others

Equally important to the lateral spacing of monitoring points is the vertical targeting of monitoring zones. Aquifer lithology and heterogeneity, the physical characteristics of site COCs (e.g., density), the downward displacement of shallow contamination with distance as a function of recharge, and other potential hydraulic influences (e.g., irrigation or supply well pumping), need to be understood and addressed during the monitoring well installation phase to allow for representative plume characterization and monitoring. A number of these topics were discussed previously in Section 5.3.

Eight rounds of ground water monitoring data should be used to demonstrate the applicability of MNA, and represent a minimum for the application of statistical methods outlined in Section 6.1.3 of this guidance. Historic SI or RI data may be used to comprise the total of eight rounds, where these data do not reflect pre-remediation conditions. Of these eight rounds, four consecutive quarterly ground water monitoring events are necessary to evaluate spatial and temporal distribution.

6.1.1 Plume Behavior

Detailed descriptions of methods to define plume behavior are provided in several sources, including the Wisconsin DNR (2003) for petroleum compounds and USEPA (1998) for chlorinated compounds. From these methods, the site investigator should be able to determine whether the ground water plume is shrinking, stable or expanding. Evidence of a shrinking or stable plume is required for MNA to be considered as a remedy.

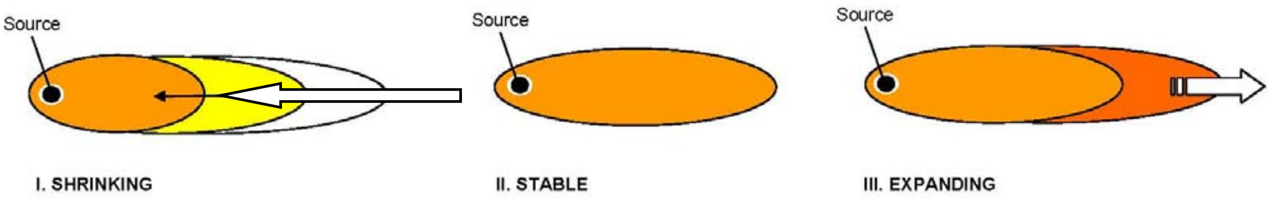
The plume behavior along the contaminant path can be considered as follows (Wisconsin DNR 2003):

I. **Shrinking:** with decreasing concentration trends over time and sentinel well concentration remains below the ground water quality standards.

II. **Stable:** if the concentration trends remain the same over time and sentinel well concentration remains below the ground water quality standards.
III. **Expanding:** if the concentration trends are increasing over time or if a sentinel well becomes impacted above the ground water quality standards.

These plume behaviors can be represented as follows:

Figure 3
Plume Behaviors



* Source: Modified from Figure 3.2 Washington State DOE (2005) – Adapted from Newell and Connor (1997)

Some example scenarios in understanding how the contaminant concentration changes related to plume stability can be outlined as follows:

- Within a shrinking plume, the concentrations at the periphery of the plume may attenuate at a faster rate than the source area due to more favorable conditions, such as higher organic carbon content (f_{oc}) and dissolved oxygen (DO) for aerobic degradation at the plume edge. This could be an occurrence in larger sized plumes (in the hundreds or thousands of feet) where the contaminant plume encounters significant variations in lithological and hydrogeological conditions from the source area out towards the plume fringe. The representation of this scenario is provided by the shrinking plume graphic in Figure 3, above.

- A stable plume may occur where the lithological, hydrogeological, and geochemical conditions provide an effective contaminant concentration reduction rate at all locations within the plume. In such a case, the areal extent of the plume remains constant and increases are not observed in downgradient monitoring wells.

- In many instances, shrinking contaminant plumes exhibit both conditions outlined in the example scenarios. There are variations of site conditions that aside from these examples could account for the shrinking or stable plume and the site investigator needs to utilize their knowledge of the contaminant and site to understand which variations of these factors are resulting in the observed field results.

A range of methods has been described in the literature to allow for the characterization of plume behavior. Typically, the investigator characterizes plume behavior through spatial and graphical methods, often supplemented with statistical analysis. More detailed methods include plume margin analysis and the application of mass flux and mass discharge techniques (Appendix C). All of these methods are designed to assess changes in source loading and/or aquifer assimilative capacity over time, and consequently, changes in the concentration, mass, or distribution of site COCs over time (Appendix C). Stable or decreasing trends in these metrics indicate an effective MNA remedy. Increasing trends may indicate that MNA is not an appropriate remedy.

Wisconsin DNR (2003) describes a method for evaluating plume stability using behavior of the plume margin, and consists of the following:

- Estimate ground water seepage velocity and contaminant velocity using Darcy's law and the application of a COC specific retardation factor (e.g., Fetter 2001);

- Determine the distance between the monitoring well closest to the edge of the contaminant plume (preferably, a clean sentinel well) and the nearest contaminated well along the contaminant flow path; and

- Based on the estimated COC velocity, determine the time frame that contaminant movement is likely to be detected between these two monitoring wells. Monitor contaminant concentrations (and optionally natural attenuation parameters) for that time period; the monitoring period should not be less than the time frame estimated from the ground water seepage velocity alone.

This analysis allows for a direct empirical assessment of whether the contaminant plume is stable, shrinking or increasing, and also forms the basis of the travel time component incorporated into Table 4 (Recommended Monitoring Well Sampling Frequency), contained in Section 7.1.

6.1.2 Contaminant Trends

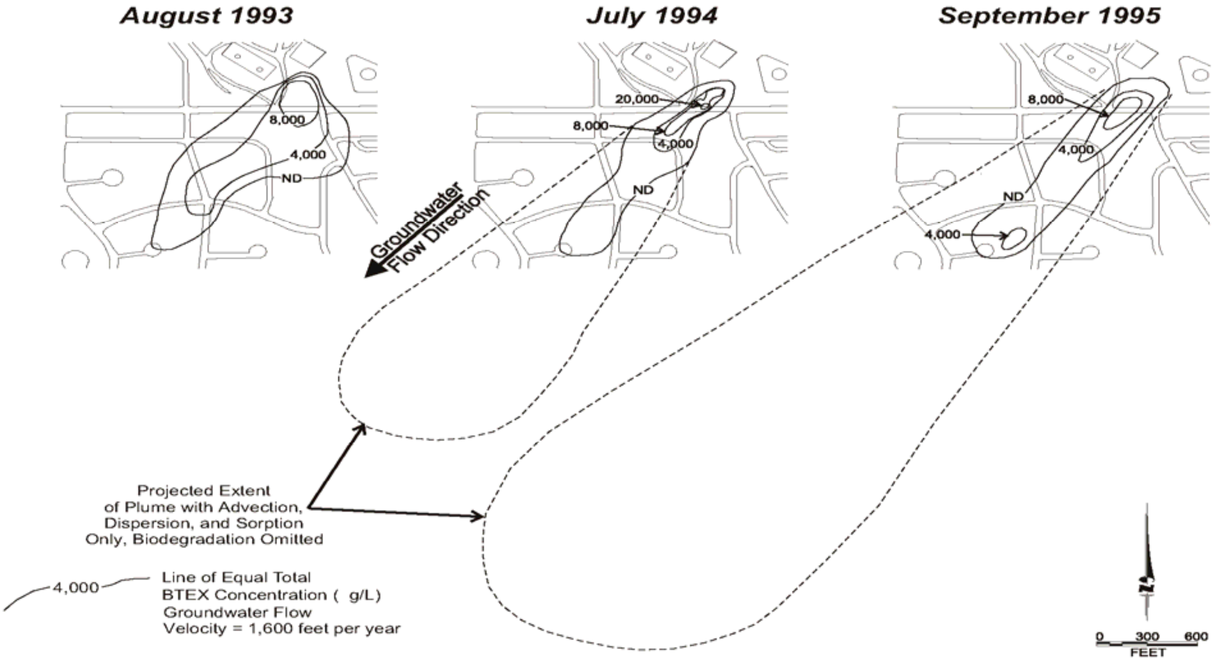
These methods are described by Wiedemeier et al. (2000), Wisconsin DNR (2003), USEPA (1998) and others, and consist of spatial plotting of plume geometry over time (alone or compared to modeled estimates of plume dimensions without COC degradation), and graphical analyses of COC concentrations at monitoring wells over time, or along the plume flow path with distance over time. As noted by Pope et al. (2004), data comparisons can be conducted by simply comparing measured values, calculated (or graphed) trends, or set values for contaminants or geochemical parameters.

6.1.2.1 Spatial Analysis

The concentration distribution of a contaminant plume is normally mapped using isopleths or contour lines (lines of equal concentration). In simple cases, these lines can be visually interpolated and drawn by hand. In more complex situations, numerical gridding techniques involving spatial statistical methods are typically used for this purpose (e.g., Golden Software Inc. Surfer). When such software is used, it is important to ensure that site hydrology and hydrogeology are accommodated; for example, contouring of water table conditions cannot occur across surface water features, and discrete vertical monitoring zones must be mapped separately.

Projection of contaminant distribution over time, with or without attenuation, retardation and/or biodegradation, can be performed with a wide range of commercially available software or freeware. In many cases, simple analytical solutions can be used to calibrate existing conditions and estimate future plume behavior; e.g., AT123D (Yeh 1981), BIOSCREEN (Newell et al. 1996), BIOCHLOR (Aziz et al. 2000, 2002), REMChlor (Falta et al. 2007), NAS (Kram, et al. 2007). Numerical flow and solute transport modeling (e.g., MODFLOW (Harbaugh, 2005) / MT3DS (Zheng and Wang, 1999)) is normally required for sites involving multiple sources, hydrogeologic conditions that vary significantly horizontally or vertically, or where dynamic conditions (e.g., pumping, seasonal recharge) must be accommodated. These software applications either plot maps of contaminant distribution directly, or provide output grid files that can be contoured. Ricker (2008) provides a straightforward method to evaluate changes in plume mass over time using volume calculations applied to mapped contaminant concentration distributions.

Figure 4
Comparison of Projected Versus Actual Plume Migration



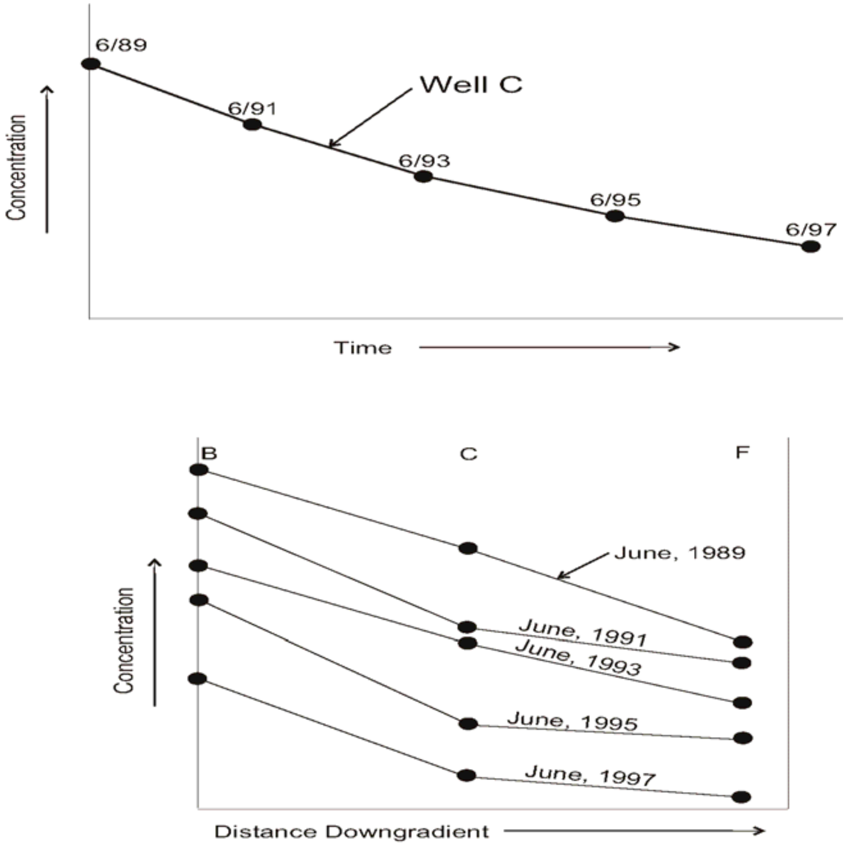
Source: Wiedemeier et al., 2000

Figure 4 is an example of the monitored behavior of a benzene, toluene, ethylbenzene, and xylenes (BTEX) plume over time (solid contour lines) compared to projections of plume migration assuming only physical transport processes (dashed lines). In this case, it appears as if steady state conditions have been achieved relative to contaminant mass loading and aquifer attenuation (biodegradation) capacity, resulting in a stable plume configuration.

6.1.2.2 Graphical Analysis

A straightforward and necessary component of the evaluation of contaminant plume characteristics is the plotting of COC concentrations over time at each monitoring location, as well as the graphing of contaminant concentrations versus distance downgradient along the plume flow path over several sampling events. Examples of these types of plots, indicating decreasing COC concentrations and a shrinking contaminant plume are provided in Figure 5 below.

Figure 5
Contaminant Concentration Plots



Source: Wiedemeier et al., 2000

Data are compared to determine if temporal and spatial trends exist within the plume and in surrounding areas. Of particular interest are trends in contaminant and degradation product concentrations, electron acceptors and donors, oxidation-reduction potential, and other general geochemical indicators. For example, a decreasing trend in tetrachloroethene (PCE) compared to an increasing trend in trichloroethene (TCE) in the same transmissive zones may indicate degradation of PCE to TCE. Trends at individual sampling points or groups of sampling points may be compared to other sampling points, or to trends in other groups of sampling points. For instance, contaminant concentrations at individual sampling points may show different trends; but evaluating trends in data from all sampling locations in the plume will determine if the plume exhibits stability or reduction in contaminant concentrations (Pope et al., 2004). Similarly, data from a group of sampling points at the downgradient limits of a plume may be compared to data from previous sampling rounds to determine if the plume seems to be stable, shrinking, or expanding (as noted under Section 6.1.1).

Detailed examples of concentration versus time and distance plots, as well as important considerations regarding relationships between water level elevation and concentration, calculation of first-order decay rates (source and plume), and regression analysis are contained in Appendix B of Wisconsin DNR (2003) and USEPA 2002 (calculation of first order rate constants).

6.1.3 Statistical Tests

Statistical procedures and models can provide a formal, quantitative method for assessing the relationship of sample measurements to characteristics of the sampled system, for using sample data to make decisions, and for predicting future states of the sampled system. The need for application of statistical tests and the nature of the tests will vary as a function of site-specific conditions and data analysis requirements.

Statistical procedures are often used to evaluate the variability associated with data, and to use estimates of variability to guide decision making processes. For example, if multiple analyses are performed, statistical procedures can be used to express a measure of the analytical variability associated with a reported contaminant concentration (e.g., 4.9 mg/L +/- 3.2 mg/L, representing the 95% confidence limits on the mean value). Statistical methods are also available to facilitate analysis and comparison of trends by considering data variability through time. For instance, changes in contaminant concentrations over space or time can be used to calculate attenuation rates, and the variability associated with those rates can be quantified with confidence intervals about the rates. These confidence intervals can be used to determine the likelihood of attaining site-related remedial goals. If all values of the attenuation rate falling within the confidence intervals lead to predictions that site remedial goals will be attained in the desired time frame, then confidence that MNA can attain remedial goals is increased.

Implementing formal methods that compare data by taking into account data variability is especially important for decision making purposes. Gibbons (1994), Gibbons et al. (2009), Gilbert (1987) and Helsel (1995) contain extensive discussions of the issues concerning use of statistics in environmental and ground water monitoring. Detailed discussions of these points, as well as step-by-step guidance on calculations for the various types of comparisons mentioned above, are contained in USEPA (1992), USEPA (2000), and USEPA (2009).

There are limitations using statistical analysis with the small number of data sets typically available during the early years of an MNA program. Where such trend analysis tests are deemed appropriate, regression analyses, the Mann-Whitney U Test, the Mann Kendall Test (including Seasonal Kendall), and Sen's non-parametric test for the slope of a trend are widely applied (Hirsch et al. 1991; USEPA/USACE 2005). The Monitoring and Remediation Optimization Systems (MAROS) software developed for the Air Force Center for Engineering and the Environment (AFCEE; formerly Air Force Center for Environmental Excellence) provides a mature application of the Mann-Kendall Test along with a range of other decision tools specific to evaluation and optimization of a long term monitoring program (Aziz et al. 2006).

In most cases, statistical procedures should be used to estimate sampling and analytical variability associated with each COC and sampling point, so that periodic or sporadic increases in COC concentration due to natural variability do not trigger contingency planning. Gilbert (1987) and Chapters 18-22 of USEPA (2009) provide detailed descriptions of the relevant topics (prediction limits, control charts and confidence intervals). Appendix E provides guidance on selection of statistical methods and more details regarding the statistical tests outlined in the following text.

Regression analysis: This is a method in which a best fit theoretical curve is applied to the analytical data to estimate the underlying functional relationships (i.e., determine variables influencing concentration values), identify the rate of concentration change, and forecast future concentrations. Linear and exponential regression analyses are commonly used for this purpose (USEPA 2011), and the theoretical details supporting their use is provided in USEPA (1992, and 2009: Section 17.3).

Linear regression analysis offers advantages where magnitude is taken into account, can work with seasonality of data, and is generally easy to compute with readily available tools and software packages. Data outliers and significant skewness can bias or invalidate the results of a trend test, and also standard linear regression methods do not account for non-detects or missing data values at selected sampling events (USEPA 2009). Regression is a parametric analysis method with several assumptions, including that regression residuals (difference between predicted regression model value and each concentration data point) are statistically independent, have constant variance, and that errors are normally distributed. The EPA 2009 guidance document notes that a minimum of 8 to 10 measurements are generally necessary to compute a linear regression.

Nonlinear regression models (e.g., exponential, logarithmic, polynomial, moving average) can be applied to predict the data trends. Nonlinear regression models utilize some form of data transformation that provides a more accurate fit for the regression line. Exponential regression is commonly utilized for petroleum compounds, since it correlates well with 1st order decay processes. Qualifications for exponential regression include the need for several rounds of data, general inability to discern slower trends, and a need for calculation of probability limits around the trend line to document that estimated significance is parametric. The EPA 2009 guidance document discusses the parameters and details for the data transformations applied for nonlinear regression models.

When examining the results of regression analysis, some of the parameters that can be calculated to determine how well the field data fits the regression equation include: the correlation coefficient (r) and the Pearson product moment correlation coefficient (R^2). The correlation coefficient (r) provides a quantitative measure of the degree of association of the parameters; that is, the strength of that association. For the Pearson correlation coefficient (R^2) calculation, the closer the R^2 value is to one (e.g., greater than 0.9 or 0.95), the better the regression can be accepted as being qualitatively useful. EPA (2002) outlines examples where the r and R^2, along with other regression statistical factors, are used for MNA assessment.

Mann-Kendall: This is a non-parametric test (Gilbert, 1987) for linear trend analysis based on the idea that if an increasing trend really exists in a data set, then the sample taken first from any randomly selected pair of measurements should on average have a lower concentration than the measurements collected at a later point. Conversely, for MNA review, this principle is applicable in the determination of a decreasing trend, where the sample first taken from a pair of measurements should on average have a higher concentration than a later collection point. The method scores pairs of measurements against each other where an earlier sample concentration greater than the latter sample point is assigned a value of +1, and an earlier sample concentration less than the latter point is assigned a value of -1 (if both sample concentrations are identical they are assigned as 0). After the scoring of data pairs, the totals are summed to produce the Mann-Kendall statistic (*S*), for which a positive value represents an upward (increasing) trend and a negative value represents a decreasing trend. S values around 0 indicate the lack of a trend. However, a calculation of coefficient of variation (CV) can be used to assess scatter in the data, such that if the calculated CV is equal to or less than unity the Mann-Kendall "no−trend" result can be used to support a stable plume hypothesis. Gilbert (1987) notes that a minimum sample size of 10 is normally required for application of the Mann-Kendall test.

In the Mann-Kendall, only the relative magnitudes of the concentration values compared to each other are used in the computation of the S value. Since actual concentration values are not used, the test is independent of absolute concentration results (i.e., not affected by gross data errors or outliers). Non-detects are assigned a common value lower than any of the detected measurements. The advantages of the test include no assumption of normality or other distribution (i.e., the test is non-parametric), ability to incorporate non-detect values, allowance for missing data, and ease of computation. Disadvantages include inability to account for seasonality (important for sites with widely varying water table fluctuations and contaminants with low solubility), and since absolute magnitude is not taken into account, large concentration changes that have a root cause outside of natural attenuation process (e.g., remedial action or source release) can be masked.

A Seasonal Kendall Test (Hirsch et al., 1982; Hirsch and Slack, 1984) is available to address situations where seasonal fluctuations are significant (Gilbert, 1987). The Seasonal Kendall test is a modification of the Mann–Kendall test that addresses short-term seasonal variability and allows evaluation of overall trends. In a seasonal Kendall test, the Mann–Kendall test is applied to each season (e.g., quarter) separately and then the results are combined for an overall test. Each season individually may show a positive trend, none of which is significant, but the overall seasonal Kendall statistic can be significant. The test has the advantages of the Mann–Kendall test, but is considered more representative of environmental monitoring conditions because it removes short-term variability caused by seasonality. If seasonal effects are identified during site characterization, or in the early stages of the long term monitoring program, continued quarterly monitoring may be warranted to support the frequency selected for LTM.

The Mann-Kendall test equations can be applied relatively simply in a spreadsheet, and a variety of organizations have well developed software, such as the Wisconsin DNR and the AFCEE

MAROS software, which both provide more robust and sensitive application of the Mann-Kendall test incorporating modifications to account for seasonal variations.

Mann-Whitney U: Is a statistical test prefaced on the theory that if two samples are drawn from the same population, the probability of the first sample being larger than the second sample is exactly 0.5, and if every sample is compared to another sample and the final probabilities arising from these comparisons do not "average out" to approximately 0.5, then it is likely that factors affecting the two samples are not the same (Cheney, 1983). For ground water analytical data, the representation would be that the factors resulting in the concentrations within the two samples from the same well may not be the same. For this test, the actual sample values are not used in the derivation of the statistical value, rather the values are ranked from either highest to lowest or lowest to highest. A Mann-Whitney statistic (U) is calculated from the ranking system, and all U results equal to or less than 3 represent a decreasing trend.

A specific adaptation of the Mann-Whitney U test (Mann and Whitney, 1947) to determine ground water data trends has historically been used by the Department. This adaptation uses eight consecutive quarterly events. Modifications of the Mann-Whitney U test are available that allow for analysis of larger datasets. For certain sites, either the Mann-Whitney U or modifications may represent an appropriate statistical test for trend analysis.

Sen Test: Sen (1968) developed a nonparametric estimator of trend that is useful for ground water monitoring applications. The method is robust to outliers, missing data, and non-detects, and can be used with small sample sizes (minimum of 8) (Gibbons et al., 2009). Sen's method for the estimation of slope requires a time series of equally spaced data. Sen's method proceeds by calculating the slope as a change in measurement per change in time:

$$Q = (x_i' - x_i) / (i' - i)$$

where:

Q = slope between data points xi' and xi
x_i' = data measurement at time i'
x_i = data measurement at time i
i' = time after time i

Upon calculation of slope (Q), Sen's estimator of slope is simply given by the median slope:

Sen's Estimator of Slope = median slope = Q'

$= Q\,[\,(N'+1) / 2\,]$ if N' is odd

$= (\,Q\,[N' / 2\,] + Q\,[\,(\,N'+2\,) / 2\,]\,) / 2$ if N' is even

where: N' = number of calculated slopes

Sen's Method also allows determination of whether the median slope is statistically different from zero. A confidence interval is developed by estimating the rank for the upper and lower confidence interval and using the slopes corresponding to these ranks to define the actual confidence interval for Q'.

Non-Detect (ND) Results: In conducting statistical analyses of analytical data, laboratory non-detect (ND) sample points are commonly encountered, and the various statistical analysis methods typically provide a specific manner in which ND values are to be used within that method. Prior to initiating any trend test on data, the investigator should identify how ND values are to be processed, and complete a conversion of the ND results within the analytical data table to method applicable values. As a general point of understanding, care needs to be taken when choosing to assess ND values between the method detection limit (MDL), the quantification limit (QL), and the reporting limit (RL). Detailed guidance on the applicability of each of these types of limits is provided in USEPA (2009).

An example of the affect of ND on linear regression is provided by USEPA (2009), where it is noted that there should be few ND values in the data set, since the concentration trend should be based on reliably quantified measurements. The presence of many NDs may result in a trend that is an artifact induced by changes in detection/quantitation/reporting limits over time or across laboratories. For example, a decreasing trend associated with numerous NDs may simply be a reflection of the fact that analytical methods have improved over time, resulting in lower RLs.

6.1.4 Mass Flux and Mass Discharge

Determining the mass flux and mass discharge may be used to evaluate the applicability of MNA. Quantifying the movement of contaminant mass through a unit cross-section at a site (mass flux) or through a cross-section that fully encompasses a plume emanating from a site (mass discharge) provides estimates of source strength, contaminant plume stability, and attenuation capacity of the aquifer. The evaluation of mass flux and mass discharge help to show the combined effects of concentration and ground water velocity on contaminant movement. The most common approach to achieve this objective is the use of transects, in which individual monitoring points are used to integrate concentration and flow data, although well capture/pump test and passive in-well flux meter methods are available (ITRC 2010). Over time, collection of these data from fixed transects or monitoring points can be assessed in a manner similar to that conducted for concentration data alone from monitoring wells, to evaluate the effectiveness of attenuation processes. The Mass Flux Toolkit software is available to simplify the mass discharge calculations when using the transect approach (Farhat et al. 2006). Appendix C provides useful information regarding spatial mass flux calculations over time.

6.2 Secondary Line of Evidence - Geochemical Conditions

The geochemical conditions that prevail in the aquifer serve as indicators of the occurrence of degradation or attenuation of contaminants. Understanding aquifer geochemical conditions is important for the determination of aquifer capacity to degrade contaminants. Geochemical parameters and their significance are discussed below.

6.2.1 Organics

Biodegradation of organic compounds in the subsurface results in measurable changes in the ground water chemistry. By measuring these changes, it is possible to document and qualitatively assess the importance of natural attenuation (natural remediation) of contaminants at a given site. The geochemical parameters described below are indicators of the occurrence of biodegradation of contaminants in the subsurface by biologically mediated processes. Appendix A of this document provides additional information regarding degradation mechanisms for organic constituents.

In general, reductive dechlorination occurs by sequential dechlorination from PCE to TCE to cDCE to VC to ethene. During this process, the chlorinated hydrocarbon is typically used as an electron acceptor (not as a source of carbon), and chlorine atoms are sequentially removed and replaced with hydrogen atoms. In this case, biodegradation is an electron-donor limited process; i.e., it is controlled by the availability of a source of carbon (for example, natural organic matter in the aquifer matrix). Chlorinated hydrocarbons can also undergo biodegradation though use as an electron donor, in which case the rate of reductive dechlorination is controlled by the availability of electron acceptors (e.g., nitrate, ferric iron, sulfate), or through cometabolic processes. Specific chemical indicator parameters are necessary to evaluate these processes, and form the basis for an understanding of reductive dechlorination processes at a site; they also represent an important component of the protocol for long term performance monitoring.

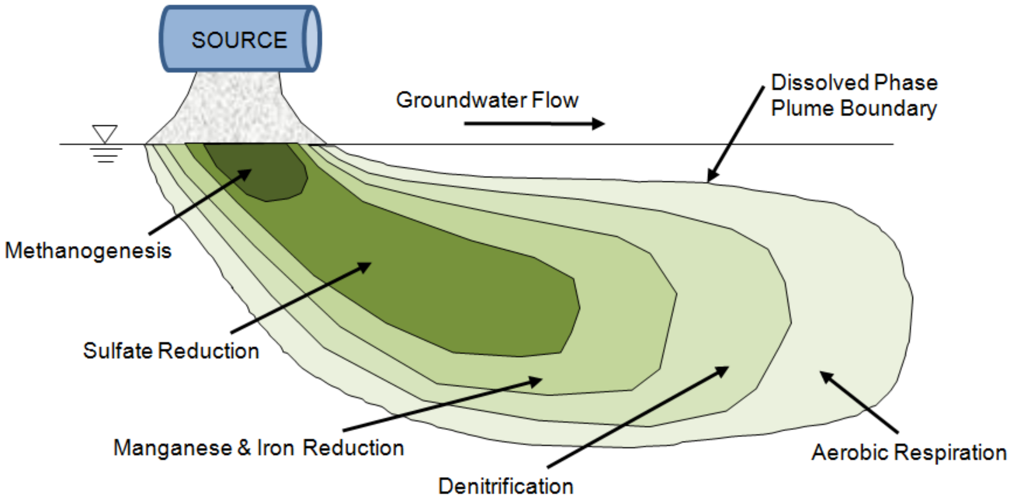
6.2.1.1 Terminal Electron Acceptors (TEA)

Degradation of organic contaminants in ground water is accomplished by biochemical oxidation-reduction reactions where one compound (electron donor) loses electrons and is oxidized and the other compound (electron acceptor) receives electrons and is reduced. If the organic contaminant is oxidized, some other compound must be reduced. The compound that is reduced (receives or gains electrons) is termed a Terminal Electron Acceptor (TEA). Oxygen, nitrate, sulfate, and ferric iron (Fe^{+3}) minerals in the aquifer can serve as TEAs. The significance of the presence of these TEAs as geochemical footprints of microbial degradation is briefly described below. Isoconcentration maps or distribution maps for all TEAs for each round of sampling would provide indications of the changes in contaminant plume configuration and allow interpretation of data in reference to degradation rates of contaminants in the aquifer.

The changes in TEAs due to progression in biological degradation in a ground water dissolved phase contamination plume are illustrated conceptually in Figure 6. As illustrated in the figure, available oxygen is consumed by microorganisms during the aerobic degradation resulting in anaerobic conditions in the core of the contamination plume and a zone of oxygen depletion along the outer margins of the plume. After dissolved oxygen has been depleted in ground water, available nitrate (NO^{-3}) will be used as an electron acceptor for anaerobic biodegradation. Nitrate reduction is followed by the reduction of Mn^{+4} and Fe^{+3} (both are electron acceptors and are reduced to Mn^{+2} and Fe^{+2}, respectively). When strong reducing conditions prevail in ground water after the depletion of oxygen, nitrate, and ferric iron, the available sulfate can be used as an electron acceptor for anaerobic degradation (refer to Table 3). Under very strong reducing conditions, methanogens (a group of anaerobes) use CO_2 as electron acceptor for biodegradation and produce methane.

Figure 6

Conceptualization of TEA Zones in Groundwater Contamination Plume



Aerobic

Dissolved Oxygen (DO) is the most preferred terminal electron acceptor (TEA) relative to others (nitrate, ferric iron, sulfate) used by microorganisms for the biodegradation of contaminants. If DO is present in ground water at concentrations above 0.5 mg/L, aerobic biodegradation is the predominant microbial process. Naturally inhabiting microorganisms in ground water couple the oxidation of an electron donor (usually organic carbon in contaminants) with the reduction of electron acceptors. In doing so, microorganisms utilize the most thermodynamically favored electron acceptor. In the case of aerobic biodegradation of fuel constituents, microorganisms utilize available oxygen as they biodegrade BTEX and other constituents, and any oxygen entering this zone is rapidly depleted. Thus, an inverse correlation between DO and BTEX concentrations is an indication that aerobic biodegradation is occurring in the subsurface.

Anaerobic

Dissolved Oxygen (DO) At DO concentrations below 0.5 mg/L, anaerobic microbes can function and reductive dechlorination can occur. After depletion of DO, anaerobic microorganisms will utilize nitrate as the TEA, followed by ferric iron (Fe^{3+}), then sulfate, and finally carbon dioxide. Measurements of DO concentrations in monitoring wells during each sampling event at a contaminated site provide essential information regarding the availability of geochemical conditions to support reductive dechlorination through microbial degradation processes.

Nitrate is the next most preferred TEA after DO. After DO has been depleted in the contaminant zone, nitrate will be used as TEA for anaerobic biodegradation of organic carbon in contaminants through denitrification. For reductive dechlorination to occur in the subsurface, nitrate concentrations in the contaminated portion of the aquifer must be less than 1.0 mg/L. Because nitrite (NO_2) is an unstable intermediate product of NO_3 reduction, presence of measurable concentrations of NO_2 in ground water is an indication of NO_3 reduction.

In ground water with high BTEX concentrations and anaerobic conditions, microorganisms capable of biodegrading BTEX will consume nitrate and thus deplete nitrate concentrations. Thus, an inverse relationship between BTEX concentrations and nitrate can be expected.

Ferric Iron (Fe^{3+}) is used as a TEA during anaerobic biodegradation of organic carbon. During this process, ferric iron is reduced to ferrous iron (Fe^{2+}), which may be soluble in water. Thus, a positive correlation between ferrous iron concentration in ground water and BTEX compounds is an indication of anaerobic biodegradation.

Sulfate (SO_4^{-2}) can be used as a TEA for anaerobic degradation of organic contaminants. Under strongly reducing conditions and after available oxygen, nitrate and ferric iron have been depleted, sulfate will be used by microorganisms as a TEA. This process results in the generation of sulfide which may precipitate from solution as ferrous sulfide. For example, under sulfate-reducing conditions and in the presence of high BTEX concentrations, sulfate demand will be high and sulfate concentrations will be depleted relative to concentrations up gradient of the BTEX contamination zone.

6.2.1.2 Degradation By-Products and other Indicators

Alkalinity in the ground water is primarily due to the presence of carbon dioxide. Carbon dioxide is produced by the metabolism of microorganisms. Increasing concentrations of carbon dioxide increase the alkalinity in the ground water. Measuring alkalinity in each round of ground water sampling and plotting the concentrations as isoconcentration contour maps would provide indication of the progress of biodegradation within the contamination plume.

Oxidation-Reduction Potential (ORP) in ground water is a measure of the oxidation-reduction (redox) state of the aquifer, and is an indicator of the relative tendency of the ground water to accept or transfer electrons. The ORP values in ground water commonly vary from -400 mv to as much as 800 mv, but certain biodegradation processes can occur only within a specified range of ORP conditions. Lower ORP values in ground water suggest the occurrence of biodegradation. A comparison of ORP values from the upgradient area of a site with the ORP values in the ground water contamination plume will indicate the areas where biodegradation is occurring.

Table 3
Geochemical Parameters Important to Anaerobic Degradation

Geochemical Parameter / Analyte	Data Use	Trend in Analyte Concentration During Biodegradation	Values Indicative of Degradation	Terminal Electron Accepting Process Causing Trend
Dissolved Oxygen	Concentrations less than about 0.5mg/L generally indicate an anaerobic pathway.	Decreases	< 0.5 mg/L	Aerobic Respiration
Nitrate	Electron acceptor for microbial respiration in the absence of oxygen	Decreases	< 1 mg/L	Denitrification
Fe^{2+}	Indication of Fe^{3+} reduction during microbial degradation of organic compounds in the absence of dissolved oxygen, nitrate, and Mn(IV).	Increases	> 1 mg/L	Fe^{3+} Reduction
Sulfate(SO_4^{2-})	Electron acceptor for anaerobic microbial respiration	Decreases	< 20 mg/L	Sulfate Reduction
Methane	The presence of methane suggests organic carbon degradation via methanogenesis	Increases	> 0.5 mg/L	Methanogenesis
Alkalinity	General water quality parameter used (1) to measure the buffering capacity of ground water, and (2) as a marker to verify that all site samples are obtained from the same ground water system.	Increases	> 2 times background	Aerobic Respiration, Denitrification, Reduction. Fe^{3+} Reduction, Sulfate Reduction
Oxidation reduction potential (ORP)	The ORP of ground water reflects the relative oxidizing or reducing nature of the ground water system. ORP is influenced by the nature of the biologically mediated degradation of organic carbon.	Decreases	< -100 mV	Aerobic Respiration, Denitrification, Reduction, Fe^{3+} Reduction, Sulfate Reduction, Methanogenesis
pH	Aerobic and anaerobic processes are pH-sensitive		Range of 5 to 9	
Chloride	General water quality parameter used as a marker to verify that site samples are obtained from the same ground water system. Final product of chlorinated solvent reduction	Increases	> 2 times background	Reductive Dechlorination or Direct Oxidation of Chlorinated Compound

Source: Adapted from Guidance on Developing a Monitored Natural Attenuation Remedial Proposal for Chlorinated Organics in Ground Water, North Carolina Hazardous Waste Section, October 4, 2000

pH, Temperature and Conductivity: The pH of ground water influences the presence and activity of the microbial population in ground water. Microorganisms capable of degrading aliphatic hydrocarbons and petroleum hydrocarbons generally prefer pH values varying from 6 to 8 standard units. Ground water temperature directly influences the metabolic activity of microorganisms in ground water. The conductivity of ground water is directly proportional to the ions in solution.

Chloride is released into ground water during the biodegradation of chlorinated hydrocarbons dissolved in ground water. This results in elevated concentrations of chloride in the contaminated zone relative to the up gradient ground water. Because of the conservative nature of chloride (chlorides do not enter into any chemical reactions and physical processes control their migration in ground water), chloride concentrations in ground water may be used as an indicator of biodegradation where source contaminant concentrations are in the parts per million range.

Degradation Products

Natural attenuation of chlorinated compounds is accompanied by production of degradation products. Different types of reactions produce different degradation products and the presence of these degradation products indicate the types of degradation reactions. Thus, the presence of specific dechlorination chain of parent and degradation products can be used as direct evidence that natural attenuation is occurring at a site (see Appendix A). It is important to document the organic compound species present at the source, in order to evaluate whether the presence of daughter products in downgradient areas is the result of ongoing biodegradation processes or simply the migration of source constituents.

It should be noted that abiotic reductive dechlorination represents a degradation pathway that may be important in some cases, and similar to the reaction of chlorinated ethenes with zero-valent iron, often does not produce the typical intermediate byproducts associated with biological degradation. As noted by Stroo and Ward (2010), USEPA (2009) and others (e.g., Ferrey et al., 2004), abiotic transformation of a range of chlorinated compounds has been documented with naturally occurring metal sulfides, including pyrite, troilite, mackinawite, and magnetite. The overall degradation pathway is referred to as “biogeochemical transformation” (AFCEE et al., 2008), because the reactive mineral may be formed as a result of both biological and chemical processes.

6.2.2 Metals & Radionuclides

Metals and radionuclides are not destroyed during attenuation. Metals and radionuclides are attenuated predominantly by immobilization in the aquifer by processes including adsorption, precipitation and decay (the latter in the case of radionuclides only). With the exception of radioactive decay, all these processes are reversible. Through adsorption and precipitation processes, the metal and radioactive contaminants partition into immobilized forms.

A thorough understanding of the geochemistry of the aquifer system and the behavior of contaminants under these conditions is crucial for evaluating the viability of natural attenuation for sites contaminated with metals and radionuclides. The geochemistry primer presented in Section 2.1 of ITRC (December 2010) publication "A Decision Framework for Applying Monitored Natural Attenuation Processes to Metals and Radionuclides in Groundwater" provides a succinct summary of the role of geochemical processes in the attenuation of metals and radionuclides, and Appendix A provides an overview of adsorption, precipitation and transformation processes (Ford et al., 2007). As a secondary line of evidence, it is important to demonstrate whether the metal or radionuclide contaminant in ground water is partitioning from the aqueous phase into the solid phase (precipitation and adsorption) to become immobilized in the aquifer. Further, the rate of attenuation of metal/radionuclide contaminant should be sufficient to account for the stability of the contaminant plume and the capacity of the aquifer must be sufficient to ensure the stability of the contaminant plume for the MNA to be a viable remedial option for a site where ground water is contaminated with metals or radionuclides.

The solubility, adsorption, and bioavailability of metals and radionuclides depend primarily on metals speciation (ion pairs or more complicated aqueous complexes) because most dissolved metals and radionuclides do not occur as independent ions in ground water. Uranium is an example which forms stable aqueous complexes by binding strongly with hydroxyl (OH^-), carbonate (CO_3^{-2}), and phosphate (PO_4^{-3}) ions. The aqueous speciation of uranium is a function of the concentrations of these ions in ground water, concentration of uranium and the pH. For example, at higher pH, carbonate (CO_3^{-2}) is the dominant species and readily complexes with uranium. ORP is another influencing factor in aqueous speciation because oxidation reduction reactions (transfer of electrons from one chemical species to another) change the oxidation state of the metals.

The potential for adsorption (through electrostatic forces) of contaminants onto the aquifer materials is dependent on the aquifer mineralogy and pH. The pH of ground water influences both aqueous speciation of metals and radionuclides and the surface properties of aquifer minerals.

Ionic strength (correlated with salinity, conductivity and total dissolved solids) of the ground water also influences adsorption of metals and radionuclides because the ionic strength affects the electrostatic surface properties of aquifer minerals.

Precipitation and dissolution of minerals depend not only on the chemical composition of the ground water and aquifer mineralogy, but also on the other reactions that are occurring in the aquifer. Use of ground water analyses (for major cations and anions) and contaminant concentrations to estimate saturation indices is valuable in making predictions as to whether the contaminant is likely to be precipitating.

Modeling should be performed to fully evaluate the geochemical conditions as secondary lines of evidence for MNA as a potential remedial option. These include the mass balance calculations, geochemical speciation calculations (includes saturation indices), as well as predictive fate and transport models. Aqueous speciation programs estimate concentrations of each contaminant species at a given pH and redox potential through consideration of bulk ground water geochemistry data (e.g., major cations, anions, other pertinent dissolved constituents, contaminant concentrations). The most widely used of these programs include PHREEQC (Version 2) and MINTEQA2 available at:

http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/index.html

http://www.epa.gov/ceampubl/mmedia/minteq/

The saturation indices output provided by these programs is also useful for making interpretations concerning what mineral is saturated or oversaturated (likely to precipitate and hence immobilize) in the aquifer system. Mass balance calculations are useful for the evaluation of MNA based on the masses of metal or radionuclide contaminants, their distribution and masses of reactants that are required to attenuate contaminant mass. Reaction path models combine speciation calculations, mass balance calculations to model the chemical reactions (between ground water and aquifer minerals) in an aquifer system and include all attenuation mechanisms. For more information visit:

http://crustal.usgs.gov/projects/aqueous_geochemistry/reaction_pathways.html

The reaction path models can be used to identify dominant attenuation mechanisms under different scenarios. It can also be used to determine the sensitivity of attenuation mechanisms to various geochemical parameters (e.g., changing pH). Thus, such models are useful for evaluating the long term stability of immobilized metal contaminants in the aquifer.

EPA’s three volume publication (USEPA, 2007a; 2007b; 2010) focuses on the natural attenuation processes of nine inorganics (including seven metals) and twelve radioactive substances. These references (described briefly below) should be consulted for a thorough understanding of the natural attenuation mechanisms of metals and radioactive substances and the approach for documenting these mechanisms.

> The first volume contains the technical requirements for assessing the potential applicability of MNA as part of a ground water remedy for plumes with non-radionuclide and/or radionuclide inorganic contaminants. Volume 1 provides a review of the physical and biogeochemical processes (e.g., sorption, precipitation, transformation, etc.) that govern contaminant transport in ground water.
>
> The second volume addresses natural attenuation of arsenic, cadmium, chromium, copper, lead, nickel, nitrate, perchlorate, and selenium and the data requirements to be met during site characterization.
>
> The third volume covers natural attenuation of radionuclides including americium, cesium, iodine, neptunium, plutonium, radium, radon, technetium, thorium, tritium, strontium, and uranium, and data requirements to be met during site characterization.

In addition, the International Atomic Energy Agency (IAEA, 2006) provides guidance relative to MNA at radioactively contaminated sites in terms of migration and retention mechanisms and the geochemistry of uranium, neptunium, technetium, cesium, strontium, thorium, radium, and lead.

Appendix A of this NJDEP MNA Technical Guidance Document provides additional information regarding stabilization mechanisms for inorganic constituents.

6.3 Tertiary Line of Evidence - Microbiological and Isotopic Studies

Microbial studies are often an additional line of evidence used to evaluate natural attenuation processes. Laboratory testing is conducted to assess whether the indigenous bacteria are capable of degrading the contaminants, or to document the isotopic fractionation resulting from microbiologically mediated reductive dechlorination. Data generated from the studies are used to directly support the presence of natural attenuation processes at the site and the ability to degrade the COCs.

EPA guidance notes that such studies are useful for sites with contaminants that do not readily degrade through biological processes, or that transform into more toxic and/or mobile forms than the parent contaminant (USEPA, 1999). Microbial studies are more commonly performed at contaminant sites with non-petroleum compounds and inorganics. Although microbial studies are less typically conducted at sites with petroleum compounds, such assays may be beneficial when the site appears to be recalcitrant to biodegradation.

Laboratories that provide analytical services to support microbiological and isotopic studies include, but are not limited to Sirem, Enoveo, Microbial Insights, Microseeps, and the Waterloo Environmental Isotope Laboratory (EIL).

6.3.1 Microbiological Tools

Molecular biological tools (MBTs) are defined as techniques that target biomarkers (specific nucleic acid sequences, peptides, proteins or lipids) to provide information about organisms and processes relevant to the assessment or remediation of contaminants (Stroo and Ward, 2010). MBTs have the potential to provide rapid and reliable measures for both a second and third line of evidence for natural attenuation and in situ bioremediation: evidence that indigenous microorganisms have the potential to transform or degrade contaminants and evidence that transformation or degradation is occurring in the field (NRC, 2000; Smets and Pritchard, 2003; USEPA, 1998).

Significant recent advances in the use of MBTs relative to the evaluation of chlorinated solvent plumes include (Stroo and Ward 2010):

- development of polymerase chain reaction (PCR) methods to identify and quantify the presence of specific DNA sequences, particularly the 16S ribosomal DNA of Dehalococcoides (genus of solvent degrading microorganisms)
- discovery of probes for trichloroethene reductase (tceA) and vinyl chloride reductase (vcrA and bvcA), allowing direct measurement of the potential for TCE dechlorination and for complete dechlorination to ethene
- development of enzyme probes to detect oxygenase enzymes capable of aerobic degradation of some solvents

The use of MBTs has also been applied to understand the degradation of recalcitrant fuel constituents, such as MTBE (e.g., Ferreira et al., 2006). Common MBTs traditionally used to evaluate sites include: (1) phospholipid fatty acids analysis (PLFA), used to provide quantitative information about overall microbiological community structure, microbial “health” and quantitative information about the biomass present; (2) denaturing gradient gel electrophoresis (DGGE), used to identify specific organisms, such as dechlorinators, and to evaluate microbial diversity; and (3) terminal restriction fragment length polymorphism (T-RFLP), also used for screening microbial diversity. Stroo and Ward (2010) note that the use of these tools has declined with the development and commercialization of quantitative PCR.

6.3.2 Isotopic Studies

Compound-specific isotopic analysis (CSIA) can be used as a powerful tool for monitoring, assessing and validating in-situ biodegradation of petroleum hydrocarbon compounds and chlorinated organic compounds in ground water. These compounds contain molecules with both heavier (e.g., C^{13}, Cl^{37}, O^{18}, H^{2}) and lighter (C^{12}, Cl^{35}, O^{16}, H) isotopes. During chemical and biological reactions, molecules with lighter isotopes tend to be consumed faster resulting in enrichment of the molecules with heavier isotopes in the unreacted substrate. This preferential enrichment of isotopes is called fractionation. Significant fractionation occurs in biological oxidation, biological reduction, abiotic degradation, in-situ chemical oxidation, and in-situ chemical reduction. Generally, no fractionation occurs in dilution, volatilization and sorption. The degree of fractionation is a function of degradation mechanisms, rate of degradation and fraction of compound degraded. The recent advances facilitate the determination of stable isotopic compositions of individual compounds at ppb concentrations in ground water. For full details of using compound-specific isotopic analysis as a tool in evaluating the biodegradation of organic compounds, the investigator is advised to refer to the USEPA publication “A Guide for Assessing Biodegradation and Source Identification of Organic Ground Water Contaminants using CSIA" (Hunkeler et al., 2008). Appendix B provides a pertinent excerpt from the referenced document.

During degradation, fractionation occurs between residual chlorinated compounds and their degradation products. Therefore, measurement of isotope ratios can provide evidence of in-situ biodegradation. For example, heavier isotope (Cl^{37}) enrichment occurs in the parent compound during the sequential degradation of PCE to ethane. Various studies have indicated that the enrichment factors increase with each step in the sequence from PCE to TCE, TCE to cis-DCE, cis-DCE to vinyl chloride, and vinyl chloride to ethane. Similarly, the heavier isotopes of oxygen (O^{18}) and hydrogen (H^{2} or deuterium) are enriched in the residual MTBE during its degradation to TBA (USEPA, 2005 and USEPA, 2007).

6.4 Protective Ground Water Remedies with Non-decreasing Levels of Ground Water Contamination

In accordance with Attachment 2 of the Department’s Issuance of Response Action Outcomes (RAO) guidance, the investigator may vary from the requirement to demonstrate a decreasing ground water contaminant trend, provided that certain conditions are met. This variance is generally applicable to historic discharges with ground water concentrations that have reached asymptotic levels. Please consult the referenced guidance document for more information.

7 REMEDIAL ACTION PERMIT FOR GROUND WATER WITH LONG TERM MONITORING

Once the source of ground water contamination has been addressed and it has been demonstrated that MNA is an appropriate remedial alternative, the investigator shall propose a Classification Exception Area (CEA) if not already established (N.J.A.C. 7:9C-1.6), and apply for a Remedial Action Permit for Ground Water (RAP-GW). Please refer to the Instructions for the application of this permit for detailed information regarding the application process. The permit requires establishing a long term monitoring (LTM) program. The following components of this Section have been developed to assist with designing the LTM program required under the permit.

Primary considerations used to develop the LTM Program include the following:

- Potential for human and ecological exposure to the ground water contamination;
- Ambient ground water quality of the area resulting from both human activities and natural conditions;
- Physical and chemical characteristics of the COCs;
- Hydrogeologic characteristics of the aquifer;
- Vertical and horizontal extent of the ground water contamination; and
- Stability of the plume

These considerations may be demonstrated using a CSM that outlines the fate and transport of the contaminants.

Components of the LTM program discussed in this technical guidance include monitoring frequency, analytical parameters, and selection of appropriate monitoring well array. The long term viability of MNA is assessed through periodic performance evaluations. If, during the LTM program, it is determined that MNA is no longer a protective remedy, the investigator must evaluate and implement an alternative remedial action (N.J.A.C. 7:26E-6.3(e)3ii). Similarly, USEPA policy requires implementation of contingency remedies if the MNA remedy is determined to be no longer protective of human health or the environment.

7.1 Long Term Monitoring Program

Monitoring required under the RAP-GW serves two purposes: (1) to evaluate the long term viability of the MNA remedy (i.e., performance well monitoring), and (2) to ensure protectiveness of the MNA remedy to potential receptors (i.e., sentinel well monitoring). Development of the monitoring schedule should incorporate both of these goals as outlined in Table 4, and as subsequently described in more detail.

Performance Monitoring Well Frequency

The monitoring frequency outlined in Table 4 has been designed to evaluate the continued viability of MNA as a protective remedy. The long term monitoring consists of more frequent sampling during the early stages to confirm predicted contaminant degradation rates, and a reduction to less frequent sampling during later stages if degradation proceeds as predicted. The technical basis for the monitoring concepts (travel time) and frequency (annual minimum)

Table 4
Recommended Monitoring Well Sampling Frequency

Situation	Performance Well Sampling Frequency	Sentinel Well Sampling Frequency	Reporting Schedule
Permit issued	Annual years 1-4 *	½ travel time to nearest receptor or annual, whichever is more frequent	With CEA Biennial Certification
After 4 years	Biennial years 5-8 *	½ travel time to nearest receptor or biennial, whichever is more frequent	With CEA Biennial Certification
After 8 years	**BTEX:** Every 8 years for the remainder of the permit. **Contaminants other than BTEX > 10X GWQS:** every 4 years **Contaminants other than BTEX < 10X GWQS:** every 8 years for remainder of the permit	½ travel time to nearest receptor or the same frequency as the performance wells, whichever is more frequent	With next scheduled CEA Biennial Certification

*** Progression through this sampling schedule is appropriate only if contaminant degradation is occurring as predicted during each monitoring event, and the remedy remains protective of receptors. If contaminant degradation is not occurring as predicted, the applicability of the MNA remedy must be revaluated in accordance with the MNA guidance.**

established in this table are contained in NJDEP (2003), Wisconsin DNR (2003), and McHugh et al. (2011).

The investigator may, with proper justification, propose a monitoring frequency that differs from the frequency outlined in Table 4 (e.g., Wehrmann et al. 1996). For instance, a biennial monitoring program may have been initiated prior to applying for a RAP-GW. Alternatively, for sites with low concentrations of fuel-related constituents remaining in an aerobic aquifer, a higher frequency than that recommended in Table 4 (i.e., quarterly) may be appropriate to rapidly document achievement of GWQS and facilitate site closure. In addition, for those cases meeting the requirements of Attachment 2 of the Issuance of Response Action Outcomes (RAO) guidance (see Section 6.4 of this document), and are reflective of an asymptotic condition, sampling frequency determinations may be based largely on the location of receptors.

Sampling performed prior to application for a RAP-GW will typically identify a seasonal/cyclical trend in contaminant concentrations and possibly plume boundaries. Long term monitoring performed at an annual or longer frequency should target the time of year expected to exhibit the highest levels of contamination based on the results of historic ground water data.

Sentinel Monitoring Well Frequency

The frequency of sentinel well sampling is conditioned on the location of potential receptors relative to the leading edge of the contaminant plume. The investigator determines the sentinel well sampling frequency by calculating the travel time to the nearest receptor using the site-specific ground water seepage velocity and the distance to the nearest receptor. The ground water seepage velocity is calculated by:

$$V_s = \frac{Ki}{n_e}$$

Where: V_s = seepage velocity, ft/day
K = hydraulic conductivity, ft/day (preferred site-specific)
i = hydraulic gradient, ft/ft (site-specific)
n_e = effective porosity, dimensionless (typically from published reference)

The investigator should use information obtained during the Receptor Evaluation performed pursuant to N.J.A.C. 7:26E-1.14 to identify the receptor location. Receptors to be considered during this evaluation include potable wells, structures subject to vapor intrusion, and environmentally sensitive natural resources. The Department realizes that the identification of receptors for the purpose of calculating a travel time to develop a monitoring frequency does not mean that these receptors require evaluation or monitoring; however, potential receptors should continue to be evaluated in accordance with the Remedial Action Protectiveness/Biennial Certifications - Ground Water requirements and other applicable regulation and guidance. Evaluation of receptors is not covered by this technical guidance and the investigator should refer to N.J.A.C. 7:26E-1.14 for direction.

The travel time is based solely on the ground water seepage velocity and location of receptors, irrespective of contaminant biodegradation or retardation. **One-half of this travel time** is used when developing the sentinel well monitoring frequency to allow time for design and implementation of an alternative remedy, should contaminants be detected above applicable standards in the sentinel well(s). If one-half of the travel time is greater than the performance monitoring frequency, then sentinel wells should be sampled at the same frequency as the performance monitoring wells. Sentinel well sampling frequency should be revaluated whenever performance monitoring is reduced in accordance with Table 4. Sampling of sentinel monitoring wells will not be required to be more frequent than quarterly.

As an example, where one-half of the travel time to the nearest receptor is 3 years, all performance and sentinel wells would be sampled annually then biennially as outlined in Table 4 above. After the initial eight years of monitoring, the performance monitoring wells would be sampled every 8 years for BTEX or other contaminants < 10X the GWQS or every 4 years for non-BTEX contaminants > 10X the GWQS; however, sentinel wells would be sampled every 3 years for the duration of the permit.

With appropriate justification, the investigator may propose a sentinel well monitoring frequency that differs from the method outlined above. Such justification may include a fate and transport model calibrated to the field data or availability of sufficient historical ground water monitoring data that demonstrate plume stability with a high degree of confidence as per this MNA Technical Guidance Document.

Reporting of sentinel well monitoring results should generally be provided at the frequency outlined above for Performance Monitoring. However, if contaminants are detected at levels above applicable standards in the sentinel well(s) during any sampling event, or impacts to receptors are identified, the Department should be notified as soon as practical or as otherwise required pursuant to regulation or guidance.

7.1.1 Analytical Parameters

The analysis of samples collected during the LTM program should include laboratory and field parameters necessary to evaluate whether natural attenuation is occurring as predicted, and to ensure the MNA remedy is protective of receptors. The suite of parameters may be modified relative to those used during the initial evaluation of the appropriateness of MNA, but should include COCs identified in the CEA for the site and degradation byproducts. Geochemical parameters may be necessary to evaluate whether aquifer conditions continue to be conducive to natural attenuation (e.g., have electron acceptors been depleted?).

7.1.2 Monitoring Well Network

The number and type of wells in the LTM program will depend upon the size and stability of the plume, relative levels of contamination, and presence of potential receptors. Monitoring will typically include source area wells, plume fringe area wells, and sentinel wells. Monitoring may also include wells perpendicular to the ground water flow direction to monitor lateral components of the plume. Wells should be positioned to evaluate the long term viability of natural attenuation and ensure protection of receptors.

7.2 Performance Evaluation of the Data

The data obtained during the LTM program needs to be evaluated for the effectiveness and protectiveness of the MNA remedy and the adequacy of the LTM program. The performance evaluation described below is in addition to the Remedial Action Protectiveness/Biennial Certification – Ground Water requirements. The following factors of the CSM need to be considered during the performance evaluation:

- Contaminant concentration trends using all available data
- Plume stability
- Hydrogeologic changes (flow direction/rate)
- Geochemical conditions
- Protectiveness to receptors

The performance evaluation should be performed after receipt of results for each round of data, and include the historical ground water data obtained during the evaluation of the applicability of natural attenuation. The evaluation will result in a decision for one of the following actions:

1) Continue the LTM program
2) Modify the LTM program
3) Implement a contingency remedy

4) Verify the goals of the MNA remedy have been met and terminate the LTM program

The following section presents each decision and under what conditions it would apply.

1) Continue the LTM Program Without Change:

The LTM Program may continue without change if contaminant concentrations (including degradation or transformation products) remain within the bounds of acceptable trends as predicted by the CSM, ground water flow characteristics are within previously identified acceptable ranges, geochemistry continues to support contaminant degradation or other natural attenuation processes, and the MNA remedy remains protective of receptors.

2) Modify the LTM Program

The LTM Program may need to be modified to better reflect changing conditions, increase the understanding of the natural attenuation processes, or further evaluate potential impacts to receptors. Changes in monitoring well network, analytical parameters, or sampling frequency may be necessary to ensure the LTM program remains protective. The investigator will need to evaluate whether the changes in conditions trigger implementation of the contingency plan (as described later in this section), or result in only a modification of the LTM program.

Changes in the LTM program such as revision to the monitoring well network, sampling frequency, or analytical parameters will require modification of the RAP-GW. However, these changes may be incorporated into the original LTM program proposed in the Permit, based on reaching certain site-specific performance goals. If these changes were incorporated into the original permit, then modification of the RA permit would not be needed. Temporary increases in monitoring frequency to verify changing conditions will generally not require modification of the permit.

If the LTM data indicates the previously established extent or duration of the CEA is no longer protective, modification to the CEA shall be submitted to the Department in accordance with the requirements of the Remedial Action Protectiveness/Biennial Certification – Ground Water. Although not required to do so, the person responsible for conducting the remediation may also submit a revised CEA to reflect a smaller extent due to a receding plume.

3) Implement a Contingency Remedy

If, during the LTM program, it is determined that MNA is no longer a protective remedy, the person responsible for conducting the remediation must evaluate and implement an alternative remedial action (N.J.A.C. 7:26E-6.3(e)3ii). This may consist of enhancing the existing MNA remedy (ITRC 2008) or implementation of a more active strategy. Criteria or triggers for determining when to implement an alternative remedial action should be outlined in the permit or remedy decision documents. These triggers are generally based on and related to the MNA remedy decision criteria. Unless imminent or verified impacts to receptors have been identified, it may be appropriate to perform verification sampling prior to implementing an alternative remedial action.

Situations that may trigger implementation of the alternative remedial action could include the following:

- Contaminant concentrations in ground water exhibit an increasing trend.
- Source area wells exhibit concentration increases indicative of a potential new discharge.
- Contaminants reach sentinel wells.
- Contaminant concentrations are not decreasing consistent with predicted rates. Milestones should be established in the LTM program (e.g., approximately 50% reduction in 5 years).
- Changes in land use and/or ground water use that will no longer make the MNA program protective. (i.e., new receptors identified, hydrogeologic conditions change).
- Changes in geochemical conditions are no longer conducive to MNA.
- Contaminants are identified at any location causing an unacceptable risk to human health or the environment.

4) Verify the goals of the MNA remedy have been met and terminate the LTM program

To lift the CEA and terminate the RAP-GW, and prior to a LSRP's issuance of an unrestricted Response Action Outcome (RAO), the person responsible for remediation must demonstrate that GWQS are not exceeded during two consecutive quarterly monitoring events (N.J.A.C. 7:26E-6.3(e)3i) at all wells included in the LTM. One of the quarterly sampling rounds should be timed to include the sampling event that typically contained the highest concentration as identified from historic sampling data.

8 REPORTING

The following general reporting outline describes the process flow for MNA cases. Please consult N.J.A.C. 7:26C, N.J.A.C. 7:26E, and other Department guidance regarding specific reporting requirements.

Remedial Action Workplan

- Provides site characterization data to support MNA (Section 6);
- Documents initial monitoring results and a preliminary evaluation of whether MNA is feasible (e.g., geochemical conditions) (Section 6);
- Documents removal, treatment, or containment of source or proposes method for addressing source prior to evaluating the applicability of MNA;
- Documents that the conditions that generally preclude MNA are not present (See Section 4.2 for evaluating these conditions);
- Outlines proposed Lines of Evidence that will demonstrate that MNA is applicable; and
- Documents that MNA would be a protective remedy.

Remedial Action Report for Limited Restricted Response Action Outcome

- Documents lines of evidence demonstrating that MNA is applicable (Section 7);
- Documents that source removal, treatment, or containment is effective;
- Documents that conditions that preclude MNA are not present (section 5.3);
- Submit CEA proposal, if not already established. CEA is established by the Department; and

- Submit application for RAP-GW with long term monitoring schedule (Section 8.1). Limited Restricted RAO issued once the permit is established by the Department.

Remedial Action Protectiveness/Biennial Certification – Ground Water

- Presents long term monitoring results;
- Documents that MNA continues to be a protective remedy (Section 8.2); and
- If proposing changes in monitoring or reporting, submit application for modification of the RAP-GW. Department issues modified Permit.

Termination of Remedial Action Permit – Ground Water

- Once GWQS have been achieved:
  - Document that GWQS have been achieved;
  - Submit CEA termination proposal. Department lifts CEA;
  - Submit RAP-GW Application with "terminate" checked; and
- Unrestricted Use RAO may be issued **for ground water** once the Permit is terminated by the Department.

9 REFERENCES

Note: Summaries of references indicated by * are provided in Appendix F.

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Appendix A

Degradation/Stabilization Processes

DEGRADATION/STABILIZATION PROCESSES

Truex, M. J., C, J, Newell, B. B. Looney, K.M. Vangelas. 2007. Scenarios Evaluation Tool for Chlorinated Solvent MNA. A Research Study of the Monitored Natural Attenuation/Enhanced Attenuation for Chlorinated Solvents Technology Alternative Project. Savannah River National Laboratory. WSRC-STI-2006-00096, Rev.2. February 2007. http://www.osti.gov/bridge/purl.cover.jsp?purl=/899964-cuFtbW/

One of the main challenges to implementing MNA is the need to cost-effectively interpret the multifaceted site specific data. To address this challenge, a team of researchers developed a "taxonomic key" to classify contaminated sites into one of thirteen scenarios based on hydrologic setting, geochemistry and a variety of modifying factors. The team developed a guidebook for each scenario to streamline characterization, modeling and monitoring. The result is a practical tool that will assist in environmental decision-making and in developing defensible environmental management strategies.

Based on the characteristics of the geochemical settings, some dechlorination reactions are very likely to occur, some are very unlikely to occur, and some may occur depending on specific circumstances. Using figures, simple "Consumer Reports" indicators, and the appropriate geochemical setting for a site, the scenario user can determine what reactions are most likely and will also know what reactions are possible depending on more detailed information.

The initial portion of this appendix excerpts a series of charts that describe key dechlorination reactions under aerobic and anaerobic conditions for the chlorinated solvents tetrachloroethene (PCE), 1,1,2,2-tetrachloroethane (1,1,2,2,-TeCA), 1,1,1,2-tetrachloroethane (1,1,1,2-TeCA), and carbon tetrachloride (CT).

Ford, Robert G., Richard T. Wilkin, and Robert W. Puls. 2007. Monitored Natural Attenuation of Inorganic Contaminants in Ground Water. Volume 1 - Technical Basis for Assessment. U.S. Environmental Protection Agency. Office of Research and Development. National Risk Management Research Laboratory. Ada, OK. EPA/600/R-07/139. October 2007.

The purpose of this series of documents, collectively titled "Monitored Natural Attenuation of Inorganic Contaminants in Ground Water," is to provide a technical resource for remedial site managers to define and assess the potential for use of site-specific natural processes to play a role in the design of an overall remedial approach to achieve cleanup objectives. Volume 1 addresses the technical basis and requirements for assessing the potential applicability of MNA as part of a ground water remedy for plumes with non-radionuclide and/or radionuclide inorganic contaminants. It consists of three sections that describe 1) the conceptual background for natural attenuation for inorganic contaminants, 2) the technical basis for attenuation of inorganic contaminants in ground water, and 3) approaches to site characterization to support evaluation of MNA.

The latter portion of this appendix excerpts pertinent technical background relative to adsorption and precipitation, the two most important stabilization processes for non-radionuclide inorganic contaminants.

HYDROGEOLOGIC SETTING

Simple Fast	*Simple Slow*	*Heterogeneous Fast*	*Heterogeneous Slow*	*Fractured/ Porous Rock*

GEOCHEMICAL SETTING

Aerobic	*Anoxic*	*Anaerobic*

KEY DECHLORINATION REACTIONS

Reaction Overview

The chart to the right shows which reactions are likely to occur, which occur but at a slow rate, and which may occur under specific conditions, and which are unlikely to occur.

Compounds Easier for Biological Degradation

- cis 1,2-DCE
- VC
- 1,2-DCA
- 1,1-DCE
- DCM
- CM

Compounds More Difficult for Biological Degradation

- PCE
- TCE
- CT
- CF

See Section 5.1 for more information about reactions

Reactions

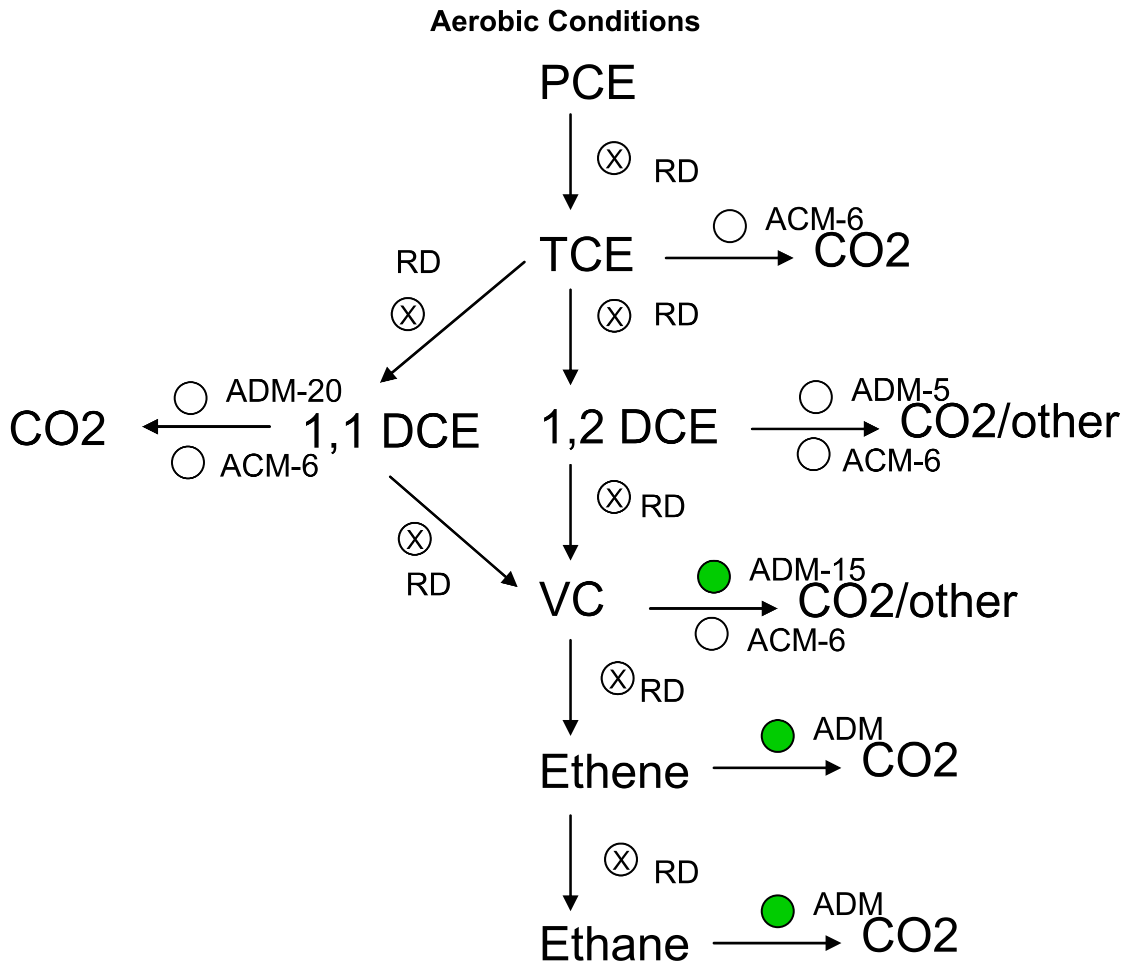
Contaminant	RD	DC	ACM	ANCM	ADM	ANDM	DHC	AH
PCE								
TCE			○					
1,2-DCE			○		○			
VC			○		●			
1,1,2,2-TcCA							●	
1,1,2-TCA			○				◒	
1,2-DCA			○		●		◒	◒
CA			○					●
1,1,1,2-TcCA							◒	
1,1,1-TCA			○				●	●
1,1-DCA			○				◒	
CA			○					●
1,1-DCE			○		○			
CT								◒
CF			○					◒
DCM			○		●			◒
CM			○		●			●

Key:

●	Highly Likely to occur
◒	Highly likely to occur, but a slow rate
○	May occur under specific conditions
▢	Highly Unlikely to occur

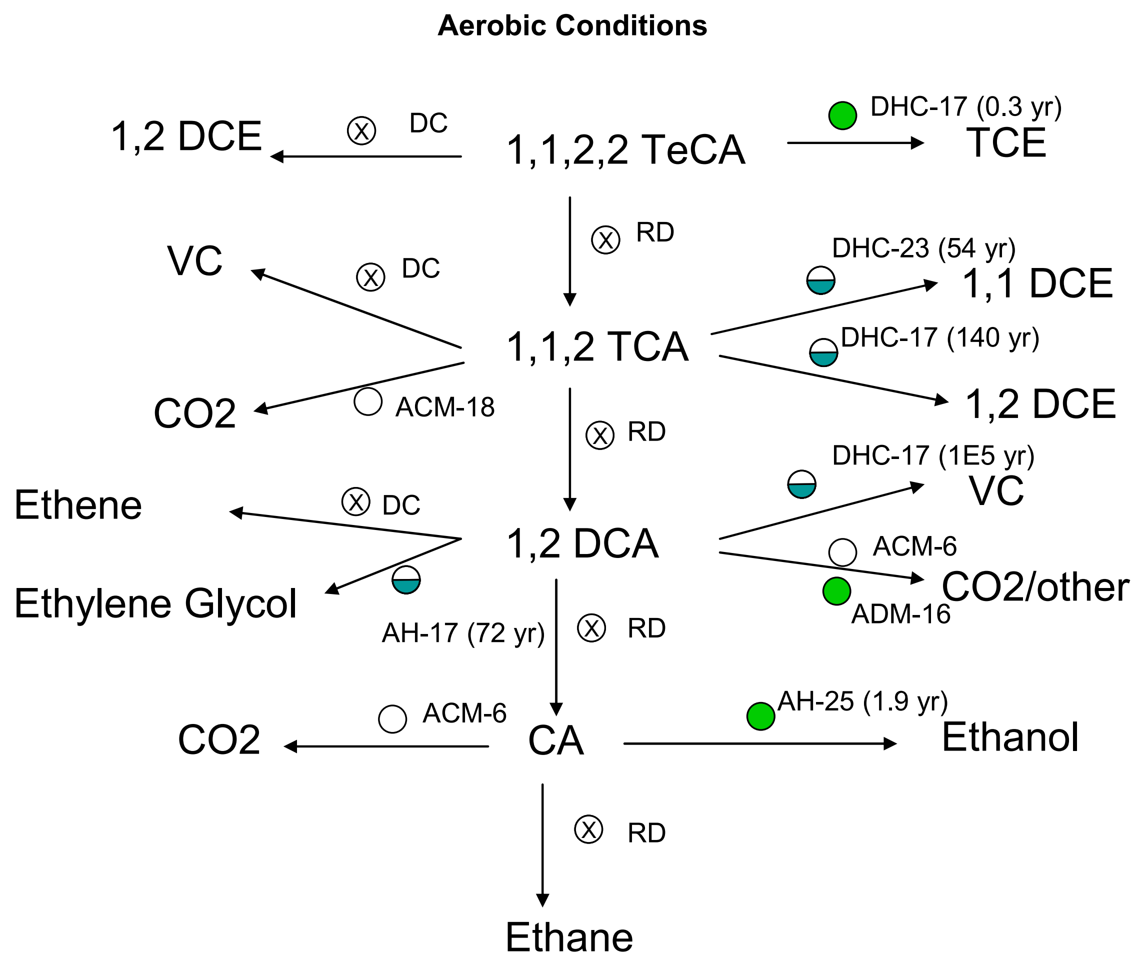
REACTIONS

ACM	Aerobic Co-Metabolism
ANCM	Anaerobic Co-Metabolism
ADM	Aerobic Direct Metabolism
ANDM	Anaerobic Direct Metabolism
DHC	Dehydrochlorination (abiotic)
AH	Abiotic Hydrolysis
DC	Dichloroelimination (biotic)
RD	Reductive Dechlorination (hydrogenolysis)



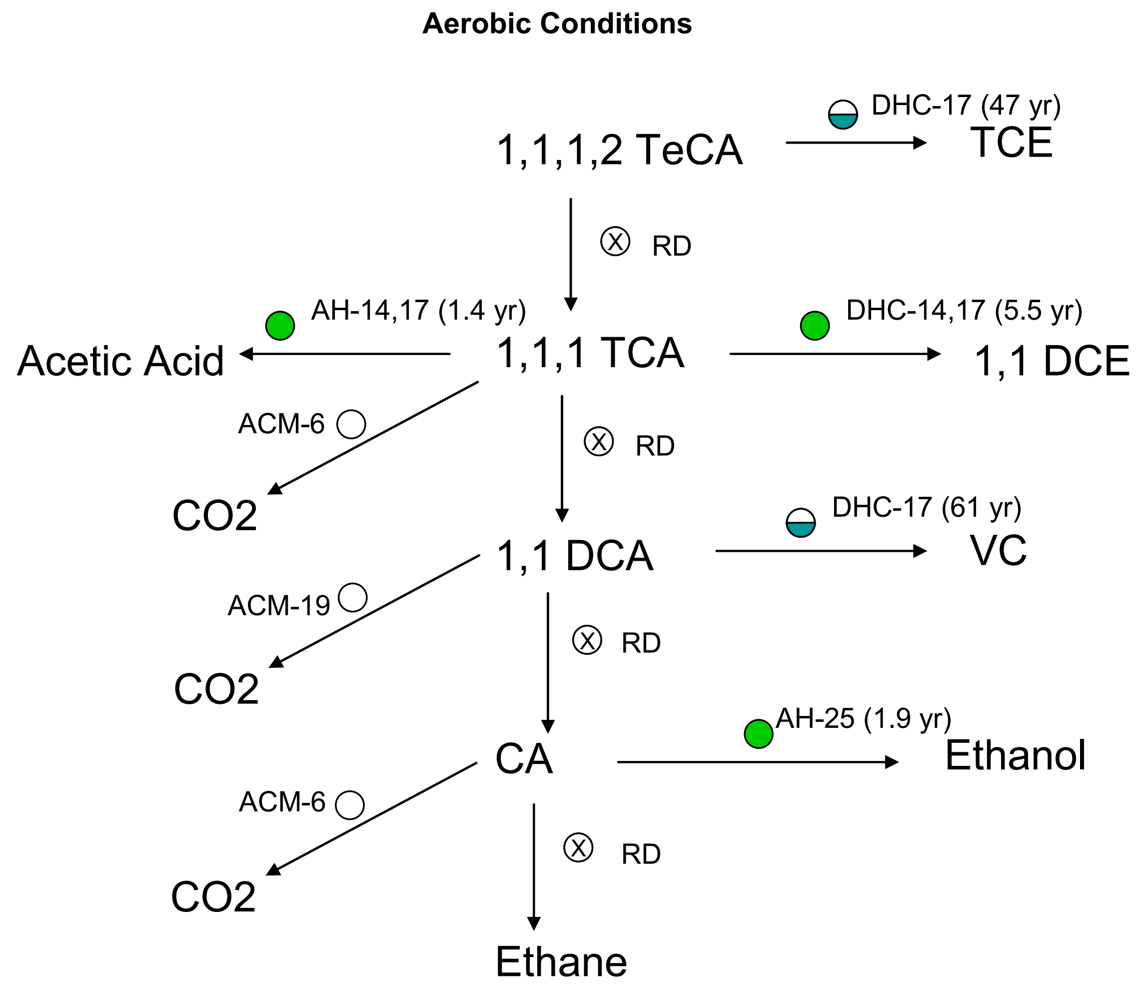
LIKELIHOOD OF REACTION	*TYPE OF REACTION*		*HALF LIVES*
	ACM:	*Aerobic Co-Metabolism*	*Numbers in parentheses (if present) indicate typical reaction half-life in years*
● ***Highly likely***	***ANCM:***	*Anaerobic Co-Metabolism*	
	ADM:	*Aerobic Direct Metabolism*	
◒ ***Highly likely, but at a slower rate***	***ANDM:***	*Anaerobic Direct Metabolism*	
	AH:	*Abiotic Hydrolysis*	***REFERENCES***
○ ***May occur under specific conditions***	***DC:***	*Dichloroelimination (biotic)*	
	DHC:	*Dehydrochlorination (abiotic)*	*Numbers next to reaction indicate reference (see page 48)*
⊗ ***Unlikely***	***RD:***	*Reductive Dechlorination*	

FIGURE 8. Dechlorination Reactions for PCE Under the Aerobic Geochemical Setting.



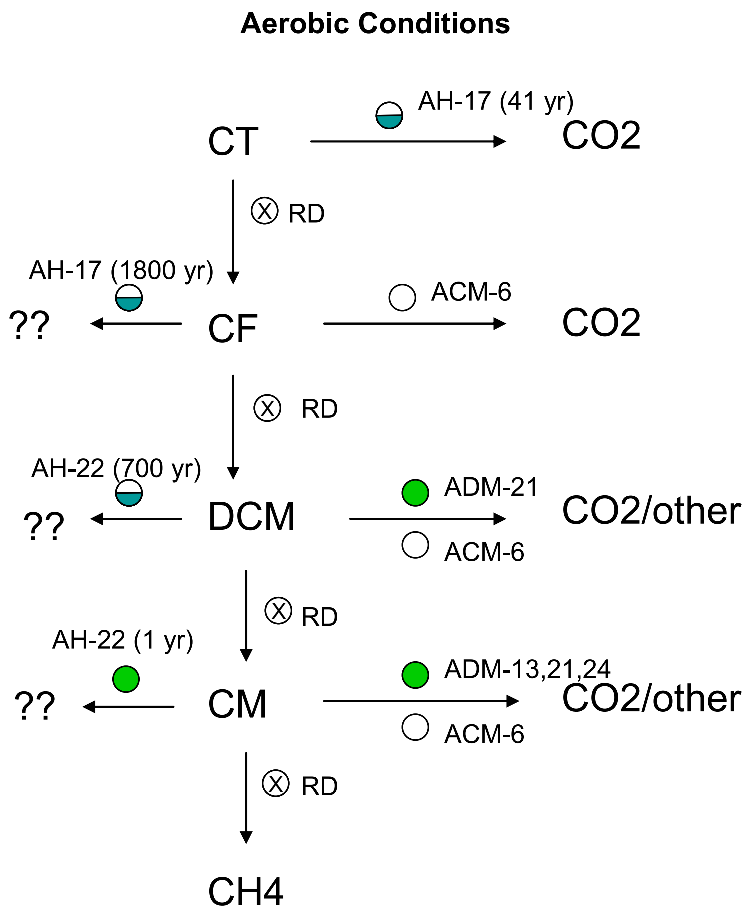
LIKELIHOOD OF REACTION	*TYPE OF REACTION*		*HALF LIVES*
	ACM:	*Aerobic Co-Metabolism*	*Numbers in parentheses (if present) indicate typical reaction half-life in years*
● ***Highly likely***	*ANCM:*	*Anaerobic Co-Metabolism*	
	ADM:	*Aerobic Direct Metabolism*	
◒ ***Highly likely, but at a slower rate***	*ANDM:*	*Anaerobic Direct Metabolism*	
	AH:	*Abiotic Hydrolysis*	***REFERENCES***
○ ***May occur under specific conditions***	*DC:*	*Dichloroelimination (biotic)*	*Numbers next to reaction indicate reference (see page 48)*
	DHC:	*Dehydrochlorination (abiotic)*	
⊗ ***Unlikely***	*RD:*	*Reductive Dechlorination*	

FIGURE 11. Dechlorination Reactions for 1,1,2,2-TeCA Under the Aerobic Geochemical Setting.



LIKELIHOOD OF REACTION	TYPE OF REACTION		HALF LIVES
	ACM:	*Aerobic Co-Metabolism*	*Numbers in parentheses (if present) indicate typical reaction half-life in years*
● ***Highly likely***	***ANCM:***	*Anaerobic Co-Metabolism*	
	ADM:	*Aerobic Direct Metabolism*	
◒ ***Highly likely, but at a slower rate***	***ANDM:***	*Anaerobic Direct Metabolism*	
	AH:	*Abiotic Hydrolysis*	***REFERENCES***
○ ***May occur under specific conditions***	***DC:***	*Dichloroelimination (biotic)*	
	DHC:	*Dehydrochlorination (abiotic)*	*Numbers next to reaction indicate reference (see page 48)*
ⓧ ***Unlikely***	***RD:***	*Reductive Dechlorination*	

FIGURE 14. Dechlorination Reactions for 1,1,1,2-TeCA Under the Aerobic Geochemical Setting.



LIKELIHOOD OF REACTION

- 🟢 ***Highly likely***
- ◒ ***Highly likely, but at a slower rate***
- ○ ***May occur under specific conditions***
- ⊗ ***Unlikely***

TYPE OF REACTION

ACM:	*Aerobic Co-Metabolism*
ANCM:	*Anaerobic Co-Metabolism*
ADM:	*Aerobic Direct Metabolism*
ANDM:	*Anaerobic Direct Metabolism*
AH:	*Abiotic Hydrolysis*
DC:	*Dichloroelimination (biotic)*
DHC:	*Dehydrochlorination (abiotic)*
RD:	*Reductive Dechlorination*

HALF LIVES

Numbers in parentheses (if present) indicate typical reaction half-life in years

REFERENCES

Numbers next to reaction indicate reference (see page 48)

FIGURE 17. Dechlorination Reactions for CT Under the Aerobic Geochemical Setting.

KEY DECHLORINATION REACTIONS

Reaction Overview

The chart to the right shows which reactions are likely to occur, which occur but at a slow rate, which may occur under specific conditions, and which are unlikely to occur.

Typically Biodegradable Parent Compounds

These compounds are typically degradable under anaerobic conditions:

- PCE
- TCE
- 1,1,1-TCA
- 1,2-DCA
- CT

Typical Daughter Products

Daughter products that may be present depending on the parent compound and the reactions listed to the right:

- TCE
- cis 1,2-DCE
- VC
- 1,2-DCA
- 1,1-DCE
- CF

See Section 5.1 for more information about reactions

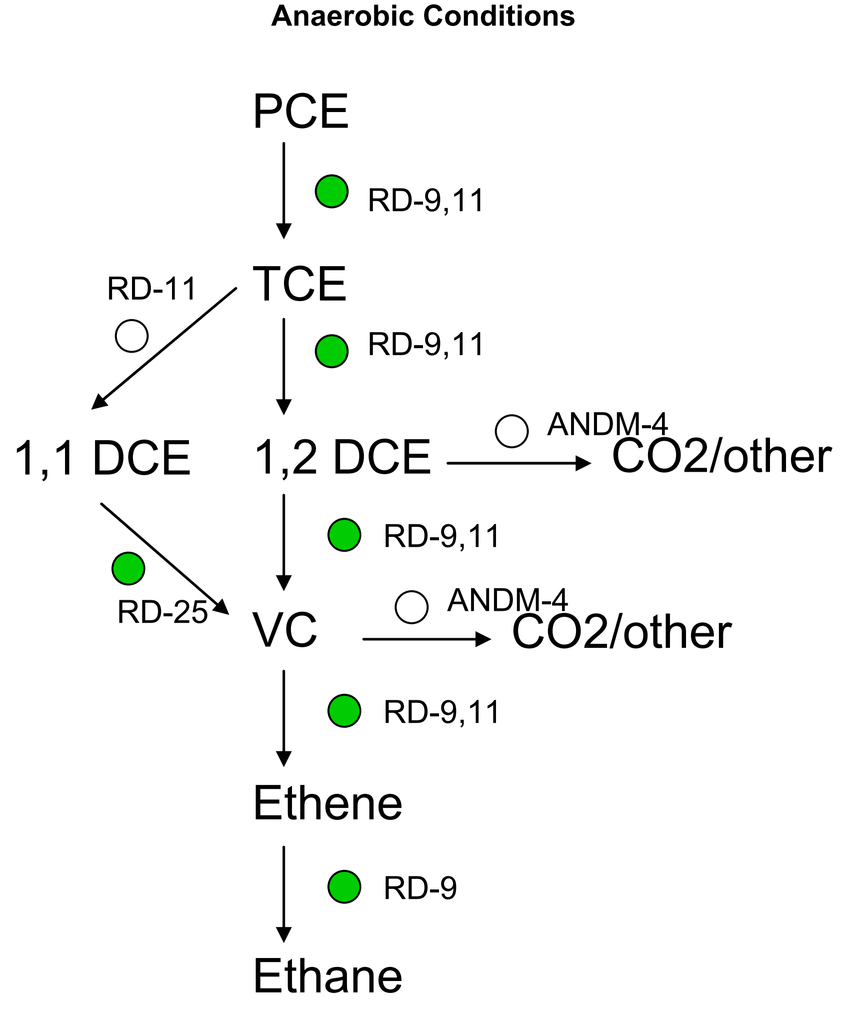
	Reactions							
Contaminant	RD	DC	ACM	ANCM	ADM	ANDM	DHC	AH
PCE	●							
TCE	●							
1,2-DCE	●					○		
VC	●					○		
1,1,2,2-TcCA	●	●					●	
1,1,2-TCA	●	●					◒	
1,2-DCA	●	●					◒	◒
CA	●							●
1,1,1,2-TcCA	○	●					◒	
1,1,1-TCA	●						●	●
1,1-DCA	●						◒	
CA	●							●
1,1-DCE	○							
CT	●			○				◒
CF	●			○				◒
DCM	○					●		◒
CM	○					○		●

Key:

- ● Highly Likely to occur
- ◒ Highly likely to occur, but a slow rate
- ○ May occur under specific conditions
- □ Highly Unlikely to occur

REACTIONS

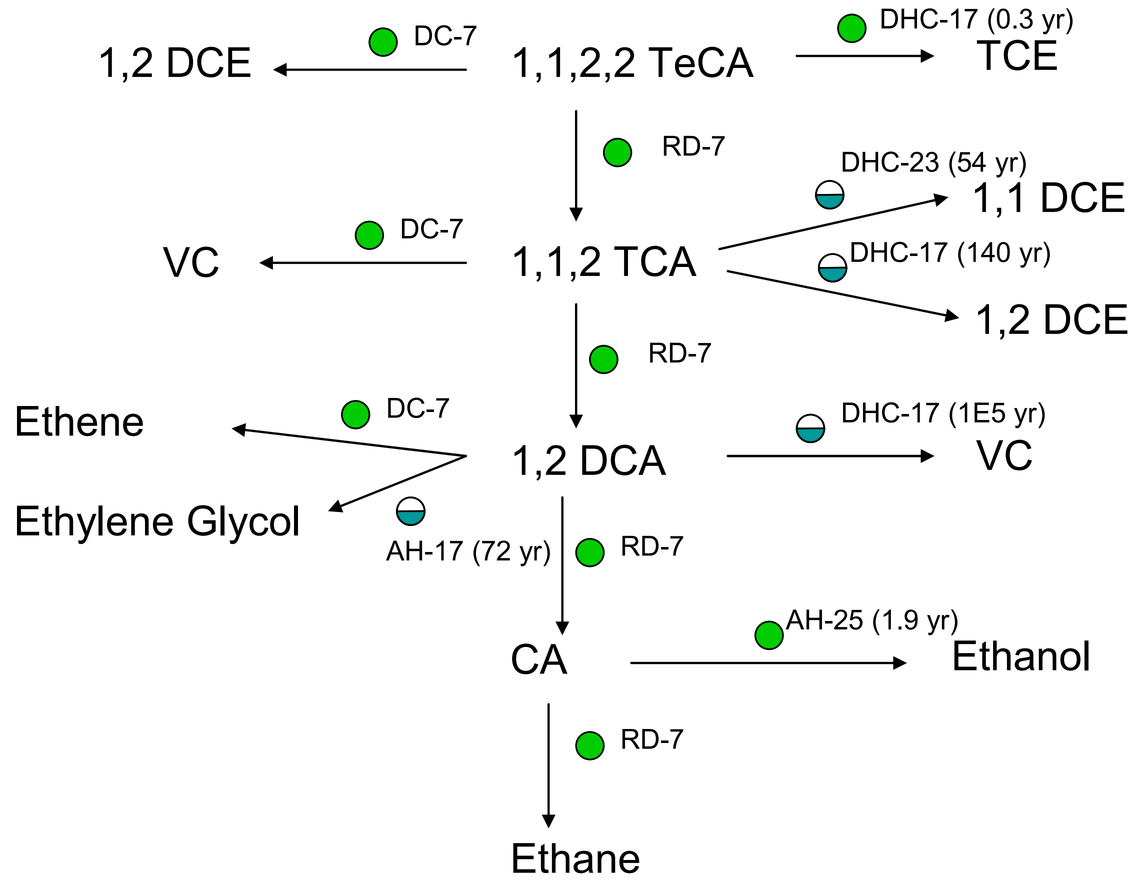
ACM	Aerobic Co-Metabolism
ANCM	Anaerobic Co-Metabolism
ADM	Aerobic Direct Metabolism
ANDM	Anaerobic Direct Metabolism
DHC	Dehydrochlorination (abiotic)
AH	Abiotic Hydrolysis
DC	Dichloroelimination (biotic)
RD	Reductive Dechlorination (hydrogenolysis)



LIKELIHOOD OF REACTION	*TYPE OF REACTION*		*HALF LIVES*
● ***Highly likely***	***ACM:***	*Aerobic Co-Metabolism*	*Numbers in parentheses (if present) indicate typical reaction half-life in years*
	ANCM:	*Anaerobic Co-Metabolism*	
◒ ***Highly likely, but at a slower rate***	***ADM:***	*Aerobic Direct Metabolism*	
	ANDM:	*Anaerobic Direct Metabolism*	
○ ***May occur under specific conditions***	***AH:***	*Abiotic Hydrolysis*	***REFERENCES***
	DC:	*Dichloroelimination (biotic)*	*Numbers next to reaction indicate reference (see page 48)*
	DHC:	*Dehydrochlorination (abiotic)*	
⊗ ***Unlikely***	***RD:***	*Reductive Dechlorination*	

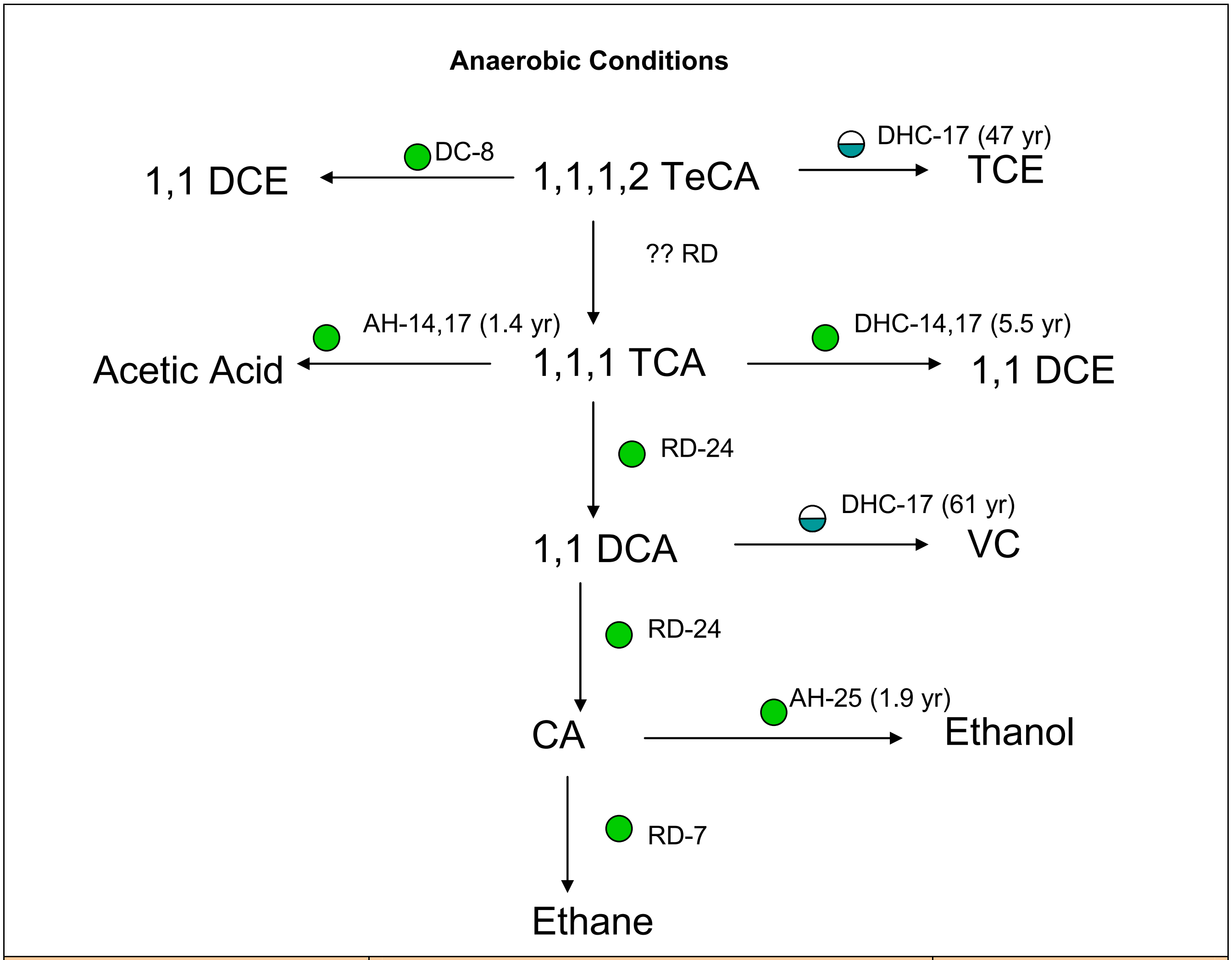
FIGURE 10. Dechlorination Reactions for PCE Under the Anaerobic Geochemical Setting.

Anaerobic Conditions



LIKELIHOOD OF REACTION	*TYPE OF REACTION*		*HALF LIVES*
	ACM:	*Aerobic Co-Metabolism*	*Numbers in parentheses (if present) indicate typical reaction half-life in years*
● ***Highly likely***	***ANCM:***	*Anaerobic Co-Metabolism*	
	ADM:	*Aerobic Direct Metabolism*	
◒ ***Highly likely, but at a slower rate***	***ANDM:***	*Anaerobic Direct Metabolism*	
	AH:	*Abiotic Hydrolysis*	***REFERENCES***
○ ***May occur under specific conditions***	***DC:***	*Dichloroelimination (biotic)*	*Numbers next to reaction indicate reference (see page 48)*
	DHC:	*Dehydrochlorination (abiotic)*	
⊗ ***Unlikely***	***RD:***	*Reductive Dechlorination*	

FIGURE 13. Dechlorination Reactions for 1,1,2,2-TeCA Under the Anaerobic Geochemical Setting.



LIKELIHOOD OF REACTION

- ● ***Highly likely***
- ◒ ***Highly likely, but at a slower rate***
- ○ ***May occur under specific conditions***
- ⊗ ***Unlikely***

TYPE OF REACTION

ACM:	*Aerobic Co-Metabolism*
ANCM:	*Anaerobic Co-Metabolism*
ADM:	*Aerobic Direct Metabolism*
ANDM:	*Anaerobic Direct Metabolism*
AH:	*Abiotic Hydrolysis*
DC:	*Dichloroelimination (biotic)*
DHC:	*Dehydrochlorination (abiotic)*
RD:	*Reductive Dechlorination*

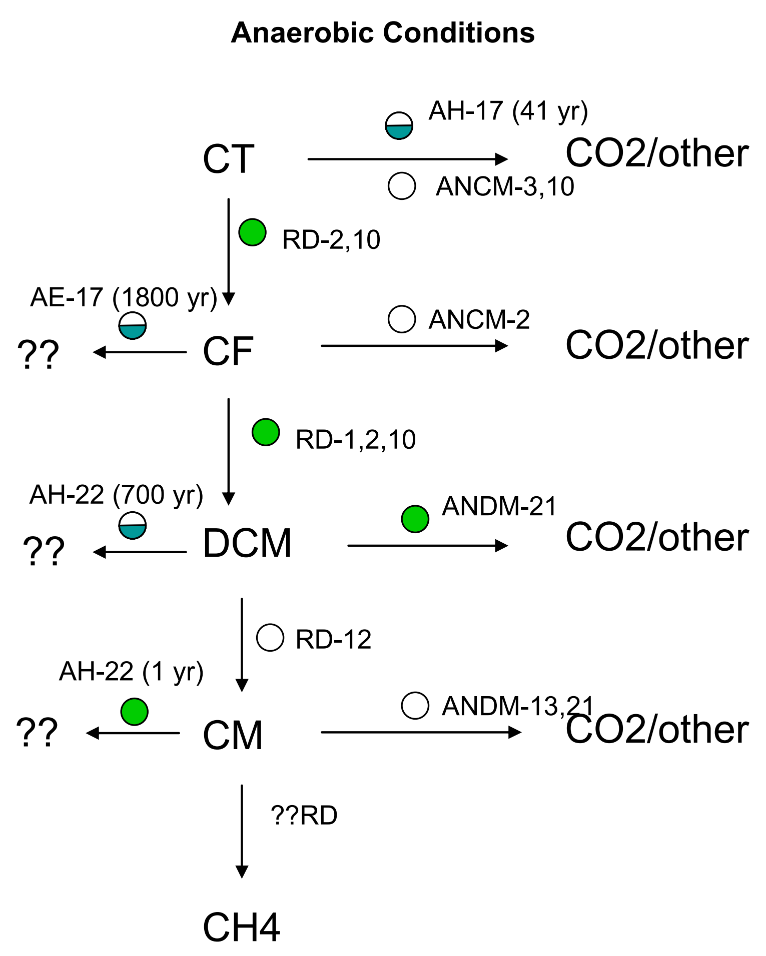
HALF LIVES

Numbers in parentheses (if present) indicate typical reaction half-life in years

REFERENCES

Numbers next to reaction indicate reference (see page 48)

FIGURE 16. Dechlorination Reactions for 1,1,1,2-TeCA Under the Anaerobic Geochemical Setting.



LIKELIHOOD OF REACTION

- ● ***Highly likely***
- ◒ ***Highly likely, but at a slower rate***
- ○ ***May occur under specific conditions***
- ⓧ ***Unlikely***

TYPE OF REACTION

ACM:	*Aerobic Co-Metabolism*
ANCM:	*Anaerobic Co-Metabolism*
ADM:	*Aerobic Direct Metabolism*
ANDM:	*Anaerobic Direct Metabolism*
AH:	*Abiotic Hydrolysis*
DC:	*Dichloroelimination (biotic)*
DHC:	*Dehydrochlorination (abiotic)*
RD:	*Reductive Dechlorination*

HALF LIVES

Numbers in parentheses (if present) indicate typical reaction half-life in years

REFERENCES

Numbers next to reaction indicate reference (see page 48)

FIGURE 19. Dechlorination Reactions for CT Under the Anaerobic Geochemical Setting.

IIB.1 Adsorption

Adsorption processes are typically categorized by the relative binding strength of interaction between the adsorbate (species in solution) and the adsorbent (aquifer solid). There is a range of binding strength for contaminant adsorption that depends on characteristics of the adsorbate, sorbent, and ground-water chemistry. However, discussions of binding strength are generally couched in terms of "weak" or "strong" adsorption processes, albeit a common convention in chemistry would categorize both the covalent and electrostatic interactions involved in adsorption as 'strong' intermolecular forces (Israelachvili ,1994). One microscopic distinction borrowed from the characterization of soluble ion pairs that is commonly used to delineate weak and strong adsorption involves the solvation properties of the adsorbate (Westall, 1986; Stumm, 1992). If solvating water molecules are interposed between the cation or anion and the surface, the adsorption complex is referred to as *outer sphere* and is considered to be weak. Conversely, if upon adsorption the adsorbate loses waters of hydration such that there are no water molecules interposed between the cation or anion and the surface, the adsorption complex is referred to as *inner sphere* and is considered to be strong (Sposito, 1984). The propensity of a cation or anion to form either an inner-sphere or outer-sphere surface complex is a function of the adsorbate, the surface functional groups of the adsorbent, and aqueous phase chemistry (e.g., pH and ionic strength).

IIB.1.1 Reactive Mineral Phases Involved in Adsorption

Important adsorbent phases commonly found in the environment include phyllosilicate minerals, metal oxyhydroxide phases, sulfide phases, and natural organic matter (Dixon and Schulze, 2002). Many phyllosilicate minerals possess a permanent negative charge as a result of the substitution of lower valence cations, i.e., Mg(II), Fe(II), Li(I) for Al(III) in the octahedral layer and/or Al(III) for Si(IV) in the tetrahedral layer (referred to as isomorphic substitution). There are two main classes of phyllosilicate minerals based on layer structure (Figure 2.5). The 1:1 mineral layer type is comprised of one Si tetrahedral layer and one Al octahedral layer, which in soils and aquifers is commonly represented by the mineral kaolinite having the general formula $[Si_4]Al_4O_{10}(OH)_8 \bullet nH_2O$. Kaolinite and related minerals generally have insignificant degrees of cation substitution within their octahedral and tetrahedral layers, and, thus generally posses a very low permanent negative charge. The 2:1 mineral type is comprised of one Al octahedral layer interposed between two Si tetrahedral layers comparable to the mica structures (Figure 2.5). The 2:1 layer class is represented by a variety of minerals, which are classified based on the location (tetrahedral vs. octahedral layer) and relative amount of isomorphic substitution. The three major mineral classes within the 2:1 layer type are illite ($M_x[Si_{6.8}Al_{1.2}](Al_3Fe_{0.25}Mg_{0.75})O_{20}(OH)_4$), vermiculite ($M_x[Si_7Al](Al_3Fe_{0.5}Mg_{0.5})O_{20}(OH)_4$), and smectite ($M_x[Si_8]Al_{3.2}Fe_{0.2}Mg_{0.6}O_{20}(OH)_4$), which display different levels

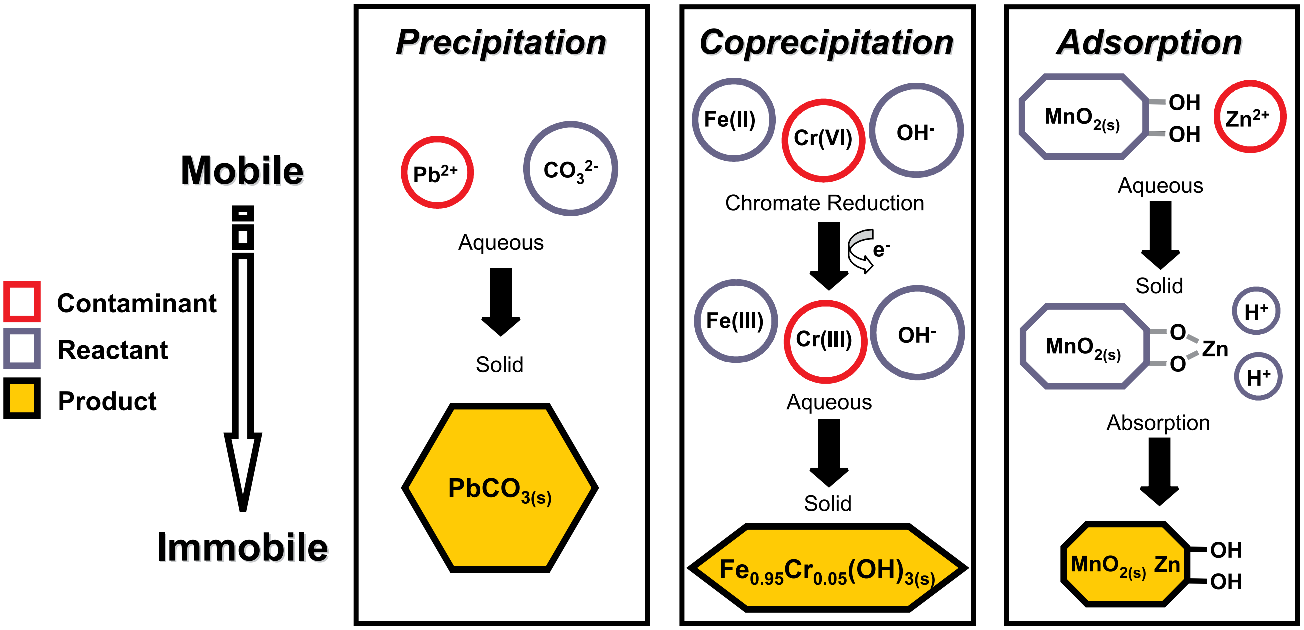


Figure 2.4 *Examples of contaminant-specific sorption processes that may lead to attenuation of the ground-water plume. Color coding is employed to distinguish the contaminant (red), aqueous or solid phase reactants (blue), and the product (yellow) of the reaction leading to contaminant attenuation. Absorption is illustrated as a possible sequential process that follows the adsorption of a contaminant onto a mineral component within aquifer solids.*

of cation substitution in their tetrahedral and octahedral layers. The permanent negative charge imparted to 2:1 clay minerals by isomorphic substitution is typically balanced through exchange reactions involving major cations in ground water (e.g., Na^+, K^+, Ca^{2+}, or Mg^{2+}; represented by "M_x" in the formulas listed above).

Contaminant sorption to phyllosilicates may occur via ion exchange or surface complexation with surface functional groups (see examples labeled "surface complex" and "ion exchange" in Figure 2.5). Due to differences in the levels of isomorphic substitution for the 1:1 and 2:1 clay mineral classes, ion exchange is usually only significant for 2:1 phyllosilicates. In addition to siloxane oxygen atoms along the basal plane, phyllosilicates possess two types of terminal ionizable OH groups, aluminol and silanol, protruding from the edge surface. These edge OH groups can form both inner- and outer-sphere complexes with metal cations and oxyanions depending on the pH of the bathing solution and on the specific characteristics of the cation or oxyanion (represented as "surface complex" in Figure 2.5).

The most important surface reactive phases for both cationic and anionic contaminants in many soil and subsurface systems are the metal oxyhydroxide phases. These phases are characterized by hexagonal or cubic close-packed O or OH anions with $Fe^{2+,3+}$, Al^{3+}, and/or $Mn^{3+,4+}$ occupying octahedral sites. These oxides are present as discrete phases and as complex mineral assemblages, being co-associated with phyllosilicates and primary minerals as coatings or with humic macromolecules. In soils and sediments the crystallinity of these phases typically varies from poorly ordered to well crystalline forms and grain size from the nanometer to micrometer scale. Among the most common Fe-oxyhydroxide phases found in soils and sediments are the poorly ordered phase ferrihydrite ($Fe_2O_3 \cdot nH_2O$), and the moderate to well crystalline phases, goethite (α–FeOOH), and hematite (α-Fe_2O_3). The most common Al oxyhydroxide phase found in soils and sediments is gibbsite (γ-$Al(OH)_3$). Additionally, poorly ordered aluminosilicates can be important reactive phases in certain soils and these include the very poorly ordered allophanes (Si/Al ratios 1:2 to 1:1) and the paracyrstalline phase, imogolite ($SiO_2 \cdot Al_2O_3 \cdot 2H_2O$). While Mn oxyhydroxides are less prevalent than Fe- and Al-oxyhydroxides in soils and sediments they are very important phases in terms of surface mediated redox reactions and because of their propensity for high metal sorption. The mineralogy of Mn is complicated by the range in Mn-O bond lengths resulting from extensive substitution of of Mn^{2+} and Mn^{3+} for Mn(IV). Thus, there exists a continuous series of stable and metastable compositions from MnO to MnO_2 forming a large variety of minerals. Among the more common Mn-oxyhydroxides are pyrolusite (β-MnO_2), the hollandite-cryptomelane family (α-MnO_2), todorokite, and birnessite (σ-MnO_2).

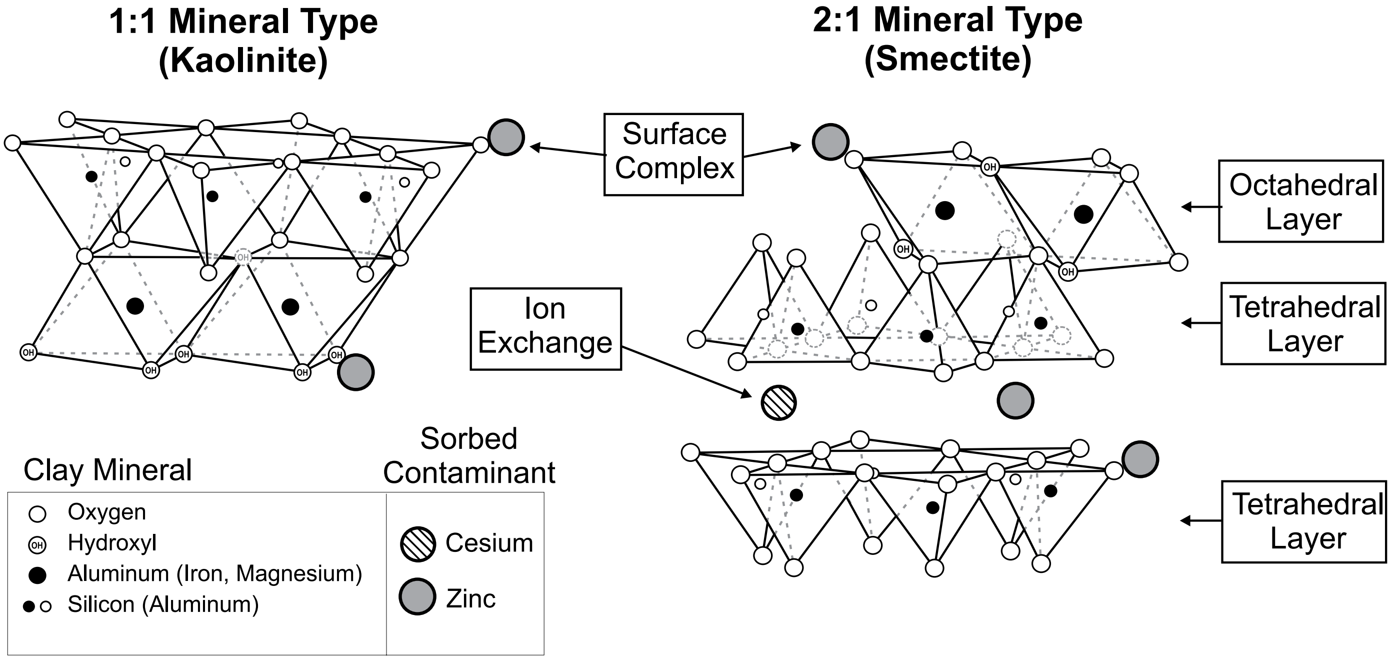


Figure 2.5 *Diagrammatic sketch of the structure of 1:1 and 2:1 phyllosilicate minerals. Also shown are hypothetical sorption reactions for zinc and cesium (ion exchange represented as 'M_x' in structural formulas for 2:1 phyllosilicates shown in text).*

IIB.1.2 Surface Functional Groups on Aquifer Solids and the Impact on Surface Charge

The reactive surface functional group for all of the metal oxyhydroxide phases is the inorganic OH moiety exposed on the outer periphery of these minerals. The reactivity of a specific metal oxyhydroxide is dependent on the surface area (S_A), surface-site density (N_S), the degree of coordination of the OH group to the bulk structure, and the point of zero charge (PZC). The charge on the mineral surface may impose either attractive or repulsive contributions to the overall adsorption reaction, depending on the type of charge possessed by the adsorbate. The properties of the sorbent that impact adsorption are controlled by both the grain size and specific structure of the oxyhydroxide phase.

The surface charge of oxyhydroxide minerals and edge sites on phyllosilicates is derived from the protonation and ionization of exposed surface hydroxyl groups, represented by $\equiv SOH_n^{n-1}$, where S represents the structural metal cation (e.g., Fe, Al, Mn) over a stoichiometric range from n= 0, 1, or 2. Thus, as a function of pH, the surface functional groups can be generally described with the following idealized nomenclature: $\equiv SOH_2^+$, $\equiv SOH^0$, and $\equiv SO^-$. The exact charge associated with the various surface functional groups is difficult to measure, so the main purpose of employing this nomenclature is to illustrate that surface charge varies as a function of ground-water chemistry. The gradual change in surface charging with pH for some common minerals is illustrated in Figure 2.6 and a discussion of surface site charging is provided below.

Natural organic matter comprised of complex polymers called humic substances, represents another very important reactive phase in aquifer solids. A variety of functional groups are present in humic substances, and, like OH functional groups of the inorganic metal oxyhydroxides, these also are characterized by pH dependent charging mechanisms. The primary functional groups associated with humic substances in terms of surface charge are carboxyl and phenolic groups, however the less abundant amino, imidazole, and sulfhydryl groups may play an important role in the sorption of certain contaminant metals when present at trace levels (Table 2.1).

Based on the previous discussion, it is apparent that the charge on aquifer solids can be grouped into two classes associated with the mechanisms that give rise to electrical charge associated with mineral surfaces or with organic functional groups. These two classes are commonly referred to as permanent (or constant) charge and variable charge.

- Constant charge - Constant charge is the predominant charge in phyllosilicate clays. Because, for the most part, these isomorphic substitutions occur during mineral formation, this charge deficit is fixed in the lattice structure and is hence unaffected by changes in electrolyte concentration or pH of the soil solution.
- Variable (pH dependent) charge - Variable charge is the predominant charge for oxyhydroxide minerals such as hematite, goethite, and gibbsite, as well as for humic substances. The metal ions in the vicinity of the surface of metal oxyhydroxide minerals are coordinatatively unsaturated, i.e. they are lewis acids, and coordinate with water molecules, which subsequently dissociate a proton leading to a surface layer of metal hydroxide functional groups. This process also occurs at the edges of phyllosilicate clays giving rise to SiOH (silanol) and AlOH (aluminol) functional groups. These surface hydroxyl groups can become positively or negatively charged by binding or dissociating a proton (i.e., protonation-deprotonation reactions):

$$S\text{—}OH + H^+ \leftrightarrows S\text{—}OH_2^+$$

$$S\text{—}OH \leftrightarrows S\text{—}O^- + H^+$$

Thus, the prevalent surface charge in aquifer solids will be dependent on the pH of ground water and the types and concentrations of ions that balance the permanent charge association with phyllosilicates. The extent to which

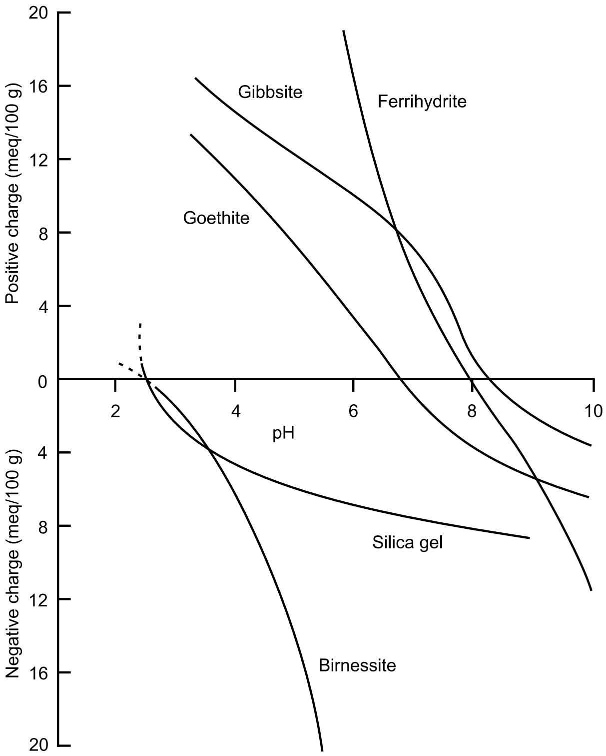
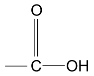
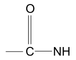
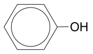
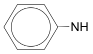


Figure 2.6 *Surface charge of some hydroxides from pH 2 to 10 measured in different electrolyte solutions shown in parentheses; positive and negative surface charge shown above and below the x-axis, respectively. Ferrihydrite [$Fe(OH)_3 \cdot nH_2O$] (0.001 M $NaNO_3$) from Hsi and Langmuir (1985); gibbsite [$Al(OH)_3$] and silica gel [$SiO_2 \cdot nH_2O$] (1.0 M CsCl) based on Greenland and Mott (1978); goethite [α-FeOOH] (0.005 M CsCl) based on Greenland and Mott (1978) (see also Hsi, 1981); birnessite (σ-MnO_2] (0.001 M $NaNO_3$) based on Catts and Langmuir (1986).*

Table 2.1 Important functional groups in humic substances that impact surface charging behavior and contaminant binding.

Functional Group	Structural Formula
Amino	$-NH_3$
Carboxyl	 $-\overset{\overset{O}{\|}}{C}-OH$
Carbonyl	 $-\overset{\overset{O}{\|}}{C}-NH$
Alcoholic hydroxyl	-OH
Phenolic hydroxyl	
Imidazole	
Sulfhydryl	-SH

protonation or deprotonation occurs is also a function of the metal ion and the local binding environment of the metal hydroxide surface group. The highly electropositive Si^{4+} in silanols precludes the protonation of the surface hydroxyl and this functional group can only dissociate a proton under pH conditions generally encountered in ground water. Aluminols, on the other hand, can be either positively or negatively charged. Various types of hydroxyls of differing reactivity have been identified spectroscopically at the surface of metal oxides.

The charge of aquifer minerals is always electrically balanced by interactions with ions of an opposite charge (counter-ions). We can define two broad classes of weak and strong interactions (outer and inner-sphere) that act to neutralize the charge developed at soil mineral surfaces.

IIB.1.3 Weak and Strong Adsorption Regimes

Weak adsorption regime - Within the weak adsorption regime, simple ion exchange is the most common mechanism and involves the electrostatic attraction of an ionic species by a negative or positive charge emanating from a mineral surface or from functional groups associated with humic substances (Sposito, 1981). Long before the structures of reactive soil minerals were determined, it was observed that, under certain circumstances, there was a reversible and stoichiometric (based on charge) replacement of major cations in soils equilibrated with concentrated neutral salt solutions according to the reaction:

$$Na_2\text{-}X_s + Ca^{2+}_{aq} \leftrightarrow Ca\text{-}X_s + 2Na^{+}_{aq}$$

Soil and sediment materials are typically characterized by their cation exchange capacity (CEC), which is defined as the quantity of cations reversibly adsorbed per unit weight of mineral and typically expressed as cmol kg^{-1}. The cation exchange capacity of 2:1 phyllosilicate clays tends to be constant over a wide pH range, since ionizable edge groups are relatively minor on a surface area basis compared to the permanent charge associated with planar sites. For 2:1 phyllosilicates, cations hydrated to differing degrees are located in the interlayer space and can be displaced by other competing cations through ion exchange reactions (see Figure 2.5). In principle, cation exchange reactions involve both inner and outer sphere complexation with planar sites, although except for the special case discussed below for large weakly hydrated monovalent cations, such as K^+ and Cs^+, both are readily reversible. Both inner and outer sphere complexes can also form with O functional groups associated with organic macromolecules and O and OH atoms associated with metal oxyhydroxides, but only the outer sphere complexes are considered weak adsorption. The major difference between phyllosilicates having substantial isomorphic substitution and metal oxyhydroxides and humic substances, is that the CEC is highly pH dependent, increasing with increasing pH. Since reactive mineral phases in soils and sediments are a composed of complex assemblages of phyllosilicates, oxyhydroxides, and humic substances, CEC is always a pH dependent property.

Strong adsorption regime - As discussed above, simple ion exchange is the predominant adsorption mechanism for phyllosilicate clays. A major exception to this is the inner-sphere sorption of larger unhydrated cations, such as K^+ and Cs^+ to oxygen atoms of two opposing siloxane ditrigonal cavities of collapsed layers of weathered micaceous minerals, such as illite, which can be classified as an 'irreversible' adsorption or as an absorption process.

At this point it is important to discuss the concept of the reversibility of adsorption. From the perspective of chemical thermodynamics, the definition of a 'reversible' process is one where the initial state of the system can be restored with no observable effects in the system *and* its surroundings (Holman, 1980). The use of the term 'irreversible' from the standpoint of adsorption mechanisms is relative and does not strictly adhere to the thermodynamic (or chemical) definition in all cases. The fixation of Cs^+ in illitic minerals is conceptually thought to proceed via an initial ion exchange reaction followed by an interlayer collapse (fast) or through the slower migration into interlayer sites in collapsed layers (absorption). Once Cs^+ is fixed within the interlayer of the clay mineral, its release is not readily reversible via displacement with competing solutes, i.e., through ion exchange mechanisms. Thus, the release of fixed Cs^+ is subsequently controlled by a process such as mineral dissolution. In this sense, the original fixation process is irreversible, since contaminant release would result from a mechanism other than the reversal of the original adsorption mechanism.

The formation of a chemical bond between an adsorbate and a functional group on the adsorbent also falls within the category of a strong adsorption regime. In general, breaking chemical bonds requires more energy than overcoming electrostatic interactions. Metal adsorption to OH functional groups of oxyhydroxide phases through surface complexation can be illustrated by the following surface reaction (Stumm, 1992; McBride, 2000):

$$=Fe\text{-}OH^{-1/2} + M(H_2O)_6^{n+} \Rightarrow =Fe\text{-}O\text{-}M(H_2O)_5^{(n-3/2)+} + H_3O^+$$

Thus, specific adsorption of cations increases the positive charge at the mineral surface when n > 1, which is generally the case for transition elements, and results in the net release of H^+ ions to the soil solution. Adsorption of anions from solution occurs by ligand exchange of a OH or H_2O at the surface functional group according the following reaction (solution anion represented by A^{n-}):

$$=\mathrm{Fe\text{-}OH} + A^{n-} \Rightarrow \mathrm{S\text{-}A}^{(n-1)-} + OH^-$$

Anion adsorption is favored by low pH, which leads to protonation of surface functional groups and makes them better leaving groups in the ligand exchange reaction.

IIB.2 Precipitation

Mineral-water reactions occur as ground water moves through porous media. These reactions may result in the removal of aquifer components due to mineral dissolution or result in the buildup to oversaturation and consequent precipitation of secondary minerals. As an outcome of mineral-water reactions along a flow path, fluid compositions and the mineralogical makeup of the solid phase will continuously evolve towards a stable or equilibrium state. Mineral precipitation processes in aquifer systems are an important group of immobilization mechanisms for inorganic contaminants in ground water.

Full treatment of precipitation processes, including coverage of relevant thermodynamic and kinetic concepts, is outside the scope of this document. The reader is referred to numerous standard textbooks in geochemistry, soil science, and aquatic chemistry (e.g., Lindsay, 1979; Stumm, and Morgan, 1981; Drever, 1982; Sposito, 1989; Stumm 1992; Morel and Hering, 1993; McBride, 1994; Sparks, 1995; Langmuir, 1997; Lasaga, 1999). The purpose of this section is to introduce key concepts and issues regarding the potential impact precipitation reactions may exert on contaminate attenuation. In general, mineral precipitation in relation to contaminant immobilization can be discussed in the context of four widely studied processes:

- Precipitation from solution: Nucleation and growth of a solid phase exhibiting a molecular unit that repeats itself in three dimensions. Homogeneous nucleation occurs from bulk solution and heterogeneous nucleation occurs on the surfaces of organic or mineral particles. Heterogeneous nucleation is thought to be more important in natural systems that are rich in reactive inorganic and biological surfaces. Precipitation may result in the formation of sparingly soluble hydroxides, carbonates, and, in anoxic systems, sulfides. Many precipitation reactions have a strong dependence on pH.
- Coprecipitation: Incorporation of an element as a trace or minor constituent within a precipitating phase. In this case, the contaminant substitutes for a more concentrated component in the crystal lattice (isomorphous substitution). This process is distinct from adsorption due to incorporation of the contaminant within the bulk structure of the major mineral phase. Examples of coprecipitation include Cr(III) in hydrous ferric oxide, Cd(II) in calcium carbonate, and As(III) in iron sulfide.
- Surface precipitation: A precipitation process intermediate between surface complexation and precipitation from bulk solution. Surface precipitation represents the continuous growth of particles formed via heterogeneous nucleation. Macroscopic studies of adsorption of some solutes, particularly di-valent and tri-valent cations, suggest that precipitation occurs at surfaces under conditions where the solid is apparently undersaturated based on solution concentrations (Dzombak and Morel, 1990).
- Mineral transformation: Adsorbed contaminants can become incorporated into minerals that form as a result of recrystallization or mineral transformation processes in soils and sediments. Transformation reactions may be accelerated or retarded by the contaminant, and in some cases mineral transformation may result in the exclusion of the impurity contaminant from the solid phase. Examples include incorporation of anions, such as As(V), into hydrous ferric oxide and transformation to Fe oxyhydroxides (e.g., Ford, 2002), coprecipitation of metals with iron monosulfide and transformation to iron disulfide (e.g., Lowers et al., 2007), and layered double hydroxides (typically with Al) as intermediates between adsorbed/surface precipitated metal ions like Ni and Zn, and metal-ion-containing aluminosilicates (e.g., Ford, 2007).

The relative importance of these processes will be determined by contaminant characteristics as well as site-specific characteristics of the plume ground-water chemistry and aquifer solids. These individual processes are discussed in more detail below.

IIB.2.1 Precipitation from Solution

Solution precipitation or crystallization can be divided into two main processes: nucleation and crystal growth. Nucleation occurs prior to growth of a mineral crystal. Both nucleation and growth processes require a system to be oversaturated in the new phase. The probability of nucleation occurring increases exponentially with the degree of oversaturation. Nucleation of a new phase is often facilitated in the presence of a surface (heterogeneous nucleation) compared to bulk solution (homogeneous nucleation). Because nucleation and growth are processes that compete for dissolved solutes, at high degrees of oversaturation the rate of nucleation may be so fast that all excess solute is partitioned into crystal nuclei. In contrast, lower levels of oversaturation can result in the growth of existing crystals without nucleation. Well-formed or euhedral crystals typically develop slowly via growth from solution at low degrees of oversaturation. During crystal growth various chemical reactions can occur at the surface of the growing mineral, such as adsorption, ion exchange, diffusion, and formation of surface precipitates. In general, the rate of crystal growth is controlled either by transport of solutes to the growing surface (i.e., transport controlled), by reactions at the surface (i.e., surface controlled), or a combination of these factors.

For the most abundant cations present in aquifers and soils, such as Al, Si, Fe, Mn, Ca, and Mg, precipitation of mineral forms is common and will in many cases control concentrations observed in solution. At contaminated sites, concentrations of ground-water contaminants are typically several orders of magnitude below the concentrations of the dominant solutes in water. At low concentrations, sorption, surface precipitation, or formation of a dilute solid solution (coprecipitation) may be the more probable removal processes for contaminant species (McBride, 1994). However, precipitation of iron-bearing or aluminum-bearing minerals, for example, can have an important affect on the transport and fate of metal and metalloid contaminants. Major mineral precipitate classes encountered in aquifers and soils are listed in Table 2.2.

The tendency for a system to support a specific precipitation or dissolution reaction can be evaluated through comparison of the equilibrium solubility constant for a given solid phase to the ion activity product calculated using ground-water chemical data. The relative magnitude of the values of the equilibrium solubility product and the calculated ion activity product provides a measure of the saturation state of ground water relative to mineral precipitation or dissolution. A conventional method for expressing the ground-water saturation state is by calculation of the saturation index, SI, which is given by (Stumm and Morgan, 1981):

$$\mathrm{SI} = \Delta G_r^0/RT + \ln Q = \ln Q/K_r$$

where ΔG_r^0 is the standard state free energy change of the reaction, R is the gas constant, T is temperature in degrees Kelvin, Q is the reaction quotient (or ion activity product), and K_r is the temperature- and pressure-dependent equilibrium constant of a reaction. Another term used frequently in place of the saturation index is the relative saturation, $\Omega = Q/K_r$. At chemical equilibrium, $\Delta G_r^0 = 0$, $Q = K_r$, and $\Omega = 1$. In this special case, the solution of interest is in equilibrium with the mineral and no dissolution or precipitation should take place. Where $\Delta G_r^0 < 0$, the mineral cannot precipitate from solution and the thermodynamic driving force is such that mineral dissolution should occur. Where $\Delta G_r^0 > 0$, the mineral will likely precipitate if there are no limiting kinetic factors (Table 2.3).

Table 2.2 Major mineral classes in aquifers and soils.

Mineral Class	Primary Mineral	Contaminant Precipitate
Hydroxides	$Al(OH)_3$, gibbsite $Fe(OH)_3$, hydrous ferric oxide FeO(OH), goethite FeO(OH), lepidocrocite	$Cu(OH)_2$ $Cr(OH)_3$ $Zn(OH)_2$
Oxides	Fe_3O_4, magnetite Fe_2O_3, hematite MnO_2, pyrolusite SiO_2, quartz	UO_2, uraninite
Carbonates	$CaCO_3$, calcite/aragonite $FeCO_3$, siderite $MnCO_3$, rhodochrosite	$CdCO_3$, otavite $ZnCO_3$, smithsonite $PbCO_3$, cerussite
Sulfates	$BaSO_4$, barite $CaSO_4 \cdot 2H_2O$, gypsum	$PbSO_4$, anglesite $RaSO_4$
Sulfides	FeS, mackinawite FeS_2, pyrite/marcasite	PbS, galena NiS, millerite HgS, cinnabar ZnS, sphalerite
Phyllosilicates	$Al_4(OH)_8Si_4O_{10}$, kaolinite $K_{1.5}Al_2(OH)_2Si_{2.5}Al_{1.5}O_{10}$, illite	$Ni_3Si_2O_5(OH)_4$, nepouite $Na_{0.3}Zn_3(Si,Al)_4O_{10}(OH)_2 \cdot 4H_2O$, sauconite

The ion activity product is a useful probe to evaluate the potential for contaminant precipitation. Some caution, however, is recommended in interpreting solution indicators as evidence for the presence of a particular precipitated solid within the plume. The observation that an ion activity product is equal to a corresponding solubility product is not unequivocal evidence that a given phase is at equilibrium or even present in the system (Sposito, 1984). Similarly, an ion activity product that is greater than a corresponding solubility product cannot be taken as confirmation that precipitation is occurring. To understand the state of a system with respect to precipitation and dissolution, it is recommended that the presence of the relevant solid phases be evaluated in addition to measuring the concentrations of solutes that participate in a precipitation reaction suspected to occur within the ground-water plume.

Table 2.3 Relationships among Q, K, and Ω.

Process	Saturation Index, log (Q/K_r)	Relative Saturation, Ω	Q, K_r
Mineral dissolution	Negative	< 1	$Q < K_r$
Mineral precipitation	Positive	> 1	$Q > K_r$
Equilibrium	0	1	$Q = K_r$

IIB.2.2 Coprecipitation

Contaminant plumes are often characterized by concentrations of dissolved solids in excess of that found in ambient ground water. These elevated dissolved solids may be derived as a component of the contaminant source or due to the dissolution of soil or aquifer solids during plume transport. Examples of these processes include interactions of acid wastes with aquifer solids leading to dissolution of aquifer minerals (e.g., carbonates or oxyhydroxides) or the development of reducing conditions driven by microbial degradation of organic contaminants that result in reductive dissolution of iron-bearing minerals. With downgradient transport, changes in ground-water chemistry or interaction with unimpacted aquifer solids may lead to precipitation of these major ground-water constituents out of solution. Contaminants may be removed from ground water at the location where precipitation of these major ground-water constituents occurs. This process is called coprecipitation, since the contaminant is sequestered within a newly formed precipitate, but only as a trace structural component within the precipitate. Examples of major precipitate classes with a coprecipitated contaminant include oxyhydroxides (e.g. $Fe_{1-x}Cr_x(OH)_{3(s)}$), carbonates (e.g., $Ca_{1-x}Cd_xCO_{3(s)}$), sulfides (e.g., $Fe_{1-x}Ni_xS_{2(s)}$), and phyllosilicates. The contaminant may be coprecipitated in a cationic or anionic form depending on ground-water chemistry and the nature of the precipitating phase.

For coprecipitates (or solid solutions) the concentration of the contaminant in ground water in contact with a precipitate may be reduced significantly below that observed for ground water in which the concentration of the contact is governed by the solubility of a precipitate in which the contaminant is a major structural component (e.g., $Ca_{1-x}Cu_xCO_{3(s)}$, coprecipitate vs. $CuCO_{3(s)}$, pure precipitate). For example, the partial molal Gibbs free energy of a binary mixture can be expressed as the sum of two components: a mechanical mixing term and a free energy of mixing term ($\Delta G_{mixture}$):

$$\bar{G}_{mixture} = \left(X_1\bar{G}_1 + X_2\bar{G}_2\right) + \Delta G_{mixture}$$

where X_1 and X_2 are the mole fractions of two components in a binary mixture. The $\Delta G_{mixture}$ term contains an ideal component that depends on X_1 and X_2 and a non-ideal component dependent on X_1, X_2, and activity coefficients in the solid phase (γ_1 and γ_2):

$$\Delta G_{mixture} = RT\left[X_1 \ln X_1 + X_2 \ln X_2\right] + RT\left[X_1 \ln \gamma_1 + X_2 \ln \gamma_2\right]$$

For an ideal solid solution, $\gamma_1 = \gamma_2 = 1$, so that $RT\,[X_1 \ln\gamma_1 + X_2 \ln\gamma_2] = 0$. Ideal mixing may be approached where the amount of substitution is very low (a dilute solid solution) or where the mixing cations are closely matched in size and charge. In this case, the $\Delta G_{mixture}$ function is a symmetrical parabola having a minimum at $X_1 = X_2 = 0.5$. Hence as a general rule, the free energy of binary mixtures is less than that of the pure, end-member components. It follows that the solubility of an ion can be lowered in a mixed ionic compound relative to the solubility of the pure compound.

Remobilization of a coprecipitated contaminant will be governed by the overall stability of the host precipitate, which may be controlled by ground water parameters such as pH and/or redox state. In most cases, the identification of a coprecipitation process cannot be made with a single line of evidence. Observations of decreased contaminant concentrations concurrent with decreases in the concentrations of major ground-water constituents such as Ca, Fe, or dissolved sulfide may be indicative of a coprecipitation event. It is recommended that this evidence be supplemented with solid phase characterization approaches, such as chemical extractions or microanalytical techniques, to confirm that coprecipitation is an attenuation mechanism.

IIB.2.3 Surface Precipitation

Surface precipitation may result when adsorption leads to high sorbate coverage at the mineral-water interface. Surface precipitation can be thought of as an intermediate stage between surface complexation and bulk precipitation of the sorbing ion in solution (Farley et al., 1985; Ford et al., 2001). At low concentrations of the sorbing metal at the mineral surface, surface complexation is the dominant process. As the concentration of the sorbate increases, the surface complexation concentration increases to the point where nucleation and growth of a surface precipitate occurs. Surface precipitation can be viewed as a special case of coprecipitation where the mineral interface is a mixing zone for ions of surface precipitate and those of the underlying substrate. It is generally believed that surface precipitation can occur from solutions that would appear to be undersaturated relative to precipitate formation based on considering solution saturation indices. The reason for this may be due in part to different equilibrium constants for surface precipitation versus precipitation from solution, or may be related to the way the mineral-water interface is modeled (Sverjensky, 2003). For example, the dielectric constant of water and therefore activity coefficients in bulk solution may be different from activity coefficients near a mineral surface. Again, the identification of a surface precipitation process cannot be made only with solution data. Solid phase characterization data, such as chemical extractions or microanalytical techniques, are needed to confirm that surface precipitation plays a role as an attenuation mechanism.

IIB.2.4 Mineral Transformation

In many cases the solids that precipitate in near surface environments are not the most thermodynamically stable phases. For example, hydrous ferric oxide, ferrihydrite, is metastable relative to the iron oxyhydroxide goethite. The preponderance of metastability in near surface environments is a consequence of the slowness of chemical reactions at temperatures typical of surficial environments. Kinetics, therefore, play an integral role in ground-water and soil geochemistry. Mineral transformation is one example of how metastable precipitates evolve toward more stable mineral phases within an aquifer. Ultimately, contaminants that are initially adsorbed onto or coprecipitated with these metastable precipitates are likely to become more resistant to remobilization if they are incorporated into the more stable transformation product.

The Ostwald Step Rule is often obeyed in low-temperature mineral formation. Precipitation of less stable and more soluble phases is followed by transformation to progressively more stable and less soluble phases. This behavior stems from the preferential formation of materials with fast precipitation kinetics over nucleation and growth of phases with slow kinetics (Stumm, 1992). Differences in precipitation kinetics are often tied to structural complexity of the precipitating mineral. Relatively simple structures are able to form rapidly whereas ordered structures, although more stable, require longer time periods to develop. Precursor phases are usually poorly crystalline and they may be chemically dissimilar to the final stable mineral. Examples that follow the Ostwald Step Rule include the precipitation of ferrihydrite and transformation to more stable iron oxyhydroxides (goethite) and iron oxides (hematite), the precipitation of mackinawite and transformation to pyrite, and the precipitation of amorphous aluminosilicates such as allophane and transformation to halloysite and kaolinite. Transformation pathways result from solution mediated processes or solid-phase transitions (Steefel and van Cappellen, 1990).

The iron monosulfide-to-iron disulfide transformation has been widely studied in the laboratory and in the field. In this example of a mineral transformation process, mackinawite ($Fe_{1+x}S$) precipitates as concentrations of dissolved sulfide and ferrous iron accumulate in pore water. It has been determined that in sulfate-reducing environments, pore water concentrations of ferrous iron and sulfide are controlled by the solubility of mackinawite. Mackinawite, however, is metastable with respect to the iron disulfides, pyrite and marcasite. The rate of transformation from mackinawite to pyrite or marcasite depends on pH and redox conditions. Metals that coprecipitate with mackinawite are likely incorporated into pyrite, which is more stable over a wide pH range and in anoxic conditions. The rate at which this transformation occurs will be governed by chemical conditions including the coprecipitation or adsorption of contaminants and other dissolved constituents from solution. Site characterization aspects relating to mineral transformation processes as an immobilization mechanism will involve determining the spatial concentration distribution of precursor phases and their more stable transformation products along with contaminant associations using mineralogical and wet chemical characterization tools.

IIB.3 Implications for Natural Attenuation Assessment

The sorption processes discussed in the preceding paragraphs may act in isolation or together to arrest contaminant migration within the aquifer. Factors that dictate which process is likely to dominate contaminant attenuation include chemical properties of the contaminant, chemical characteristics of the ground water, and properties of the aquifer solids. Due to the complexities of directly identifying the immobilized form of the contaminant, it is likely that multiple lines of evidence will be needed to adequately discern the controlling attenuation reaction. These lines of evidence will include the evaluation of patterns in ground-water chemistry that point to potential precipitation or coprecipitation reactions, evaluation of aquifer solids to determine patterns in contaminant and solid component associations, and the use of chemical speciation or reaction models to assess if ground-water and aquifer solid characteristics are consistent with observed contaminant attenuation. Additional perspective on possible sorption processes for specific contaminants is provided in the contaminant-specific chapters included in Volume 2 and 3 of this document.

IIC. Microbial Impacts on Inorganic Contaminant Attenuation

The chemical characteristics of ground water and properties of the aquifer mineral components are, in part, influenced by microbial reactions. Microbial activity within the aquifer may also play a more direct role in controlling contaminant speciation and migration. The influence of microbial reactions may be more pronounced in contaminant plumes that also contain degradable organic contaminants such as hydrocarbons or chlorinated solvents. In these instances, the plume geochemistry may differ significantly from that observed in ambient ground water at a site. If microbial reactions play a significant role in contaminant attenuation, it may be necessary to gather information on the degree that

Appendix B

Compound Specific Isotope Analysis

COMPOUND SPECIFIC ISOTOPE ANALYSIS (CSIA)

Hunkeler, Daniel, Rainer U. Meckenstock, Barbara Sherwood Lollar, Torsten C. Schmidt, and John T. Wilson. 2008. A Guide for Assessing Biodegradation and Source Identification of Organic Ground Water Contaminants Using Compound Specific Isotope Analysis (CSIA). U.S. Environmental Protection Agency. Office of Research and Development. National Risk Management Research Laboratory, Ada, OK. EPA 600/R-08/148. December 2008.

An evaluation of the contribution of natural biodegradation or abiotic transformation processes in ground water is usually crucial to the selection of Monitored Natural Attenuation (MNA) as a remedy for a site. Documentation that the organic contaminant is actually being degraded is important for performance monitoring of MNA, performance monitoring of active in situ bioremediation, and performance monitoring of many other active remedial technologies. Stable isotope analyses can provide unequivocal documentation that biodegradation or abiotic transformation processes actually destroyed the contaminant.

When organic contaminants are degraded in the environment, the ratio of stable isotopes will often change, and the extent of degradation can be recognized and predicted from the change in the ratio of stable isotopes. Recent advances in analytical chemistry make it possible to perform Compound Specific Isotope Analysis (CSIA) on dissolved organic contaminants such as chlorinated solvents, aromatic petroleum hydrocarbons, and fuel oxygenates, at concentrations in water that are near their regulatory standards.

This appendix excerpts Section 4 of this document: “Interpretation of Stable Isotope Data from Field Sites”.

4.0

Interpretation of Stable Isotope Data from Field Sites

This section is intended for contractors and consultants that will evaluate data on stable isotope ratios, and produce a report for the site manager and the regulatory staff. It is also intended for regulators who will review the report. This section presents a simple equation (the Rayleigh equation) that may be used to predict the extent of biodegradation of an organic compound from changes in the value of the stable isotopic ratio ($\delta^{13}C$ or $\delta^{2}H$). This section discusses conditions that are necessary to apply the Rayleigh equation to predict biodegradation of an organic contaminant in ground water samples from field sites. It discusses the different assumptions that are necessary to calculate the extent of biodegradation, and evaluates situations where the various assumptions are most appropriate. It compares rates of biodegradation extracted from concentration data from monitoring wells to rates of biodegradation extracted from CSIA analyses. The section illustrates the use of CSIA analyses to estimate field-scale rates of biodegradation when it is impossible or misleading to extract the rates from data on attenuation of concentrations. It discusses the effect of heterogeneity of flow and of the rate of biodegradation on stable isotopic ratios, and it provides recommendations to minimize the confounding effect of heterogeneity on the estimate of biodegradation.

4.1. Prerequisites for Application of Isotope Data to Demonstrate and Quantify Biodegradation

Sherwood Lollar et al. (1999) suggested four criteria that must be met to apply CSIA to provide evidence for biodegradation in the field. These original criteria, with two additional criteria, form the basis for the recommendations below and hence will be discussed in some detail.

In the course of many biochemical and abiotic reactions, molecules containing the lighter isotopes exclusively (i.e. ^{12}C) tend to react more rapidly compared to molecules containing the heavy stable isotope (i.e. ^{13}C). As the reaction proceeds, the ratio of stable isotopes in the material that remains behind, in the material that has not gone through the reaction, will therefore change. The more the reaction proceeds the more pronounced the isotope shift in the ratio of ^{13}C to ^{12}C will be. This change in the ratio of stable isotopes is called stable isotope fractionation and can be expressed as the stable isotope fractionation factor alpha (α) as described in Equation 4.1:

$$\alpha = \mathrm{R}_a/\mathrm{R}_b = \left(1000 + \delta^{13}C_a\right)/\left(1000 + \delta^{13}C_b\right) \qquad \textbf{4.1}$$

where R is the stable isotope ratio ($^{13}C/^{12}C$) of the compound, and the subscripts *a* and *b* may represent a compound at time zero (t_0) and at a later point (t) in a reaction; or a compound in a source zone, versus a down gradient well. For many organic contaminants, stable isotope fractionation during biotic and abiotic degradation can also often be quantitatively described by the Rayleigh equation (Equation 4.2)

$$\mathrm{R} = \mathrm{R}_0\, f^{(\alpha-1)} \qquad \textbf{4.2}$$

where R is the stable isotope ratio ($^{13}C/^{12}C$) of the compound at time t, R_0 is the initial isotope value of the compound and *f* is the ratio (C/C_0) of the concentrations of the compound at time t and zero.

As discussed in Section 2, the stable isotope ratio is reported in the delta notation, where the ratio is normalized to the ratio in a standard.

Equation 4.2 can be rearranged to produce Equation 4.3 (Section 7 for details)

$$f = e^{(\delta^{13}C_{groundwater} - \delta^{13}C_{source})/\varepsilon} \qquad \textbf{4.3}$$

where $\delta^{13}C_{\mathrm{groundwater}}$ is the measure of the isotope ratio in the organic contaminant in the sample of ground water, $\delta^{13}C_{\mathrm{source}}$ is the isotopic ratio in the un-fractionated organic contaminant before biodegradation has occurred, and epsilon (ε) is the stable isotope enrichment factor as defined in Equation 4.4.

$$\varepsilon = (\alpha - 1) * 1000 \qquad \textbf{4.4}$$

The larger the fractionation during the reaction, the more negative is the corresponding value of epsilon. Throughout this Guide we will use the stable isotope enrichment factor (ε) to make all the data easily comparable.

The next few sections discuss in detail the criteria that must be met to apply CSIA to provide evidence for biodegradation in the field.

4.1.1. Does Biodegradation of the Compound Produce Isotope Fractionation?

For CSIA to be useful, laboratory studies must have demonstrated that significant fractionation does occur during biodegradation (see Table 8.1 for a compendium of information on enrichment factors during biodegradation). While this basic principle has been established for a wide range of organic contaminants (including chlorinated ethylenes and ethanes, aromatic hydrocarbons such as the BTEX compounds, lower molecular weight alkanes, MTBE, TBA, and some PAHs), it is not true for all compounds under all circumstances. For example, high molecular weight petroleum hydrocarbons tend to be isotopically conservative because any fractionation due to biodegradation is generally "diluted" by the large number of non-reactive carbon atoms. Similarly, for some compounds under specific conditions (i.e. aerobic toluene biodegradation) significant carbon isotope fractionation is observed only if the degradation pathway proceeds by reactions that attack the methyl group rather than reactions that attack the benzene ring (Morasch et al., 2002).

4.1.2. Is the Observed Extent of Fractionation Significant?

To be significant, the extent of fractionation must be greater than the total analytical uncertainty. In addition, the observed difference in the values of $\delta^{13}C$ must exceed the spatial and temporal variability introduced by different sources of contamination at the site, by the mixing of ground water flow lines, and by what are typically the minor effects of processes such as sorption or volatilization. As demonstrated in Section 2.4, the total analytical uncertainty for $\delta^{13}C$ analyses is typically ± 0.5‰. As a result, the observed fractionation must be at a minimum > 1‰. To ensure reliable interpretation, we recommend that fractionation on the order of 2‰ be used as a criterion for positive identification of degradation in order to minimize the possibility of an erroneous interpretation. Provided that other causes for the differences in the stable isotope values can be excluded, there is a qualitative indication of biodegradation or transformation along a flow path in ground water when the values of $\delta^{13}C$ in the compounds of interest in the down gradient wells are enriched (less negative) by 2‰ compared to values of $\delta^{13}C$ in the up gradient well.

It is important to appreciate that this criterion of 2‰ will be met at very different levels of biodegradation, depending on the extent of fractionation during degradation of a given compound. For example, due to the large enrichment factors (ε) associated with reductive dechlorination of TCE, observed fractionation exceeds 2‰ at a very early stage of biodegradation, when < 20% is degraded or > 80% is still remaining (Panel A of Figure 4.1). In contrast, for petroleum hydrocarbons such as benzene and toluene, the important but more subtle carbon isotope effects observed during degradation are such that significant fractionation > 2‰ is only discernable when biodegradation has proceeded more extensively and almost 60% of the original contaminant mass has been degraded, as illustrated in Panel B of Figure 4.1 (Ahad et al., 2000; Mancini et al., 2003; Meckenstock et al., 1999; Morasch et al., 2004). Several studies suggest that for compounds with small enrichment factors for carbon, such as the aromatic hydrocarbons, the larger enrichment factors (ε) associated with hydrogen isotope fractionation may make coupling of CSIA for carbon and hydrogen the best approach to identify biodegradation (Fischer et al., 2008; Gray et al., 2002; Mancini et al., 2003; Mancini et al., 2008a).

Once biodegradation is documented in a qualitative fashion, the next step is an evaluation of whether isotopic variation can be used to quantitatively calculate the extent of biodegradation and to derive biodegradation rates based on the CSIA data.

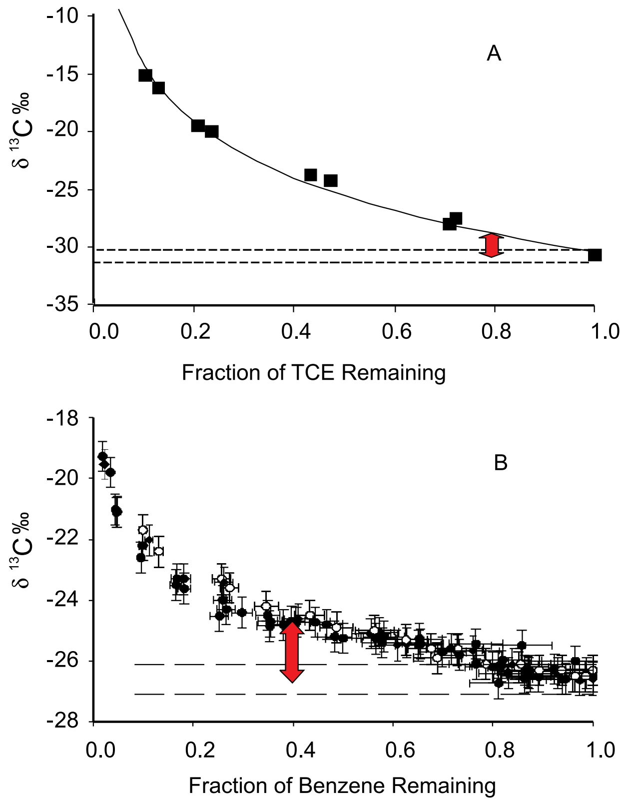


Figure 4.1. Degradation of (A) TCE and (B) benzene by enrichment cultures. The stable carbon isotope ratios in the substrate that remains after biodegradation are plotted against the fraction of the original concentration remaining. Data for TCE degradation are after Sherwood Lollar et al. (1999) and for benzene after Mancini et al. (2003). Dotted lines represent ± 0.5 ‰ around the $\delta^{13}C_0$ value of TCE and of benzene, respectively. The vertical solid red arrow represents the extent of fractionation necessary to recognize biodegradation in field data (2‰).

4.1.3. Is the Observed Fractionation Reproducibly and Accurately Correlated to a Distinct Process?

If fractionation is to be used to predict degradation, the isotopic enrichment factor for a particular contaminant that is degraded by a particular process or pathway must be reproducible from one study to the next. The results of extensive research have shown this criterion to be necessary for valid interpretation of data on $\delta^{13}C$.

Published information on laboratory-derived, compound specific enrichment factors that were determined for biodegradation processes under various redox conditions is available from recent review articles (Elsner et al., 2005; Mancini et al., 2003; Meckenstock et al., 2004; Morrill et al., 2006; Schmidt et al., 2004). Many values are summarized in Table 8.1. Enrichment factors are also available on the internet at www.isodetect.de, and this website will provide updated information over time. The web page is available in either German or English. For the English Language website; select the link for the English Website from the menu, follow the link to *isotope enrichment*, and follow the link to *table Isofrac*. In the experiments listed in Table 8.1, either single strains or mixed bacterial cultures degraded the compounds as the sole carbon source using a single electron acceptor (e.g. oxygen, nitrogen, sulfate). For the same compound and the same biochemical pathway of degradation, the agreement among the enrichment factors determined by the different studies is quite good, reflecting the fact that, to first approximation, the main controlling influence on fractionation is the reaction mechanism (e.g. bond breakage).

For many of the compounds in Table 8.1, different laboratories and different studies report a range of enrichment factors for the same biodegradation process. Table 4.1 below summarizes data from Table 8.1 to compare the total range of values published to date for reductive dechlorination of chlorinated ethenes. Carbon isotope fractionation during reductive dechlorination of chlorinated ethenes is perhaps the most extensively studied system to date, with the values in Table 4.1 reflecting experiments done by a large number of different groups worldwide with a wide range of different microbial consortia and microcosm conditions.

Table 4.1. Ranges of carbon isotope enrichment factors for microbial reductive dechlorination of chlorinated ethenes published in the literature to date (Bloom et al., 2000; Cichocka et al., 2007; Hunkeler et al., 2002; Lee et al., 2007; Slater et al., 2001). See also Table 8.1.

Compound	**Range of α values**	**Range of ε (‰)**
TCE	0.9975 to 0.9771	-2.5 to –22.9
cis-DCE	0.9859 to 0.9789	-14.1 to –21.1
VC	0.9785 to 0.9689	-21.5 to –31.1

While variation in the range of published enrichment factors for a given degradation reaction are very important from the point of view of understanding the details of the reaction mechanism, the variation in published values does not necessarily introduce a large uncertainty into the estimate of the fraction remaining after degradation (*f*) as calculated using Equation 4.2 or 4.3.

For instance, the total analytical uncertainty in measured $\delta^{13}C$ values is typically ±0.5‰ for carbon CSIA for many of the hydrocarbon contaminants investigated to date. Total uncertainty in (*f*), the fraction of contaminant remaining, is at a minimum the analytical uncertainty associated with typical VOC concentration analyses. While under optimized performance, VOC concentrations can be determined to a precision of ±5%; typically, commercial VOC analyses are ±20 to 30%. In the estimate of (*f*) using Equation 4.2, uncertainty in the second or third decimal place in the exponent (α-1) does not contribute as much uncertainty as does the uncertainty in the direct calculation of (*f*) caused by uncertainty in the analysis of VOC concentrations. This can be shown by calculating the propagation of errors for the individual parameters in the Rayleigh equation (Griebler et al., 2004b). More examples and discussion are provided in Section 4.2.3.4a.

Data published to date suggests that the rate of biodegradation does not seem to significantly impact the observed enrichment factor ε (Mancini et al., 2006; Morasch et al., 2001). The dominant controlling parameter on fractionation is the reaction mechanism. As is predicted from theoretical principles of isotope fractionation, degradation pathways or reaction mechanisms can have characteristic stable isotope enrichment factors based on the bonds that are broken. Variations between the stable isotope enrichment factors for one pathway compared to another are one of the most important factors influencing stable isotope fractionation during biodegradation. This principle is a well-established foundation of stable isotope geochemistry, having been demonstrated for microbial methanogenesis via different pathways in a landmark paper in 1985 (Whiticar and Faber, 1985) and elucidated for photosynthesis by C3 versus C4 metabolic pathways more than twenty years ago (O'Leary, 1981). It follows that conditions that control the dominant degradation pathway can control the characteristic fractionation pattern, and the value of the isotopic enrichment factor. For compounds that degrade under different reaction mechanisms under aerobic versus anaerobic conditions, the characteristic isotopic fractionation observed varies with redox conditions. This has been quite extensively studied for MTBE (Hunkeler et al., 2001a; Kolhatkar et al., 2002; Kuder et al., 2002; Kuder et al., 2005; Rosell et al., 2007; Zwank et al., 2005), benzene and toluene (Ahad et al., 2000; Fischer et al., 2007; Fischer et al., 2008; Hunkeler et al., 2001b; Mancini et al., 2003; Mancini et al., 2008a; Meckenstock et al., 2004; Morasch et al., 2001; Morasch et al., 2002; Morasch et al., 2004) and is recently being elucidated for the chlorinated ethenes (Chartrand et al., 2005; Chu et al., 2004). Even under similar redox conditions, if different microbial populations use different degradation pathways, each can result in a reproducible and distinct value for the isotopic enrichment factor, as has been shown for aerobic biodegradation of 1,2-dichlorethane (Hirschorn et al., 2004), aerobic biodegradation of toluene (Morasch et al., 2002), and aerobic biodegradation of MTBE (Rosell et al., 2007).

In most aerobic degradation pathways, the first step is usually an activation of the molecules by an oxygenase reaction to introduce hydroxyl, epoxide or other reactive oxygen-containing groups. For some compounds, there are several types of oxygenase reactions, and the extent of isotope fractionation can depend on the particular oxygenase reaction that is responsible for biodegradation. In the case of aromatic hydrocarbons this may range from undetectable fractionation of stable isotopes of carbon for reactions that are carried out by dioxygenase enzymes that attack the π-electron system of the aromatic ring to strong fractionation caused by reactions carried out by monooxygenase enzymes that attack the ring or methyl groups. Practical recommendations for assessing the uncertainty introduced by the range of available fractionation factors are discussed in detail in Section 4.4.

4.1.4. Do Non-Degradative Processes Influence the Observed Isotope Fractionation?

In order to use CSIA to understand the degradation of contaminants, the isotope fractionation during degradation must be readily discernable from isotope effects associated with other subsurface processes that do not destroy the contaminant, such as volatilization, dissolution and sorption. Isotope fractionation during volatilization (Harrington et al., 1999; Ward et al., 2000); dissolution (Dempster et al., 1997; Hunkeler et al., 2004; Slater et al., 1999; Ward et al., 2000); diffusion (Hunkeler et al., 2004; Bouchard et al., 2008) and sorption (Harrington et al., 1999; Kopinke et al., 2005; Meckenstock et al., 1999; Schuth et al., 2003; Slater et al., 2000) is typically small or is indiscernible outside of the analytical uncertainty typical for CSIA (±0.5‰ for carbon isotopes; ±5‰ for hydrogen). During sorption of contaminants to carbonaceous material, a hydrogen isotope shift of only 8‰ was observed after 95% of the contaminant was sorbed (Schuth et al., 2003). Significant hydrogen isotopic effects were only observed in laboratory experiments where aromatic hydrocarbons underwent near complete vaporization or sorption, in excess of 95% removal (Schuth et al., 2003; Wang and Huang, 2003). Hence, Wang and Huang (2003) noted that large isotopic shifts might be relevant to processes such as air sparging and to studies in the unsaturated zone, but large isotopic shifts are not likely to be significant in most natural systems where extensive mass loss due to volatilization or sorption is unusual. In a recent study documenting carbon isotope fractionation due to diffusion, Bouchard et al. (2008) demonstrated that even in the unsaturated zone where diffusive effects on isotope composition might be expected to be most pronounced compared to the saturated zone, diffusive effects were only observable if measured within a few days of the spill, and where measurements could be done at a very fine spatial scale.

4.1.5. Do Abiotic Degradation Processes Occur and Produce Isotope Effects for the Compound of Interest?

The relative importance of biodegradation versus processes of abiotic degradation at the site must be considered. In the past few years, the principles of Rayleigh controlled isotope fractionation of organic contaminants in ground water have been shown to apply to abiotic degradation as well as biodegradation (Bill et al., 2001; Elsner et al., 2007a; Elsner et al., 2008; Hofstetter et al., 2008; Slater et al., 2002; VanStone et al., 2004; VanStone et al., 2008; Zwank, et al., 2005). Zero valent iron is widely used in active remediation of ground water contamination. While much research is still underway to understand the precise reaction mechanisms associated with degradation of chlorinated ethenes on zero valent iron, CSIA indicates that the mechanisms are similar to the familiar mechanisms associated with biodegradation, and that different abiotic degradation mechanisms are associated with different characteristic patterns of fractionation.

Traditionally, rates of natural abiotic degradation in ground water were thought to be insignificant unless they were enhanced through abiotic remediation schemes such as the addition of zero valent iron. This view is changing. There have been several recent studies of the role of abiotic reactions with minerals and the role of microbially-mediated abiotic reactions at field sites (Bradley and Chapelle, 1997; Butler and Hayes, 1999; Cervini-Silva et al., 2001; Ferrey et al., 2004; Lee and Batchelor, 2002; McCormick and Adrians, 2004).

The possibility of abiotic degradation introduces the challenge of distinguishing between the effects of abiotic and biotic isotopic fractionation in any system where both types of degradation may be significant. Liang et al. (2007) noted that the isotope fractionation during abiotic degradation of PCE and TCE by FeS was much greater than the fractionation during anaerobic biodegradation of PCE and TCE. Reduced iron sulfides such as FeS can be an important component of aquifer sediments at hazardous waste sites. Liang et al. (2007) warn that the use of an enrichment factor appropriate for biodegradation instead of the factor appropriate for the abiotic mechanism may overestimate the true extent of degradation at field scale. A similar pattern of smaller biological enrichment factors compared to abiotically-mediated degradation has been identified for MTBE and 1,1,1-TCA (Elsner et al., 2007a; 2007b) and PCE (Lee et al., 2007; Nijenhuis et al., 2005; Slater et al., 2001; Slater et al., 2003), suggesting that additional rate-limiting factors in biochemical reactions require more in depth research. VanStone et al., (2008) and Elsner et al., (2008) discuss the potential of using CSIA to distinguish between abiotic and biodegradation processes where both types of processes may be important.

4.1.6. Is the Rayleigh Equation an Appropriate Model to Describe the Data Set?

For compounds that are intermediates in degradation pathways, such as the products of reductive dechlorination of chlorinated ethylenes, a straightforward application of the Rayleigh equation (Equation 4.2) is not strictly possible. The isotope ratio in the intermediate compound will change due to the combined effects of isotopic fractionation during its production from the parent compound and isotopic fractionation due to its own continuing degradation. There is one important exception. The Rayleigh equation can be used when complete transformation of the parent compound occurs prior to further degradation of the intermediate compound (Morrill et al., 2005).

When production and degradation of the intermediate compound occurs simultaneously, a more complex isotope evolution occurs that can be evaluated using multistep reactive transport models (van Breukelen et al., 2005; Morrill et al., 2006). Quantitative information on biodegradation can be obtained by fitting an analytical model (Beranger et al., 2005) or numerical model (van Breukelen, et al., 2005) that describes the isotope evolution during sequential processes to the measured isotope data. Van Breukelen et al. (2005) used a simple one dimensional model to provide insight in the rates of transformation of parent and intermediate compounds. The simulation of different degradation scenarios such as various degrees of degradation or different relative rates of biodegradation for different steps in a multi-step process can also be very useful as a benchmark for a semi-quantitative interpretation of isotope data.

For certain chlorinated solvents the situation is even more complex because the degradation pathways of different compounds can converge and produce the same daughter products (Kirtland et al., 2003). For example, trichloroethylene (TCE) can be produced from biological reductive dechlorination of tetrachlorethylene (PCE), or through an abiotic reaction from 1,1,2,2-tetrachlorethane. If several potential parent compounds are present in ground water at the same time, it is difficult to interpret the behaviour of the compound from CSIA. Due to these complexities, the conceptual model for biodegradation at a site should distinguish those compounds that are only present as parent compounds from those compounds which might be present both as parent and daughter compounds. See for example Hirschorn et al., (2007). Section 4.2 covers the appropriateness of a Rayleigh model in more detail with respect to field data.

4.2. Recommended Steps for the Quantification of Biodegradation Based on CSIA

4.2.1. Site Characterization

Use of CSIA is no silver bullet and will be most useful and cost effective when applied within the context of the hydrological, geological, geochemical and microbiological parameters at the site. The factors that affect contaminant transport and degradation over time as well as space must be identified and evaluated. This includes the important geohydrological parameters (ground water flow direction, hydraulic conductivity, hydraulic gradient) and geochemical conditions (concentrations of oxygen, nitrate or sulfate within the plume). Ultimately, a conceptual site model can be developed that will reveal practicable remediation goals that are capable of protecting existing or potential receptors from contamination. Iterative generation and interpretation of field data from a general survey is necessary to identify the major compartments of the plume (the source, the fringe, the center line, and the mixing zones) as well as the most relevant processes that contribute to natural attenuation.

4.2.2. Evaluate Field Data for the Fit to the Rayleigh Model

The Rayleigh model (Equation 4.2 and 4.2) predicts that a plot of $\delta^{13}C$ or $\delta^{2}H$ on the logarithm of the concentration remaining should be a straight line. If field data are plotted as described above, and the data follow a straight line, then a single process for biodegradation or abiotic transformation likely controls the concentrations at field scale, as illustrated in Figure 4.2. This is called a Rayleigh correlation. Dilution, dispersion, sorption, volatilization, and mixing between contaminant sources with different values of $\delta^{13}C$ or $\delta^{2}H$ will cause the data to fall off of the straight line.

Given the importance of dilution and dispersion at field scale, it might intuitively seem likely that no set of realistic field data would show a Rayleigh correlation. However, case studies and evolving field experience have in fact shown that a significant number of sites do have field data that fit the Rayleigh model (Abe and Hunkeler, 2006; Griebler et al., 2004b; Kolhatkar et al., 2002; Morrill et al., 2005). The existence of such a correlation indicates that biodegradation or abiotic transformation is the significant process that controls changes in concentrations of contaminants.

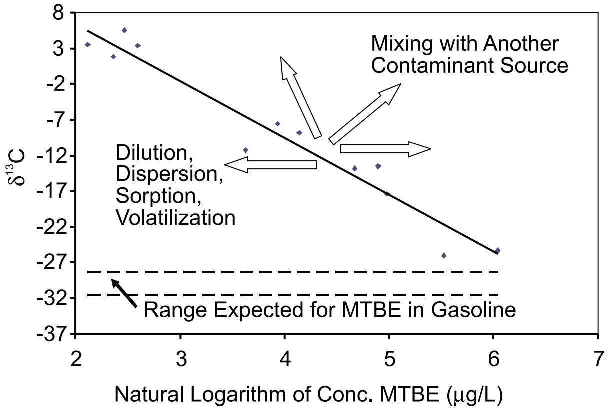


Figure 4.2. Testing field data on CSIA and concentrations of contaminants for fit to the Rayleigh equation. Deviations from a straight regression line in the plot of $\delta^{13}C$ on the natural logarithm of concentration can indicate that processes other than degradation control the concentrations of contaminants. Example data plotted for Table 1 of Kolhatkar et al. (2002). The dotted lines bound the values of $\delta^{13}C$ that are expected for MTBE that was blended into gasoline.

The first recommendation for using CSIA to quantify biodegradation is to plot the δ^{13}C of the compound against the natural logarithm of the concentration of the compound to determine if these parameters show a Rayleigh correlation as illustrated in Figure 4.2. This "test" is simply the first step in determining if the Rayleigh controlled fractionation inherent in Equation 4.2 is an appropriate model for the site. There is no need to take the location of the respective wells into account on this level when performing the Rayleigh analysis because the location does not influence the calculation. However, data points that drastically fall of the straight regression line can be identified and might be evaluated further for other processes that influence the compound apart from biodegradation, such as dilution in the monitoring well, dispersion along the flow path, or volatilization. A strong correlation to the Rayleigh model adds considerable confidence to the application of CSIA data to understand the behaviour of a contaminant at a site.

Variations in the length and elevation of the screened interval of monitoring wells can cause a well to produce ground water that is either dominated by the plume of contamination, or cause the well to produce water that has a small contribution from the plume and a major contribution from clean ground water above or below the plume. Details of well construction can have a strong effect on the concentration of the organic compound in water produced by the well. A poor correlation to the Rayleigh model may be due to these incidental perturbations in the concentration that are created by the monitoring wells. As a result, a poor correlation does not automatically disqualify a site for the application of CSIA to understand the transformation processes.

4.2.3. Determination of the Primary Isotope Signature ($\delta^{13}C_{source}$ or $\delta^{2}H_{source}$)

The primary isotopic signature is the isotopic ratio of the organic contaminant of concern before it is fractionated by biodegradation processes or abiotic transformations. The ideal approach would be to measure the isotopic signature of the primary contaminant that was spilled at the site. However, this is rarely feasible. Nor is measurement of $\delta^{13}C_{source}$ or $\delta^{2}H_{source}$ for the most recent spill necessarily relevant at many sites where there has been a history of multiple spills or leakage.

There are three basic approaches to determination of $\delta^{13}C_{source}$ or $\delta^{2}H_{source}$. One approach compares values of δ^{13}C or δ^{2}H for contaminants in ground water to values of δ^{13}C or δ^{2}H reported in the literature. The second and third approaches are entirely site specific. They compare δ^{13}C or δ^{2}H for contaminants in different samples of ground water to determine the extent of degradation between points in space (between different wells) or points in time (temporal variation within a single well) at a specific site.

4.2.3.1. Value of $\delta^{13}C_{source}$ or $\delta^{2}H_{source}$ Based on Literature.

In the routine case where samples of the actual spilled material are neither available nor relevant, the approach is to make an assumption for $\delta^{13}C_{source}$ or $\delta^{2}H_{source}$ based on published values in the literature for undegraded pure product. This is not unreasonable for petroleum hydrocarbons, or for anthropogenic compounds such as chlorinated ethenes produced from petroleum hydrocarbon feedstocks, because the range of δ^{13}C for petroleum hydrocarbons is well characterized and relatively well constrained. As degradation proceeds, a point is reached where the value of δ^{13}C or δ^{2}H may be more positive (more enriched in ^{13}C or ^{2}H) than any reported value from commercially available products. When the value of δ^{13}C or δ^{2}H in the field is more positive than the range in the pure substance, degradation at the site is evident (compare Figure 4.2).

4.2.3.2. Values of $\delta^{13}C_{source}$ or $\delta^{2}H_{source}$ Based on Most Negative Value at the Site

Because biodegradation induces a shift of the residual compound to less negative values of δ^{13}C or δ^{2}H, the most negative values measured for the organic contaminant in ground water at the site can be the best estimate of the original values of $\delta^{13}C_{source}$ or $\delta^{2}H_{source}$. While this approach can work well for compounds for which the fractionation due to biodegradation is large (tens of ‰) relative to the variation in assumed $\delta^{13}C_{source}$, the approach is not recommended for compounds such as benzene and toluene for which the error in the assumption of $\delta^{13}C_{source}$ will be large with respect to a relatively small changes in δ^{13}C caused by biodegradation.

4.2.3.3. Values of $\delta^{13}C_{source}$ or $\delta^{2}H_{source}$ Based on Point to Point or Time to Time Comparisons

Quantifying the relative amount of biodegradation between wells, or in a given well over time, is compelling since it involves fewer assumptions than the literature-based approach. It does, however, require a good hydrogeological and geological understanding of the site. In this approach, one can select wells for $\delta^{13}C_{source}$ or $\delta^{2}H_{source}$ that sample the known source zone. As an example, the wells might be screened across an interval with non aqueous phase liquids (NAPL) that act as the source of ground water contaminant. Wells in the source area would be expected to produce water with the highest concentrations of contaminants. Since biodegradation produces more enriched (less negative) $\delta^{13}C$ values, such wells may be assumed to represent the least degraded material at the site.

It is important to note that this approach will provide a conservative estimate of the extent of biodegradation. If undegraded compound is in fact being added to the plume through mixing, desorption, or continued dissolution of NAPL, the addition of this more isotopically negative $\delta^{13}C$ material will minimize the observed fractionation effects produced by biodegradation (Abe and Hunkeler, 2006, Morrill et al., 2005). While continued dissolution of NAPL close to the source zone may result in a complete suppression of the fractionation signal of biodegradation, the calculation can at least provide a conservative upper boundary on C/Co. The true fraction remaining may be less than the estimate.

The most thorough approach would be to calculate the extent of biodegradation using all three approaches for determining $\delta^{13}C_{source}$. If the three estimates agree, the extent of biodegradation is well constrained. In several case studies this was indeed the situation because the source well $\delta^{13}C$ values were not only the most negative $\delta^{13}C$ values at the site, but they were within the published range for undegraded pure product (Sherwood Lollar et al., 2001).

4.2.3.4. Selection of an Appropriate Enrichment Factor

This Guide assumes that the isotope enrichment factors derived from laboratory microcosm studies are applicable to the field. In contaminant hydrology, the removal of organic contaminants in traditional laboratory microcosm studies is commonly used to predict the removal in field scale plumes. The assumptions made in extrapolating isotope enrichment factors to the field are equivalent to the assumptions made in extrapolating data on contaminant degradation from laboratory microcosm studies to predict the behaviour of a plume at field scale.

As discussed in Section 4.1.3, there are two important sources of uncertainty in extrapolation of enrichment factors. The value of the enrichment factor is sensitive to the biodegradation pathway (and hence to parameters such as redox conditions and microbial populations) and to the reproducibility of fractionation factors under any given set of conditions for any given biodegradation reaction pathway. The selection and evaluation of enrichment factors from the literature is a two step process. First, use site specific data on geochemical parameters to determine the most probable pathway for metabolism (or abiotic transformation) of the contaminant at field scale. Then search the literature (Table 8.1) for published enrichment factors for the compound of interest under the relevant redox conditions.

The variation in published enrichment factors for a given set of conditions is a measure of the reproducibility of the enrichment factor. One option to deal with the variation in published enrichment factors is to select the largest enrichment factor in the literature to estimate the extent of biodegradation at field scale. In this case, the “largest” enrichment factor is the most negative factor, the factor with the largest absolute value. For a given change in the value of $\delta^{13}C$ or $\delta^{2}H$, the largest enrichment factor will predict the largest value for the fraction remaining after biodegradation and will predict the smallest extent of biodegradation. As a result, the largest value for the enrichment factors will provide the most conservative estimate of the extent of biodegradation. When the difference in values of $\delta^{13}C$ between the source and the down gradient monitoring wells is small (2‰ to 5‰), the value selected for the enrichment factor can have a stronger influence on the extent of biodegradation predicted from Equation 4.3.

A second option to deal with variation in the published values of the enrichment factors is to calculate a lower boundary on the extent of biodegradation using the highest published enrichment factor, an upper boundary using the lowest published enrichment factor, and a best estimate of bioremediation using the mean of all the enrichment factors, then compare the predictions of the extent of bioremediation. When this approach was applied to data from studies of bioremediation of TCE and *cis*-DCE at spill sites at Dover Air Force Base in Dover, Delaware, USA and at Kelly Air Force Base in San Antonio, Texas, USA, the difference between the upper and lower boundaries on the extent of biodegradation was small (Morrill et al., 2005, Sherwood Lollar et al., 2001).

A third option is to calculate the mean and the standard deviation of the enrichment factors, and then use statistical techniques to estimate propagation of error to determine the effect of the variation in published values for the enrichment factor on the estimate of the extent of biodegradation.

Reactions with large fractionation factors (ε more than an absolute value of 3‰) allow a more sensitive quantification of biodegradation, while reactions with small fractionation factors (ε smaller than an absolute value of 1‰) require a large degree of biodegradation (>90%) before a significant isotopic difference between source and monitoring wells can be resolved (Ahad et al., 2000). As a general principle, as the difference between $\delta^{13}C$ and $\delta^{13}C_{source}$ becomes larger, the uncertainty in the calculation of the extent of biodegradation becomes smaller.

Figure 4.3 compares the relative effect of the value of the isotopic enrichment factor, and the value of $\delta^{13}C_{source}$, on the predicted extent of biodegradation. When the value of $\delta^{13}C$ is close to the value of $\delta^{13}C_{source}$, the estimate of the extent of biodegradation is more sensitive to the value of $\delta^{13}C$. When the value of $\delta^{13}C$ is further away from the value of $\delta^{13}C_{source}$, the estimate of the extent of biodegradation is more sensitive to the value of the enrichment factor ε.

One may be tempted to use fractionation data from a contaminated field site to determine implicit isotope enrichment factors. Although some scientific studies have practiced this approach (Steinbach et al., 2004), it cannot be recommended as a general procedure. The complexity of hydrogeological and microbial processes in the field will give only a crude estimate of the enrichment factor compared to well-controlled laboratory experiments and will certainly introduce additional uncertainty. Therefore, it is advisable to take appropriate laboratory-derived enrichment factors from the literature.

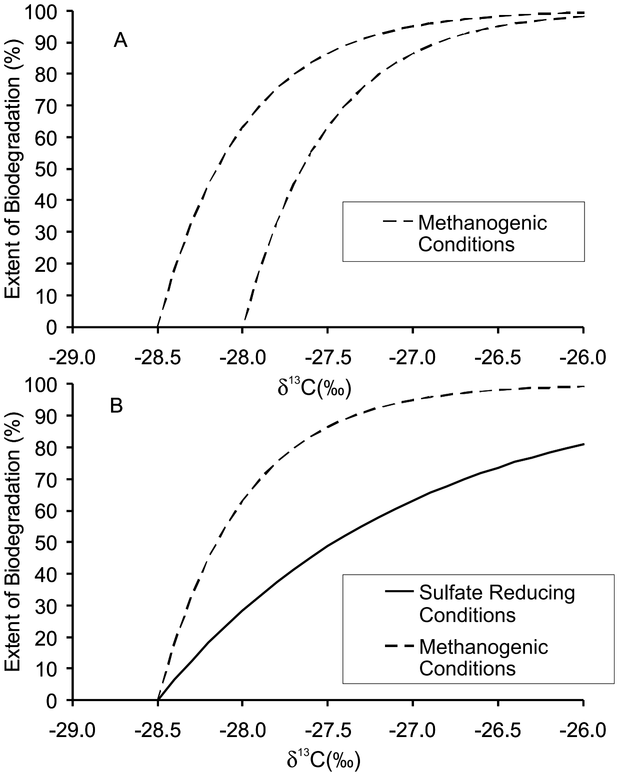


Figure 4.3. Relative influence of different values for $\delta^{13}C_{source}$ (Panel A) and different values for the isotopic enrichment factor ε (Panel B) on the calculated extent of toluene biodegradation. The extent of biodegradation is expressed in percent of the material originally present, calculated as $B = (1-f)$, where f is the fraction remaining as calculated from Equation 4.3. The dashed lines are estimates of the extent of biodegradation from $\delta^{13}C$ for biodegradation of toluene under methanogenic conditions where ε = -0.5‰ with two different values for $\delta^{13}C_{source}$. The solid line is an estimate of the extent of biodegradation under sulfate-reducing conditions where ε = -1.5‰.

4.2.3.5. Estimating an Enrichment Factor when none is Available.

Although the literature on isotope enrichment factors is expanding rapidly, there may be occasions when an isotopic enrichment factor for a particular compound is not available in the literature. The following material describes an approach that may be used to estimate an isotopic enrichment factor from the data available for similar compounds.

Stable isotopic fractionation occurs at a distinct chemical bond within a molecule, where the enzymatic reaction takes place. A heavy isotope at an adjacent position might still affect the reaction but to a much lower extent (referred to as a secondary isotope effect) and can usually be neglected. Heavy atoms further distant from the reactive position have no influence on isotope fractionation. As a first approximation, only the atom in the reactive position of the molecule undergoes isotope fractionation. However, in CSIA the isotopic composition of all of the atoms of a respective element in the molecule is measured (e.g. all carbon atoms).

The stable isotope effect is therefore "diluted" by the number of atoms at non-reactive positions of a compound. One can distinguish between the intrinsic isotope enrichment factor (ε_i) which considers only the isotope shifts at the reactive position and the overall isotope enrichment factor (ε) which determines the isotope fractionation of the entire molecule. Details of this approach can be found in Elsner et al. (2005) and Morasch et al. (2004). The relation of (ε_i) and (ε) follows Equation 4.5, where (n) is the total number of atoms of a particular element in the molecule.

$$\varepsilon = \varepsilon_i / n \qquad \textbf{\textit{4.5}}$$

From the stable isotope enrichment factors and the intrinsic factors published for anaerobic or aerobic degradation of mineral oil constituents and chlorinated solvents it is apparent that CSIA can be successfully applied to recognize isotope fractionation in compounds with no more than twelve to thirteen carbon atoms. For larger molecules, the expected isotope shifts will be so strongly diluted that they fall into the range of the experimental error of the isotope analysis (Morasch et al., 2004).

Expressing fractionation as the intrinsic enrichment factor (ε_i) reveals that the same biochemical reactions produce similar intrinsic enrichment factors for different compounds. Anaerobic degradation of BTEX compounds and methylnaphthalene provide a good example. The primary enzyme reaction in the anaerobic degradation pathways of methylated aromatic hydrocarbons (toluene, xylene, methylnaphthalene) is always a fumarate addition to the methyl group by glycyl radical enzymes. The intrinsic carbon isotope enrichment factors have been shown to be similar (Morasch et al., 2004).

If there is no published value for the isotope enrichment factor (ε) for a compound, but the biochemical reaction of the primary degradation step is known, it should be possible to use literature values for the intrinsic enrichment factors (ε_i) of similar compounds to estimate an isotope enrichment factor (ε) for the compound. Such estimates have been shown to be in the same range of accuracy as those obtained from laboratory experiments with the respective compounds (Meckenstock et al., 2004; Morasch et al., 2004; Zwank et al., 2005).

As an example, a representative carbon isotope enrichment factor for toluene which can be taken from the literature is -1.7‰. As toluene contains 7 carbon atoms the intrinsic enrichment factor ε_i for the reactive carbon position is -1.7‰ * 7 = -11.9‰ (Table 8.1). Imagine that we require an enrichment factor for xylene. Because the initial reaction of the degradation pathway of xylene is similar to toluene degradation we will make an assumption that the intrinsic enrichment factor ε_i for xylene is the same as for toluene (ε_i = -11.9‰). For the overall enrichment factor ε we divide the estimate of ε_i by 8 (xylene contains 8 carbon atoms) to produce an estimate for the enrichment factor of -11.9‰ / 8 = - 1.5‰. This estimate is exactly equivalent to the only value that is available in the literature for a pure culture study of the anaerobic biodegradation of xylene (Morasch et al., 2004; Table 8.1). However, Table 8.1 also reveals that the variation of fractionation factors determined for anaerobic xylene degradation is quite large.

4.2.3.6. Concurrent Application of CSIA Analysis for Different Elements (Two-Dimensional Analysis).

For some contaminants, such as MTBE and benzene, there is a fundamental difference in the enzymatic mechanism for biodegradation under aerobic and anaerobic conditions, and the difference in enzymatic mechanism is reflected in a large difference in the values of the enrichment factors (ε) under aerobic or anaerobic conditions. As discussed in Section 4.1.5 and Section 4.2.3.4, depending on the compound, different values of ε may have an effect on the predicted extent of biodegradation, and the implications should be investigated as in the example in Figure 4.3.

If field measurements of $\delta^{13}C$ are to be used to estimate the extent of degradation, it is necessary to know the mechanism of degradation to be able to select the correct value of ε. Frequently it is not possible from conventional site characterization data to unequivocally associate biodegradation with either the aerobic mechanism or the anaerobic mechanism. However, it may be possible to identify the mechanism of degradation from the concurrent enrichment of both carbon and hydrogen isotopes. Kuder et al. (2005) compared the enrichment of carbon and hydrogen during biodegradation of MTBE in anaerobic microcosms and in field samples from gasoline spill sites in the USA. In a plot of δ^2H for MTBE against $\delta^{13}C$ for MTBE, the data from the field sites had the same distribution as the distribution of the data from the anaerobic microcosm study (Figure 4.4).

Zwank et al. (2005) made the same comparisons of δ^2H against $\delta^{13}C$ for MTBE contamination in ground water at a former industrial landfill in South America, and established that MTBE degraded under anaerobic conditions at that site as well. Zwank et al. (2005) applied the term "two-dimensional analysis" to describe the concurrent CSIA for both carbon and hydrogen, and offered the approach as a useful tool to distinguish the pathway of biodegradation of MTBE in ground water at field scale.

The dotted line in Figure 4.4 projects the values of δ^2H and $\delta^{13}C$ for MTBE that would be expected from values of ε_C of -2.4‰ and ε_H of -30‰. These values are the extremes in the range reported in Gray et al. (2002) for aerobic biodegradation of MTBE by strain PM1 or mixed cultures that resembled PM1 in their behavior. These organisms degrade MTBE by oxidation of the methyl group with an oxygenase enzyme. Because oxygenase enzymes act by extracting a proton from the methyl group, there is a very strong enrichment of deuterium in the residual MTBE. To provide the most conservative estimate in Figure 4.4, the projections of δ^2H and $\delta^{13}C$ expected in MTBE in ground water start from the most positive values of δ^2H and $\delta^{13}C$ determined in MTBE in gasoline as reported in Kuder et al. (2005).

The actual distribution of δ^2H against $\delta^{13}C$ for MTBE at field scale was very different than the distribution that would be expected from aerobic biodegradation of MTBE. The actual distribution of δ^2H corresponds to ε_H of -11.5‰. Zwank et al. (2005) reported an estimate of ε_H of -15.6‰ at the site in South America. The actual distribution of $\delta^{13}C$ corresponds to a value of ε_C in the range -8.9‰ to -10.2‰.

The first step in anaerobic biodegradation of MTBE is hydrolysis of the ether bond (Kuder et al., 2005; Zwank et al., 2005). In the hydrolysis reaction, there is strong enrichment of ^{13}C in the carbon atoms involved in the ether bond. Because the hydrogen atoms are not directly involved, there is much less fractionation of hydrogen.

Rosell et al. (2007) compared the distribution of δ^2H against $\delta^{13}C$ for MTBE during aerobic degradation by two cultures that metabolized MTBE through a different pathway that involves attack on the ether bond. The value of ε_H was -0.2‰ for strain L108 and +5‰ for strain IFP2001. In these organisms, the values of ε_H are much lower than is the case for organisms like PM1. Enrichment of δ^2H and $\delta^{13}C$ during aerobic biodegradation by these organisms is projected as the solid line in Figure 4.4. The values used in the projection were ε_C of -1.48‰ and ε_H of -0.2‰. There was considerable overlap of the field data of Kuder et al. (2005) and plausible values of δ^2H and $\delta^{13}C$ that would be expected from aerobic biodegradation of MTBE by organisms similar to strains L108 and IFP2001. As a consequence, Rosell et al. (2007) warn against uncritical comparison of δ^2H and $\delta^{13}C$

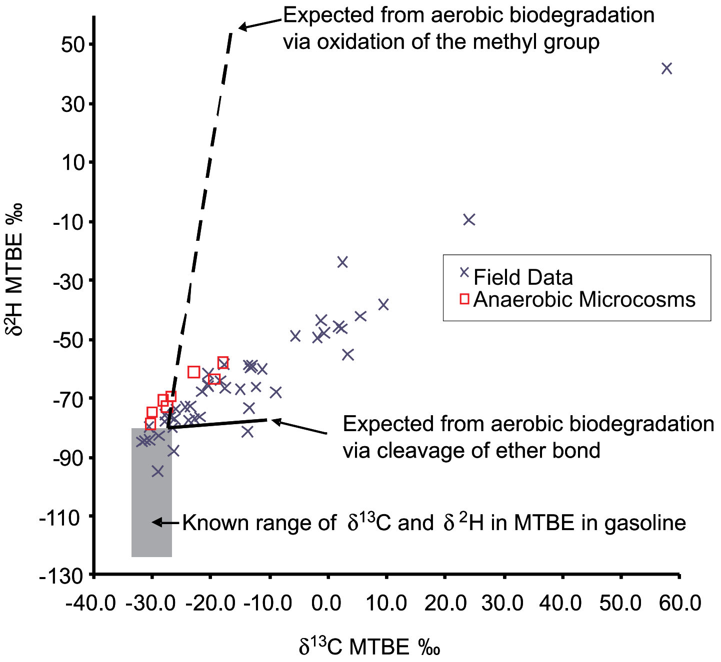


Figure 4.4. Concurrent analysis of $\delta^{13}C$ in MTBE and δ^2H in MTBE in ground water to associate natural biodegradation of MTBE in ground water with an anaerobic process, which allows the selection of an appropriate value for the enrichment factor (ε) to be used to estimate the extent of biodegradation of MTBE.

in MTBE in the field to infer the primary pathway for biodegradation.

The length of the solid line in Figure 2.4 is the range of values of δ^2H and $\delta^{13}C$ that would be expected in MTBE when MTBE is degraded from an initial high concentration of 100,000 µg/L to 1 µg/L. Only 5% of gasoline spill sites in the USA have initial concentrations of MTBE above 100,000 µg/L, and 1 µg/L is the lower limit for determination of δ^2H and $\delta^{13}C$ in MTBE in water samples. The solid line in Figure 4.4 represents the plausible range of δ^2H and $\delta^{13}C$ that would be expected during aerobic biodegradation of MTBE by organisms similar to strains L108 and IFP2001. By examination of Figure 4.4, and allowing for uncertainty in the estimation of δ^2H of 10‰ and $\delta^{13}C$ of 0.5‰, the two dimensional approach proposed by Zwank et al. (2005) can be used to distinguish anaerobic biodegradation of MTBE whenever the value of δ^2H in MTBE in the field sample is more positive than -67‰ and $\delta^{13}C$ is more positive than -9‰.

Similar success has been reported recently for determining benzene biodegradation pathways (Fischer et al., 2007; Fischer et al., 2008; Mancini et al., 2008a). The approach will find wider use, and have more validity, as more data are available on the concurrent enrichment of δ^2H and $\delta^{13}C$ in organic contaminants by different microorganisms under different geochemical conditions.

4.3. Conversion of Calculated Extent of Biodegradation (1-f) to Biodegradation Rates

At many hazardous waste sites, mathematical models are used to predict the transport of contaminants in ground water from source areas to potential receptors such as drinking water wells. These models are calibrated using estimates of the rate of biodegradation of the contaminant in ground water. Most commonly the rates of biodegradation are extracted from field monitoring data. These conventional approaches compare changes in concentration of the contaminant with travel time along a flow path in an aquifer.

One valuable application of CSIA is an independent evaluation of the rates of biodegradation of contaminants. Section 7.3 derives equations that can be used to calculate the rates of biodegradation or abiotic transformation at field scale from an estimate of the fraction remaining after biodegradation (C/Co) and from some assumptions about flow paths and ground water flow rates for the site. This approach combines the uncertainty in the estimates of the hydrogeological parameters with any uncertainties in the estimate of the extent of biodegradation based on CSIA and Equation 4.3. Nonetheless, several recent case studies have shown good agreement between biodegradation rates extracted from isotope studies and rates derived by conventional approaches that are based on changes in concentrations in monitoring wells along a flow path in the aquifer (van Breukelen et al., 2005; Fischer et al., 2006; Hirschorn et al., 2007; Morrill et al., 2005). A key point to emphasize is that CSIA typically provides a more conservative estimate of the degradation rate compared to the conventional approach (Abe and Hunkeler, 2006; Chartrand et al., 2005; Morrill et al., 2005).

4.4. Using Estimates of Rates of Biodegradation to Predict Plume Behaviour

In the conventional approach, the extent of removal along a flow path is estimated by dividing the concentration of contaminant in a down gradient well (C_t) by the concentration in an up gradient well (C_0). Often at field scale, monitoring wells are screened vertically across plumes, and produce samples of the contaminated plume that are diluted with clean water from above or below the plume. Occasionally a well will only sample the top or bottom of a plume. In this case the apparent attenuation of concentrations of contaminants has a strong component of dilution, and data on concentrations cannot be used in the conventional approaches to estimate the extent of removal.

Fischer et al. (2006) provided an approach for solving this problem by taking the concentration that is actually measured in the down gradient well C_t and the measured values of $\delta^{13}C$ in the two wells, to calculate a theoretical value for C_0 using the Rayleigh equation. The difference between the calculated theoretical value of C_0 and the measured value of C_t provides an estimate of the amount of compound that was degraded that is independent of dilution or other non destructive processes that can lead to a reduction of the contaminant concentration (Fischer et al., 2006). Because the estimate of the extent of biodegradation provided by CSIA is independent of the concentration of the contaminant in the ground water sample, the extent of biodegradation from the CSIA analyses and the estimated travel time from the source of contaminant to a well can be used to estimate the rate of biodegradation along the flow path.

The behaviour of contaminants in most plumes is heterogeneous, with extensive biodegradation in some regions and little or no biodegradation in others. When a plume is heterogeneous, it is best to consider the behaviour of the contaminant in each flow path, instead of trying to predict the average behaviour of the entire plume. The approach will be illustrated with data from a plume of MTBE from a gasoline spill at a site in Dana Point, California, USA (Figure 4.5). Additional details of this case study are described in section 6 of an EPA report (Wilson et al., 2005a).

The direction of ground water flow for separate rounds of sampling is presented as flow arrows in Figure 4.5. The length of each arrow is proportional to the distance ground water would move in one year under the hydraulic gradient during that particular round of sampling. The length was calculated by multiplying the hydraulic gradient by the average hydraulic conductivity (11 meters per day), then dividing by an estimate of porosity (0.25).

After the spill of gasoline was discovered, the leaking underground storage tanks and most of the surrounding fill material were excavated. However, residual gasoline in the aquifer acts as a continuing source of MTBE in ground water. The highest concentrations of MTBE are immediately down gradient of the underground storage tanks (Figure 4.5). A second source is associated with the distribution lines to the south-eastern dispenser island.

Table 4.2 compares the concentrations of MTBE in selected monitoring wells to the fraction of MTBE remaining as predicted from Equation 4.3 using the $\delta^{13}C$ of MTBE in the ground water in each well and a value of -27.4‰ for the $\delta^{13}C$ that would be expected for MTBE in gasoline. This value is the most positive $\delta^{13}C$ value that has been published for MTBE in gasoline (O'Sullivan et al., 2003). To be conservative, the most negative enrichment factor available in the literature was used in the calculations (ε = -14.6‰; Somsamak et al., 2006). This approach provided the most conservative estimate

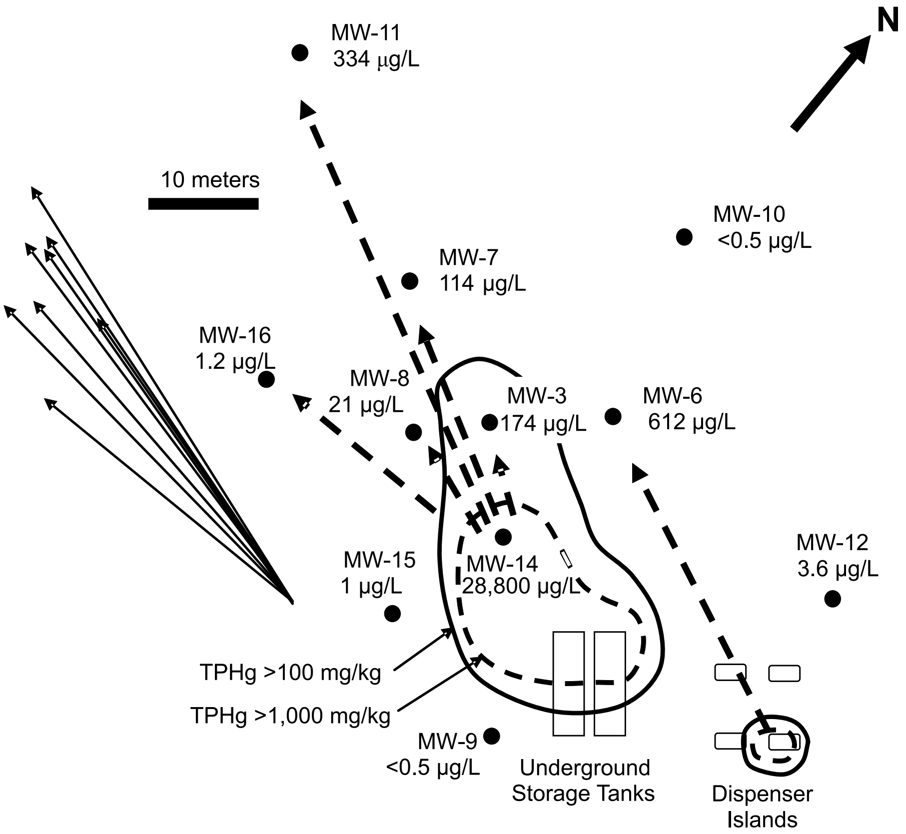


Figure 4.5. Concentration of MTBE in selected monitoring wells at a gasoline spill site in Dana Point, California, USA in 2004. The cluster of arrows is a flow rose indicating the direction and distance ground water would move in one year based on the elevation of the water table in monitoring wells on particular sampling dates. The dashed arrows indicate possible flow paths between wells. Concentrations are MTBE in ground water. TPHg is the Total Petroleum Hydrocarbons in the range of constituents of gasoline.

of the fraction of MTBE remaining compared to the MTBE that was originally present in the gasoline spilled to the aquifer.

Table 4.2 reveals that the most conservative approach to calculate C/Co must have underestimated the true extent of biodegradation at this site. Well MW-11 had a value of $\delta^{13}C$ for MTBE that was even more negative than the value assumed for MTBE in the gasoline that was spilled. The true value of $\delta^{13}C$ for MTBE in the gasoline that was spilled may have been even more negative than -28.9‰. This most conservative approach was taken because this study was conducted as part of a risk evaluation, and the rates extracted from the CSIA analyses were the only rates available. If the purpose of the study were to validate other rates of biodegradation that were extracted from conventional approaches, it would have been appropriate to use estimates of $\delta^{13}C_{source}$ that were more likely to be representative of the true $\delta^{13}C_{source}$.

The most contaminated well at the site (MW-14 in Figure 4.5) is located in an area that had 9,000 mg/kg of Total Petroleum Hydrocarbons in the range of constituents of gasoline (TPHg). Wells MW-3 and MW-8 are further down gradient of the source of MTBE associated with the underground storage tanks (Figure 4.5). The $\delta^{13}C$ of MTBE in wells MW-3 and MW-8 is much more enriched in ^{13}C than MTBE in gasoline with values of +8.5‰ and +38.0‰ respectively. The fraction remaining corresponds to 91% and 99% biodegradation of MTBE. The attenuation in concentration of MTBE in wells MW-3 and MW-8 compared to well MW-14 can be attributed to biodegradation.

Well MW-6 appears to be cross gradient to the source of MTBE associated with the underground storage tanks (compare the flow arrows in Figure 4.5). However, well MW-6 is directly down gradient of the secondary source associated with the dispenser islands. The behaviour of MTBE in well MW-6 is very similar to wells MW-3 and MW-8. The $\delta^{13}C$ of MTBE (-1.6‰) is highly enriched relative to MTBE in gasoline, and the predicted fraction remaining corresponds to 83% biodegradation of MTBE.

Wells MW-7 and MW-11 are even further down gradient of the source of MTBE. The concentrations of MTBE are low, and it would be tempting to attribute the low concentrations to biodegradation. However, the $\delta^{13}C$ of MTBE in these wells is even more depleted in ^{13}C (-27.3‰, -28.9‰) than the $\delta^{13}C$ in MW-14, the most contaminated well. The $\delta^{13}C$ of MTBE in these wells falls near or within the range of $\delta^{13}C$ expected for MTBE in gasoline. Hence, there is no evidence from the $\delta^{13}C$ of MTBE that biodegradation contributed to attenuation of MTBE in these two down gradient wells.

Because the isotope fractionation provides a direct estimate of the fraction of contaminant remaining after biodegradation, the rate constant for biodegradation can be calculated from the removal

Table 4.2. Rates of natural biodegradation of MTBE in ground water moving along a flow path to monitoring wells. The rates were calculated from the estimated seepage velocity of ground water and the fraction of MTBE remaining after biodegradation.

Well	**MTBE (µg/L)**	**$\delta^{13}C$ MTBE (‰)**	**Fraction MTBE Remaining (C/C_o)**	**Distance from MW-14 (meters)**	**Rate of Degradation with Distance (per meter)**	**Rate of Degradation with Time (per year)**
MW-14	28,800	-21.6	0.67	0		
MW-3	174	8.5	0.085	9.6	0.26	9.4
MW-8	21	38.0	0.0113	11.7	0.38	14.1
MW-7	114	-27.3	0.995	23.0	0.00021	0.0077
MW11	334	-28.9	1.11	44.1	0	0
				Distance from Dispenser Island (meters)		
MW-6	612	-1.6	0.171	31.1	0.057	2.1

of contaminant along the flow path in the aquifer, the distance between wells, and an estimate of the interstitial seepage velocity. If biodegradation follows a pseudo first order rate law, the rate of attenuation can be expressed directly as a first order rate of attenuation with distance, or the rate of attenuation with distance can be multiplied by an estimate of the seepage velocity of ground water to calculate a rate of attenuation with time of travel. The rate of attenuation with distance is calculated following Equation 4.6. Attenuation with time follows Equation 4.7.

$$\lambda_{\text{with distance}} = -\ln\left(f\right)/d \qquad \mathbf{4.6}$$

$$\lambda_{\text{with time}} = -\ln\left(f\right)*v/d \qquad \mathbf{4.7}$$

In Equation 4.6 and 4.5, λ is the rate of natural biodegradation, *f* is the fraction of contaminant remaining predicted from Equation 4.3, *d* is the distance along the flow path between the up gradient well and the down gradient well, and *v* is the ground water seepage velocity.

The average hydraulic conductivity at the site in Dana Point, California is 11 meters per day. The average hydraulic gradient over eight rounds of sampling was 0.0023 meter per meter. Assuming the effective porosity is 0.25, the average ground water seepage velocity should be near 37 meters per year. Table 4.2 presents the rates of biodegradation of MTBE along flow paths between the most contaminated well (MW-14), and down gradient wells MW-3, MW-7, MW-8, and MW-11, and between the secondary source at the pump island and down gradient well MW-6. In wells MW-3 and MW-8, the first order rate of degradation is rapid, on the order of 0.3 per meter of travel, or 10 per year of residence time. In well MW-6, the rate of biodegradation is about ten fold slower. In well MW-7, the rate of biodegradation was one thousand fold slower, and in well MW-11 biodegradation was not detected at all.

The field rates estimated for wells MW-3, MW-6 and MW-8 are in good agreement with laboratory rates reported in the literature. The rate of anaerobic biodegradation of MTBE in a microcosm study constructed with material from a gasoline spill in Parsippany, New Jersey, varied from 11 ± 2.3 per year to 12 ± 2.9 per year (Wilson et al., 2005b). The rate of anaerobic MTBE biodegradation in a microcosms study constructed with core material from a JP-4 jet fuel spill in Elizabeth City, North Carolina, was 3.02 ± 0.52 per year and 3.5 ± 0.65 per year (Wilson et al., 2000).

The distance travelled before the concentration of contaminant reaches a particular goal (d_{further}) can be calculated by rearranging Equation 4.7 to produce Equation 4.8. In Equation 4.8, *F* is the ratio of the goal to the existing concentration in the monitoring well.

$$d_{\text{further}} = -\ln(F)/\lambda_{\text{with distance}} \qquad \mathbf{4.8}$$

If *F* is calculated by dividing the U.S. EPA advisory limit of 20 µg/L by the concentration of MTBE remaining in monitoring wells MW-3, MW-6, or MW-8 (Table 4.2), and if the first order rates of biodegradation also apply to the flow path that is down gradient of the monitoring wells, then the plume would move 8.4 meters past MW-3, and 60 meters past MW-6. Biodegradation had essentially already brought the concentration of MTBE to the limit in well MW-8.

In contrast, the first order rate of biodegradation in well MW-7 (Table 4.2) is much slower. At a rate of 0.00021 per meter, starting at a concentration of 114 µg/L, the MTBE plume would be expected to move 8,300 meters further down gradient before it reached the advisory limit of 20 µg/L.

In well MW-11, biodegradation of MTBE could not be established based on the δ^{13}C for MTBE in the ground water. The concentration of dissolved oxygen in water from well MW-1 was 0.65 mg/L, the concentration of Iron(II) was 0.2 mg/L, and the concentration of methane was 0.018 mg/L. Conditions were not favourable for aerobic biodegradation. The only processes that can be reasonably expected to attenuate MTBE further down gradient of MW-11 are dilution and dispersion. It would appear that while the biodegradation of MTBE in the core of the plume was rapid and extensive, MTBE in the periphery of the plume was not degraded.

As a consequence of the spatial heterogeneity in the rate of biodegradation, the extent of the plume would be seriously underestimated if a single rate constant for biodegradation was applied to the maximum concentration of MTBE in the source area. On the other hand, the maximum extent of the plume was seriously overestimated if biodegradation was ignored. At this point in the evolution of risk evaluation, a conservative course of action is to recognize that plumes are heterogeneous. An independent estimate of the extent of MTBE contamination further down gradient should be made for each well used in the risk evaluation, based on the concentration of MTBE in each well, and the rate of biodegradation in the flow path leading to each well.

4.5. Effect of Heterogeneity in Biodegradation in the Aquifer on Stable Isotope Ratios

The rate and extent of biodegradation may be heterogeneously distributed in an aquifer. As ground water moves away from a source of contamination, the organic contaminants are removed in flow paths where biodegradation is rapid and extensive, and persist in flow paths where biodegradation is weak or absent. This effect can confuse the interpretation of a shift in the isotopic ratio in the residual organic contaminant. As the contaminant is degraded in the flow paths where biodegradation is rapid and extensive, the residual contaminant is fractionated. However, the concentration of the contaminant that is fractionated is reduced much faster than the concentration of contaminant that is not fractionated. With time and distance away from the source area, the total mass of contaminant that is contributed by the flow paths that degrade the contaminant will decline compared to the flow paths that do not degrade the contaminant. Eventually, the contribution of the fractionated contaminant to the total concentration of contaminant is negligible. Even though a large proportion of the total mass of contaminant has been removed in the aquifer, the stable isotope ratio of the residual material closely resembles the ratio in the material that was released from the source. An analysis of stable isotope ratios in contaminants in water from a monitoring well that blended the flow paths would suggest that the contaminant had not fractionated, and had not been biologically degraded. This situation is illustrated in Figure 4.6.

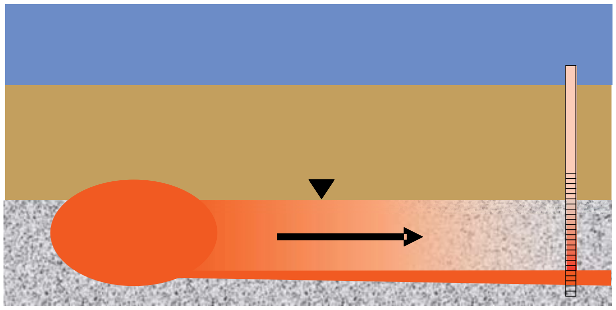


Figure 4.6. Hypothetical illustration of a heterogeneous plume, where a monitoring well that produces ground water from some flow paths where biodegradation of an organic contaminant is rapid and extensive (upper part of the saturated zone), and other flow paths where biodegradation of the organic contaminant is absent.

Figure 4.7 presents a thought experiment that illustrates the effect. In the thought experiment, the isotope enrichment factor for anaerobic biodegradation of MTBE in an aquifer is -12‰, and MTBE in various proportions of the ground water is not degraded. Initially, the $\delta^{13}C$ in the total mass of MTBE increases as biodegradation progresses in the aquifer. Eventually, the total mass of ^{13}C in MTBE in the regions where MTBE is degrading becomes less than the total mass of ^{13}C in MTBE in the regions where MTBE is not degrading. From that point forward, the $\delta^{13}C$ in the total mass of MTBE decreases as biodegradation proceeds in the aquifer. Eventually the $\delta^{13}C$ in residual MTBE returns to the initial $\delta^{13}C$, even though a small fraction of the original mass of MTBE remains. If a shift in the stable isotope ratio was the only criterion to estimate biodegradation, the contribution of biodegradation could be seriously underestimated or missed altogether.

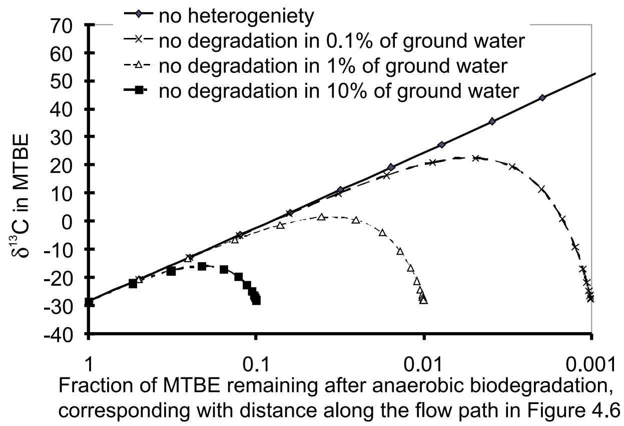


Figure 4.7. Theoretical experiment of the effect of heterogeneity in biodegradation on the stable isotope ratio for carbon in residual MTBE in water produced from a monitoring well, when MTBE does not degrade in certain portions of the aquifer as depicted in Figure 4.6. The Y-axis shows the calculated values for $\delta^{13}C$ of MTBE that is a mixture of MTBE from a flow path with biodegradation and MTBE from a flow path with no biodegradation.

The scenario described above is an extreme case where we have either 100% biodegradation or 0% in different sections of the aquifer. However, there have been recent publications that tried to assess the problem of heterogeneity in a mathematical model, and an *in situ* tracer test where biodegradation was monitored by several methods and the estimate based on stable isotope fractionation was verified in the field (Abe and Hunkeler, 2006; Fischer et al., 2006). Both studies concluded that the influence of spatial heterogeneities in a gravel sediment aquifer was not significant for the calculation of biodegradation. For other sites with more complex heterogeneity, these potential effects should be considered; biodegradation might be significantly underestimated. In any case, situations that protect a portion of the contaminant from fractionation, such as unreactive flow paths or sorption to organic matter, will cause an underestimate of the extent of biodegradation (Kopinke et al., 2005).

4.6. Recommended Practices to Minimize the Confounding Effects of Heterogeneity

Water samples for determination of stable isotope ratios should be acquired from wells with short screen intervals, or from temporary push wells or from cluster wells with small screens. Whenever possible, the depth interval of the well screen should be compared to the lithology of the aquifer, and only wells that are screened across a single unit in the aquifer should be sampled. Often, the very top layer of an anoxic contaminated aquifer will be oxic. This can result from diffusion of oxygen into the ground water from the capillary fringe, or from recharge of aerobic uncontaminated ground water from surface precipitation. Avoid sampling wells that are screened across the water table.

Wells should be purged to the minimum extent necessary to bring geochemical parameters to stability. If the geochemical parameters do not stabilize after three casing volumes have been purged, purging should stop at that point and the ground water should be sampled. If the well water is not in geochemical equilibrium, there is reasonable chance that the well will blend organic contaminants that have been fractionated to different extents.

Use geochemical parameters to recognize the “footprint” of a contaminant plume when the contaminant of interest has been extensively degraded and may not be present at high concentrations in the ground water. As an example, the “footprint” of a plume from a fuel spill often has high concentrations of methane, alkalinity and iron(II), and low concentrations of soluble electron acceptors such as sulfate, nitrate, or oxygen. The “footprints” are expressed in aquifers in both horizontal view (two dimensional space) and with depth. Select locations and depth intervals for CSIA where the geochemical parameters indicate that they are in the “footprint” of the plume, even though they may have lower concentrations of the contaminant of concern.

Appendix C

Contaminant Mass Example Calculations

CONTAMINANT MASS EXAMPLE CALCULATIONS

A. **Contaminant Mass**: Appendix A: Guidance On Natural Attenuation For Petroleum Releases, Wisconsin DNR, March 2003

B. **Mass Flux:** Appendix D (pg 108-112): Guidance on Remediation of Petroleum-Contaminated Ground Water By Natural Attenuation, Washington State DOE, July 2005

A. **Contaminant Mass**: Appendix A: Guidance On Natural Attenuation For Petroleum Releases, Wisconsin DNR, March 2003

A-3 Estimating Contaminant Mass and Distribution in the Subsurface

Estimates of contaminant mass may be necessary when:

- Comparing the cost effectiveness of various remedial options.
- Estimating the time frame for site cleanup is critical for future site development.
- Monitoring results alone cannot establish the effectiveness of natural attenuation.
- Using predictive fate and transport modeling.

Estimates of contaminant mass can be based on the volume of product released, if this is known. This section describes one approach to estimating contaminant mass based on soil and groundwater samples from the contaminated site. Other approaches, such as estimates of residual saturation of petroleum hydrocarbons in the soil and saturated material, can be used (Weidmeier, et.al., 1999; Huntley, et.al., 1994).

A. Distribution of Petroleum Contaminants

Petroleum can reside in a number of locations and phases in the subsurface. Lyman, et.al. (EPA, 1992) lists 13 physiochemical-phase loci representing where and how petroleum can reside in the subsurface. Typical site investigations identify concentrations of contaminant in the soil vapor phase, on the soil surfaces, interstitial pore space of the soil sample, and in the groundwater. Liquid product floating on the water table is also identified. An important phase that is often not investigated is the mass of residual contaminant trapped at and below the water table, even though a significant quantity of mass often resides in this phase.

The primary mass of petroleum product in the subsurface is usually liquid petroleum floating on the water table or trapped as residual product in vadose (unsaturated soil) or saturated zone pore space. This liquid and residual petroleum product is the source of continued dissolution of contaminants into groundwater. Microbes do not readily degrade free phase or residual phase product, so naturally occurring biodegradation does not easily or quickly reduce the supply of petroleum in the source zone. In general, if the petroleum fraction is not physically or chemically removed, it will continue to dissolve contaminants into the groundwater until an “aged” mixture of relatively non-volatile, non-soluble petroleum remains. The presence of liquid and/or residual petroleum has the following implications for natural attenuation:

- The ultimate extent of a groundwater plume will be dictated by contaminant type, solubility of the contaminant, concentration of contaminants in the petroleum product, geologic/hydrogeologic characteristics of the site and geochemical and biological characteristics of the groundwater and subsurface solids.
- After reaching maximum extent (dictated by site-specific conditions), a “stable” plume will remain until the soluble portion of the petroleum is depleted to the point that the degradation of dissolved contaminant outstrips the flux of the contaminant from the petroleum source. The weathering of subsurface petroleum can take many decades, depending upon the original mass of petroleum released.

Quantifying contaminant mass and distribution in the subsurface can be used to assess the effectiveness of natural attenuation processes. Gallagher (1995) divides the source zone into 4 compartments: unsaturated soil zone (vadose zone), free product, smear zone below the water table and groundwater zone (dissolved phase). The vast majority of soluble contaminant resides in the unsaturated soil, free product and smear zone below the water table, with the least amount of mass in the dissolved phase. Mass of GRO/DRO may represent total contaminant mass in the source zone. Total hydrocarbon mass can be estimated from GRO/DRO results. Soluble mass calculations should be based on the soluble portion of the source zone contaminants, such as BETX (benzene, ethylbenzene, tolutene, xylenes), MTBE (methyl tertiary-butyl ether), TMB (trimethyl benzenes), 1,2-DCA (1,2-dichloroethane), Naphthalene, etc.

B. Calculating Contaminant Mass

Various methods can be used to assess contaminant mass remaining at a site, including knowledge of the petroleum volume released. The method presented here is based on the Florida Petroleum Cleanup Program's RNA Tool Kit Guidance Manual. This analysis presumes uniform stratigraphy but can be used for non-uniform stratigraphy. The analysis is based upon defining a soil or saturated zone volume associated with each sampling point. The vertical sampling interval (the length of soil cores or well screen length) will define the "layers" used in this method. The soil/saturated zone layers used for the volume estimate are not always related to site stratigraphy, but may be related. In some cases the vertical sampling intervals will correspond to stratigraphic units. Heterogeneous subsurface environments require more sampling and model layers to determine mass distribution than homogeneous environments.

The procedure to estimate areas associated with each sampling point is the Thiessen Polygon Method. The method assumes that the concentration measured at a given point represents the concentration in the soil out to a distance halfway to all adjacent sampling points. Areas associated with each sampling point are defined by constructing a Thiessen polygon network. The polygon network is formed by perpendicular bisectors of lines connecting adjacent sampling points (Dupont, et.al., 1996). An example of the mass calculation follows at the end of this section.

1. Mass in Free Product

Section NR 708.13 requires removal of free product to the maximum extent practicable. After removal of free product, a floating layer may remain that is not removable. These layers may vary from a "sheen" to several inches in thickness. If free product is present, the mass of contaminant in the free product should be calculated.

Methods to calculate volume of floating product and mass contained in the free product are beyond the scope of this guidance. See references by Lundegard and Mudford (1998); Farr, Houghtalen and McWhorter (1990); Huntley, et. al. (1994), and others for discussions of calculating volume of free product in the subsurface.

2. Contaminant Mass in the Unsaturated Source Zone

Using the selected investigation method, collect and analyze soil samples to determine contaminant concentrations both laterally and vertically from the original release. For this analysis, the unsaturated (vadose) zone extends in depth from the ground surface to the present water table and laterally from the highest contamination to non-detectable levels.

a. Map the vadose zone based on vertical sampling interval. Each soil sample will represent a soil depth interval and a soil area. Therefore, it is necessary to collect enough soil samples to represent the entire contaminated vadose zone. Determine the thickness of each soil interval.

b. Use the Thiessen Polygon method to determine the area associated with each sample for each depth interval (soil layer). Use the area-weighted mean technique to determine the average contaminant concentration within the contaminated area for each soil layer. In the area-weighted mean technique, each data point is correlated with an area represented by that data point. The equation for the area-weighted mean for n data points each associated with an area, A, is:

$$\overline{c}_v = \frac{(c_1 A_1 + c_2 A_2 + \ldots + c_n A_n)}{(A_1 + A_2 + \ldots + A_n)}$$

where: $\overline{c}_v$ = area weighted concentration for a given depth interval in the vadose zone (M/M)
$c_1, c_2, \ldots c_n$ = concentration of each sample within the depth interval (M/M)
$A_1, A_2, \ldots A_n$ = individual area associated with each sample in the depth interval (L^2)

c. Multiply the average concentration by the total contaminated area for the depth interval by the depth of the soil layer. The units will be concentration • volume (e.g., m^3 • mg/Kg).

$$\overline{c}_v \times (A_1 + A_2 + \ldots A_n) \times d = \text{concentration} \bullet \text{volume for depth interval}$$

where: d = depth of sample interval (soil layer) (L)

d. Sum the concentration • volume results for each layer. Multiply the result by soil density (eg., g/cm^3) to arrive at mass of contaminant in the vadose zone.

$$\left[\sum_{i=1}^{\ell} \left[\overline{c}_v{}^i \times \left(A_1{}^i + A_2{}^i + \ldots A_n{}^i\right) \times d^i\right]\right]\rho = M_s$$

where: i = number of soil intervals (soil layers), where i =1 to ℓ
A_n^i = area represented by n^{th} sample in the i^{th} layer (L^2)
d^i = thickness of the i^{th} layer (L)
ρ = density of soil (M/L^3)
M_s = mass of contaminant in vadose zone (M)

3. Contaminant Mass in the Saturated Source Zone (Smear Zone below the Water Table)

Collect and analyze contaminated saturated media from beneath the water table. Extend samples vertically to non-detect levels. The contaminated saturated source zone, referred to here as the "smear zone below the water table", is delineated vertically between the existing water table and lowest water table level. If the groundwater has been pumped or otherwise significantly lowered, the lowest groundwater level will define the source zone for saturated materials. Determine lateral extent of the contaminated saturated source zone as listed below.

a. Lateral extent of the contaminated saturated source zone:
   i. Area delineated by floating product, based on current or historical detection of free product; or
   ii. Area with hydrocarbons above a predetermined threshold value. For gasoline, total BETX levels greater than 3,000 ug/l in groundwater may represent the contaminated saturated source zone (Gallagher, 1995). The 3,000 ug/l cut off is used by Gallagher because "it is within 1 and 10 percent of BETX solubility" from gasoline.

b. Use the process listed in #2 above for the unsaturated soil zone to determine the area weighted average soil concentration for the saturated zone.

c. Multiply the saturated source zone concentration ($\bar{c}_{sz}$) by the area of the contaminated saturated soils (A_1, A_2, … A_n) by the depth of saturated soil contamination by the soil density to calculate a source mass for the saturated zone.

$$\left(\bar{c}_{sz} \times (A_1 + A_2 + \ldots A_n) \times d_{sz}\right)\rho = M_{sz}$$

where:

$\bar{c}_{sz}$ = area weighted concentration in saturated zone materials (M/M)
A_1, A_2, … A_n = individual area associated with each sample in saturated zone materials (L^2)
d_{sz} = depth of saturated zone materials (L)
ρ = density of saturated zone materials (M/L^3)
M_{sz} = mass of contaminant in saturated zone materials (M)

4. Contaminant Mass in the Dissolved Phase in the Source Zone

In general, the contaminant mass dissolved in the groundwater is negligible compared to the soil source zone and can be ignored when there is significant contamination of the soil and saturated media.

a. Determine the area of the dissolved source zone. Generally, the area of source zone groundwater corresponds to the area of the saturated source zone contamination. If a saturated source zone does not exist at a site, groundwater concentrations more than 3,000 ppb total BETX should be included in the dissolved phase mass for the source area.

b. Determine the depth of groundwater contamination within the source area. Depth should be determined from the initial investigation. Wetted screen length should not be used unless it is known that this represents the depth of groundwater contamination. A depth of 5 feet, or the vertical extent of the upper stratigraphic unit, which ever is less, can be assumed to be the depth of groundwater contamination if other information on depth is not available.

c. Determine the area-weighted mean of the groundwater contamination within the source zone, using the procedure listed in #2 above for unsaturated soils.

d. Multiply the mean groundwater concentration ($\bar{c}_{gw}$), by the source area ($A_1, A_2, \ldots A_n$), by the depth of groundwater contamination at the source, by the porosity of the geologic media to obtain dissolved contaminant mass.

$$\left(\bar{c}_{gw} \times (A_1 + A_2 + \ldots A_n) \times d_{gw}\right)\theta = M_{gw}$$

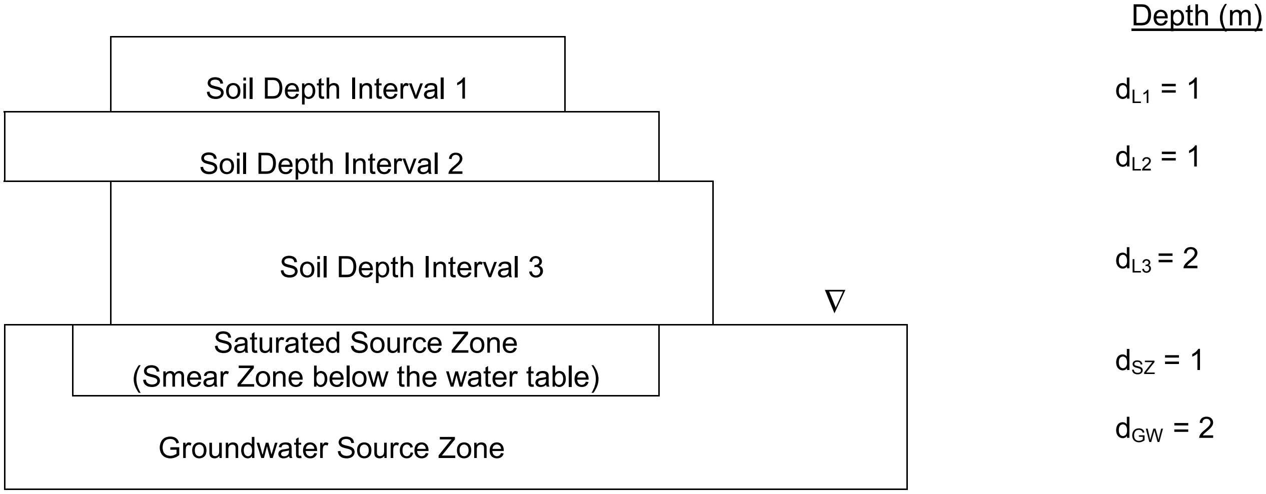
where:

$\bar{c}_{gw}$ = area weighted concentration for groundwater in the source zone groundwater (M/L^3)
$A_1, A_2, \ldots A_n$ = individual area associated with each sample in source zone groundwater (L^2)
d_{gw} = depth of contaminated source zone groundwater (L)
θ = porosity of saturated geologic media in source zone
M_{gw} = mass of contaminant dissolved in source zone groundwater (M)

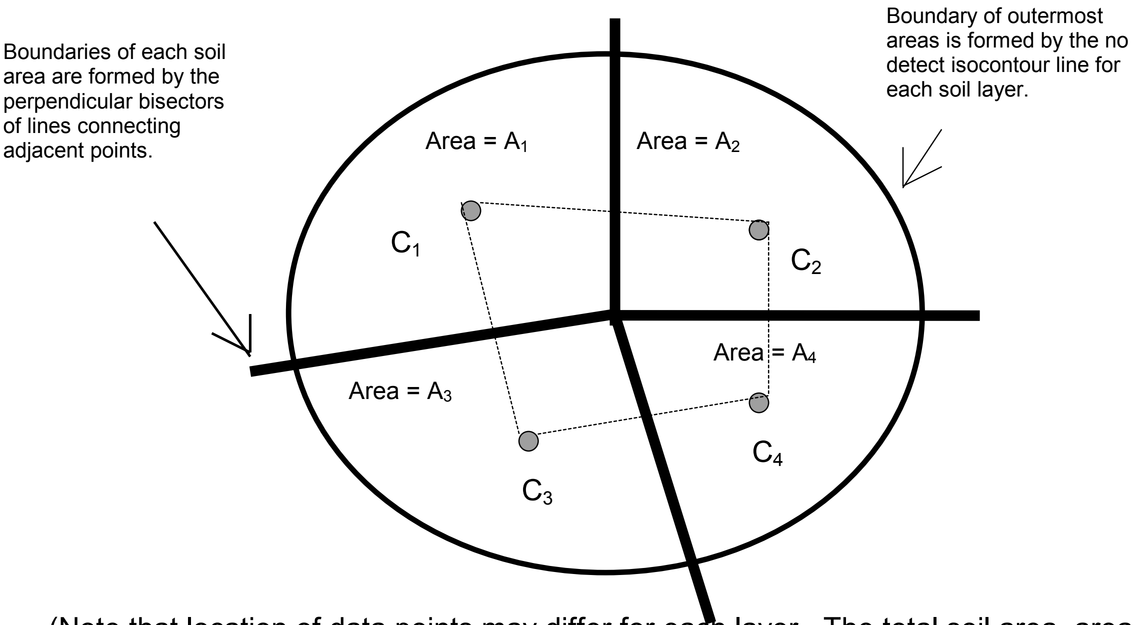
C. Example Calculation of Source Mass

This example assumes that no free product exists at the facility. This example is based upon BETX as the primary soluble contaminants at the facility. It will usually be necessary to calculate the total mass of GRO/DRO in the source zone and the mass of all soluble contaminants at the site, e.g., MTBE, TMB, etc.

Cross-section of Contaminant Source:



Plan View of Contaminant Source: Thiessen Polygon Network



(Note that location of data points may differ for each layer. The total soil area, area associated with each sample and soil interval depth may differ for each layer.)

1. Contaminant Mass in Unsaturated Source Zone.

   a. Determine area associated with each sample point using the Thiessen Polygon Method. In this example, there are 4 sample points in each layer associated with the source zone.

Table A-2

Areas Determined from Thiessen Polygon Method

Layers	thickness (m)	Area 1 (m^2)	Area 2 (m^2)	Area 3 (m^2)	Area 4 (m^2)	Total Area (m^2)	Total Volume (m^3)
L1	1	30	25	25	20	100	100
L2	1	35	30	30	25	120	120
L3	2	25	20	35	25	105	210
SZ	1	20	25	30	20	95	95
GW	2	40	30	35	30	135	270

where:
L1 = uppermost unsaturated source soil interval
L2 = middle unsaturated source soil interval
L3 = deepest unsaturated source soil interval
SZ = saturated source soil zone (“smear zone below the water table”)
GW = dissolved source groundwater zone

Table A-3

Area-Weighted Mean and Concentration-Volume for Unsaturated Soil Layers

Layers	C1 (mg/Kg)	C2 (mg/Kg)	C3 (mg/Kg)	C4 (mg/Kg)	Area-Weighted Average (mg/Kg)	Volume • Area-Weighted Ave. Conc. (m^3 • mg/kg)
L1	300	200	500	400	345	34,500
L2	800	900	1050	1100	950	114,000
L3	1,500	2,000	2,300	2,500	2,100	441,000
					SUM	589,500

   b. Calculate the area-weighted mean for soil intervals (layers) 1,2 & 3.

$$\overline{c}_v = \frac{(c_1 A_1 + \ldots + c_4 A_4)}{(A_1 + \ldots + A_4)}$$

Example for soil interval (layer) 1:

$$\bar{c}_{L1} = \frac{\left[\left(300\frac{mg}{kg}\times 30\,m^2\right)+\left(200\frac{mg}{kg}\times 25\,m^2\right)+\left(500\frac{mg}{kg}\times 25\,m^2\right)+\left(400\frac{mg}{kg}\,g\times 20\,m^2\right)\right]}{\left[30\,m^2\ +25\,m^2+25\,m^2+20\,m^2\right]} = 345\frac{mg}{Kg}$$

c. Multiply the area-weighted mean by the total contaminated area in each soil interval and by the depth of each soil layer.

$$\bar{c}_{L1}\times(A_1+A_2+\ldots A_n)\times d_{L1} = \text{concentration} \bullet \text{volume for soil layer } 1$$

Example calculation for soil interval (layer) 1:

$$345\frac{mg}{Kg}\times 100\,m^2\times 1\,m\ =\ 34{,}500\,m^3\bullet\frac{mg}{Kg}$$

Table A-4

Sum of Concentration-Volume for Unsaturated Soil Layers

Layer	Area-Weighted Ave. (mg/Kg)	Layer depth (m)	Total Area (m^2)	Volume • Area-Weighted Ave. Conc. (m^3•mg/Kg)
L1	345	1	100	34,500
L2	950	1	120	114,000
L3	2,100	2	105	441,000
			SUM	589,500

d. Multiply the sum of the volume-concentration calculation by soil bulk density (usually 1.65 g/cm^3 = 1,650 Kg/m^3).

$$\left[\sum_{i=1}^{l}\left[\bar{c}_v{}^i\times\left(A_1{}^i+A_2{}^i+\ldots A_n{}^i\right)\times d^{\,i}\right]\right]\rho = \text{mass of contaminant in vadose zone}$$

Example calculation:

$$589{,}500\frac{m^3 \bullet mg}{Kg} \times 1{,}650\frac{Kg}{m^3} \times \frac{Kg}{1 \times 10^6 mg} = 973\ Kg$$ of total BETX in the unsaturated soil zone

2. Contaminant Mass in Saturated Source Zone (Smear Zone below the Water Table). Calculate as with unsaturated soil.

<u>Given Data Set</u>:

Area weighted average total BTEX concentration:	8,000 mg/Kg
Area of source zone:	95 m^2
Vertical extent of saturated source zone:	1 m
Soil bulk density:	1.65 g/cm^3 = 1650 Kg/m^3

$$8000\frac{mg}{Kg} \times 95m^2 \times 1m \times 1650\frac{Kg}{m^3} \times \frac{Kg}{1 \times 10^6 mg} = 1254\,Kg$$ of total BETX in saturated source zone soils.

3. Contaminated Mass in Groundwater Source Zone.

a. Determine if the wetted screen length of monitoring wells corresponds to the contaminated groundwater zone. If it is known that well screens extend beyond the zone of contaminated groundwater (thereby diluting the contaminated groundwater) correct the groundwater concentrations by multiplying the ratio of the wetted screen length to the affected groundwater thickness.

<u>Example:</u>

Wetted screen length: 3 meters

Vertical extent of groundwater contamination: 2 meters

Contaminant concentration (total BETX): 20,000 ug/l

Correction: $20{,}000 ug / l \times \frac{3}{2} = 30{,}000 ug / l$

b. Calculate the area-weighted mean for groundwater in the source zone. Use the Thiessen Polygon Method to associate an area of groundwater with each monitoring well in the source area. The formula for the area weighted mean is:

$$\bar{c}_{gw} = \frac{(c_1 A_1 + \ldots + c_4 A_4)}{(A_1 + \ldots + A_4)}$$

c. Multiply the area weighted mean groundwater concentration by the area of source groundwater contamination by the depth of groundwater contamination by the porosity.

$$\bar{c}_{gw} \times A_{gw} \times d_{gw} \times \theta = \text{total BETX dissolved in groundwater in the source zone}$$

Example:
Area weighted mean: 30,000 ug/l = 30 g/m^3

$$30{,}000 \frac{ug}{l} \times \frac{g}{1 \times 10^{6}\ ug} \times \frac{l}{1 \times 10^{-3}\ m} = 30 \frac{g}{m^{3}}$$

Area of source: 135 m^2
Depth of groundwater contamination in source area: 2 m
Porosity: 35%

$$30 \frac{g}{m^{3}} \times 135 m^{2} \times 2 m \times .35 \times \frac{Kg}{1 \times 10^{3}\ g} = 2.8\, Kg \approx 3\, Kg$$

4. Total Mass in Source Zone.

Sum soluble contaminant mass of the three source zone compartments, the unsaturated soils, saturated materials and groundwater.

	Total BETX		Percent of Total
Soil Source Zone:	973	Kg	44%
Saturated Source Zone:	1,254	Kg	56%
Groundwater Source Zone:	3	Kg	0.1%
Sum:	2,230	Kg	100%

B. **Mass Flux:** Appendix D (pg 108-112): Guidance on Remediation of Petroleum-Contaminated Ground Water By Natural Attenuation, Washington State DOE, July 2005 quarters of data are divided into two groups representing the first four quarters (designated with an "A") and the last four quarters (designated with a "B"). For each individual "A" concentration, the numbers of "B" concentrations that occur below the "A" concentration are counted. The four values (either zero or some positive number) are summed together to obtain the U-statistic. For the purpose of the Mann-Whitney U method tests, non-detect values are considered zero. If two or more concentrations are identical, two vertical columns are constructed. In the first column, the tying "B" concentration is ranked first, and in the second column the tying A concentration is ranked first. An interim U is calculated for each column and the average of the interim U values is used as the final U value (Weidemeir et al., 1999).

If $U \leq 3$, the null hypothesis is rejected, and it is concluded with at least 90% confidence that the concentration for the individual contaminant has decreased with time at that well. If $U > 3$, the null hypothesis is accepted, and it cannot be concluded with at least 90% confidence that the concentration for the individual contaminant has decreased with time at that well.

D.5 Spatial Mass Flux Calculation Over Time

Contaminant mass flux is the rate at which a contaminant passes through a defined cross-sectional area in the ground water system per unit time. A mass flux calculation is a useful and cost-effective tool to evaluate the effectiveness of a natural attenuation remedy.

Once the contaminant mass leaves the source zone, the total flux within the plume should remain constant as the plume migrates down-gradient, unless mass is removed by natural attenuation processes. When the magnitude of the mass flux varies at different locations within a plume, this may be an indicator of natural attenuation. Mass flux calculations can provide insights into the nature, strength, and longevity of the source zone, and can be used for:

- Refining the conceptual site model;
- Evaluating plume status;
- Demonstrating contaminant mass loss;
- Estimating biodegradation rate constants; and
- Evaluating the potential impacts to receptors.

Several methods (Nichols and Roth, 2004) can be used to estimate contaminant mass flux. These include:

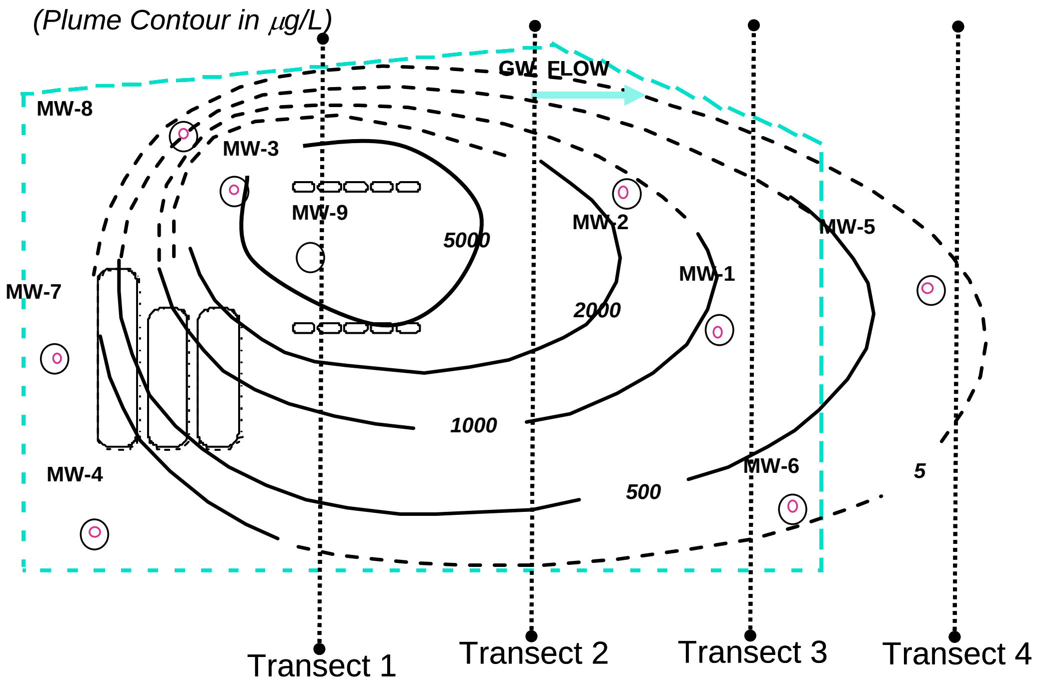
- Using multi-transects of monitoring wells across a plume as shown in Figure D.5;
- Capturing a plume by supply wells or remedial extraction wells;
- Using *in-situ*, down-hole flux meters; and
- Using solute transport modeling in combination with field data collection and interpretation.

This guidance describes the mass flux method with multi-transects of monitoring wells. This method relies on ground water samples from single or multi-level monitoring well data interpolated along a transect across the plume, perpendicular to ground water flow. A vertical cross-section across the transect is divided into any number of sub-areas, each presenting a discrete area of uniform ground water concentration and flow. The total mass flux is the sum of the fluxes from each of these sub areas, as illustrated in Figure D.5. Examples of mass flux methods can be found in Suarez and Rifai (2002), Wiedemeier et al. (1999), NRC (2000), Buscheck et al. (2003), and Nichols and Roth (2004).

Contaminant mass flux is the product of the rate of ground water discharge and the concentration of the contaminant at specified transects along the plume. The steps in a mass flux computation can be summarized as follows:

1. Drawing several transects (or lines) perpendicular to the flow and at various distances down-gradient from the source. These serve as control planes. Each transect of single or multi-level monitoring wells should extend sufficiently in distance both laterally and vertically, in order to define the width and thickness of the plume;
2. Determining the distance between two consecutive contours crossing each transect (within the study area);
3. Estimating volume (and mass) of ground water passing through each line between two consecutive contours for all the contaminant ground water concentrations along a transect;

Figure D.5. Mass Flux Method



4. Estimating the mass flux of the contaminant crossing a transect (i) using the following equation (Eq. D.1);

$$MF_i = C_i * (A_i n_e v_{gw} \rho_{water}) \quad \text{(Eq. D.1)}$$

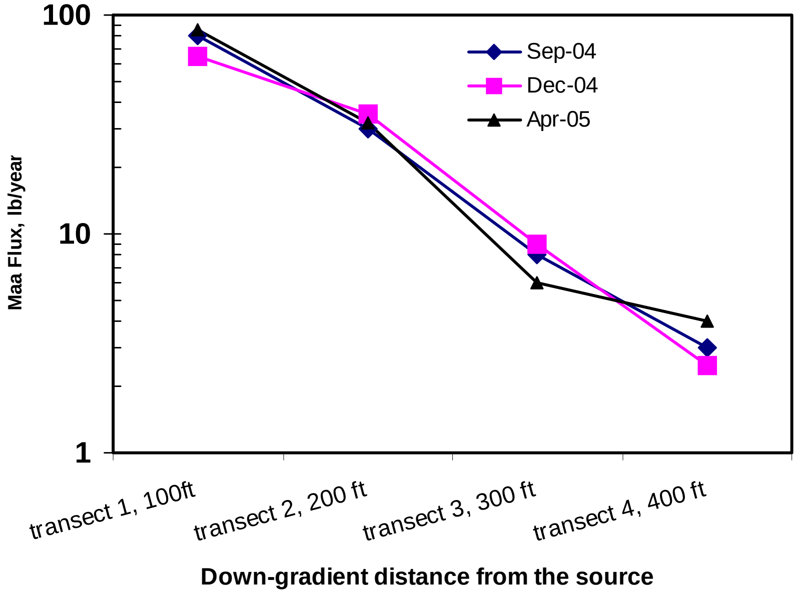
5. Calculating the contaminant mass for each two consecutive contour lines along the transect and adding up the mass; and
6. Comparing the mass flux change at each transect over time.

Although a lower-resolution approach with single-level monitoring wells can be applied, multi-level monitoring well data allow for a more refined, detailed concentration and flow profile.

Evaluating plume status:

Mass flux of the plume can help in assessing plume stability when multiple sampling events for multiple transects are conducted. This calculation involves contaminant mass flux (movement) across plume transects. To use this method, calculate the mass flux for each consecutive contour line along multiple transects as shown below and add up the mass annually as shown in Figure D.5, then compare the mass flux change at each transect to determine the trend in mass changes along the plume over time as shown in Figure D.6.

Figure D.6. Mass Flux versus Down-gradient Distance for Multiple Transects over Time



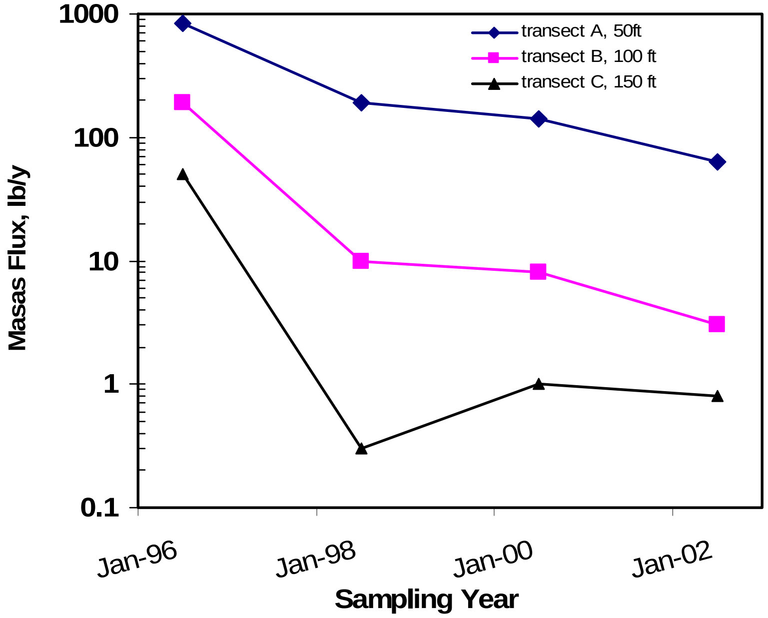
For example, the plots for mass flux versus distance over time shown in Figure D.6 demonstrate the stable plume. Figure D.7 indicates that the plume is shrinking, as exhibited by a mass flux that is declining spatially and temporally. The observed spatial and temporal loss of contaminant mass could be attributed to biodegradation and/or source decay.

Estimating biodegradation rate constants and demonstrating contaminant mass loss due to biodegradation:

An estimated biodegradation rate constant can be calculated by using a quantitative mass flux approach. The mass flux approach is a tool for estimating mass loading from the source zone and concurrent mass attenuation within the plume. This method is most applicable to situations in which the plume is stable. See NRC (2000) and Bockelmann et al. (2003) for more details.

As ground water flows past a source area, it is loaded with dissolved petroleum hydrocarbons through contact with the free product and smear zone.

Figure D.7. Mass Flux versus Sampling Time over Multiple Transects



Therefore, the loading rate can be used as an estimate for the biodegradation rate constant for a stable plume. The mass of dissolved phase which enters the ground water system per unit of time will be the product of the average contaminant concentration in and below the source area and the flow of contaminated ground water in and below the source area. For an expanding plume, the actual biodegradation rate constant would be somewhat less than that calculated for a steady-state plume, and for a shrinking plume it would be somewhat more. The dissolved contaminant loading rate has two components:

- The dissolved phase added to the ground water that flows horizontally through the smear zone below the water table, and
- The dissolved phase added to the ground water beneath the smear zone, caused primarily by vertical dispersion and vertical advection.

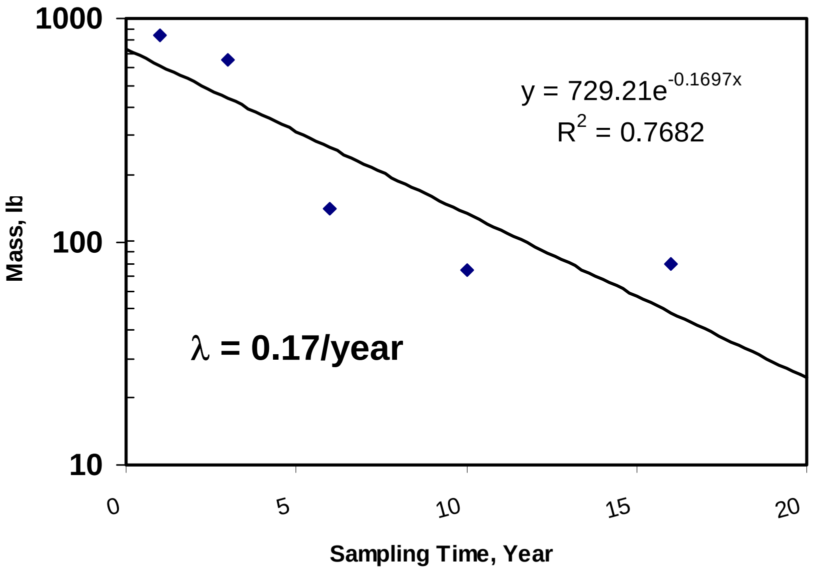
For both of these zones, an average concentration is estimated and multiplied by the ground water flow rate through the zone. The calculation results in the mass of dissolved petroleum hydrocarbons contributed for each zone. Based on stable plume conditions, this rate (Eq. D.2) can be equated to a biodegradation rate constant as shown below.

$$\lambda = -\ln\left(\frac{MF_s}{MF_d}\right) * \frac{1}{\Delta t} \tag{Eq. D.2}$$

Biodegradation rate constant can be calculated by plotting the natural log of mass flux through different transects perpendicular to the flow as a function of the average ground water travel time between the adjacent transects. This method usually also requires a dense well network and accurate aquifer thickness. Mass flux method assumes 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 down-gradient distance between the control planes), the greater the uncertainty of both the contaminant concentration and mass and the contaminant travel time.

For a shrinking plume, biodegradation rate constant derived from mass changes is calculated from change in the total dissolved mass over time for a shrinking plume. A biodegradation rate constant for the contaminant plume is estimated using a plot of dissolved mass as a function of time (Suarez and Rifai, 2002). The rate is calculated as the slope of the best-fit line. Data from Figure D.8 indicate that biodegradation rate constant is occurring at the site at a rate of 0.17/year.

Figure D.8. Estimation of Biodegradation Rate Constant from Mass Change over Time



Evaluating the potential impacts to receptors:
At a site where there is the potential for receptor well impacts, mass flux estimates may be used to predict receptor well concentrations expected in the supply well using the equation – Eq. D.3 (Einarson and Mackay, 2001) below:

$$C_{sw} = \frac{MF_i}{Q_{sw}} \qquad \text{(Eq. D.3)}$$

Appendix D

Aquifer Characteristics

This appendix provides basic guidance for the estimation of aquifer characteristics necessary to describe site hydrogeology in support of the implementation of MNA.

1 Hydraulic Gradient

The calculation of site specific hydraulic gradient (change in hydraulic head elevation with change in distance) is necessary to understand the orientation and velocity of ground water flow. Water level measurements are made against reference elevations in monitoring well casings (typically the top of the inner well casing), and are normally collected during each ground water sampling event (prior to well purging). As with contaminant concentration data, hydraulic head data are normally plotted as isopleths (elevation contours), and the same caveats described in Section 6.1.2.1 of the MNA Technical Guidance relative to the mapping of those data apply here. In the case of hydraulic head data, however, water surface elevations from stream and/or tidal gages can (and should) be incorporated into the mapping of the unconfined aquifer hydraulic surface, if such features are present on site. The horizontal head distribution should be mapped separately within discrete monitoring zones (e.g., overburden and bedrock, confined and unconfined aquifers). Vertical gradients should be determined where monitoring clusters have been installed; the centers of the saturated well screens (which will vary for water table wells) are used to define the vertical distance between the wells[1]. If migration of contaminants through low permeability sediments (e.g., aquitards) represents an important consideration in an MNA remedy, diffusion or vertical flow of contamination may dominate, and therefore vertical gradients and head distribution may be more important to understand than lateral flow components.

2 Hydraulic Conductivity

Hydraulic conductivity (K) is a measure of a porous media's ability to transmit water under a given hydraulic gradient, and is a key, site-specific parameter necessary for the estimation of ground water seepage velocity and travel time. Horizontal hydraulic conductivity is normally estimated through the performance of instantaneous discharge (slug) tests or aquifer (pumping) tests in monitoring wells. Slug tests influence only a very small portion of the aquifer adjacent to the monitoring well, and extrapolation of these data to large areas of a site must be done with caution; slug test data are typically believed to be representative of aquifer conditions only within one order of magnitude. For this reason, efforts should be made to ensure that testing is comprehensive (for example, including multiple wells, and using both slug insertion and slug extraction methods below the water table), and that electronic water level monitoring equipment (pressure transducer and datalogger) provide a full record, especially in sandy aquifers where response time may be extremely rapid. In addition to the standard references cited previously (e.g., Fetter, 2001), Midwest Geosciences Group (www.midwestgeo.com) provides educational materials to improve the performance of slug testing and the accuracy of the derived data.

Pumping tests will normally be performed at a site only when an active ground water treatment or hydraulic control remedy is deemed necessary. Hydraulic conductivity data derived from such

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[1] See http://www.epa.gov/athens/learn2model/part-two/onsite/vgradient.html

tests, which influence a much larger volume of the aquifer than possible from slug tests, is generally of high quality and is assumed to be representative. Guidance for the performance of pumping tests and interpretation of derived data is contained in several well-established texts (Sterrett, 2007; Kruseman and de Ridder, 1992). Software programs and associated user's guides for the solution of pumping test data also contain much useful information; e.g., Aquifer Test Pro (www.swstechnology.com) or AQTESOLV (www.aqtesolv.com).

3 Porosity

The porosity of earth materials is the percentage of void space in rock or soil. Effective porosity (η_e) represents the porosity available for fluid flow, and excludes pores that are not large enough to contain water molecules and those that are not interconnected. Effective porosity is also referred to as the "effective porosity for flow" (n_{eff}) (Bear and Verruuijt, 1987), dynamic porosity, kinematic porosity and transport porosity. For water molecules, η_e is considered to be equivalent to total porosity in coarse soils (sands and gravels) (Fetter, 2001), although this is a poor assumption in soils with a high degree of silts/clay present. Since the Darcy seepage velocity equation includes the effective porosity term, an estimate of η_e is necessary to evaluate contaminant travel time. Newell et al. (1996) cite the following ranges for effective porosity from a number of sources (Walton, 1985; Wiedemeier et al., 1995; Domenico and Schwartz, 1990):

Clay: 0.01 - 0.20
Silt: 0.01 - 0.30
Fine Sand: 0.10 - 0.30
Medium Sand: 0.15 - 0.30
Coarse Sand: 0.20 - 0.35
Gravel: 0.10 - 0.35
Sandstone: 0.005 - 0.10
Unfractured Limestone: 0.001- 0.05
Fractured Granite: 0.00005 - 0.01

4 Organic Carbon Content

The fraction of the aquifer soil matrix comprised of natural organic carbon (f_{oc}) is an important characteristic in the assessment of organic constituent transport. More natural carbon means more sorption of organic constituents on the aquifer matrix, and increased attenuation of contaminant transport. If the fraction organic carbon value is used to demonstrate the applicability of MNA (through solute transport modeling), it can be measured by collecting a sample of aquifer material from an uncontaminated area and performing the appropriate laboratory analysis (e.g., Lloyd-Kahn; Walkley-Black; ASTM Method 2974-87). Typical literature values of f_{oc} range from 0.0002 - 0.02 (0.02 – 2.0 percent) (Newell et al., 1996); if unknown, a default value of 0.001 (0.10 percent) is often used (e.g., ASTM, 1995). Extensive New Jersey-specific data are also available to define a range of f_{oc} within both surface and subsurface soils (BEM, 1997; BEM, 1998; BEM, 2002; Dooley, 2001).

Appendix E

Trend Analysis and Statistical Tests

TREND ANALYSIS AND STATISTICAL TESTS

A. **Selection of Statistical Method:** Chapter 8 (pg 8-1): Statistical Analysis Of Groundwater Monitoring Data At RCRA Facilities - Unified Guidance, EPA 530/R-09-007, March 2009

B. **Linear Regression:** Chapter 17 (pg 17-23): Statistical Analysis Of Groundwater Monitoring Data At RCRA Facilities - Unified Guidance, EPA 530/R-09-007, March 2009
- **Method Summary** (pg 8-31)
- **Procedure** (pg 17-25)
- **Example** (pg 17-26)

C. **Mann-Kendall:** Chapter 17 (pg 17-30): Statistical Analysis Of Groundwater Monitoring Data At RCRA Facilities - Unified Guidance, EPA 530/R-09-007, March 2009
- **Method Summary** (pg 8-32)
- **Procedure** (pg 17-32)
- **Example** (pg 17-33)

D. **Seasonal Mann-Kendall:** Chapter 14 (pg 14-37): Statistical Analysis Of Groundwater Monitoring Data At RCRA Facilities - Unified Guidance, EPA 530/R-09-007, March 2009
- **Method Summary** (pg 8-21)
- **Procedure** (pg 14-37)
- **Example** (pg 14-38)

E. **Mann-Whitney U:** Appendix C: New Jersey Administrative Code 7:26E – Technical Requirements for Site Remediation, NJDEP, April 2010

A. **Selection of Statistical Method:** Chapter 8 (pg 8-1): Statistical Analysis Of Groundwater Monitoring Data At RCRA Facilities - Unified Guidance, EPA 530/R-09-007, March 2009

CHAPTER 8. SUMMARY OF RECOMMENDED METHODS

This chapter provides a quick guide to the statistical procedures discussed within the Unified Guidance. The first section is a basic road map designed to encourage the user to ask a series of key questions. The other sections offer thumbnail sketches of each method and a matrix of options to help in selecting the right procedure, depending on site-specific characteristics and constraints.

8.1 SELECTING THE RIGHT STATISTICAL METHODS

Choosing appropriate statistical methods is important in developing a sound groundwater monitoring statistical program. The statistical test(s) should be selected to match basic site-specific characteristics such as number and configuration of wells, the water quality constituents being measured, and general hydrology. Statistical methods should also be selected with reference to the statistical characteristics of the monitored parameters — proportion of non-detects, type of concentration distribution (*e.g.*, normal, lognormal), presence or absence of spatial variability, *etc.*

Because site conditions and permit requirements vary considerably, no single "cookbook" approach is readily available to select the right statistical method. The best strategy is to consider site-specific conditions and ask a series of questions. A table of recommended options (**Table 8-1**) and summary descriptions is presented in **Section 8.2** to help select an appropriate basic approach.

The first question is: what stage of monitoring is required? Detection monitoring is the first stage of any groundwater monitoring program and typically involves comparisons between measurements of background and compliance point groundwater. Most of the methods described in this document (*e.g.*, prediction limits, control charts, tests for trend, *etc.*) are designed for facilities engaged in detection monitoring. However, it must be determined whether an interwell (*e.g.*, upgradient-to-downgradient) or an intrawell test is warranted. This entails consideration of the site hydrology, constituent detection rates, and deciding whether separate (upgradient) wells or past intrawell data serves as the most appropriate and representative background.

Compliance/assessment monitoring is required for facilities that no longer meet the requirements of a detection monitoring program by exhibiting statistically significant indications of a release to groundwater. Once in compliance/assessment, compliance point measurements are typically tested against a fixed GWPS. Examples of fixed standards include Maximum Concentration Limits [MCL], risk-derived limits or a single limit derived from background data. The most appropriate statistical method for tests against GWPS is a lower confidence limit. The type of confidence limit will depend on whether the regulatory standard represents an average concentration; an absolute maximum, ceiling, or upper percentile; or whether the compliance data exhibit a trend over time.

In cases where no fixed GWPS is specified for a particular constituent, compliance point data may be directly compared against background data. In this situation, the most appropriate statistical method is one or another detection monitoring two- or multiple-sample tests using the critical design limit as the GWPS (discussed in **Section 7.5**).

Corrective action is reserved for facilities where evidence of a groundwater release is confirmed above a GWPS. In these situations, the facility is required to submit an appropriate remediation plan to the Regional Administrator and to institute steps to insure adequate containment and/or clean-up of the release. Remediation of groundwater can be very costly and also difficult to measure. EPA has not adopted a uniform approach in the setting of clean-up standards or how one should determine whether those clean-up standards have been attained. Some guidance on this issue is given in the EPA document, ***Methods for Evaluating the Attainment of Cleanup Standards, Volume II: Groundwater*** (EPA, 1992).

The null hypothesis in corrective action testing is reversed from that of detection and compliance/assessment monitoring. Not only is it assumed that contamination is above the compliance or clean-up standard, but corrective action should continue until the average concentration level is below the clean-up limit for periods specified in the regulations. For any fixed-value standard (e.g., the GWPS or a remediation goal) a reasonable and consistent statistical test for corrective action is an *upper* confidence limit. The type of confidence limit will depend on whether the data have a stable mean concentration or exhibit a trend over time. For those well constituents requiring remediation, there will be a period of activity before formal testing can take place. A number of statistical techniques (e.g. trend testing) can be applied to the data collected in this interim period to gauge prospects for eventual GWPS compliance. **Section 7.5** describes corrective action testing limitations involving a two-sample GWPS.

Another major question involves the statistical distribution most appropriate to the observed measurements. Parametric tests are those which assume the underlying population follows a known and identifiable distribution, the most common examples in groundwater monitoring being the normal and the lognormal. If a specific distribution cannot be determined, non-parametric test methods can be used. Non-parametric tests do not require a known statistical distribution and can be helpful when the data contain a substantial proportion of non-detects. All of the parametric tests described in the Unified Guidance, except for control charts, have non-parametric counterparts that can be used when the underlying distribution is uncertain or difficult to test.

A special consideration in fitting distributions is the presence of non-detects, also known as left-censored measurements. As long as a sample contains a small fraction of non-detects (*i.e.*, no more than 10-15%), simple substitution of half the reporting limit [RL] is generally adequate. If the proportion of non-detects is substantial, it may be difficult or impossible to determine whether a specific parametric distributional model provides a good fit to the data. For some tests, such as the *t*-test, one can switch to a non-parametric test with little loss of power or accuracy. Non-parametric interval tests, however, such as prediction and tolerance limits, require substantially more data before providing statistical power equivalent to *parametric* intervals. Partly because of this drawback, the Unified Guidance discusses methods to adjust datasets with significant fractions of non-detects so that parametric distributional models may still be used (**Chapter 15**).

The Unified Guidance now recommends a single, consistent D*ouble Quantification rule* approach for handling constituents that have either never been detected or have not been recently detected. Such constituents are *not* included in cumulative annual *site-wide false positive error rate* [SWFPR] computations; and no special adjustment for non-detects is necessary. Any confirmed quantification (*i.e.*, two consecutive detections above the RL) at a compliance point provides sufficient evidence of groundwater contamination by that parameter.

A key question when picking a test for detection monitoring is whether traditional background-to-downgradient interwell or single-well intrawell tests are appropriate. If intrawell testing is appropriate, historical measurements form the individual compliance well's own background while future values are tested against these data. Intrawell tests eliminate any natural spatial differences among monitoring wells. They can also be used when the groundwater flow gradient is uncertain or unstable, since all samples being tested are collected from the same well.

Possible disadvantages to intrawell tests also need to be considered. First, if the compliance well has already been impacted, intrawell background will also be impacted. Such contaminated background may provide a skewed comparison to later data from the same well, making it difficult to identify contaminated groundwater in the future. Secondly, if intrawell background is constructed from only a few early measurements, considerable time may be needed to accumulate a sufficient number of background observations (via periodic updating) to run a statistically powerful test.

If a compliance well has already been impacted by previous contamination, trend testing can still indicate whether conditions have deteriorated since intrawell background was collected. For sites historically contaminated above background, the only way to effectively monitor compliance wells may be to establish an historical intrawell baseline and measure increases above this baseline.

Besides trend tests, techniques recommended for intrawell comparisons include intrawell prediction limits, control charts, and sometimes the Wilcoxon rank-sum test. The best choice between these methods is not always clear. Since there is no non-parametric counterpart to control charts, the choice will depend on whether the data is normal or can be normalized via a transformation. New guidance for control charts shows they also can be designed to incorporate retesting. For sites with a large number of well-constituent pairs, intrawell prediction limits can incorporate retesting to meet specific site-wide false positive rate and statistical power characteristics. Parametric intrawell prediction limits can be used with background that is normal or transformable to normality; non-parametric versions can also be applied for many other data sets.

If interwell, upgradient-to-downgradient tests are appropriate, the choice of statistical method depends primarily on the number of compliance wells and constituents being monitored, the number of observations available from each of these wells, and the detection rates and distributional properties of these parameters. If a very small number of comparisons must be tested (*i.e.*, two or three compliance wells versus background, for one or two constituents), a *t*-test or Wilcoxon rank-sum test may be appropriate if there are a sufficient number of compliance measurements (*i.e.*, at least two per well).

For other cases, the Unified Guidance recommends a prediction limit or control chart constructed from background. Whenever more than a few statistical tests must be run, retesting should be incorporated into the procedure. If multiple observations per compliance well can be collected during a given evaluation period, either a prediction limit for 'future' observations, a prediction limit for means or medians, or a control chart can be considered, depending on which option best achieves statistical power and SWFPR targets, while balancing the site-specific costs and feasibility of sampling. If only one observation per compliance well can be collected per evaluation, the only practical choices are a prediction limit for individual observations or a control chart.

8.2 TABLE 8-1 INVENTORY OF RECOMMENDED METHODS

Chapter 9. Exploratory Tools

Statistical Method	Chapter	Use
Time Series Plot	**§9.1**	Plot of measurement levels over time; Useful for assessing trends, data inconsistencies, etc.
Box Plot	**§9.2**	Graphical summary of sample distribution; Useful for comparing key statistical characteristics in multiple wells
Histogram	**§9.3**	Graphical summary of sample distribution; Useful for assessing probability density of single data set
Scatter Plot	**§9.4**	Diagnostic tool; Plot of one variable vs. another; Useful for exploring statistical associations
Probability Plot	**§9.5**	Graphical fit to normality; Useful for raw or transformed data

Chapter 10. Fitting Distributions

Statistical Method	Chapter	Use
Skewness Coefficient	**§10.4**	Measures symmetry/asymmetry in distribution; Screening level test for plausibility of normal fit
Coefficient of Variation	**§10.4**	Measures symmetry/asymmetry in distribution; Screening tool for plausibility of normal fit; Only for non-negative data
Shapiro-Wilk Test	**§10.5.1**	Numerical normality test of a single sample; for $n \le 50$
Shapiro-Francía Test	**§10.5.2**	Numerical test of normality for a single sample; Supplement to Shapiro-Wilk; Use with $n > 50$
Filliben's Probability Plot Correlation Coefficient	**§10.6**	Numerical test of normality for a single sample; Interchangeable with Shapiro-Wilk; Use with $n \le 100$; Good supplement to probability plot
Shapiro-Wilk Multiple Group Test	**§10.7**	Extension of Shapiro-Wilk test for multiple samples with possibly different means and/or variances; Good check to use with Welch's *t*-test

Chapter 11. Equality of Variance

Statistical Method	Chapter	Use
Box Plots (side-by-side)	**§11.1**	Graphical test of differences in population variances; Good screening tool for equal variance assumption in ANOVA
Levene's Test	**§11.2**	Numerical, robust ANOVA-type test of equality of variance for ≥ 2 populations; Useful for testing assumptions in ANOVA
Mean-SD Scatter Plot	**§11.3**	Visual test of association between SD and mean levels across group of wells; Use to check for proportional effect or if variance-stabilizing transformation is needed

Chapter 12. Outliers

Statistical Method	Chapter	Use
Probability Plot	**§12.1**	Graphical fit of distribution to normality; Useful for identifying extreme points not coinciding with predicted tail of distribution
Box Plot	**§12.2**	Graphical screening tool for outliers; quasi-non-parametric, only requires rough symmetry in distribution
Dixon's Test	**§12.3**	Numerical test for single low or single high outlier; Use when $n \le 25$
Rosner's Test	**§12.4**	Numerical test for up to 5 outliers in single dataset; Recommended when $n \ge 20$; User must identify a specific number of possible outliers before running

Chapter 13. Spatial Variation

Statistical Method	Chapter	Use
Box Plots (side-by-side)	**§13.2.1**	Quick screen for spatial variability; Look for noticeably staggered boxes
One-Way Analysis of Variance [ANOVA] for Spatial Variation	**§13.2.2**	Test to compare means of several populations; Use to identify spatial variability across a group of wells and to estimate pooled (background) standard deviation for use in intrawell tests; Data must be normal or normalized; Assumption of equal variances across populations

Chapter 14. Temporal Variability

Statistical Method	Chapter	Use
Time Series Plot (parallel)	**§14.2.1**	Quick screen for temporal (and/or spatial) variation; Look for parallel movement in the graph traces at several wells over time
One-way ANOVA for Temporal Effects	**§14.2.2**	Test to compare means of distinct sampling events, in order to assess systematic temporal dependence across wells; Use to get better estimate of (background) variance and degrees of freedom in data with temporal patterns; Residuals from ANOVA also used to create stationary, adjusted data
Sample Autocorrelation Function	**§14.2.3**	Plot of autocorrelation by lag between sampling events; Requires approximately normal data; Use to test for temporal correlation and/or to adjust sampling frequency
Rank von Neumann Ratio	**§14.2.4**	Non-parametric numerical test of dependence in time-ordered data series; Use to test for first-order autocorrelation in data from single well or population
Darcy Equation	**§14.3.2**	Method to approximate groundwater flow velocity; Use to determine sampling interval guaranteeing physical independence of consecutive groundwater samples; Does not ensure statistical independence
Seasonal Adjustment (single well)	**§14.3.3**	Method to adjust single data series exhibiting seasonal correlations (*i.e.*, cyclical fluctuations); At least 3 seasonal cycles must be evident on time series plot
Temporally-Adjusted Data Using ANOVA	**§14.3.3**	Method to adjust multiple wells for a common temporal dependence; Use adjusted data in subsequent tests
Seasonal Mann-Kendall Test	**§14.3.4**	Extension of Mann-Kendall trend test when seasonality is present; At least 3 seasonal cycles must be evident

Chapter 15. Managing Non-Detect Data

Statistical Method	Chapter	Use
Simple Substitution	**§15.2**	Simplest imputation scheme for non-detects; Useful when ≤ 10-15% of dataset is non-detect
Censored Probability Plot	**§15.3**	Probability plot for mixture of non-detects and detects; Use to check normality of left-censored sample
Kaplan-Meier	**§15.3**	Method to estimate mean and standard deviation of left-censored sample; Use when ≤ 50% of dataset is non-detect; Multiple detects and non-detects must originate from same distribution
Robust Regression on Order Statistics	**§15.4**	Method to estimate mean and standard deviation of left-censored sample; Use when ≤ 50% of dataset is non-detect; Multiple detects and non-detects must originate from same distribution
Cohen' Method and Parametric Regression on Order Statistics	**§15.5**	Other methods to estimate mean and standard deviation of left-censored sample; Use when ≤ 50% of dataset is non-detect; Detects and non-detects must originate from same distribution and there must be a single censoring limit

Chapter 16. Two-sample Tests		
Statistical Method	Chapter	Use
Pooled Variance *t*-Test	**§16.1.1**	Test to compare means of two populations; Data must be normal or normalized, with no significant spatial variability; Useful at very small sites in upgradient-to-downgradient comparisons; Also useful for updating background; Population variances must be equal
Welch's *t*-Test	**§16.1.2**	Test to compare means of two populations; Data must be normal or normalized, with no significant spatial variability; Useful at very small sites in interwell comparisons; Also useful for updating background; Population variances can differ
Wilcoxon Rank-Sum Test	**§16.2**	Non-parametric test to compare medians of two populations; Data need not be normal; Some non-detects OK; Should have no significant spatial variability; Useful at very small sites in interwell comparisons and for certain intrawell comparisons; Also useful for updating background
Tarone-Ware Test	**§16.3**	Extension of Wilcoxon rank-sum; non-parametric test to compare medians of two populations; Data need not be normal; Designed to accommodate left-censored data; Should have no significant spatial variability; Useful at very small sites in interwell comparisons and for certain intrawell comparisons; Also useful for updating background

Chapter 17. ANOVA, Tolerance Limits, & Trend Tests		
Statistical Method	Chapter	Use
One-Way ANOVA	**§17.1.1**	Test to compare means across multiple populations; Data must be normal or normalized; Should have no significant spatial variability if used as interwell test; Assumes equal variances; Mandated in some permits, but generally superceded by other tests; Useful for identifying spatial variation; RMSE from ANOVA can be used to improve intrawell background limits
Kruskal-Wallis Test	**§17.1.2**	Test to compare medians across multiple populations; Data need not be normal; some non-detects OK; Should have no significant spatial variability if used as interwell test; Useful alternative to ANOVA for identifying spatial variation
Tolerance Limit	**§17.2.1**	Test to compare background vs. ≥ 1 compliance well; Data must be normal or normalized; Should have no significant spatial variability if used as interwell test; Alternative to ANOVA; Mostly superceded by prediction limits; Useful for constructing alternate clean-up standard in corrective action
Non-parametric Tolerance Limit	**§17.2.2**	Test to compare background vs. ≥ 1 compliance well; Data need not be normal; Non-Detects OK; Should have no significant spatial variability if used as interwell test; Alternative to Kruskal-Wallis; Mostly superceded by prediction limits
Linear Regression	**§17.3.1**	Parametric estimate of linear trend; Trend residuals must be normal or normalized; Useful for testing trends in background or at already contaminated wells; Can be used to estimate linear association between two random variables
Mann-Kendall Trend Test	**§17.3.2**	Non-parametric test for linear trend; Non-detects OK; Useful for documenting upward trend at already contaminated wells or where trend already exists in background
Theil-Sen Trend Line	**§17.3.3**	Non-parametric estimate of linear trend; Non-detects OK; Useful for estimating magnitude of an increasing trend in conjunction with Mann-Kendall test

Chapter 18. Prediction Limit Primer

Statistical Method	Chapter	Use
Prediction Limit for m Future Values	**§18.2.1**	Test to compare m measurements from compliance well against background; Data must be normal normalized; Useful in retesting schemes; Can be adapted to either intrawell or interwell tests; No significant spatial variability allowed if used as interwell test
Prediction Limit for Future Mean	**§18.2.2**	Test to compare mean of compliance well against background; Data must be normal or normalized; Useful alternative to traditional ANOVA; Can be useful in retesting schemes; Most useful for interwell (*e.g.*, upgradient to downgradient) comparisons; No significant spatial variability allowed if used as interwell test
Non-Parametric Prediction Limit for m Future Values	**§18.3.1**	Non-parametric test to compare m measurements from compliance well against order statistics of background; Non-normal data and/or non-detects OK; Useful in non-parametric retesting schemes; Should have no significant spatial variability if used as interwell test
Non-parametric Prediction Limit for Future Median	**§18.3.2**	Test to compare median of compliance well against order statistics of background; Non-normal data and/or non-detects OK; Useful in non-parametric retesting schemes; Most useful for interwell (*e.g.*, upgradient to downgradient) comparisons; No significant spatial variability allowed if used as interwell test

Chapter 19. Prediction Limit Strategies with Retesting

Statistical Method	Chapter	Use
Prediction Limits for Individual Observations With Retesting	**§19.3.1**	Tests individual compliance point measurements against background; Data must be normal or normalized; Assumes common population variance across wells; No significant spatial variability allowed if used as interwell test; Replacement for traditional ANOVA, extends Dunnett's multiple comparison with control (MCC) procedure; Allows control of SWFPR across multiple well-constituent pairs; Retesting explicitly incorporated; Useful at any size site
Prediction Limits for Means With Retesting	**§19.3.2**	Tests compliance point means against background; Data must be normal or normalized; Assumes common population variance across wells; No significant spatial variability allowed if used as interwell test; Replacement for traditional ANOVA, extends Dunnett's multiple comparison with control (MCC) procedure; More flexible than a series of intrawell t-tests if used as intrawell test; Allows control of SWFPR across multiple well-constituent pairs; Must be feasible to collect ≥2 resamples per evaluation period to incorporate retesting; 1-of-1 scheme does not require explicit retesting
Non-Parametric Prediction Limits for Individual Observations With Retesting	**§19.4.1**	Non-parametric test of individual compliance point observations against background; Non-normal data and/or non-detects OK; No significant spatial variability allowed if used as interwell test; Retesting explicitly incorporated; Large background sample size helpful
Non-Parametric Prediction Limits for Medians With Retesting	**§19.4.2**	Non-parametric test of compliance point medians against background; Non-normal and/or non-detects OK; No significant spatial variability allowed if used as interwell test; Large background sample size helpful; Must be feasible to collect ≥ 3 resamples per evaluation period to incorporate retesting; 1-of-1 scheme does not require explicit retesting

Chapter 20. Control Charts		
Statistical Method	Chapter	Use
Shewhart-CUSUM Control Chart	**§20.2**	Graphical test of significant increase above background; Data must be normal or normalized; Some non-detects OK if left-censored adjustment made; At least 8 background observations recommended; Viable alternative to prediction limits; Retesting can be explicitly incorporated; Control limits can be set via published literature or Monte Carlo simulation

Chapter 21. Confidence Intervals		
Statistical Method	Chapter	Use
Confidence Interval Around Normal Mean	**§21.1.1**	Data must be normal; Some non-detects OK if left-censored adjustment made; Used in compliance/assessment or corrective action to compare compliance well against fixed, mean-based groundwater standard; Should be no significant trend; 4 or more observations recommended
Confidence Interval Around Lognormal Geometric Mean	**§21.1.2**	Data must be lognormal; Some non-detects OK if left-censored adjustment made; Used in compliance/assessment or corrective action to compare compliance well against fixed, mean-based groundwater standard; Should be no significant trend; 4 or more observations recommended; Geometric mean equivalent to lognormal median, smaller than lognormal mean
Confidence Interval Around Lognormal Arithmetic Mean	**§21.1.3**	Data must be lognormal; Some non-detects OK if left-censored adjustment made; Used in compliance/assessment or corrective action to compare compliance well against fixed, mean-based groundwater standard; Should be no significant trend; 4 or more observations recommended; Lognormal arithmetic mean larger than lognormal geometric mean
Confidence Interval Around Upper Percentile	**§21.1.4**	Data must be normal or normalized; Some non-detects OK if left-censored adjustment made; Used in compliance/assessment to compare compliance well against percentile-based or maximum groundwater standard; Should be no significant trend
Non-Parametric Confidence Interval around Median	**§21.2**	For non-normal, non-lognormal data; Non-detects OK; Used in compliance/assessment or corrective action to compare compliance well against fixed, mean-based groundwater standard; Should be no significant trend; 7 or more observations recommended
Non-Parametric Confidence Interval Around Upper Percentile	**§21.2**	For non-normal, non-lognormal data; Non-detects OK; Used in compliance/assessment or corrective action to compare compliance well against percentile-based or maximum groundwater standard; Should be no significant trend; Large background sample size helpful
Confidence Band Around Linear Regression	**§21.3.1**	Use on data with significant trend; Trend residuals must be normal or normalized; Used in compliance/assessment or corrective action to compare compliance well against fixed groundwater standard; ≥ 8 observations recommended
Non-parametric Confidence Band Around Theil-Sen Line	**§21.3.2**	Use on data with significant trend; Non-normal data and/or non-detects OK; Used in compliance/assessment or corrective action to compare compliance well against fixed groundwater standard; Bootstrapping of Theil-Sen trend line used to construct confidence band

B. **Linear Regression:** Chapter 17 (pg 17-23): Statistical Analysis Of Groundwater Monitoring Data At RCRA Facilities - Unified Guidance, EPA 530/R-09-007, March 2009

- **Method Summary** (pg 8-31)
- **Procedure** (pg 17-25)
- **Example** (pg 17-26)

When to use: A non-parametric tolerance limit can be used in place of the Kruskal-Wallis test for detecting contaminated groundwater. It is more flexible than Kruskal-Wallis since 1) as few as one new measurement per compliance well is needed to run a tolerance limit test, and 2) no post-hoc testing is necessary to identify which compliance wells are elevated over background. Most uses of tolerance limits have been superseded by prediction limits, due to difficulty of incorporating retesting into tolerance limit schemes. However, when a clean-up limit cannot or has not been specified in corrective action, a tolerance limit can be computed on background and used as a site-specific alternate concentration limit [ACL].

Steps involved: 1) Compute a large order statistic from background and set this value as the upper tolerance limit; 2) calculate the confidence and coverage associated with the tolerance limit; 3) collect one or more observations from each compliance well and test each against the tolerance limit; and 4) identify a well as contaminated if any of its observations exceed the tolerance limit.

Advantages/Disadvantages: 1) Tolerance limits are likely to be used only infrequently to be used as either interwell or intrawell tests. Prediction limits or control charts offer better control of false positive rates, and less is known about the impact of retesting on tolerance limit performance; and 2) non-parametric tolerance limits have the added disadvantage of generally requiring large background samples to ensure adequate confidence and/or coverage. For this reason, it is strongly recommended that a parametric tolerance limit be constructed whenever possible.

LINEAR REGRESSION (SECTION 14.4)

Basic purpose: Method for detection monitoring and diagnostic tool. It is used to identify the presence of a significantly increasing trend at a compliance point or any trend in background data sets.

Hypothesis tested: H_0 — No discernible linear trend exists in the concentration data over time. H_A — A non-zero, (upward) linear component to the trend does exist.

Underlying assumptions: Trend residuals should be normal or normalized, equal in variance, and statistically independent. If a small fraction of non-detects exists (≤10-15%), use simple substitution to replace each non-detect by half the reporting limit [RL]. Test homoscedasticity of residuals with a *scatter plot* (**Section 9.1**).

When to use: Use a test for trend when 1) upgradient-to-downgradient comparisons are inappropriate so that intrawell tests are called for, and 2) a control chart or intrawell prediction limit cannot be used because of possible trends in the intrawell background. A trend test can be particularly helpful at sites with recent or historical contamination where it is uncertain to what degree intrawell background is already contaminated. The presence of an upward trend in these cases will document the changing nature of the concentration data much more accurately than either a control chart or intrawell prediction limit, both of which assume a stable baseline concentration.

Steps involved: 1) If a linear trend is evident on a time series plot, construct the linear regression equation; 2) subtract the estimated trend line from each observation to form residuals; 3) test residuals for assumptions listed above; and 4) test regression slope to determine whether it is significantly different from zero. If so and the slope is positive, conclude there is evidence of a significant upward trend.

Advantages/Disadvantages: Linear regression is a standard statistical method for identifying trends and other linear associations between pairs of random variables. However, it requires approximate normality of the trend residuals. Confidence bands around regression trends can be used in compliance/assessment and corrective action to determine compliance with fixed standards even when concentration levels are actively changing (*i.e.*, when a trend is apparent).

MANN-KENDALL TEST FOR TREND (SECTION 17.3.2)

Basic purpose: Method for detection monitoring and diagnostic tool. It is used to identify the presence of a significant (upward) trend at a compliance point or any trend in background data.

Hypothesis tested: H_0 — No discernible linear trend exists in the concentration data over time. H_A — A non-zero, (upward) linear component to the trend does exist.

Underlying assumptions: Since the Mann-Kendall trend test is a non-parametric method, the underlying data need not be normal or follow any particular distribution. No special adjustment for ties is needed.

When to use: Use a test for trend when 1) interwell tests are inappropriate so that intrawell tests are called for, and 2) a control chart or intrawell prediction limit cannot be used because of possible trends in intrawell background. A trend test can be particularly helpful at sites with recent or historical contamination where it is uncertain if intrawell background is already contaminated. An upward trend in these cases documents changing concentration levels more accurately than either a control chart or intrawell prediction limit, both of which assume a stationary background mean concentration.

Steps involved: 1) Sort the data values by time of sampling/collection; 2) consider all possible pairs of measurements from different sampling events; 3) score each pair depending on whether the later data point is higher or lower in concentration than the earlier one, and sum the scores to get Mann-Kendall statistic; 4) compare this statistic against an α-level critical point; and 5) if the statistic exceeds the critical point, conclude that a significant upward trend exists. If not, conclude there is insufficient evidence for identifying a significant, non-zero trend.

Advantages/Disadvantages: The Mann-Kendall test does not require any special treatment for non-detects, only that all non-detects can be set to a common value lower than any of the detects. The test is easy to compute and reasonably efficient for detecting (upward) trends. Exact critical points are provided in the Unified Guidance for $n \leq 20$; a normal approximation can be used for $n > 20$. 3) A version of the Mann-Kendall test (the seasonal Mann-Kendall, **Section 14.3.4**) can be used to test for trends in data that exhibit seasonality.

THEIL-SEN TREND LINE (SECTION 17.3.3)

Basic purpose: Method for detection monitoring. This is a non-parametric alternative to linear regression for estimating a linear trend.

Hypothesis tested: As presented in the Unified Guidance, the Theil-Sen trend line is not a formal hypothesis test but rather an estimation procedure. The algorithm can be modified to formally test whether the true slope is significantly different from zero, but this question will already be answered if used in conjunction with the Mann-Kendall procedure.

Kendall test for trend and the *Theil-Sen trend line*. These methods can be particularly valuable when constructing trends on data sets containing non-detects.

PROCEDURE

Step 1. Construct a time series plot of the compliance point measurements. If a discernible trend is evident, compute a linear regression of concentration against sampling date (time), letting x_i denote the ith concentration value and t_i denote the ith sampling date. Estimate the linear slope $\hat{b}$ with the formula:

$$\hat{b} = \sum_{i=1}^{n} \left(t_i - \bar{t}\right) \cdot x_i \Big/ (n-1) \cdot s_t^2 \qquad [17.21]$$

This estimate then leads to the regression equation, given by:

$$\hat{x}_t = \bar{x} + \hat{b} \cdot \left(t - \bar{t}\right) \qquad [17.22]$$

where $\bar{t}$ denotes the mean sampling date, s_t^2 is the variance of sampling dates, $\bar{x}$ is the mean concentration level, and $\hat{x}_t$ represents the estimated mean concentration at time t.

Note: though the variable t above represents time, it could just as easily signify another variable, perhaps a second constituent for which an association with x is estimated.

Step 2. Compute the regression residual at each sampling event i with equation [17.23]:

$$r_i = x_i - \hat{x}_i \qquad [17.23]$$

Check the set of residuals for lack of normality and significant skewness using the techniques in **Chapter 10**. Also, plot the residuals against the estimated regression values ($\hat{x}_i$) to check for non-uniform vertical thickness in the scatter cloud. Make a similar check by plotting the residuals against the sampling dates (t_i).

If the residuals are non-normal and substantially skewed and/or the scatter clouds appear to have a definite pattern (*e.g.*, funnel-shaped; "U"-shaped; or, residuals mostly positive on one end of graph and mostly negative on the other end, instead of randomly scattered around the horizontal line $r = 0$), repeat **Steps 1** and **2** after first attempting a normalizing transformation.

Step 3. Calculate the estimated variance around the regression line (also known as the *mean squared error* [MSE]) with equation [17.24]:

$$s_e^2 = \frac{1}{n-2} \sum_{i=1}^{n} r_i^2 \qquad [17.24]$$

Step 4. Compute the standard error of the linear regression slope coefficient using the s^2_e result from Step 3 in equation [17.25]:

$$se(\hat{b}) = \sqrt{s^2_e \Big/ \sum_{i=1}^{n} (t - \bar{t})^2} \qquad [17.25]$$

Step 5. Test whether the trend is significantly different from zero by forming the *t*-statistic ratio in equation [17.26]:

$$t_b = \hat{b} \big/ se(\hat{b}) \qquad [17.26]$$

This *t*-statistic (t_b) has n–2 degrees of freedom [*df*]. Given a level of significance (α), choose the critical point (t_{cp}) for the test as the (1– α) × 100th percentage point of the Student's *t*-distribution with (n–2) *df* or $t_{cp} = t_{1-\alpha,n-2}$. Compare t_b against the critical point. If $t_b > t_{cp}$, conclude that the slope of the trend is both positive and significantly different from zero at the α-level of significance. If $t_b < -t_{cp}$, conclude there is a significant decreasing trend. If neither exists, there is insufficient evidence of an increasing or decreasing trend.

►EXAMPLE 17-5

The following groundwater chloride measurements (n = 19) were collected over a five-year period at a solid waste landfill. Test for a significant trend at the α = 0.01 level using linear regression.

Sample Date	Chloride (ppm)	Elapsed Days	Residuals
2002-03-18	11.5	76	−0.25
2002-05-14	12.6	133	0.67
2002-08-22	13.8	233	1.56
2003-02-12	12.3	407	−0.48
2003-05-29	12.8	513	−0.30
2003-08-18	13.2	594	−0.15
2003-11-20	14.1	688	0.45
2004-02-19	13.3	779	−0.63
2004-04-26	13.1	846	−1.04
2004-07-29	13.2	940	−1.23
2004-11-09	15.3	1043	0.56
2005-02-24	15.0	1150	−0.08
2005-06-14	15.2	1260	−0.22
2005-08-23	15.8	1330	0.17
2005-10-17	16.1	1385	0.30
2006-02-08	15.1	1499	−1.06
2006-04-27	16.4	1577	0.00
2006-08-10	17.7	1682	0.98
2006-10-26	17.7	1759	0.74

SOLUTION

Step 1. Check for an apparent trend on a time series plot (**Figure 17-2**). Since the chloride values are increasing in reasonably linear fashion, compute the tentative regression line using equations [17.21] and [17.22]. To compute the slope estimate, first convert the sample dates to elapsed days using a starting date prior to the first event. In this case, choose an arbitrary starting date of 2002-01-01 as zero and compute the elapsed days as listed in the table above.

Using elapsed days as the time variable, compute the sample mean and variance to get:

$$\bar{t} = 941.79 \text{ days}$$

$$s_t^2 = 279374.3 \text{ days}^2$$

Then compute the tentative slope as:

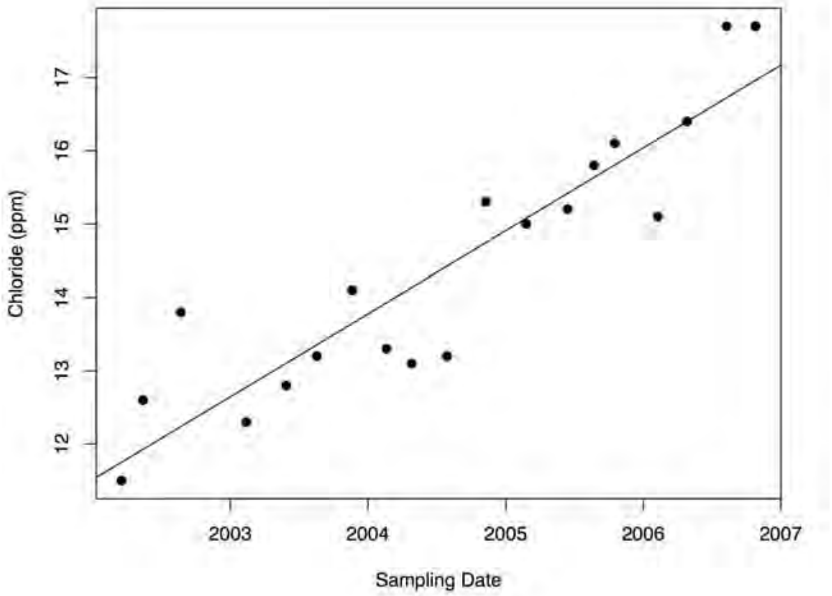
$$\hat{b} = [(76-941.79)\cdot 11.5 + \ldots + (1759-941.79)\cdot 17.7]/[(19-1)\cdot 279374.3] = .0031$$

and the regression line itself as:

$$\hat{x}_t = \bar{x} + \hat{b}\cdot(t-\bar{t}) = 14.432 + .0031\cdot(t-941.79)$$

where the mean chloride value is $\bar{x} = 14.432$ ppm. The regression line is overlaid on the scatter plot in **Figure 17-2**.

Figure 17-2. Time Series Plot of Chloride (ppm) Overlaid With Linear Regression



Step 2. Calculate the regression residual at each sampling event using equation [17.23]. This involves computing an estimated concentration along the regression line for each sampled time (t) and then subtracting from the observed concentration. For example, the residual at t = 407 is

$$x_t - \hat{x}_t = 12.3 - 12.78 = -0.48$$

All the residuals are listed in the table above. Then check the residuals for normality, homoscedasticity, and lack of association with the predicted values from the regression line.

Figure 17-3 is a probability plot of the residuals, indicating good agreement with normality. **Figure 17-4** is a scatter plot of the residuals versus sampling date and **Figure 17-5** is a scatter plot of the residuals versus predicted values from the trend line. Both of these last plots do not exhibit any particular trends or patterns with sampling date or the trend line predicted values; the residuals are fairly randomly scattered.

Step 3. Compute the MSE of the regression using the squared residuals in equation [17.24] to get

$$s_e^2 = \frac{1}{n-2} \cdot \sum_{i=1}^{n} r_i^2 = \frac{1}{17} \cdot \left[(-.25)^2 + (.67)^2 + \ldots + (.74)^2\right] = 0.5628$$

Step 4. Calculate the standard error of the regression slope coefficient using equation [17.25]:

$$se(\hat{b}) = \sqrt{s^2{}_e \Big/ \sum_{i=1}^{n} (t-\bar{t})^2} = \sqrt{.5628 \Big/ \left[(76-941.79)^2 + \ldots + (1759-941.79)^2\right]} = .00033$$

Step 5. Form the *t*-statistic ratio with formula [17.26] to get:

$$t_b = \hat{b} \Big/ se(\hat{b}) = 0.0031/0.00033 = 9.39$$

Since α = 0.01, compare this value to a critical point equal to the 99th percentile of a Student's *t*-distribution with $(n–2) = 17$ degrees of freedom, that is, $t_{cp} = t_{.99,17} = 2.567$. Since the *t*-statistic is substantially larger than the critical point, conclude the upward trend is significant at the 1% α-level. ◄

Figure 17-3. Probability Plot of Chloride Regression Residuals

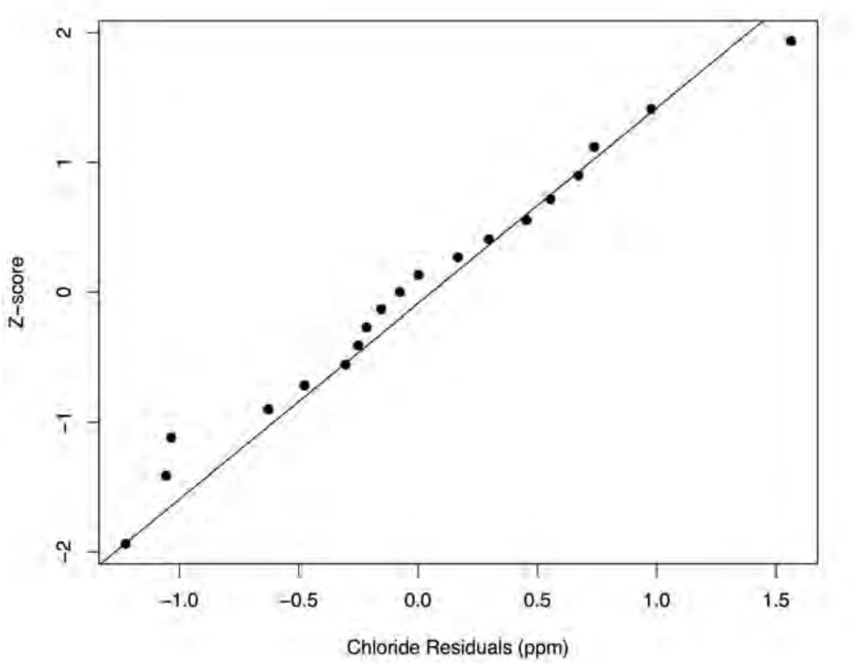


Figure 17-4. Scatter Plot of Chloride Residuals vs. Sampling Date

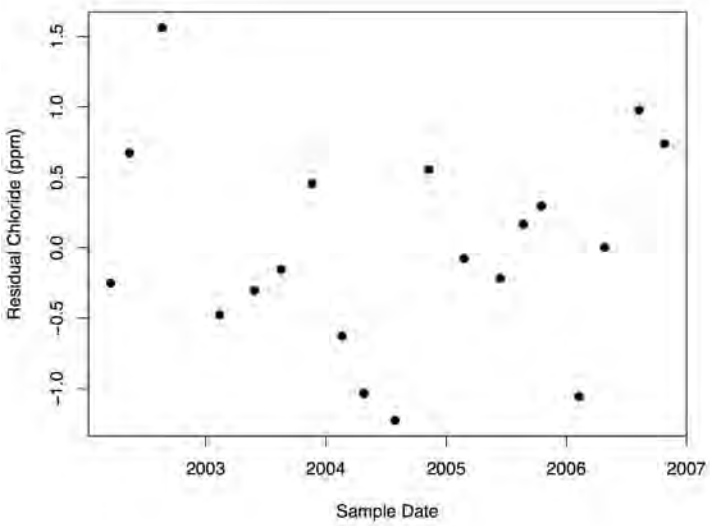
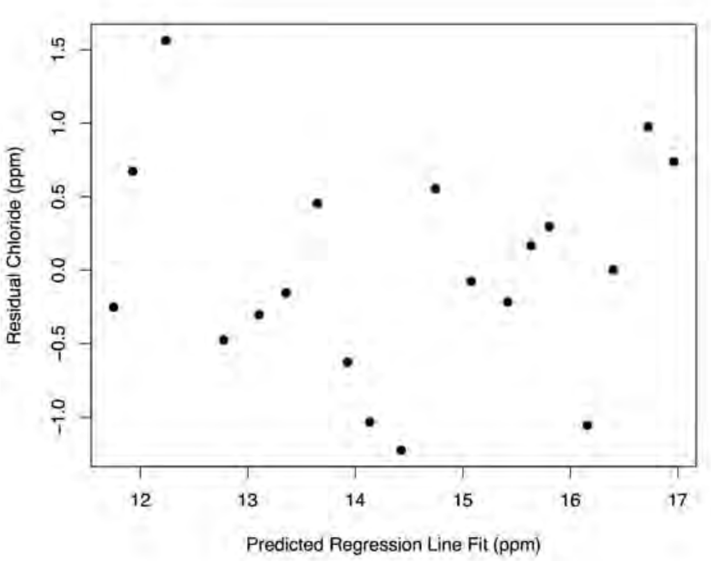


Figure 17-5. Scatter Plot of Chloride Residuals vs. Predicted Regression Fits



17.3.2 MANN-KENDALL TREND TEST

BACKGROUND AND PURPOSE

The Mann-Kendall test (Gilbert, 1987) is a non-parametric test for linear trend, based on the idea that a lack of trend should correspond to a time series plot fluctuating randomly about a constant mean level, with no visually apparent upward or downward pattern. If an *increasing* trend really exists, the sample taken first from any randomly selected pair of measurements should on average have a *lower* concentration than the measurement collected at a later point. The Mann-Kendall statistic is computed by examining all possible pairs of measurements in the data set and scoring each pair as follows. An earlier measurement less in magnitude than a later one is assigned a value of 1. If an earlier value is greater in magnitude than a later sample, the pair is tallied as –1; two identical measurement values are assigned 0.

After scoring each pair in this way and adding up the total to get the Mann-Kendall statistic (S), a positive value of S implies that a majority of the differences between earlier and later measurements are positive, suggestive of an upward trend over time. Likewise, a negative value for S implies that a majority of the differences between earlier and later values are negative, suggestive of a decreasing trend. A value near zero indicates a roughly equal number of positive and negative differences. This would be expected if the measurements were randomly fluctuating about a constant mean with no apparent trend.

To account for randomness and inherent variability in the sample, the Mann-Kendall test is based on the critical ranges of the statistic S likely to occur under stationary conditions. The larger the absolute

C. **Mann-Kendall:** Chapter 17 (pg 17-30): Statistical Analysis Of Groundwater Monitoring Data At RCRA Facilities - Unified Guidance, EPA 530/R-09-007, March 2009
    - **Method Summary** (pg 8-32)
    - **Procedure** (pg 17-32)
    - **Example** (pg 17-33)

Advantages/Disadvantages: Linear regression is a standard statistical method for identifying trends and other linear associations between pairs of random variables. However, it requires approximate normality of the trend residuals. Confidence bands around regression trends can be used in compliance/assessment and corrective action to determine compliance with fixed standards even when concentration levels are actively changing (*i.e.*, when a trend is apparent).

MANN-KENDALL TEST FOR TREND (SECTION 17.3.2)

Basic purpose: Method for detection monitoring and diagnostic tool. It is used to identify the presence of a significant (upward) trend at a compliance point or any trend in background data.

Hypothesis tested: H_0 — No discernible linear trend exists in the concentration data over time. H_A — A non-zero, (upward) linear component to the trend does exist.

Underlying assumptions: Since the Mann-Kendall trend test is a non-parametric method, the underlying data need not be normal or follow any particular distribution. No special adjustment for ties is needed.

When to use: Use a test for trend when 1) interwell tests are inappropriate so that intrawell tests are called for, and 2) a control chart or intrawell prediction limit cannot be used because of possible trends in intrawell background. A trend test can be particularly helpful at sites with recent or historical contamination where it is uncertain if intrawell background is already contaminated. An upward trend in these cases documents changing concentration levels more accurately than either a control chart or intrawell prediction limit, both of which assume a stationary background mean concentration.

Steps involved: 1) Sort the data values by time of sampling/collection; 2) consider all possible pairs of measurements from different sampling events; 3) score each pair depending on whether the later data point is higher or lower in concentration than the earlier one, and sum the scores to get Mann-Kendall statistic; 4) compare this statistic against an α-level critical point; and 5) if the statistic exceeds the critical point, conclude that a significant upward trend exists. If not, conclude there is insufficient evidence for identifying a significant, non-zero trend.

Advantages/Disadvantages: The Mann-Kendall test does not require any special treatment for non-detects, only that all non-detects can be set to a common value lower than any of the detects. The test is easy to compute and reasonably efficient for detecting (upward) trends. Exact critical points are provided in the Unified Guidance for $n \leq 20$; a normal approximation can be used for $n > 20$. 3) A version of the Mann-Kendall test (the seasonal Mann-Kendall, **Section 14.3.4**) can be used to test for trends in data that exhibit seasonality.

THEIL-SEN TREND LINE (SECTION 17.3.3)

Basic purpose: Method for detection monitoring. This is a non-parametric alternative to linear regression for estimating a linear trend.

Hypothesis tested: As presented in the Unified Guidance, the Theil-Sen trend line is not a formal hypothesis test but rather an estimation procedure. The algorithm can be modified to formally test whether the true slope is significantly different from zero, but this question will already be answered if used in conjunction with the Mann-Kendall procedure.

Once the standard deviation of S has been derived, the standardized Z-statistic for an increasing (or decreasing) trend is formed using the equation:

$$Z = \left(|S| - 1\right) \Big/ SD\left[S\right] \qquad [17.29]$$

Note that although the expected mean value of S is zero, applying the continuous normal to the discrete S distribution is an approximation. Therefore, a *continuity correction* is made to Z by first subtracting 1 from the absolute value of S. The final Z-statistic can then be compared to an α-level critical point taken from **Table 10-1** in **Appendix D** to complete the test.

PROCEDURE

Step 1. Order the data set by sampling event or time of collection, x_1, x_2, to x_n. Then consider all possible differences between distinct pairs of measurements, $(x_j - x_i)$ for $j > i$. For each pair, compute the *sign* of the difference, defined by:

$$\operatorname{sgn}\left(x_j - x_i\right) = \begin{cases} 1 & \text{if } \left(x_j - x_i\right) > 0 \\ 0 & \text{if } \left(x_j - x_i\right) = 0 \\ -1 & \text{if } \left(x_j - x_i\right) < 0 \end{cases} \qquad [17.30]$$

Pairs of tied values including non-detects, will receive scores of zero using equation [17.30].

Step 2. Compute the Mann-Kendall statistic S using equation [17.31]:

$$S = \sum_{i=1}^{n} \sum_{j=i+1}^{n} \operatorname{sgn}\left(x_j - x_i\right) \qquad [17.31]$$

In equation [17.31] the summation starts with a comparison of the very first sampling event against each of the subsequent measurements. Then the second event is compared with each of the samples taken after it (*i.e.*, the third, fourth, fifth, *etc.*). Following this pattern is probably the most convenient way to ensure that all distinct pairs are tallied in forming S. For a sample of size n, there will be $n \cdot (n-1)/2$ distinct pairs.

Step 3. If $n \le 10$, and given the level of significance (α), determine the critical point s_{cp} from **Table 17-5 of Appendix D.** If $S > 0$ and $|S| > s_{cp}$, conclude there is statistically significant evidence of an increasing trend at the α significance level. If $S < 0$ and $|S| > s_{cp}$, conclude there is statistically significant evidence of a decreasing trend. If $|S| \le s_{cp}$, conclude there is insufficient evidence to identify a significant trend.

Step 4. If $n > 10$, determine the number of groups of ties (g) and the number of tied values in each group of ties (t_j). Then use equation [17.27] to compute the standard deviation of S and equation [17.29] in turn to compute the standardized Z-statistic.

Step 5. Given the significance level (α), determine the critical point z_{cp} from the standard normal distribution in **Table 10-1** in **Appendix D**. Compare Z against this critical point. If $Z > z_{cp}$, conclude there is statistically significant evidence at the α-level of an increasing trend. If $Z < -z_{cp}$, conclude there is statistically significant evidence of a decreasing trend. If neither exists, conclude that the sample evidence is insufficient to identify a trend.

►EXAMPLE 17-6

Test for a significant upward trend using the Mann-Kendall procedure in the following set of sulfate measurements (ppm) collected over several years.

Sample No.	**Sampling Date (yr.mon)**	**Sulfate Conc. (ppm)**	**Sample No.**	**Sampling Date (yr.mon)**	**Sulfate Conc. (ppm)**
1	89.6	480	13	93.1	590
2	89.8	450	14	93.6	550
3	90.1	490	15	94.1	600
4	90.3	520	16	94.6	700
5	90.6	485	17	95.1	570
6	90.8	510	18	95.6	610
7	91.1	510	19	95.8	650
8	91.3	530	20	96.1	620
9	91.6	510	21	96.3	830
10	91.8	560	22	96.6	720
11	92.1	560	23	96.8	590
12	92.6	540			

SOLUTION

Step 1. Construct a time series plot of the sulfate observations to check for a possible trend as in **Figure 17-6**. A clearly rising concentration pattern is seen, although the variability in the measurements appears greater toward the end of the sampling record than at the beginning.

Step 2. Compute the difference between each distinct pair of measurements and determine the sign of the difference, using equation [17.30]. Then sum up the signs with equation [17.31]. Note that to make sure all the distinct pairs have been summed, begin with the first listed observation and compare it to each of values below it. Then take the second listed value and compare it to each of the remaining ones below it, *etc*. The Mann-Kendall statistic becomes:

$$S = \operatorname{sgn}(450-480) + \operatorname{sgn}(490-480) + \ldots + \operatorname{sgn}(590-720) = 194$$

Step 3. Since the sample size $n = 23 > 10$, form the normal approximation to the Mann-Kendall statistic. Because there are some ties in the data, use equation [17.27] to compute the approximate standard deviation. Among the sulfate measurements, there are three groups of ties with 3, 2, and 2 tied values in each set respectively (at values 510, 560, and 590). The adjusted standard deviation is then:

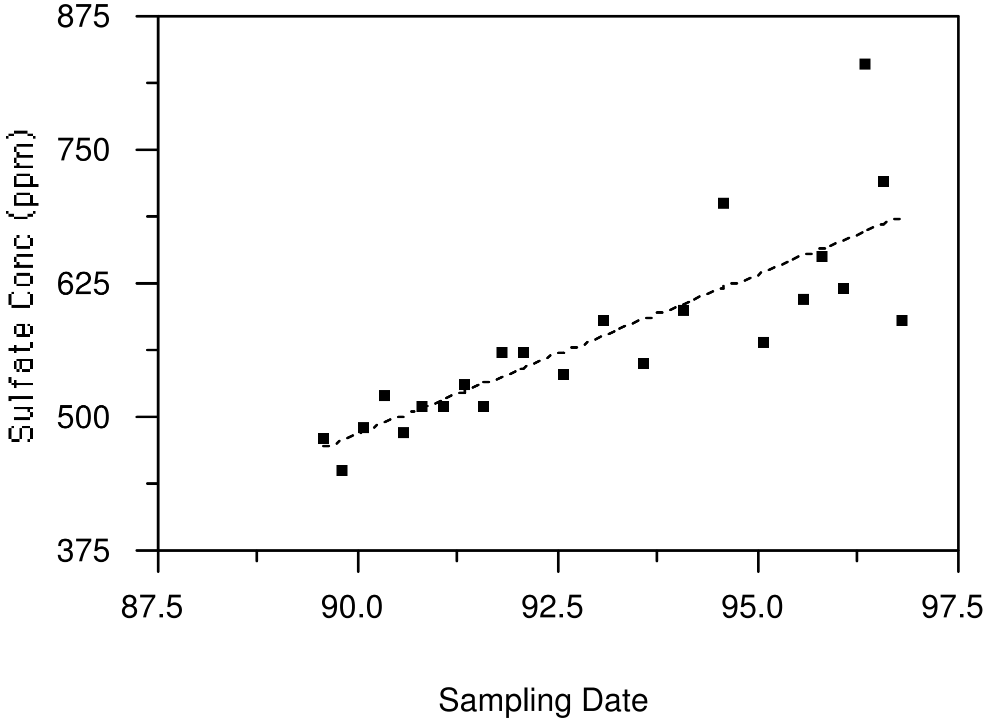
$$SD[S] = \sqrt{\frac{1}{18}\cdot\left[23\cdot(23-1)(2\cdot 23+5) - \{3\cdot(3-1)(2\cdot 3+5) + \ldots + 2\cdot(2-1)(2\cdot 2+5)\}\right]} = 37.79$$

Finally, using equation [17.29], the normalized Mann-Kendall statistic is:

$$Z = (|194| - 1)/37.79 = 5.11$$

Step 4. The Z statistic can be compared to a critical point from the standard normal distribution in **Table 10-1** in **Appendix D**. As large as it is, the test statistic is bigger than the critical point for any usual significance level, suggesting that the trend appears to be real and not just a chance artifact of the sample. ◀

Figure 17-6. Time Series Plot of Sulfate Concentrations (ppm)



17.3.3 THEIL-SEN TREND LINE

BACKGROUND AND PURPOSE

The Mann-Kendall procedure is a non-parametric test for a significant slope in a linear regression of the concentration values plotted against time of sampling. But the Mann-Kendall statistic S does not indicate the *magnitude* of the slope or estimate the trend line itself even when a trend is present. This is slightly different from parametric linear regression, where a test for a significant slope follows naturally from the estimate of the trend line. Even a relatively modest slope can be statistically distinguished from zero with a large enough sample. It is best to first identify whether or not a trend exists, and then determine how steeply the concentration levels are increasing over time for a significant trend. The *Theil-Sen trend line* (Helsel, 2005) is a non-parametric alternative to linear regression which can be used in conjunction with the Mann-Kendall test.

The Theil-Sen method handles non-detects in almost exactly the same manner as the Mann-Kendall test. It assigns each non-detect a common value less than any other detected measurement (*e.g.*,

D. Seasonal Mann-Kendall: Chapter 14 (pg 14-37): Statistical Analysis Of Groundwater Monitoring Data At RCRA Facilities - Unified Guidance, EPA 530/R-09-007, March 2009

- **Method Summary** (pg 8-21)
- **Procedure** (pg 14-37)
- **Example** (pg 14-38)

Steps involved: 1) Using a time series plot of the data series, separate the values into common sampling events for each year (*e.g.*, all January measurements, all third quarter values, *etc.*); 2) compute the average of each subgroup and the overall mean of the dataset; and 3) adjust the data by removing the seasonal pattern.

Advantages/Disadvantages: The seasonal correction described in the Unified Guidance is relatively simple to perform and offers a more accurate standard deviation estimates compared to using unadjusted data. Removal of the seasonal component may reveal other previously unnoticed features of the data, such as a slow-moving trend. A fairly long data series is required to confirm the presence of a recurring seasonal cycle. Furthermore, many complex time-related patterns cannot be handled by this simple correction. In such cases, consultation with a professional statistician may be necessary.

SEASONAL MANN-KENDALL TEST FOR TREND (SECTION 14.3.4)

Basic purpose: Method for detection monitoring. It is used to identify the presence of a significant (upward) trend at a compliance point when data also exhibit seasonal fluctuations. It may also be used in compliance/assessment and corrective action monitoring to track upward or downward trends.

Hypothesis tested: H_0 — No discernible linear trend exists in the concentration data over time. H_A — A non-zero, (upward) linear component to the trend does exist.

Underlying assumptions: Since the seasonal Mann-Kendall trend test is a non-parametric method, the underlying data need not be normal or follow a particular distribution. No special adjustment for ties is needed.

When to use: Use when 1) upgradient-to-downgradient comparisons are inappropriate so that intrawell tests are called for; 2) a control chart or intrawell prediction limit cannot be used because of possible trends in the intrawell background, and 3) the data also exhibit seasonality. A trend test can be particularly helpful at sites with recent or historical contamination where it is uncertain if background is already contaminated. An upward trend in these cases will document the changing concentration levels more accurately than either a control chart or intrawell prediction limit, both of which assume a stationary background mean concentration.

Steps involved: 1) Divide the data into separate groups representing common sampling events from each year; 2) compute the Mann-Kendall test statistic (S) and its standard deviation ($SD[S]$) on each group; 3) sum the separate Mann-Kendall statistics into an overall test statistic; 4) compare this statistic against an α-level critical point; and 5) if the statistic exceeds the critical point, conclude that a significant upward trend exists. If not, conclude there is insufficient evidence for identifying a significant, non-zero trend.

Advantages/Disadvantages: 1) The seasonal Mann-Kendall test does not require any special treatment for non-detects, only that all non-detects be set to a common value lower than any of the detected values; and 2) the test is easy to compute and reasonably efficient for detecting (upward) trends in the presence of seasonality. Approximate critical points are derived from the standard normal distribution.

The overriding point is that data should be deseasonalized when a cyclical pattern might obscure the random deviations around an otherwise stable average concentration level, or to more clearly identify an existing trend. However, a linear trend is inherently indicative of a changing mean level. Such data should not be de-trended before it is determined what the trend likely represents, and whether or not it is itself *prima facie* evidence of possible groundwater contamination.

A similar trend both in direction and slope may be exhibited by background wells *and* compliance wells, perhaps suggestive of sitewide changes in natural groundwater conditions. Residuals from a one-way ANOVA for temporal effects (**Section 14.2.2**) can be used to simultaneously create adjusted values across the well network (**Section 14.3.3.2**). Linear trends are just as easily identified and adjusted in this way as are parallel seasonal fluctuations or other temporal effects.

14.3.4 IDENTIFYING LINEAR TRENDS AMIDST SEASONALITY: SEASONAL MANN-KENDALL TEST

BACKGROUND AND PURPOSE

Corrections for seasonality or other cyclical patterns over time in a single well are discussed in **Section 14.3.3.1**. These adjustments work best when the long-term mean at the well is stationary. In cases where a test for trend is desired and there are also seasonal fluctuations, **Chapter 17** tests may not be sensitive enough to detect a real trend due to the added seasonal variation.

One possible remedy is to use the seasonal correction in **Section 14.3.3.1** and illustrated in **Example 14-8**. The seasonal component of the trend is removed prior to conducting a formal trend test. A second option is the seasonal Mann-Kendall test (Gilbert, 1987).

The seasonal Mann-Kendall is a simple modification to the Mann-Kendall test for trend (**Section 17.3.2**) that accounts for apparent seasonal fluctuations. The basic idea is to divide a longer multi-year data series into subsets, each subset representing the measurements collected on a common sampling event (*e.g.*, all January events or all fourth quarter events). These subsets then represent different points along the regular seasonal cycle, some associated with peaks and others with troughs. The usual Mann-Kendall test is performed on each subset separately and a Mann-Kendall test statistic S_i formed for each. Then the separate S_i statistics are summed to get an overall Mann-Kendall statistic S.

Assuming that the same basic trend impacts each subset, the combined statistic S will be powerful enough to identify a trend despite the seasonal fluctuations.

REQUIREMENTS AND ASSUMPTIONS

The basic requirements of the Mann-Kendall trend test are discussed in **Section 17.3.2**. The only differences with the seasonal Mann-Kendall test are that 1) the sample should be a multi-year series with an observable seasonal pattern each year; 2) each ‘season’ or subset of the overall series should include at least three measurements in order to compute the Mann-Kendall statistic; and 3) a normal approximation to the overall Mann-Kendall test statistic must be tenable. This will generally be the case if the series has at least 10-12 measurements.

PROCEDURE

Step 1. Given a series of measurements from each of T sampling events on each of K years, label the observations as x_{ij}, for i = 1 to T, and j = 1 to K. Then x_{ij} represents the measurement from the ith sampling event during the jth year.

Step 2. For each distinct sampling event (i), form a seasonal subset by grouping together observations x_{i1}, x_{i2},...., x_{iK}. This results in T separate seasons.

Step 3. For each seasonal subset, use the procedure in **Section 17.3.2** to compute the Mann-Kendall statistic S_i and its standard deviation $SD[S_i]$. Form the overall seasonal Mann-Kendall statistic (S) and its standard deviation with the equations:

$$S = \sum_{i=1}^{T} S_i \qquad [14.24]$$

$$SD\left[S\right] = \sqrt{\sum_{i=1}^{T} SD^2\left[S_i\right]} \qquad [14.25]$$

Step 4. Compute the normal approximation to the seasonal Mann-Kendall statistic using the equation:

$$Z = \left(\left|S\right| - 1\right) \Big/ SD\left[S\right] \qquad [14.26]$$

Step 5. Given significance level, α, determine the critical point z_{cp} from the standard normal distribution in **Table 10-1** of **Appendix D**. Compare Z against this critical point. If $Z > z_{cp}$, conclude there is statistically significant evidence at the α-level of an increasing trend. If $Z < -z_{cp}$, conclude there is statistically significant evidence of a decreasing trend. If neither, conclude that the sample evidence is insufficient to identify a trend.

►EXAMPLE 14-10

The data set in **Example 14-8** replicated below indicated both clear seasonality and an apparent increasing trend. Use the seasonal Mann-Kendall procedure to test for a significant trend with $\alpha = 0.01$ significance.

	Analyte Concentrations				
	1983	1984	1985	S_i	$SD[S_i]$
January	1.99	2.01	2.15	3	1.915
February	2.10	2.10	2.17	2	1.633
March	2.12	2.17	2.27	3	1.915
April	2.12	2.13	2.23	3	1.915
May	2.11	2.13	2.24	3	1.915
June	2.15	2.18	2.26	3	1.915
July	2.19	2.25	2.31	3	1.915
August	2.18	2.24	2.32	3	1.915
September	2.16	2.22	2.28	3	1.915
October	2.08	2.13	2.22	3	1.915
November	2.05	2.08	2.19	3	1.915
December	2.08	2.16	2.22	3	1.915
				$S = 35$	$SD[S] = 6.558$

SOLUTION

Step 1. Form a seasonal subset for each month by grouping all the January measurements, all the February measurements, and so on, across the 3 years of sampling. This gives 12 seasonal subsets with $n = 3$ measurements per season. Note there are no tied values in any of the seasons except for February.

Step 2. Use equations [17.30] and [17.31] in **Section 17.3.2** to compute the Mann-Kendall statistic (S_i) for each subset. These values are listed in the table above. Also compute their sum to form the overall seasonal Mann-Kendall statistic, giving $S = 35$.

Step 3. Use equation [17.28] from **Section 17.3.2** for all months but February to compute the standard deviation of S_i. Since $n = 3$ for each of these subsets, this gives

$$SD\left[S_i\right] = \sqrt{\frac{1}{18}n(n-1)(2n+5)} = \sqrt{\frac{1}{18}3\cdot 2\cdot 11} = 1.915$$

For the month of February, one pair of tied values exists. Use equation [17.27] to compute the standard deviation for this subset:

$$SD\left[S_i\right] = \sqrt{\frac{1}{18}\left[n(n-1)(2n+5) - \sum_{j=1}^{g} t_j\left(t_j - 1\right)\left(2t_j + 5\right)\right]} = \sqrt{\frac{1}{18}\left[3\cdot 2\cdot 11 - 2\cdot 1\cdot 9\right]} = 1.633$$

List all the subset standard deviations in the table above. Then use equation [14.25] to compute the overall standard deviation:

$$SD\left[S\right] = \sqrt{\sum_{i=1}^{12} SD^2\left[S_i\right]} = \sqrt{11\cdot(1.915)^2 + (1.633)^2} = 6.558$$

Step 4. Compute a normal approximation to S with equation [17.29]:

$$Z = (35 - 1)/6.558 = 5.18$$

Step 5. Compare Z against the 1% critical point from the standard normal distribution in **Table 10-1** of **Appendix D**, $z_{.01} = 2.33$. Since Z is clearly larger than $z_{.01}$, the increasing trend evidence in **Figure 14-15** is highly significant. ◄

E. **Mann-Whitney U:** Appendix C: New Jersey Administrative Code 7:26E – Technical Requirements for Site Remediation, NJDEP, April 2010

APPENDIX C - Mann-Whitney U-Test*

The random variable to be analyzed shall be the concentrations of the individual contaminants of concern in each individual monitoring well. The statistic to be evaluated is the Mann-Whitney "U". The test shall be a Mann-Whitney U-test with the size of the test equal to 0.1. The hypotheses (H) to be tested are:

H_0: $\hat{\theta}_1 \leq \hat{\theta}_2$ (null hypothesis)
H_1: $\hat{\theta}_1 > \hat{\theta}_2$ (alternate hypothesis)

where $\hat{\theta}_2$ represents the stochastic size of the population of each individual contaminant during the most recent 12 month period of sampling and $\hat{\theta}_1$ represents the stochastic size of the population of each individual contaminant during the previous 12 month period. The test is applied to each contaminant in each individual monitoring well. In other words, if benzene and trichloroethene are the contaminants of concern, and there are four monitoring wells involved in the sampling program, then a total of eight Mann-Whitney tests are to be performed (benzene in each of the four monitoring wells and trichloroethene in each of the four monitoring wells).

The U statistic shall be evaluated as follows:

1. The test is applied to eight consecutive quarters of analytical data for each individual contaminant in each individual monitoring well.

2. For each quarter of data, annotate the concentration of the specific contaminant in the specific monitoring well with either a "b" for the most recent four quarters or an "a" for the four quarters from the previous 12 month period.

3. Vertically arrange the eight contaminant concentrations, with notations, in order of increasing value: the lowest value on the top, and the greatest value on the bottom.

4. For each individual "a" concentration, count the number of "b" concentrations that occur below that "a" concentration in the column.

5. Add the four values (zero or some positive number) obtained for Step 4 to calculate the "U" value.

6. All values of non-detectable (ND) or values detected below the limits of quantitation are to be ranked as "zero." It is required that appropriate detection levels/quantitation limits be achieved.

7. If two or more concentrations are identical, then two vertical columns are necessary. In the first column, rank tying "b" concentrations first, and in the second column rank tying "a" concentrations first. Calculate an interim "U" for each column ("Ua" and "Ub"). The average of these interim values is the actual "U". This is shown in Example 2, below.

The hypotheses shall be tested as follows:

1. If "U" is three or less, the null hypothesis is rejected, and it is concluded, with at least 90 percent confidence, that the concentration for the individual contaminant has decreased with time at the specific monitoring well.

2. If "U" is greater than three, the null hypothesis is accepted, and it cannot be concluded, with 90 percent or greater confidence, that the concentration for the individual contaminant has decreased with time at the specific monitoring well.

* Adapted from Mann, H. B. and Whitney, D.R., 1947, On a test of whether one of two random variables is stochastically larger than the other., Ann. Math. Statist., 18, pp. 52-54.

EXAMPLE 1: All data points are numerically unique

1. Individual Contaminant: TCE
   Individual Monitoring Well: MW-1

2. Monitoring quarters:

	$\hat{\theta}_1$ [Year 1]				$\hat{\theta}_2$ [Year 2]			
Sampling Round:	1	2	3	4	5	6	7	8
Sampling Result: (ppb) (concentration)	506a	1021a	612a	265a	543b	261b	77b	379b

3. 77b
   261b
   265a
   379b
   506a
   543b
   612a
   1021a

4. 265a=2, 506a=1, 612a=0, 1021a=0

5. 2+1+0+0=3, U=3

Conclusion: “U” is three, therefore the null hypothesis is rejected, and it is concluded, with 90 percent or greater confidence, that the first sampling set ($\hat{\theta}_1$) is greater than the second sampling set ($\hat{\theta}_2$), and therefore that the concentration for the specific contaminant in the specific monitoring well has decreased over the period of the ground water monitoring program.

EXAMPLE 2: two or more numerically identical data points

1. Individual Contaminant: TCE
   Individual Monitoring Well: MW-1

2. Monitoring quarters:

	$\hat{\theta}_1$ [Year 1]				$\hat{\theta}_2$ [Year 2]			
Sampling Round:	1	2	3	4	5	6	7	8
Sampling Result: (ppb) (concentration)	28a	NDa	61a	NDa	63b	NDb	77b	79b

3.

a]	b]
NDb	NDa
NDa	NDa
NDa	NDb
28a	28a
61a	61a
63b	63b
77b	77b
79b	79b

4. a] NDa=3, NDa=3, 28a=3, 61a=3
   b] NDa=4, NDa=4, 28a=3, 61a=3

5. a] 3+3+3+3=12 Ua=12 ==> U=13.0
   b] 4+4+3+3=14 Ub=14

Conclusion: "U" is thirteen, therefore we accept the null hypothesis, and we cannot conclude, with 90 percent or greater confidence, that the first sampling set ($\hat{\theta}_1$) is greater than the second sampling set ($\hat{\theta}_2$), and we cannot conclude that the concentration for that specific contaminant has decreased with time.

Appendix F

Selected Reference Summaries

Use of Monitored Natural Attenuation at Superfund RCRA Corrective Actions, and Underground Storage Tank Sites

USEPA Office of Solid Waste and Emergency Response
April 1999
http://www.epa.gov/oust/directiv/d9200417.pdf

Synopsis:

The purpose of the document is to clarify EPA's policy regarding the use of monitored natural attenuation (MNA) for the cleanup of contaminated soil and groundwater at sites in EPA programs. MNA of contaminants related to petroleum, chlorinated solvents, inorganics including radionuclides are addressed. The document deals mainly with the policy surrounding MNA as a site remedy and provides little technical guidance on the use of MNA. EPA expects that source control and long term performance monitoring will be fundamental components of any MNA remedy. The guidance discusses the appropriateness of MNA as a remedy in an effort to ensure that MNA is selected and implemented properly. Identifying a reasonable timeframe for remediation is outlined in relation to deciding where MNA is an appropriate remedy. The use of performance monitoring as a tool to evaluate the MNA remedy is outlined. The guidance identifies the need for contingency remedies.

Concepts Presented & Relevance to Natural Attenuation:

EPA stresses that MNA should not be considered the default or presumptive remedy and that MNA is not applicable to every site. Furthermore, MNA does not imply that active remediation is infeasible or technically implacable. The guidance notes that MNA is most appropriate when used in conjunction with other remedial measures (e.g., source control, ground water extraction) or as a follow up to active remediation. Reasonable remedial time frames should be considered in determining where MNA is an appropriate remedy. A comparison of restoration alternatives from aggressive to passive will provide information on appropriate time periods needed to clean up ground water.

Methods & Techniques:

Adequate site characterization data and analysis is necessary to support MNA as a remedy. In addition, a detailed conceptual site model is necessary to evaluate MNA as a potential remedy for a site. EPA stresses that source control is necessary at all sites, including sites with MNA as a remedy. When MNA is the chosen remedy performance monitoring is a necessary element of the remedy. The monitoring should at a minimum determine the rate of attenuation and how the rate is changing with time. The monitoring should continue until the remedial objectives are achieved and maybe beyond to ensure stability of the ground water contaminants. The guidance stresses that a contingency remedy shall be included as a backup to MNA and can be implemented if the chosen remedy fails to perform as anticipated. One or more triggers should be established that can signal unacceptable performance of the remedy and the need to implement the contingency remedy.

Data/Information that can be used in MNA Evaluations:

The guidance outlines lines of evidence that should be evaluated in order to determine whether MNA is a viable remedy. The following lines of evidence were provided.

1. Historic ground water data demonstrates a clear and meaningful trend.
2. Hydrogeologic and geochemical data demonstrate natural attenuation.
3. Data from the field or microcosm that directly demonstrate natural attenuation.

Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water

USEPA
September 1998
http://www.epa.gov/superfund/health/conmedia/gwdocs/protocol.htm

Synopsis:

The EPA guidance provides for a systematic approach to determining if MNA is a suitable remedy for the chlorinated sites. The approach involves the initial MNA site screening using available data from the site and development of a conceptual site model. If this initial review identifies that MNA could be a suitable remedy, the next step would be to conduct a site characterization to fill data gaps and to refine the conceptual site model. The site characterization focuses on ground water monitoring and aquifer testing. Once the characterization is complete, the conceptual site model is further refined and modeling of the plume can be conducted. The document references and includes excerpts from the EPA publication "Use of Monitored Natural Attenuation at Superfund RCRA Corrective Actions, and Underground Storage Tank Sites". The document stresses the need to treat or contain product, evaluate receptors and develop a long term monitoring plan.

Concepts Presented & Relevance to Natural Attenuation:

The document provides a good understanding of the degradation pathways for chlorinated solvents including a figure 2.2 on reductive dehalogenation. Table 2.3 provides a comprehensive list if analytical parameters that are necessary for the evaluation of biodegradation and the text provide details on each parameter. The document calls for quarterly monitoring for the first year followed by an appropriate sampling frequency that considers seasonal variations, flow direction and velocity.

Methods & Techniques:

The EPA document does not focus on statistical reductions in concentrations such as the current NJDEP guidance. EPA focuses on the development of the conceptual site model and its refinement by further investigation and data collection. The final step is to use a suitable fate and transport model to supplement the conceptual site model. EPA notes that the results of the modeling are only as accurate as the original data therefore a thorough site characterization is necessary.

Data/Information that can be used in MNA Evaluations:

EPA provides a through evaluation of the degradation mechanisms for chlorinated solvents. The ground water monitoring parameter list in Table 2.3 along with the text describing each of the parameters is a good summary of ground water data requirements. The guidance does call for treatment or containment of source areas.

EPA GROUNDWATER ISSUE: NATURAL ATTENUATION OF HEXAVALENT CHROMIUM IN GROUNDWATER AND SOILS

USEPA
EPA/540/5-94/505
October 1994
http://www.epa.gov/tio/tsp/download/natatt.pdf

Synopsis:

This document summarizes the geochemistry of chromium in soil and ground water, describes the potential for natural attenuation of hexavalent chromium in soil and ground water, and provides a means for determining the potential for natural attenuation. The document highlights the ability of natural ground water environments to reduce hexavalent chromium to less toxic and mobile forms, primarily through abiotic reduction pathways.

Concepts Presented & Relevance to Natural Attenuation:

The document provides a detailed description of the chemical processes associated with potential natural attenuation of hexavalent chromium. Evaluation of the appropriateness of natural attenuation is primarily accomplished through assessment of aquifer geochemistry, including soil mineral composition. For natural attenuation, it must be demonstrated that:

- There are natural reductants present within the aquifer,
- The amount of hexavalent chromium and other reactive constituents do not exceed the capacity of the aquifer to reduce them,
- The rate of hexavalent chromium reduction is greater than the rate of transport of the aqueous hexavalent chromium from the site,
- The chromium remains immobile,
- There is no net oxidation of trivalent chromium to hexavalent chromium (not common).

The document describes tests that are appropriate to evaluate these criteria.

Data/Information that can be used in MNA Evaluations:

This document is specific to natural attenuation of hexavalent chromium.

Monitored Natural Attenuation of MTBE as a Risk Management Option at Leaking Underground Storage Tank Sites

USEPA - John T. Wilson, Philip M. Kaiser and Cherri Adair
January 2005
EPA/6/6000/R/R-0-044/1/177990
http://www.epa.gov/nrmrl/pubs/600r04179/600r04179.pdf

Synopsis:

This report reviews the current state of knowledge on the transport and fate of Methyl Tertiary Butyl Ether (MTBE) in ground water, with emphasis on the natural processes that can be used to manage the risk associated with MTBE in ground water or that contribute to natural attenuation of MTBE as a remedy. It provides recommendations on the site characterization data that are necessary to manage risk or to evaluate MNA of MTBE, and it illustrates procedures that can be used to work up data to evaluate risk or assess MNA at a specific site with respect to MTBE.

Concepts Presented & Relevance to Natural Attenuation:

The primary degradation product of MTBE is TBA. At many sites, the onset of anaerobic biodegradation of MTBE can be recognized by a change in the ratio of TBA to MTBE. However, because TBA is also added to gasoline, TBA accumulations does not provide convening evidence of biodegradation of MTBE.

Stable carbon isotopes (^{12}C and ^{13}C) in MTBE are fractionated when MTBE is biologically degraded. As biodegradation proceeds, the MTBE that has not been degraded has a progressively greater proportion of the heavy carbon isotope ^{13}C, compared to the more common isotope ^{12}C. Stable isotope analyses make it possible to accurately measure the change in the ratio of the isotopes (^{12}C and ^{13}C) in MTBE in water at low concentrations. The fractionation of the MTBE that has not degraded becomes the equivalent to a "metabolic product" that is used to document biodegradation.

The isotope ratio mass spectrometer does not measure the ratio of the stable carbon isotopes directly to each other. Rather, it measures the deviation of the ratio in the sample from the ratio in a standard substance that is used to calibrate the instrument. The substance used as the international standard for stable carbon isotopes has a ratio of ^{13}C to ^{12}C of 0.0112372. The conventional notation for the ratio of ^{13}C to ^{12}C in a sample ($\delta^{13}C$) reports the ratio in terms of its deviation from the ratio in the standard. The units for $\delta^{13}C$ are parts per thousand, often represented as ‰ , or per mil, or per mill (see below):

$$\delta^{13}C_{\text{(Sample)}}\ \text{(per mil)} = \{ [(^{12}C/13C)_{\text{Sample}} - (^{12}C/^{13}/C)_{\text{Standard}})] \div (^{12}C/^{13}/C)_{\text{Standard}} \} \times 1000$$

Available data shows that $\delta^{13}C$ values range from -28.4 per mil (least biodegraded) to 52.2 per mil (most biodegraded)

Monitored Natural Attenuation of Inorganic Contaminants in Ground Water, Volume 1, Technical Basis for Assessment

USEPA Office of Research and Development National Risk Management
Edited by: Robert G. Ford, Richard T. Wilkin, Robert W. Plus
October 2007
EPA/600/R-07/139
http://www.epa.gov/nrmrl/pubs/600R07139/600R07139.pdf

Synopsis:

The document addresses the technical basis and requirements for assessing the potential applicability of MNA as part of a ground-water remedy for plumes with non-radionuclide and/or radionuclide inorganic contaminants. Three topics have been addressed in separate sections: 1) the conceptual background for natural attenuation for inorganic contaminants, 2) the technical basis for attenuation of inorganic contaminants in ground water, and 3) approaches to site characterization to support evaluation of MNA.

Concepts Presented and Relevance to Natural Attenuation:

Detailed discussion is provided on the importance of acquiring site-specific data that define ground water hydrogeology and chemistry, the chemical and mineralogical characteristics of aquifer solids, and the aqueous and solid phase chemical speciation of contaminants within the ground water plume boundary and the relevance of each of these to natural attenuation of inorganic contaminants.

Emphasis is placed on the need to collect site-specific data supporting evaluation of the long-term stability of immobilized inorganic contaminants. Also included is discussion on the role of analytical models as one of the tools that may be employed during the site characterization process.

This document is limited to evaluations performed in porous-media settings.

Methods & Techniques:

A tiered analysis approach is presented to assist in organizing site characterization tasks in a manner designed to reduce uncertainty in remedy selection and to address four primary evaluations relevant to natural attenuation. These are summarized in Table 1.

Data/Information that can be used in MNA Evaluations:

Section III of this publication provides site characterization details to support MNA evaluations. These include geologic and hydrogeologic data acquisition; contaminant quantification, distribution and speciation; model representations to interpret contaminant sorption observations;
Characterization of redox conditions in the ground water system and their implications to natural remediation.

Table 1: Synopsis of site characterization objective to be addressed throughout the tiered analysis process and potential supporting data types and/or analysis approaches associated with each tier.

Tier		Potential Data Types and Analysis
I	Demonstrate active contaminant removal from ground water	• Ground water flow direction (calculation of hydraulic gradients); aquifer hydrostratigraphy • Contaminant concentrations in ground water and aquifer solids • General ground water chemistry data for preliminary evaluation of contaminant degradation
II	Determine mechanism and rate of attenuation	• Detailed characterization of system hydrology (spatial and temporal heterogeneity; flow model development) • Detailed characterization of ground water chemistry • Subsurface mineralogy and/or microbiology • Contaminant speciation (ground water & aquifer solids) • Evaluate reaction mechanism (site data, laboratory testing, develop chemical reaction model)
III	Determine system capacity and stability of attenuation	• Determine contaminant & dissolved reactant fluxes (concentration data & water flux determinations) • Determine mass of available solid phase reactant(s) • Laboratory testing of immobilized contaminant stability (ambient ground water; synthetic solutions) • Perform model analyses to characterize aquifer capacity and to test immobilized contaminant stability (hand calculations, chemical reaction models, reaction-transport models)
IV	Design performance monitoring program and identify alternative remedy	• Select monitoring locations and frequency consistent with site heterogeneity • Select monitoring parameters to assess consistency in hydrology, attenuation efficiency, and attenuation mechanism • Select monitored conditions that “trigger” re-evaluation of adequacy of monitoring program (frequency, locations, data types) • Select alternative remedy best suited for site-specific conditions

Guidance on Natural Attenuation for Petroleum Releases

Wisconsin Department of Natural Resources
March 2003
http://www.dnr.state.wi.us/Org/aw/rr/archives/pubs/RR614.pdf

Synopsis:

The guidance was developed by the Wisconsin Department of Natural Resources to address natural attenuation at petroleum releases. The document is broken into four sections, (1) the site investigation, (2) data analysis, (3) monitoring requirements and (4) site closure. The site investigation evaluates receptors, soil and ground water characterization and determining the plume behavior. Data analysis identifies three lines of evidence to evaluate natural attenuation as a remedy. The lines of evidence include (1) a decreasing trend in contaminants, (2) evaluation of geochemical conditions and (3) microbial studies. The monitoring section outlines monitoring of contaminants and geochemical parameters for eight quarters followed by yearly monitoring. The site closure section outlines closure of the site under the Wisconsin regulations.

Concepts Presented & Relevance to Natural Attenuation:

The document focuses on the development and refinement of the conceptual site model. The initial site model should identify the history and nature of the contamination, the factors affecting contaminant movement and receptor identification. The document identifies the need for source zone identification along with removal or treatment. The guidance outlines certain conditions where MNA should not to be used as a sole remedy for ground water contamination. These conditions include sites with an advancing ground water plume, sites with bedrock contamination, sites with contaminated receptors and sites with free product. The document also discusses restoring ground water in a reasonable time frame. Sites are considered to be remediated in a reasonable time frame if the following criteria are satisfied. The criteria include source zone action, demonstrated effectiveness of MNA, no receptor impacts and no land use changes during remediation.

Methods & Techniques:

The document identifies a two-step process for well installation as part of the evaluation of the ground water plume for the natural attenuation remedy. The process starts with temporary well installation to help in the evaluation of locations for the second step placement of permanent wells. At a minimum, the guidance calls for wells located along the center line of the plume. The monitoring section outlines monitoring of contaminants and geochemical parameters for eight quarters followed by yearly monitoring. Evaluation of plume behavior is achieved with four methods. First, is the field assessment of the plume margins, followed by graphical analysis, statistical tests and last is the evaluation in low permeability. From the data generated, the contaminant plume can be characterized as either receding, stable or advancing.

Data/Information that can be used in MNA Evaluations:

The document provides details on three lines of evidence. The primary line of evidence is to evaluate the degradation rate of contaminants and outlines five different methods for the evaluation. The methods include (1) batch flushing, (2) concentration versus time plots, (3) concentration versus distance plots, (4) concentration versus travel time plots and (5) use of the Mann-Kendall statistical analysis. Two methods are outlined to estimate contaminant decay rate in the source zone. The methods are mass flux and first order decay. The secondary line of evidence involves the evaluation of geochemical parameters. It consists of using the geochemical conditions within the aquifer to verify that natural attenuation is occurring. The third line of evidence is the use of microbial studies of which the document outlines five methods. The five methods are assay of microorganisms, using a conservative tracer, using fate and transport models, sampling for metabolites in ground water and soil testing over time. The appendices of the document provide information on the methods outlined in this section.

MONITORED NATURAL ATTENUATION OF GROUNDWATER CONTAMINATION AT BROWNFIELDS/VOLUNTARY CLEANUP PROGRAM SITES

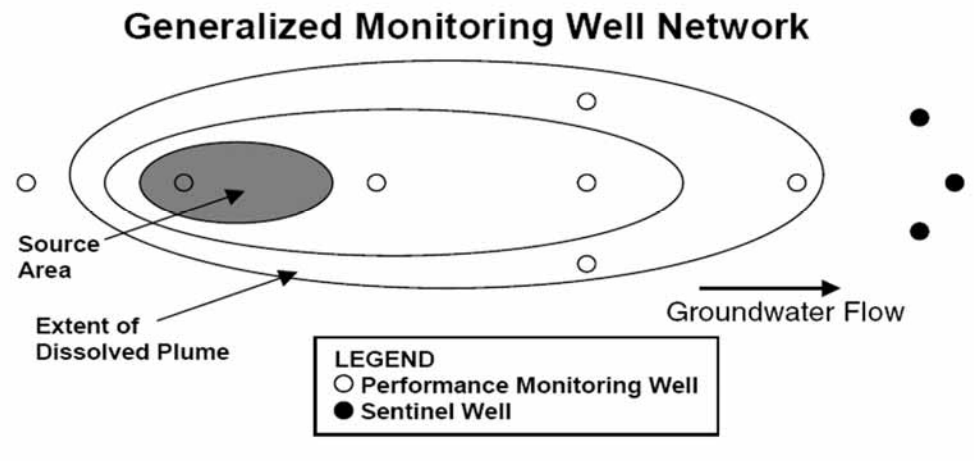
Missouri Department of Natural Resources, Hazardous Waste Program Fact Sheet
01/2007
http://www.dnr.mo.gov/pubs/pub2110.pdf

Synopsis:

The document is a fact sheet that provides information on MNA at Brownfields/Voluntary Cleanup sites in Missouri. The fact sheet stresses that MNA is not a “Do Nothing” remedy, outlines advantages and disadvantages of MNA and identifies the need for more comprehensive site characterization (relative to active remedies) to support MNA. The fact sheet requires Conceptual Site Model development, MNA applicability screening, performance monitoring, and contingency planning. Closure criteria are identified for plumes within a single property and plumes that extend off-site.

Concepts Presented and Relevance to Monitored Natural Attenuation:

Defines MNA as “reliance on natural processes to achieve ground water cleanup goals within a reasonable time frame, and before the contaminants present an unacceptable risk to human health and the environment, or exceed approved cleanup levels at established points of compliance.” There is no specific definition of reasonable time frame provided. For site characterization, the document defines minimum well network “for most sites” to include an upgradient well, at least one transect of wells screened within the longitudinal axis of the plume, one transect screened within the transverse axis of the plume, a source area well, and one or more sentinel wells; see below.



Data/Information that can be used in MNA Evaluations:

The document identifies indicator parameters for MNA sampling programs (in addition to primary and daughter product constituents): hydrogen, methane, ethane, ethene, oxygen, redox, pH, conductivity, organic carbon, iron, manganese, chloride, nitrate, sulfate, hydrogen sulfide, alkalinity, etc. Analytical models are also identified to develop preliminary estimates of contaminant migration and attenuation over time (BIOSCREEN, BIOCLOR).

Methods and Techniques

Two lines of evidence to evaluate MNA as a remedy: (1) decreasing trend in contaminant mass and concentration over time, and (2) existence of geochemical and hydrogeologic conditions favorable for MNA. The estimate of contaminant biodegradation/attenuation rate is a critical component of determining whether MNA will be an adequate remedy.

Performance monitoring must include the following:

- Demonstrate that natural attenuation is progressing as predicted;
- Verify that the plume is not expanding;
- Identify any toxic and/or mobile transformation products;
- Verify no unacceptable impact to downgradient receptors;
- Detect significant changes in relevant environmental conditions;
- Detect any new releases of contaminants;
- Demonstrate the efficacy of any institutional controls used; and
- Verify the attainment of cleanup goals.

Contingency planning includes specification of measures to be taken that will function as a back-up in the event that MNA fails to perform as anticipated, including intensification of monitoring activities, active enhance of MNA processes, use of engineered barriers, or employment of active remedial techniques. Contingency planning triggers include:

- Plume contaminant concentrations exhibit an unpredicted increasing trend;
- Plume contaminant concentrations do not decrease at a sufficiently rapid rate to meet cleanup goals within an acceptable time frame;
- Plume contaminants are detected in sentinel wells; and
- Changes in land and/or ground water use that affects the protectiveness of the MNA remedy.

Closure for on-site plumes: (1) ground water contaminant levels across the entire plume achieve “Tier 1” GWQS; (2) where levels exceed “Tier 1” GWQS, combination of institutional controls and “Tier 3” (risk-based) approach acceptable on a site-specific basis. Closure for on-site/off-site plumes as the same as above except that access agreements must be obtained for all off-site properties and affected properties must accept institutional controls if “Tier 1” GWQS are not achieved.

Examples of Approved Groundwater Corrective Measures for Solid Waste Management Facilities

North Carolina Department of Environment and Natural Resources
Division of Waste Management Solid Waste Section
June 2008
http://portal.ncdenr.org/c/document_library/get_file?uuid=5bd5c76f-7648-4ab1-b8d7-118476f38181&groupId=38361

Synopsis:

Examples of ground water remedial alternatives are presented including MNA. The MNA section of the document discusses conditions where MNA cannot be used as a sole groundwater remedy. The document provides requirements for MNA monitoring well networks and sampling parameters and provides for the evaluation of MNA effectiveness as well as contingency planning. North Carolina recommends EPA's guidance on MNA.

Concepts Presented and Relevance to Monitored Natural Attenuation:

Conditions where MNA cannot be used as a sole ground water remedy include:

- Capacity of the system is unable to control migration of contaminants,
- Contaminated media difficult to assess,
- Contaminant concentrations exceed ground water standards beyond point of compliance,
- Points of exposure other than property boundary are impacted,
- Mobile free product is present and no remedial method to address free product removal has been proposed,
- Exposure pathways exist (such as soil leachate to ground water, ground water to indoor air inhalation) and no active remediation method has been proposed to eliminate them,
- Contaminants do not readily biodegrade,
- Fractured bedrock contamination,
- Contamination has impacted receptors or creates imminent threat to receptors,
- Source water protection areas,
- Well head protection areas.

Baseline sampling is conducted on a semiannual basis for at least two calendar years. The monitor well network consists of compliance wells, performance wells and sentinel wells. Sampling parameters required for baseline sampling: Dissolved Oxygen, Nitrate, Iron, Sulfate, Sulfide, Methane, Ethene, Ethane, ORP,TOC/ BOD/COD, CO2 , Alkalinity, Chloride, Hydrogen, Volatile Fatty Acids, pH, Temperature, Conductivity, Turbidity. The parameters and sampling frequency may be reevaluated after the baseline sampling events. Any changes to the list need to be approved by the State. In addition to the baseline sampling requirements, North Carolina requires performing an EPA approved MNA screening model with ability to measure mass flux during each semiannual baseline event.
The document outlines MNA effectiveness evaluation that includes the requirement to demonstrate that reduction of contaminant concentrations is caused by chemical or biological attenuation and that sampling results show the plume has stabilized horizontally and vertically and is not migrating. In addition, there is a requirement to show a statistical reduction in the contaminant concentrations along specific flow paths and determine plume stability (chemical, biological, and physical) in evaluating trends along specific flow lines within the plume and along the plume boundary.

North Carolina has specific submittal requirements. The MNA effectiveness evaluation report must be submitted at least once per five calendar years. In the five calendar years, ten MNA sampling events should have been conducted. The submission requirement coincides with the minimum number of independent sampling data points required for most statistical analyses. After the baseline sampling events have been completed, an EPA approved MNA screening model is required at least annually to simulate the ground water remediation and to determine the mass flux and mass balance.

An approved MNA program needs to include a contingency plan that specifies triggering events and responses to those triggering events. The document emphasizes that uncertainty associated with estimated rates of attenuation over extended periods of time is a major consideration with MNA.

PADEP Fate and Transport Analysis Tools

Pennsylvania Department of Environment Protection

http://www.portal.state.pa.us/portal/server.pt?open=514&objID=552019&mode=2

Synopsis:

Pennsylvania DEP has developed a Technical Guidance Manual to assist responsible parties in satisfying their site remediation requirements (Act 2 and the regulations, Chapter 250). The manual provides suggestions and examples of how to best approach site characterization and remediation. The manual is divided into five sections: Section I provides an overview for determining which standard or which other statutes may be applicable to your site. Section II outlines the procedures for meeting the requirements of each standard. Section III discusses the appropriate interfaces with other applicable statutes. Section IV provides general technical guidance's augmenting the information in Section II and hyperlinks to other helpful documents are listed in Section V.

The Fate and Transport Analysis Tools are presented in Section IV to help one predict the concentrations of contaminants at one or more locations in the future, assess potential remediation alternatives, evaluate natural attenuation remedies and associated monitoring requirements, assure continued attainment of the relevant standard, estimate ground water chemical flux used in mass balance calculations for attainment of surface water standards and assess post-remediation care requirements and termination.

Concepts Presented & Relevance to Natural Attenuation:

When the site characterization is completed and the conceptual model has been developed, selection of an appropriate computer code can be made. Pennsylvania DEP has prepared three spreadsheets that can be used in the performance of a fate and transport analysis. They are QUICK_DOMENICO.XLS, FASTBACK.XLS and SWLOAD.XLS.

These may be used in the development of the MNA plan.

Methods and Techniques:

QUICK_DOMENICO.XLS calculates the concentration anywhere in the plume at any time. The Domenico equation results are about one to three orders of magnitude higher than those produced by other models such as AT123D and MODFLOW/MT3D. Therefore, these are very conservative results.

The Domenico equation has some drawback because it under estimates contaminant mobility unless the equation is run until the peak concentration is observed. This works as long as biodegradation is not simulated. Although as travel times increase, so does biodegradation. Exaggerated travel times produce inflated amounts of biodegradation and as such the lowest contaminant concentrations. This makes the Domenico equation the least conservative model.

FASTBACK.XLS calculates the steady-state source concentration given the receptor concentration and location. The Fatback4 spreadsheet was frequently misused to generate source concentrations as a substitute for proper characterization of the source area. To encourage proper site characterization of the source areas, the PA DEP has discontinued support for the Fatback4 spreadsheet and removed the link from their web site.

SWLOAD.XLS uses a rearrangement of the Domenico equation to calculate the concentration at different points in the cross-section of the plume at any distance from the source at any time. These concentrations are added and multiplied by the GW flux and used to estimate the mass loading of a particular contaminant from the diffuse GW flow to a surface water body.

Technical Guide for PENTOX describes the technical methods contained in PENTOXSD for performing waste-load allocation analyses and for determining recommended single discharge National Pollutant Discharge Elimination System effluent limits. It contains a listing of the current input data (both required and optional) and describes how these data are used. It contains discussions of important technical considerations that are pertinent to the determination of effluent limits.

Buffer1 is a spreadsheet that can be used to estimate the potential contaminant concentration entering ground water resulting from migration of a contaminant in vadose soil of a given thickness and with a given contaminant concentration.

Buscheck Alcantar is a spreadsheet that calculates a lambda value for the centerline of a plume with a continuous source at steady-state conditions. This model has a help document coming soon.

Data/Information that can be used in MNA Evaluations:

This reference is a list of tools used in complying with PA DEP regulation. This reference does not readily make a link from the Fate and Transport models to MNA. The models may be used to assist in predictions for a MNA program. Section IV of these PA DEP regulations further details the use of such models and cautions the user of the importance of site-specific parameters for input values. In addition, the PA DEP requires that the models be “audited” to compare the actual data collected to what was predicted. They also list the general reporting format when a computer model is used.

This part of the guidance then goes into the use of statistical methods to determine compliance and cleanup. http://www.elibrary.dep.state.pa.us/dsweb/Get/Document-66832/253-0300-00%20Section%20IV.pdf

Guidance for GW Monitoring for Demonstrating Compliance with the Connecticut Remediation Standard Regulations

Connecticut DEP BWM Remediation Division

3/17/06

http://www.ct.gov/dep/lib/dep/site_clean_up/guidance/GWM_Guidance_for_Demonstrating_Compliance_with_CT_RSR.pdf

Synopsis:

This guidance document provides a summary and commentary of Connecticut's (CT) DEP ground water monitoring requirements in order to demonstrate compliance during remediation, not for site investigations. The actual requirements are found in the Remediation Standard Regulations (RSRs) Section 22a-133k-3. The guidance follows the same numbering of sections and subsections as the RSRs. This guidance document also includes the CT DEP's expectations and rational in circumstances where ground water monitoring beyond the minimum requirements would be warranted.

Concepts Presented & Relevance to Natural Attenuation:

CT has two types of remediation ground water monitoring requirements: Compliance Monitoring and Post-Remediation Monitoring. Compliance monitoring is required after a plume has been documented. Post-remediation monitoring only applies where remediation has been performed. This includes soil remediation and ground water remediation, including, but not limited to natural remediation.

The Compliance Monitoring section includes a table that lists the regulation citation, the duration of sampling i.e., 4 consecutive quarters, 12 consecutive months, etc. and the sampling objective.

The Post-remediation Monitoring section includes the duration of monitoring required which is dictated by the water usage of the aquifer/area. It does not state the frequency of sampling, only the length of time, but it does recognize that quarterly is nearly always acceptable.

They have designated drinking water areas where the remediation standard is background (classified as GA) and non-drinking water areas (classified as GB) where the Ground Water Protection Criteria (GWPC) are the remediation standards.

In GA areas, the GWPC may be acceptable as opposed to background, if there is a steady state or diminishing plume. Also, if it is determined to be technically impracticable to remediate the plume to background, then the GWPC may be used.

A surface water section is included if a plume is determined to be discharging to a surface water body, including wetlands, intermittent streams, headwaters and tidal flats where more stringent SW protection criteria exists. In addition, there is a volatilization criteria section that is intended to measure vertically beneath the building. Not much further commentary was available about the volatilization criteria as complexities associated with interpretation and application had not been identified at the time of writing. (3/06).

The applicability of the GWPC section included a Q & A portion that included natural attenuation as a remedial strategy.

In addition, there was a section concerning pollutants not included in their GWPC. Guidance was given on how to calculate a criterion and request approval of it from the CT DEP. Again a Q & A section was included.

Data/Information that can be used in MNA Evaluations:

The post-remediation requirements apply to MNA, but do not directly speak to the requirements for MNA. A document geared directly to MNA monitoring requirements would be a useful addition to this document. The Q & A sections of this document are especially helpful. In addition, following the regulations numbering system in the guidance document was helpful to the reader.

BIOCHLOR Chlorinated Solvent Plume Database Report

Air Force Center for Environmental Excellence
June 2000
http://www.afcee.af.mil/shared/media/document/AFD-070926-071.pdf

Synopsis:

Numerous free public domain ground water, vadose zone and remediation technology-specific models and tools have been developed by the Air Force Center for Environmental Excellence (AFCEE). Two that are widely used are BIOSCREEN and BIOCHLOR. Other tools were also listed and generally described.

Concepts Presented and Relevance to Natural Attenuation:

BIOCHLOR is a screening model that simulates remediation by natural attenuation of dissolved solvents at chlorinated solvent release sites. BIOCHLOR includes three different model types:

- Solute transport without decay,
- Solute transport with biotransformation modeled as a sequential first-order decay process and
- Solute transport with biotransformation modeled as a sequential first-order decay process with two different reaction zones (i.e., each zone has a different set of rate coefficient values).

The software, programmed in the Microsoft Excel spreadsheet environment and based on the Domenico analytical solute transport model, has the ability to simulate one-dimensional advection, three-dimensional dispersion, linear adsorption, and biotransformation via reductive dechlorination (the dominant biotransformation process at most chlorinated solvent sites). Reductive dechlorination is assumed to occur under anaerobic conditions and dissolved solvent degradation is assumed to follow a sequential first-order decay process.

BIOCHLOR is a database of chlorinated solvent plume characteristics. Key characteristics of parent and daughter chlorinated contaminants were identified within the database. The relationship of parent and daughter chlorinated contaminants to the hydrogeologic and environmental variables were examined. The results help determine plume length, which may determine the likelihood of off-site migration. This tool can be very effective in determining the ability for natural attenuation.

BIOSCREEN is a screening model that simulates remediation through natural attenuation of dissolved hydrocarbons. This model uses Microsoft Excel and is based on the Domenico model. This model simulates advection, dispersion, adsorption, aerobic and anaerobic reactions. Three model types are used:

- solute transport without decay
- solute transport with biodegradation modeled as first-order decay
- solute transport with biodegradation modeled as an instantaneous biodegradation reaction with multiple soluble electron acceptors including DO, nitrate and sulfate

This model is widely used in the industry to answer two questions:

- How far will the dissolved contaminant plume extend if no engineered controls or further source zone reduction measures are implemented?
- How long will the plume persist until natural attenuation processes cause it to dissipate?

Other programs available for free downloads are:

- Bioslurping Cost Estimating Program (NFESC)
- Bioventing Design Tool (BVDT) = active remediation
- Cost Estimating Tool for Enhanced Anaerobic Bioremediation of Chlorinated Solvents = active remediation
- CSMoS Ground Water Modeling Software
- Geostatistical Long-Term Monitoring Optimization Algorithm

- Hydrogeologic Model Description and Selection = See: http://www.afcee.af.mil/shared/media/document/AFD-070926-076.ppt
- Monitoring and Remediation Optimization System (MAROS) =This software provides a strategy for formulating appropriate long-term ground water monitoring programs that can be implemented at lower costs. MAROS is a decision support tool based on statistical methods applied to site-specific data that accounts for relevant current and historical site data as well as hydrogeologic factors (e.g., seepage velocity) and the location of potential receptors (e.g., wells, discharge points, or property boundaries). Based on this site-specific information the software suggests an optimization plan for the current monitoring system in order to efficiently achieve the termination of the monitoring program.
- Simulation/Optimization Modeling System - (SOMOS) =aids in optimally managing water resources
- Source Depletion Decision Support System = active DNAPL Remediation
- SourceDK
- Mass Flux Toolkit = This is a Microsoft® Excel based software tool that enables users to learn about different mass flux approaches, calculate mass flux from transect data, and apply mass flux values to manage ground water plumes. With the mass flux data, the progress of natural attenuation and remediation systems can be demonstrated more vividly and directly.

Data/Information that can be used in MNA Evaluations:

BIOCHLOR and BIOSCREEN are applicable models that could be considered for use in determining if MNA is applicable.

Note that in the BIOCHLOR AFCEE document the acronym “RNA” is used for remediation through natural attenuation.

The Mass Flux Toolkit also provides valuable information for MNA evaluations.

DESIGNING MONITORING PROGRAMS TO EFFECTIVELY EVALUATE THE PERFORMANCE OF NATURAL ATTENUATION

Air Force Center for Engineering and the Environment (now: Engineering and the Environment), Technology Transfer Division,
January 2000
http://www.afcee.af.mil/shared/media/document/AFD-071211-021.pdf

Synopsis:

The document is a technical manual that identifies strategies to: (1) define sample collection points, analytical protocols, and sampling frequency, and (2) evaluate plume stability and behavior. Plume stability and behavior is evaluated primarily through statistical tools contained in the AFCEE Long Term Monitoring Decision Support Software System (LTM-DSSS). The LTM-DSSS has subsequently been replaced with the more comprehensive Monitoring and Remediation Optimization System (MAROS) software.

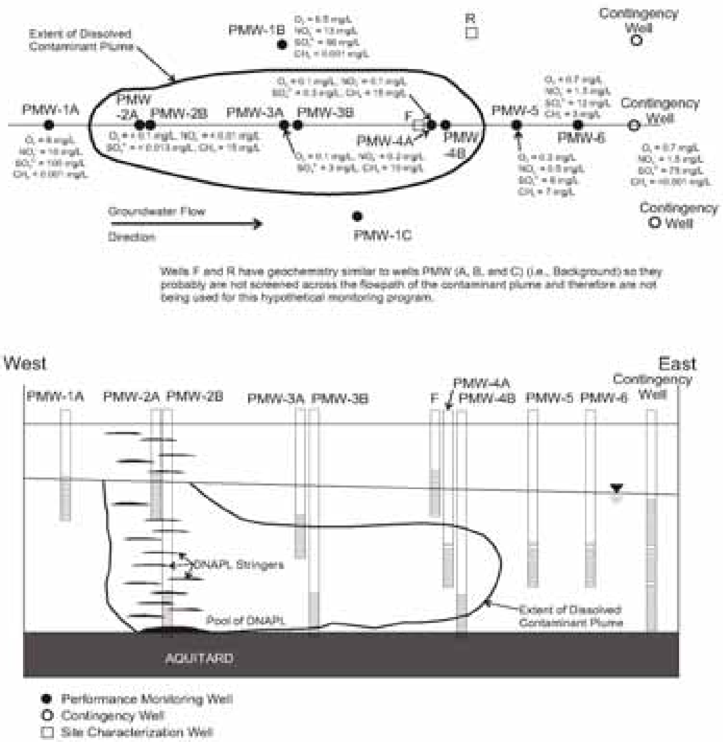
Concepts and Experimental Data Presented and Relevance to Monitored Natural Attenuation:

The document identifies three types of environmental monitoring: (1) site characterization (baseline) to describe distribution of contamination and forecast future behavior, (2) validation monitoring to determine if predictions based on site characterization are accurate, and (3) long-term monitoring to ensure that the behavior of the contaminant plume does not change. The document describes how to effectively and efficiently specify the location, frequency and types of analyses required to meet objectives of validation and long-term monitoring.

The document notes that where the groundwater flow field cannot be determined with certainty (e.g., fractured bedrock), the evaluation of MNA and the design of a monitoring program can be problematic. The most critical factors to consider when developing a monitoring program are the distance to the potential receptor and the ground water seepage velocity. A contingency plan is identified as an integral component of the monitoring plan.

Data/Information that can be used in MNA Evaluations:

The document outlines two types of wells used for validation and long-term monitoring: performance monitoring wells (PMWs) and contingency wells. PMWs are located upgradient from, within, and just downgradient from the plume; used to verify predictions made during the evaluation of natural attenuation. Contingency wells are placed beyond the maximum predicted lateral and downgradient boundaries for the plume, and upgradient of known or potential receptor points. Geochemical data should be used to confirm that downgradient wells are sampling ground water that was once contaminated (e.g., depleted electron acceptors and elevated metabolic byproducts). Examples were provided of lateral and vertical distribution of monitoring points



Wells F and R have geochemistry similar to wells PMW (A, B, and C) (i.e., Background) so they probably are not screened across the flowpath of the contaminant plume and therefore are not being used for this hypothetical monitoring program.

Figure 2.2
Locating Monitoring Wells Using Contaminant and Geochemical Data (DNAPL)
(Modified from Wiedemeier *et al.*, 1999)

for alternative contaminant scenarios that include geochemical and spatial considerations. The stresses that identify location and number of monitoring wells are highly dependent on site-specific conditions.

Analytical protocols are outlined in Sample Table (Table 2-1) which provides example of analytical test program for validation and long-term monitoring programs, including: (1) contaminants and daughter products, (2) electron acceptors (DO, nitrate, Fe(III), sulfate, carbon dioxide), (3) metabolic byproducts (Fe(II), carbon dioxide, methane, ethane, ethene, alkalinity, lowered ORP, chloride, hydrogen), and (4) general water quality parameters (pH, temperature, conductivity).

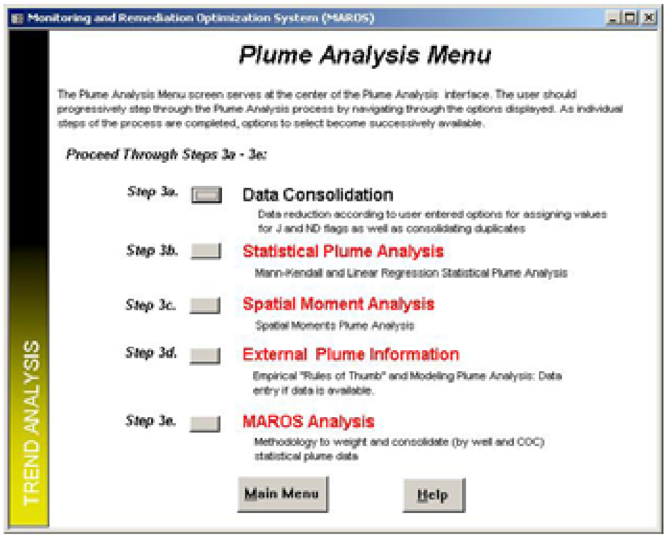
The sampling frequency was identified as quarterly for the first year, with subsequent modification based on first year results. A sampling protocol of annual or less frequent monitoring is often appropriate after the first year. One method to estimate sampling frequency is to divide the distance between leading edge of plume and a downgradient contingency well by the seepage velocity.

The document is strongly supportive of passive diffusion samplers/bags (PDBs) to minimize cost and provide time-averaged or equilibrium data.

Methods and Techniques:

Graphical techniques for evaluating plume stability include:
(1) isopleth maps of contaminant concentration over time,
(2) contaminant concentration versus time for individual monitoring well; and
(3) contaminant concentrations versus distance downgradient for several wells along a flow path for multiple sample events.

The document identifies Thiessen analysis or similar spatial analysis tools which can be used to calculate the center of mass of the plume over time. Statistical techniques for evaluating plume stability include the non-parametric Mann-Whitney U (Wilcoxon Rank-Sum) and Mann-Kendall tests. The document references the NJDEP application of the Mann-Whitney U (identified as a relatively low-power test that may misclassify datasets with declining trend). Extensive discussion of these tests is provided within the context of the LTM-DSSS software, currently MAROS, which is available in Microsoft (MS) Office XP/2000, Office 2003, and Office 2007 versions (all require MS Access, the Office database application, as well as MS Excel). In addition to evaluating plume stability, MAROS also contains tools to allow for siting and optimization of the monitoring well network. The document also references the "RNA Tool Kit" (Groundwater Services, Inc.) which performs a more sophisticated application of the Mann-Kendall, using a calculated confidence level and the coefficient of variance of the sample data to classify any data set as declining, probably declining, stable, no trend, probably increasing, or increasing. This software is no longer available as a separate package, but has been incorporated into MAROS.



Plume Analysis Menu

The Plume Analysis Menu screen serves at the center of the Plume Analysis interface. The user should progressively step through the Plume Analysis process by navigating through the options displayed. As individual steps of the process are completed, options to select become successively available.

Proceed Through Steps 3a - 3e:

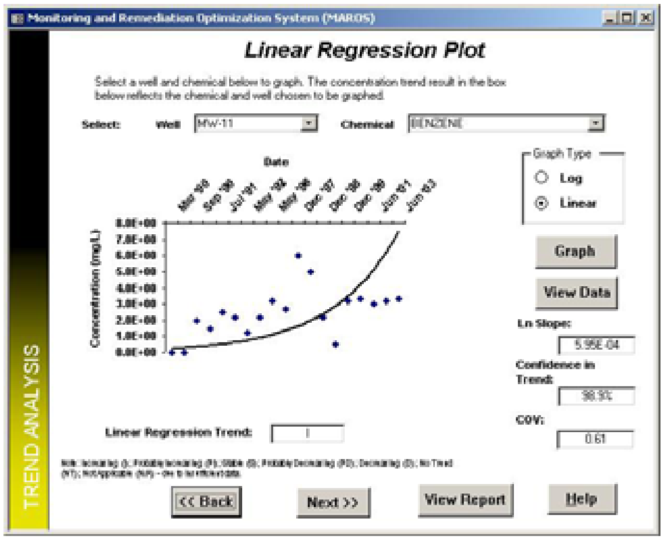
Step 3a. Data Consolidation
Data reduction according to user entered options for assigning values for J and ND flags as well as consolidating duplicates

Step 3b. Statistical Plume Analysis
Mann-Kendall and Linear Regression Statistical Plume Analysis

Step 3c. Spatial Moment Analysis
Spatial Moments Plume Analysis

Step 3d. External Plume Information
Empirical "Rules of Thumb" and Modeling Plume Analysis: Data entry if data is available.

Step 3e. MAROS Analysis
Methodology to weight and consolidate (by well and COC) statistical plume data



Linear Regression Plot

Select a well and chemical below to graph. The concentration trend result in the box below reflects the chemical and well chosen to be graphed.

Select: Well MW-11 Chemical BENZENE

Graph Type: ○ Log ● Linear

Ln Slope: 5.95E-04

Confidence in Trend: 98.9%

COV: 0.61

Linear Regression Trend: I

Note: Increasing (I); Probably Increasing (PI); Stable (S); Probably Decreasing (PD); Decreasing (D); No Trend (NT); Not Applicable (N/A) - Due to insufficient data

SCENARIOS EVALUATION TOOL FOR CHLORINATED SOLVENT MNA

Savannah River National Laboratory-SNRL
REF: WSRC-STI-2006-00096, Rev. 2
FEBRUARY 7, 2007
http://sti.srs.gov/fulltext/WSRC-STI-2006-00096.pdf

Synopsis:

One of the main challenges to implementing MNA is the need to cost-effectively interpret the multifaceted site-specific data. To address this challenge, a team of researchers developed a "taxonomic key" to classify contaminated sites into one of 13 scenarios based on hydrologic setting, geochemistry and a variety of modifying factors. The team developed a guidebook for each scenario to streamline characterization, modeling and monitoring. The result is a practical tool that will assist in environmental decision-making and in developing defensible environmental management strategies.

Concepts Presented and Relevance to Monitored Natural Attenuation:

Over the past 30 years, much progress has been made in the remediation of chlorinated solvents in the subsurface, but the physical and chemical properties of these compounds make it difficult to rapidly reach low regulatory limits in ground water. In 2003, the Department of Energy funded a science-based technical project using EPA's technical protocol (EPA, 1998) and directives (EPA, 1999) on MNA as the basis to introduce supporting concepts and new scientific developments. Three topic areas were identified for further development: (1) mass balance as the central framework for attenuation based remedies, (2) Enhanced Attenuation (EA), which represents a transition step between primary treatment and MNA, and (3) new characterization and monitoring tools. Each of these topics is documented in stand-alone reports (WSRC-STI-2006-00082, WSRC-STI-2006-00083, and WSRC-STI-2006-00084).

The Scenarios Evaluation Tool supports the topic areas of characterization and monitoring and Enhanced Attenuation, with characterization and monitoring being the primary development area. The objective of the study was to develop a guide to provide practitioners with an appropriate level of site specificity to assist in planning/supporting characterization, modeling, and implementation of MNA and EA. The tool consists of a user's guide and 13 scenarios that are built around general site conditions and hydrogeologic conditions. By applying a "taxonomic system", the scenario that best describes a plume (or a segment of a plume) can be selected. The scenario contains information about how to proceed with MNA evaluation for the type of plumes.

Data/Information that can be used in MNA Evaluations:

A Scenario is a particular combination of five different generic hydrogeologic settings and three geochemical environments, and each Scenario includes up to four modifying factors (see table on next page). Once a particular site has been characterized, the user is referred to one of 13 Scenarios, which contain detailed data relevant to the design of a monitoring program and an evaluation of the effectiveness of MNA for the particular site conditions. The Scenarios document provides a wealth of specific information for each of the "Primary Info" and "Modifying Factor" options, to assist in selecting the appropriate condition for a particular site. For example, relative to selecting the "Hydrogeologic Setting", the document provides several rules of thumb, including the following: "The median groundwater seepage velocity from a survey of 400 contaminant sites around the country was 88 ft/yr (Newell et al., 1990). An unconsolidated site significantly faster than 88 ft/yr would likely be classified as one of the "faster" flow regimes, while a site slower than 88 ft/yr would likely be classified as one of the "slower" flow regimes." The document also provides an extremely detailed and complete series of dechlorination reaction charts (with preferential pathways) for PCE; 1,1,1,2-TeCA, 1,1,2,2-TeCA; and CT under anaerobic, anoxic, and aerobic geochemical settings.

Primary Info	Why Important	Options
Hydrogeologic Setting	Nature of the hydrogeologic regime that will shape the groundwater contaminant plume	Simple, fast flow regime
		Simple, slow flow regime
		Heterogeneities, fast flow
		Heterogeneities, slow flow
		Fractured or porous rock
Geochemical Environment	Summarizes the geochemistry that will control which degradation processes are active	Aerobic
		Anoxic
		Anaerobic
Modifying Factors	**Why Important**	**Options**
Source Strength	Potential to produce and maintain plume	Strong
		Medium
		Weak
Source Type	Influences application of EA and longevity of source	Vadose Zone Source
		Submerged Source
		Mixed Vadose/Submerged Source
Travel Time to Receptor	Provides indication of "safety factor" associated with applying MNA/EA; influences intensity of monitoring program	Travel time < 2 years
		Travel time 2-5 years
		Travel time > 5 years
Plume Stability	Indicates current state of plume, which dictates level of evaluation needed to determine if MNA is viable	Expanding or perturbed (e.g., influenced by pumping)
		Stable
		Shrinking

Methods and Techniques

Once the Scenario has been selected, the user is referred to the appropriate Scenario module, where the following information is provided:

- Scenario Description
    - Hydrogeologic Setting
    - Geochemical Setting
- Key Dechlorination Reactions
- Effect of Modifying Factors
- Will MNA Work?
    - Potential for MNA Processes to Control Plume
    - Key Sustainability Concept
- How do I Characterize This Type of Site?
    - Actions Needed to Determine MNA Viability
    - Key Monitoring Concepts
    - Key Uncertainty Concepts
- How Do I Analyze Data?
- What About Costs and Enhancements?
    - Cost Considerations
    - Key Enhanced Attenuation Concepts
    - Key Source Control Concepts

STANDARD GUIDE FOR REMEDIATION OF GROUND WATER BY NATURAL ATTENUATION AT PETROLEUM RELEASE SITES

ASTM International E1943-98 (Reapproved 2004)
June 2004
(not available online)

Synopsis:

This document provides a practical and streamlined process for determining the appropriateness of remediation by natural attenuation and implementing remediation by natural attenuation at petroleum release sites. The document does not address bioremediation, enhanced attenuation, or natural attenuation of non-petroleum constituents.

Concepts Presented and Relevance to Monitored Natural Attenuation:

The document was developed to address natural attenuation of petroleum releases; therefore, the entire document is relevant to MNA. The document states that remediation by MNA may be used in the following situations:

- As the sole remedial action at sites where immediate threats to human health, safety, and the environment do not exist or have been mitigated, and constituents of concern are unlikely to impact a receptor;
- As a subsequent phase of remediation after another remedial action has sufficiently reduced concentrations/mass in the source area so that plume impacts on receptors are unlikely; or
- As part of a multi-component remediation plan.

Implementation of NAA should include:

- Ensuring that site characterization activities focus on collecting information required to evaluate and implement MNA;
- Evaluating information to understand MNA processes present at the site;
- Determining whether MNA is the most appropriate and cost-effective remedial alternative with a reasonable probability of achieving remedial goals; and
- Monitoring remedial progress.

The document acknowledges that MNA is not a presumptive remedy.

The document outlines a ‘lines of evidence’ approach for demonstrating that natural attenuation is occurring. Primary, secondary, and optional lines of evidence are discussed. Primary evidence includes constituent of concern data used to define the plume as shrinking, stable, or expanding. Secondary evidence includes geochemical indicators of naturally occurring biodegradation and estimates of natural attenuation rates. Optional lines of evidence include transport modeling, estimation of assimilative capacity, and microbiological studies.

Data/Information that can be used in MNA Evaluations:

Figure 1 (page 7) provides a flowchart for evaluating the appropriateness and progress of natural attenuation. Each step in the flow chart is described in the standard with several appendixes providing additional more detailed guidance of the steps. The standard (12 pages) and appendixes (29 pages) are well written.

Methods and Techniques:

- Appendix X1: What is Remediation by MNA?
  - Provides overview of process, including physical, chemical, and biological
- Appendix X2: Site Characterization for Evaluation of MNA
  - Describes 23 types of characterization data needed for MNA.
- Appendix X3: Monitoring Considerations

- MNA performance monitoring should include, at a minimum, one upgradient, two or three plume wells (outside of free product zones), and one downgradient well
    - Plume well placement is discussed depending on the type of evidence used to demonstrate attenuation rates (mass-balance approach, concentration-vs.-time approach, or concentration-vs.-distance approach)
    - Downgradient well should be placed to warn of potential impact to receptor
- Monitoring frequency should be established based on site-specific factors (characteristic of plume, ground water velocity, water table fluctuations, distance to receptor)
    - As a general rule, enough information can be gathered in one year of quarterly monitoring to establish a relationship between BTEX and terminal electron acceptors
    - More than one year of monitoring may be necessary to establish whether the plume is stable, shrinking, or expanding
    - Acknowledgement that existing long term monitoring data may be sufficient

Appendix X4: Sampling Considerations and Analytical Methods for MNA Indicators

Provides detailed table of indicator parameters for the three lines of evidence

Appendix X5: Interpretation of MNA Indicators

Based on the three lines of evidence

Appendix X6: Quantifying MNA Rates

Provides several approaches to quantify MNA rates.

- Mass Balance Approach
    - Quantitative approach for estimating mass loading from source zone and concurrent mass attenuation within the plume.
    - Most applicable to stable or shrinking plumes
    - Provides method
- Concentration vs. Time/Distance Approaches
    - Concentration vs. Time applicable to a shrinking plume
    - Concentration vs. Distance applicable to a stable plume
    - Can be demonstrated through graphical or regression techniques
    - Equation provided
- One-Dimensional Analytical Solution for a Stable Plume
- One, Two, and Three-Dimensional Analytical Models

Appendix X7: Example Problems

Two examples are provided, one using primary lines of evidence and one using both primary and secondary lines of evidence.

Use and Measurement of Mass Flux and Mass Discharge

Interstate Technology & Regulatory Council
Integrated DNAPL Site Strategy Team
August 2010
http://www.itrcweb.org/guidancedocument.asp?TID=82

Synopsis:

The document presents the following information:

- concepts and theory of mass flux and mass discharge
- applications for using mass flux and mass discharge information, and
- methods for measuring mass flux and mass discharge.

The purpose is to improve decision making for contaminated ground water sites so that decisions evaluate source or plume strength at a given time and location. The evaluation of mass flux and mass discharge help to show the combined effects of concentration and ground water velocity on contaminant movement.

Concepts Presented and Relevance to Monitored Natural Attenuation:

Mass flux and mass discharge information can provide another tool for sites considering MNA. Reliable mass flux and mass discharge estimates often require more detailed site characterization of hydraulic conductivity and ground water flow.

Methods & Techniques:

Methods to measure mass flux and mass discharge are presented in Section 4. These include transect methods, well capture/pump test methods, passive flux meters, transects based on isocontours, and solute transport models. Transect testing has been the most common method employed.

Data/Information that can be used in MNA Evaluations:

Table 3-1 summarizes how mass flux and mass discharge data can be applied. For the purposes of MNA evaluations, useful portions of the table and corresponding document text include site characterization / conceptual site model, exposure assessment, remediation selection, performance monitoring, and compliance monitoring.

Table 4-3 lists solute transport models used for estimating mass flux. Models include Bioscreen, Biochlor, Biobalance, various Modflows, and RemChlor.

Appendix G

Glossary

GLOSSARY

Aerobic means living, active, or occurring only in the presence of oxygen.

Alkalinity describes the capacity to accept protons (acid) while maintaining the pH above a predetermined value. Ground-water alkalinity may be increased as carbon dioxide emitted during biodegradation causes bicarbonate production.

Anaerobic means living, active, or occurring only in the absence of oxygen.

Attenuation means a lessening in concentration or mass.

Attenuation Capacity means the capacity of the aquifer to sustain attenuation of the mass of contaminant within the ground-water plume in support of cleanup objectives.

Degradation product means a compound that results directly from the degradation of another compound. For example *cis*-1,2-dichloroethene (*cis*-1,2-DCE) is commonly a degradation product of trichloroethene (TCE).

Diffusion describes the process by which ionic and molecular species move from a region of higher concentration to a region of lower concentration.

Dispersion describes the phenomenon by which a solute in flowing ground water mixes with uncontaminated water, becoming reduced in concentration. Dispersion is due both to differences in water velocity at the pore level and differences in the rate at which water moves through different strata. Also refers to statistical measures of how widely a set of data vary.

Electron acceptor means a compound capable of accepting electrons during oxidation-reduction reactions. Microorganisms obtain energy by transferring electrons from electron donors such as organic compounds (or sometimes reduced inorganic compounds such as sulfide) to an electron acceptor. An electron acceptor is a compound that is relatively oxidized and include oxygen, nitrate, ferric iron (III), manganese (IV), sulfate, carbon dioxide, or in some cases the chlorinated aliphatic hydrocarbons such as perchloroethene (PCE), TCE, DCE, and vinyl chloride.

Electron donor means a compound capable of supplying (giving up) electrons during an oxidation-reduction reaction. Microorganisms obtain energy by transferring electrons from electron donors such as organic compounds (or sometimes reduced inorganic compounds such as sulfide) to an electron acceptor. Electron donors are compounds that are relatively reduced and include fuel hydrocarbons and native organic carbon.

Long Term Monitoring (LTM) is a site-specific groundwater sampling program that specifies the location, frequency, and type of samples and measurements necessary to evaluate whether the natural attenuation remedy is performing as expected, is capable of attaining remediation objectives, and is protective of human health and the environment. LTM refers specifically to the monitoring performed after the Remedial Action Permit for Ground Water is issued by the Department, and is a component of the Monitoring, Maintenance, and Evaluation (N.J.A.C. 7:26C-7.4(a)) plan required under the permit.

Metabolic By-product is a product of the reaction between an electron donor and an electron acceptor. Metabolic by-products can include volatile fatty acids, daughter products of chlorinated aliphatic hydrocarbons, methane, chloride, carbon dioxide, and water.

Monitored natural attenuation (MNA) refers to the reliance on natural attenuation processes to achieve site-specific remedial objectives.

Natural attenuation processes means a remediation approach including a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil and ground water. These in-situ processes include biodegradation, dispersion, dilution, sorption, volatilization, and chemical or biological stabilization, transformation, or destruction of contaminants.

Oxidation is chemical process that results in a net loss of electrons in an element or compound.

Retardation means any process that acts to inhibit the movement of a solute in ground water, such that the solute travels more slowly than the ground water itself.

Sorption describes movement of a substance from the aqueous phase to the solid phase, whether by adsorption, absorption, fixation or precipitation. Sorption may be reversible or irreversible.

Substrate refers to a substance(s) that provides growth and energy requirements for cells.

Terminal electron acceptor (TEA) is a compound or molecule that accepts an electron (is reduced) during metabolism (oxidation) of a carbon source. Under aerobic conditions molecular oxygen is the terminal electron acceptor. Under anaerobic conditions a variety of terminal electron acceptors may be used. In order of decreasing redox potential, these TEAs include nitrate, manganese (IV), ferric iron (III), sulfate, and carbon dioxide.

Appendix H

Acronyms

ACRONYMS

AOC	Area of Concern
ARRCS	Administrative Requirements for the Remediation of Contaminated Sites
BTEX	Benzene, Toluene, Ethylbenzene, and Xylenes
CEA	Classification Exception Area
CSM	Conceptual Site Model
COC	Contaminant of Concern
CSIA	Compound-Specific Isotopic Analysis
DO	Dissolved Oxygen
DNAPL	Dense Non-Aqueous Phase Liquid
GWQS	Ground Water Quality Standards
IEC	Immediate Environmental Concern
IAEA	International Atomic Energy Agency
ISRA	Industrial Site Recovery Act
ITRC	Interstate Technology and Regulatory Council
LNAPL	Light Non-Aqueous Phase Liquid
LTM	Long Term Monitoring
LSRP	Licensed Site Remediation Professional
MBT	Molecular Biological Tools
MDL	Method Detection Limit
MIP	Membrane Interface Probe
MNA	Monitored Natural Attenuation
MTBE	Methyl Tertiary Butyl Alcohol
ND	Non-Detect
NJDEP	New Jersey Department of Environmental Protection
ORP	Oxidation Reduction Potential
QL	Quantification Limit
RAO	Response Action Outcome
RAP-GW	Remedial Action Permit for Ground Water
RL	Reporting Limit
SRRA	Site Remediation Reform Act
TEA	Terminal Electron Acceptor
TDS	Total Dissolved Solids
USACE	US Army Corps of Engineers
USEPA	United States Environmental Protection Agency
UST	Underground Storage Tank