WISCONSIN
DEPT. OF NATURAL RESOURCES

Remediation
and
Redevelopment
Program

Guidance
On Natural Attenuation
For Petroleum Releases

Biodegradation

Sorption

Dispersion
and Dilution

Processes of
NATURAL
ATTENUATION

Volatilization
(Evaporation)

Chemical
Reactions

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Purpose

This document provides technical guidance for evaluating natural attenuation processes in remediating groundwater contaminated with petroleum products. The theories and processes of natural attenuation are dealt with in many references, some of which are listed at the end of this document. This guidance covers the application of natural attenuation for remediating petroleum contaminated groundwater, including: site investigation, selecting natural attenuation as a remedy, designing a monitoring well network, developing a monitoring plan, monitoring groundwater, evaluating data, and site closure requirements.

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

Applicability and Limitations

This guidance is applicable to sites with petroleum-contaminated soil and groundwater or sites with only contaminated groundwater. This guidance does not address sites where only the soil is contaminated. (For guidance on natural attenuation of sites with only soil contamination, refer to "Naturally Occurring Biodegradation as a Remedial Action Option for Soil Contamination", Department publication, PUBL-SW-515-95.) THIS GUIDANCE IS NOT INTENDED FOR CONTAMINANTS OTHER THAN PETROLEUM COMPOUNDS. Portions of this guidance are not applicable to certain sites that qualify for closure under Com 46/NR 746, Wis. Adm. Code. Please refer to Com 46/NR 746 to determine which sections of this guidance are not applicable.

This guidance is intended to help owners, consultants and regulators assess natural attenuation processes at specific sites and understand what role these processes may play in the cleanup of the site. When considering remedial alternatives, the capacity of natural attenuation processes to remediate contamination should be compared with other cleanup remedies and the best combination of alternatives chosen which result in a cost-effective and timely cleanup.

Recommendations of this guidance are applicable to sites in various stages of the cleanup process – sites that have just been discovered, sites where the site investigation has been completed, and sites where a remedy has been implemented and natural attenuation is being assessed to address the residual contamination. Historical data should be used to the extent possible to assess the effectiveness of natural attenuation processes. Occasionally, sites with completed site investigations may need additional monitoring wells and/or piezometers or additional soil or groundwater sampling and analysis to assess natural attenuation as a remedy. Decisions on the need to collect additional site data should be based upon an assessment of site data gaps and the ability to demonstrate that natural attenuation processes will be effective in meeting remediation goals.

The Wisconsin Administrative Code requirements governing the application of natural attenuation include ch. NR 140, Groundwater Quality and the NR 700 Series, Environmental Protection--Investigation and Remediation, Wis. Adm. Code. This guidance specifically references various sections of these codes. For sites with soil and groundwater contamination, natural attenuation of contaminants in groundwater can serve as a "performance standard" for the soil contamination. See the Department's "Interim Guidance on Soil Performance Standards", Publication RR-528-97, for further information.

Other Relevant Guidance Documents

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

- Interim Guidance for Selection of Natural Attenuation for Groundwater Restoration and Case Closure Under Section NR 726.05(2)(b), Publication RR-530-97
- Interim Guidance on Use of Leaching Tests for Unsaturated Contaminated Soils to Determine Groundwater Contamination Potential, Publication RR-523-97
- Interim Guidance on Soil Performance Standards, Publication RR-528-97
- Guidance for Documenting the Investigation of Utility Corridors for Petroleum Releases, Publication RR-649-00
- Close Out Guidance on the Use of Deed and Groundwater Use Restrictions and Deed Notices, PUBL-RR-606
- Implementation Guidance for NR 746/Comm 46, Emergency Rule, anticipated availability last quarter 1999.
- Department of Health and Family Services' (DHFS) "Chemical Vapor Intrusion and Residential Indoor Air", 2003.

This list will be expanded as additional guidances are developed.

The DNR guidances may be obtained by:
    A. Sending a request to: Public Information Requests, Bureau for Remediation and Redevelopment, Department of Natural Resources, P.O. Box 7921, Madison, WI 53707.
    B. Calling the publication request line at (608)-264-6009.
    C. Downloading the files from the internet at www.dnr.state.wi.us/org/aw/rr/errhw/.
The DHFS guidance can be found at http://www.dhfs.state.wi.us/eh/Air/

Guidance Revisions

This guidance will be updated as needed. Comments and concerns may be sent to "Guidance Revisions", Dale Ziege - RR/3, WDNR, P.O. Box 7921, Madison, WI 53707, phone number 608-267-7533.

Disclaimer

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

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

Interim Guidance on
Natural Attenuation for Petroleum Releases

Introduction

Natural attenuation is a broad term that encompasses a number of naturally occurring processes that degrade contaminants and limit their movement in the subsurface. Natural attenuation processes can control contaminant movement in many environmental media, including, soil, sediment, air, surface water, groundwater, etc. This guidance specifically addresses the reliance on natural attenuation processes in groundwater to control and remediate petroleum contaminants. These processes include dilution, dispersion, sorption, precipitation, volatilization, biodegradation/biotransformation, and abiotic degradation/transformation.

Biodegradation, which relies upon microorganisms to convert contaminants to less harmful compounds, is the primary natural attenuation mechanism for reducing the mass and concentration of petroleum contaminants. To convert ("eat") contaminants, microorganisms require the proper environmental conditions, nutrients and electron acceptors. Nutrients, which include trace levels of phosphorus, potassium, nitrogen, etc., are usually available within most soil and groundwater systems. The availability of electron acceptors usually controls the extent of contaminant biodegradation, therefore, it is important to assess electron acceptor distribution and concentration in groundwater. Microorganisms use electron acceptors (e.g., oxygen, nitrate, iron, and sulfate) to "breathe".

Consider an example of natural biodegradation. An underground gasoline tank leaks gasoline into the surrounding soils. The gasoline will migrate downward under gravity and rainfall will leach the more soluble portion (such as benzene, toluene, ethylbenzene, and xylenes) of the gasoline into the soils. Microorganisms in the soil will begin to degrade these compounds. The rate of biodegradation will depend on the amount of contaminant released, the rate of movement through the soils and the presence of appropriate environmental conditions. Oxygen is usually present in the unsaturated soil to support biodegradation processes. If the release is large enough, contaminants dissolved in water seeping through the soil, or even pure petroleum product from the spill, may reach the groundwater (also known as the saturated zone). Groundwater will transport the contaminants downgradient from the release (source zone) and naturally occurring microorganisms in the groundwater will degrade the soluble petroleum contaminants to an extent largely limited by the availability of electron acceptors. Oxygen is readily depleted in groundwater so that aerobic degradation processes are limited to the fringes of a contaminant plume. Anaerobic processes (degradation that relies upon electron acceptors other than oxygen) will account for most of the biodegradation that occurs within the contaminant plume.

Some petroleum compounds are only slowly degradable by microorganisms, or may not be degradable at all. The chemical structure of the contaminant, the concentration and competition between contaminants, and the ability of the natural microbes to "eat" a contaminant while "breathing" various electron acceptors, control the speed and extent of degradation. For instance, benzene is most easily degraded under aerobic (oxygen) conditions. Benzene does degrade under anaerobic conditions, but more slowly than if oxygen were present. At some contaminated sites, benzene has been shown to not degrade at all (Davis, et.al.,1999). In general, it has been found that toluene and xylenes degrade more

readily than benzene and ethylbenzene. Another petroleum contaminant, methyl tertiary butyl ether (MTBE), degrades very slowly, if at all, and does not sorb (or cling) to soil surfaces. Because of these properties, MTBE moves rapidly and tends to persist in groundwater.

Natural attenuation includes many other processes besides biological degradation. The processes of dilution, dispersion, sorption, precipitation, volatilization and abiotic degradation/transformation all serve to reduce the concentration of contaminants in groundwater and soils. These processes are particularly important for contaminants that are not subject to biodegradation, such as lead. Tetraethyl lead (TEL) was added to gasoline as an anti-knock agent from the 1920s until the 1970s. The organic portion of TEL will decompose abiotically as well as through microbiological processes. The breakdown products of TEL (which includes elemental lead) are strongly sorbed to soil organic matter and may sorb strongly to soil mineral surfaces. In addition, elemental lead is subject to chemical complexation and precipitation. All of these processes serve to limit the concentration and mobility of lead in groundwater (Rhue, et.al., 1992).

The length of time needed to cleanup petroleum contaminants by means of natural attenuation depends on the mass of contaminant in the environment, the availability of electron acceptors and the ability of the existing microbial population to degrade the contaminants. To achieve site cleanup goals within a reasonable period of time, source control actions are almost always needed in conjunction with natural attenuation. Source control actions include tank removal, removal of free product to the extent practical, and removal or treatment of highly contaminated soil, which can constitute a long-term contaminant source. <u>Assessment of natural attenuation as a remedy should take place after source control actions are complete</u>.

This guidance document discusses approaches to site investigation, data assessment, and groundwater monitoring as part of assessing natural attenuation processes. Many approaches are available to assess natural attenuation processes and each site will present site-specific challenges. This document should be used as a guide to help establish the effectiveness of natural attenuation. <u>Do not use this document as a checklist of tasks that must be completed at every petroleum-contaminated site</u>.

SECTION 1

SITE INVESTIGATION NEEDS

Adequate site characterization lays the foundation for demonstrating the effectiveness of natural attenuation. Chapter NR 716, Wis. Adm. Code, sets out the requirements for site investigations. To show the effectiveness of natural attenuation, site-specific data should demonstrate that natural attenuation will reduce contaminant mass and concentrations to acceptable regulatory limits within a reasonable period of time. A thorough site investigation, along with proper monitoring, will lay the foundation for demonstrating the effectiveness of natural attenuation as a remedial option.

All of the site investigation recommendations of this section may not be needed for every petroleum release site. However, collecting the appropriate information early in the site investigation process should reduce overall site costs and result in better decision making.

I.   Formation of a Conceptual Model

A conceptual model is a three dimensional understanding of the contaminant source, groundwater flow characteristics and hydraulic properties, dissolved contaminant distribution and solute transport system. The conceptual model should address how site-specific natural attenuation processes perform to protect human health and clean up the environment. An initial site conceptual model should be developed based on existing site information, much of which may be qualitative. As data is gathered, the site conceptual model should be modified to reflect a growing understanding of site geology, pathways of contaminant movement, natural attenuation processes effective at the site, etc. The evolving site conceptual model should govern the need for quantitative data collection.

In formulating the initial site conceptual model, gather as much existing data as possible from available resources, such as: USGS 7.5 minute quadrangle maps, Water Supply Papers, regional groundwater flow maps, maps of local geology and soils, history of site use including contaminant types and hazardous substance releases, etc. The initial conceptual model should address, at a minimum, the following areas:

1. History and Nature of Contamination. This includes site location; history of site use; contaminant source zones; age of contaminant release; the types and amounts of contaminant released, including an estimate of contaminant mass; likely environmental media affected; other nearby sources of contamination; estimated extent of contamination; the likelihood that contamination has moved beyond the property boundaries; physical/chemical characteristics of the contaminants; biodegradability of the contaminants; etc.

2. Factors Affecting Contaminant Movement. This includes local topography; expected soil type; local stratigraphy/lithology; expected groundwater flow direction(s) including variability in flow directions; existence of preferential flow paths (both natural and manmade, e.g.,

fractured bedrock, presence of utility trenches); estimated hydraulic conductivities and horizontal and vertical gradients; variation in groundwater gradients over time, etc. The Department's "Guidance on Documenting the Investigation of Utility Corridors for Petroleum Releases", RR-649, may be useful when determining whether utility corridors are a contaminant pathway.

3. <u>Contaminant Receptors</u>. This includes location of existing public and private potable wells, well head protection areas, well fields and high capacity wells; groundwater discharge areas; surface waters; threatened or endangered species or habitats; floodplains; and wetlands; as well as possible changes in land use.

The conceptual model allows the investigator to identify additional data requirements necessary to define the geologic and hydrogeologic system, contaminant source, extent and degree of contamination, natural attenuation processes, and human and environmental impact of the contamination.

II.   Identify Receptors

A.   Determine Location of Receptors

Determine the presence of receptors near the contaminated site, using maps, municipal public works departments, or other resources. A receptor search should include identification of:

- Public wells or well fields within 1,000 feet of the site.
- High capacity pumping wells (e.g., irrigation wells, industrial wells) within 1,000 feet of the site.
- Private wells within 100 feet of the site.
- Surface water bodies that may serve as a discharge location for groundwater contaminants within 1,000 feet of the site.
- Basements and other subsurface enclosed structures within 100 feet of the site.

Site specific conditions, such as high groundwater velocity and/or recalcitrant contaminants, may require that receptors be identified beyond the distances listed here. Once receptors are identified, determine whether the contaminants pose a threat to the receptor, considering likely pathways and site specific factors such as: screened intervals of pumping wells; field screening data (such as soil vapor surveys near building foundations); contacting nearby residents for indoor air complaints, etc. Develop a monitoring plan that includes appropriate monitoring of the likely receptors.

For municipal wells, well fields or high capacity wells drawing water from an unconfined aquifer near the contaminant site, calculate a capture zone for the well(s) to determine if the contaminant site is within the capture zone. If one exists, a well head protection map may be used to determine the well head protection area. If the contaminated site is within the capture zone (or well head protection area), actions may be necessary to protect the well field, high capacity well or municipal well and to reduce contaminant mass and movement to the extent possible.

B. Information Sources for Identifying Receptors

The Wisconsin DNR's Bureau of Drinking Water and Groundwater maintains computerized well construction reports for all private wells constructed after January 1, 1998 and for community and municipal wells. For well location or geologic information, please contact the appropriate regional DNR water supply specialist. To access private well construction reports prior to January 1998, call the Wisconsin Geologic and Natural History Survey at (608) 262-7430. Regional staff in the Bureau of Drinking Water and Groundwater can be contacted to identify locations of nearby public and private wells and can identify established well head protection areas and associated capture zones, if these have been calculated.

The Department of Health and Family Services (DHFS) has developed guidance for consultants evaluating the vapor intrusion pathway. "Chemical Vapor Intrusion and Residential Indoor Air" is available from DHFS, at http://www.dhfs.state.wi.us/eh/Air/.

In all cases, in order to comply with the requirements of s. NR 716.11(5), Wis. Adm. Code, the investigator needs to evaluate site-specific geologic and hydrogeologic characteristics in assessing the potential receptors. This should include consulting county hydrogeologic maps for regional groundwater flow patterns, groundwater divides, etc. to identify at-risk receptors.

III. Soil & Groundwater Characterization

Adequate site characterization is essential to determine the capacity of natural attenuation processes to control and remediate contamination. When natural attenuation is being considered as a partial or sole remedy for a site, site investigation needs are generally greater than if active remedies are applied. This is because active remedies impose an external control on contaminant migration and/or reduction. In addition, the effectiveness of active remedies to achieve site cleanup goals can usually be assessed within a relatively short time. When natural attenuation processes are relied upon as a cleanup mechanism, a thorough understanding of the processes controlling contaminant movement and degradation are required because no active intervention is controlling the movement of environmental contaminants. In addition, the time frame for achieving site cleanup goals using natural attenuation may be considerably longer than if an active remedy had been implemented. When characterizing a site for the use of natural attenuation, determine:

- The three-dimensional (3-D) extent and estimate of total mass of contaminants in the "source zone" (area of petroleum product release, where product may be trapped in soil and the saturated zone).
- Contaminant migration pathways, including the most conductive water bearing units.
- The 3-D extent, concentration and behavior of the dissolved contaminant plume, including hydrogeologic controls on groundwater and contaminant flow and rates of groundwater and contaminant flow.
- Observed contaminant decay rate due to natural attenuation processes.
- The existence of impacted or threatened receptors.

This guidance focuses on the aspects of site characterization that are particularly critical when assessing natural attenuation processes. The investigator should design the site investigation

for site size and complexity, including a detailed assessment of the site geology/hydrogeology, contaminant properties, and identification of receptors. The requirements of a full site investigation are beyond the scope of this guidance. (See chapter NR 716, Wis. Adm. Code, and "Contents of Site Investigation Reports for Petroleum Contaminated Sites", RR-628-01 for more information).

A.   Source Zone Characterization

There are four major components of the contaminated source zone: contaminated soils; free petroleum product (sometimes referred to as LNAPL - light non-aqueous phase liquid); contaminated saturated materials beneath the water table; and dissolved contaminants in groundwater. Contaminant distribution in these four components must be understood to properly assess the effectiveness of natural attenuation and determine whether cleanup goals will eventually be met.

To assess contaminant distribution, sample the source zone to determine the 3-D degree and extent of contamination. Accelerated site characterization techniques (which include any technology that produces field generated analytical data) or standard soil borings/monitoring wells should be used to sample and assess the source zone stratigraphy and contaminant distribution, including assessing source zones that may cross property boundaries and rights-of-way. This information can also be used to estimate contaminant mass and ultimately predict a time frame for groundwater cleanup.

1. Perform multi-level sampling of soils[1], saturated material[2] and groundwater within the source zone to characterize the soil type, depth of contamination, preferential groundwater flow paths, contaminant type and contaminant mass.
    a. Visually observe samples for contamination. Field screen all samples for the presence of VOCs, using hand held detectors or other methods. Use of field GC (gas chromatography), FID for field headspace analysis, or other real time analytical techniques to identify contaminants is encouraged to guide the site investigation. Submit a minimum of 10% of samples analyzed by field methods to a ch. NR 149 certified laboratory for confirmation analysis of the appropriate contaminants.
    b. Describe the soil and saturated zone material, including: grain size, lithology, fractures, geologic origin, moisture content, layering, color, odor, etc. Quantitatively determine grain size distribution and fraction organic carbon content[3], for representative soil and saturated zone material. As appropriate, determine effective porosity based on literature values for soil type.
    c. Extend soil sampling below the depth of contamination, including below the water table. Sample and analyze for soluble contaminants in the unsaturated soil and saturated material in order to assess the extent and mass of the contaminants in the source zone.

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[1] Soil is defined in NR 700.03(58) as "unsaturated organic material, derived from vegetation and unsaturated, loose, incoherent rock material, of any origin, that rests on bedrock other than foundry sand, debris and any industrial waste".
[2] Saturated material is any subsurface material that is saturated with groundwater.
[3] Fraction organic carbon (f_{oc}) should be determined on uncontaminated soil and saturated material.

2. Identify the depth and areal extent of free product, if present. Where free product is present, free product removal shall be conducted to the maximum extent practicable (as required by ss. NR 708.13 and NR 722.09(2), Wis. Adm. Code).

3. Identify the depth and areal extent of trapped residual petroleum product in the soil and saturated zone material (that is, the depth and areal extent of the "smear zone".) Visually inspect the samples and use analytical techniques to determine contamination levels in the "smear zone".

4. Sample groundwater at the water table in the source zone to determine if groundwater contamination exists at the site. Field screen groundwater for contamination and analyze selected samples at a NR 149 certified laboratory for contaminants of concern.

5. Sample groundwater in the source zone for geochemical indicators of natural attenuation. Use field analytical methods to the extent possible.

B.   Source Zone Contaminant Mass Distribution & Interim Measures

Using the site investigation results, responsible parties must determine if interim or immediate actions are necessary, as required in ch. NR 708, Wis. Adm. Code. Interim actions must be taken to protect receptors if these have been affected or are likely to be affected by contaminants. If an interim action or an active remedy is necessary, natural attenuation assessment should take place _after_ completion of the remedial action.

Estimate the mass of BETX, MTBE, and TMBs (the relatively soluble contaminants) and the mass of total hydrocarbon in the source zone from the original contaminant release, if this is known. For sites where significant contamination remains in the subsurface and monitoring results alone cannot establish the effectiveness of natural attenuation, it may be necessary to estimate the mass of soluble and total subsurface contaminants from soil and groundwater contaminant concentrations. Contaminant mass estimates can help determine the expected source lifetime, aid in assessing the effectiveness of natural attenuation, and allow investigators to compare the cost effectiveness of alternate remedial technologies. Appendix A contains a description of contaminant mass calculation and an example calculation.

C.   Groundwater Characterization

1. Defining the Degree and Extent of Groundwater Contamination. Accelerated site characterization techniques are encouraged to help determine the degree and extent of the dissolved groundwater contaminant plume, including the vertical distribution of the plume. Accelerated site characterization techniques can be used to help evaluate stratigraphy and guide the placement of permanent monitoring wells.
   a. If accelerated site characterization is used, collect groundwater samples at various depths downgradient of the source zone (see Fig. A-4 in Appendix A). Suggested sample intervals:
      i.   if the water table < 30 feet below ground surface, groundwater sample interval should not exceed 2 to 5 feet.

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ii. if the water table > 30 feet below ground surface, groundwater sample interval may be 5 feet.
b. Identify contaminant flow pathways.
c. Field screen groundwater samples for contamination. Install monitoring wells according to ch. NR 141, and analyze groundwater samples in a NR 149 certified laboratory for contaminants of concern.
d. Sample groundwater upgradient, within the dissolved plume, sidegradient and downgradient of the dissolved plume for geochemical indicators of natural attenuation. Use field analytical methods to the extent possible.

2. Installation of Permanent Monitoring Wells. The placement of permanent monitoring wells at a site is critical to establishing the effectiveness of natural attenuation. The results of the accelerated site characterization effort should determine the appropriate location of monitoring wells and piezometers. Appendix A discusses considerations when installing water table monitoring wells and piezometers, including:
   a. Location of monitoring wells with respect to the contaminant plume. Base monitoring well locations on the complexity of the site geology and the plume configuration. If possible, locate two or more monitoring wells approximately along the center flow line of the plume.
   b. Spacing of monitoring wells. Monitoring wells need to be spaced to reflect groundwater flow velocity, contaminant characteristics and the dynamics of plume movement. Demonstrating the effectiveness of natural attenuation involves determining changes in groundwater quality along the groundwater flowpath(s). Therefore, spacing of monitoring wells will, in part, dictate the length of time monitoring is needed to show the effectiveness of natural attenuation processes.
   c. Placement of monitoring well screens. While free phase petroleum tends to float on the water table, dissolved phase petroleum contaminants move with groundwater flow. Dissolved contaminants can move to deeper levels in a groundwater flow system due to infiltration of rainwater and downward vertical gradients. Assess permeability of site soils, surface conditions, and location in the hydrologic flow system to determine whether a piezometer is needed. Appendix A provides further guidance on when piezometers are needed at a site.

3. Groundwater Monitoring. During the site investigation, determine the contaminants of concern at the site and monitor for evidence of contaminant decay.
   a. Monitor contaminant types and levels, including:
      i. Volatile Organic Compounds (VOCs) during the first round and petroleum volatile organic compounds (PVOCs) and any other VOCs detected, thereafter; lead, if leaded gasoline was ever used at the site; and DRO to evaluate whether polycyclic aromatic hydrocarbons (PAHs) should be analyzed during subsequent sampling rounds.
      ii. Include in long-term monitoring compounds at the site that are of regulatory concern (i.e., contaminants detected at or above NR 140 Preventive Action Limits) as well as all parameters detected that do not have a PAL or ES in ch. NR 140.
   b. Monitor geochemical indicator parameters. Geochemical indicators of natural attenuation can indicate the presence of appropriate site conditions for natural attenuation, provide evidence of subsurface biological activity, and help determine monitoring well placement. Section 3 and Appendix C contains further information on monitoring the parameters listed below.

i. Monitor geochemical parameters most likely to indicate electron acceptors are being used, including: dissolved oxygen, nitrate, dissolved manganese, ferrous iron, sulfate, and methane.

ii. Monitor geochemical parameters that indicate appropriate site conditions for natural attenuation, including: alkalinity, oxidation-reduction potential (ORP), pH, temperature and specific conductivity.

iii. Collect and analyze at least 2 quarterly rounds of each geochemical parameter. Monitor dissolved oxygen, pH, temperature, and specific conductivity during all sampling rounds. Continue to monitor other geochemical parameters found to be most useful for indicating natural attenuation at the site, based on a site-specific evaluation. See Table 3-1 in Section 3 for a recommended monitoring schedule.

iv. Field analyze geochemical indicators, to the extent possible. Field test kits, probes and other field techniques are acceptable methods. Section 3 contains information on test methods. Results of geochemical analysis are very sensitive to sample collection procedures; therefore, consider the quality of sampling collection and handling when assessing analytical data.

4. Initial Assessment of the Effectiveness of Natural Attenuation. Using the data from the site investigation, assess the likelihood that natural attenuation can be considered as a possible remedy for the soil and groundwater contamination. Section 2 and Appendix B of this document include methods for conducting this assessment. Results of the assessment should be included in the site investigation report.

D.   Chemical/Physical Properties of the Contaminants

The chemical and physical properties of the contaminants are critical for determining plume behavior and whether natural attenuation processes will reduce contaminant concentration and mass to achieve site cleanup goals. Appendix D contains typical chemical properties of common petroleum contaminants.

1. Benzene, Ethylbenzene, Toluene, Xylenes (BETX). These aromatic hydrocarbons are the most common contaminants of concern at petroleum sites and can naturally biodegrade under most subsurface conditions. The rate of degradation can vary significantly from site to site. Benzene usually degrades more slowly than ETX and there are conditions where benzene may be recalcitrant to biodegradation. Schreiber (1999) summarizes the biodegradability of each BETX compound relative to the available terminal electron acceptor.

2. Methyl Tertiary Butyl-Ether (MTBE) and Other Fuel Oxygenates. MTBE is highly soluble, does not readily sorb to soil surfaces and tends to be recalcitrant to biodegradation. MTBE moves readily with groundwater flow and is typically found on the leading edge of the contaminant plume. The "disappearance" of MTBE can be due to the contaminant moving beyond the groundwater monitoring network rather than the loss of contaminant from the groundwater system. The presence of MTBE at a site may require additional monitoring efforts to determine whether natural attenuation processes will remediate MTBE plumes.

3. 1,2 - Dichloroethane (1,2 - DCA). Leaded gasolines, no longer produced, contained 1,2-DCA. 1,2-DCA is degradable to carbon dioxide and water under aerobic as well as anaerobic conditions. 1,2-DCA is not strongly retarded in the aquifer matrix and can migrate significantly beyond the source zone.

4. 1,2-Dibromoethane (EDB). EDB was used as a lead scavenger, particularly in aviation fuels and leaded gasoline. EDB is volatile and readily leaches from soil, but can be trapped in soil micropores and persist for many years. The primary degradation processes in groundwater are biodegradation and hydrolysis. The rate of these processes varies greatly from site to site.

5. Trimethylbenzenes (TMB). These compounds can be recalcitrant to degradation under anaerobic conditions. The three isomers of TMB (1,2,3-TMB, 1,2,4-TMB, and 1,3,5-TMB) have soil sorption (K_{oc}) values higher than benzene. However, under certain condtions, TMB's have been used as a conservative tracer within petroleum plumes to estimate the degradation rate of other petroleum products (Wiedemeier, et.al., 1999).

6. Polycyclic Aromatic Hydrocarbons (PAHs). These compounds are composed of 2 to 7 fused aromatic rings. The longer chain, higher molecular weight PAHs are relatively resistant to biodegradation. However, PAHs are only slightly soluble and have a high affinity for soil surfaces. The majority of PAHs remain in weathered petroleum in the source zone after the more soluble and biodegradable petroleum components have been removed.

7. Lead (Pb). Natural attenuation processes do not reduce the total mass of metals in the subsurface. However, processes of adsorption, ion exchange, precipitation and complexation with organic matter limit the mobility of lead and reduce the mass of lead in the groundwater. The amount of dissolved lead in groundwater depends on pH, the concentration of dissolved salts and colloid formation. (GWRTC, 1997)

IV. Determining Dissolved Plume Behavior

A. Methods to Define Behavior of a Dissolved Contaminant Plume

The behavior of the plume margin is of utmost concern when defining dissolved contaminant plume behavior. Determine the 3-D extent of contamination by monitoring the source zone, properly locating water table wells and piezometers to intersect the flow lines of the contaminant plume, and monitoring the leading edge of the plume. The site's hydrogeology and type of contaminants govern the period of time that is needed to define plume behavior.

Several options to evaluate plume behavior are detailed below to determine whether or not the plume margin is expanding, contracting or remaining relatively stable. The tools discussed below may be used to assist in defining plume behavior, however, data within a source area or within the plume itself is not a valid substitute for defining and monitoring the location of the downgradient plume margin over time.

1. Field Assessment of the Plume Margin to Determine Plume Behavior
   a. Calculate groundwater and contaminant velocities along the preferential groundwater flow pathway.

   Groundwater velocity:

   $$v = \frac{K \, \Delta h}{n_e \, \Delta l}$$

   where: v = groundwater velocity (L/T)
             K = hydraulic conductivity (L/T)

n_e = effective porosity

$\dfrac{\Delta h}{\Delta l}$ = hydraulic gradient

Contaminant velocity:

$$V_c = \dfrac{v}{R}$$

where: v_c= velocity of the contaminant (L/T)
             v = groundwater velocity (L/T)
             R = retardation factor (unitless),
                     (See App. B for calculation of retardation)

  b. Determine the distance between the monitoring well closest to the edge of the contaminant plume (preferably, this will be a clean, sentinel well) and the nearest contaminated well along the contaminant flow path (see Figure 1).
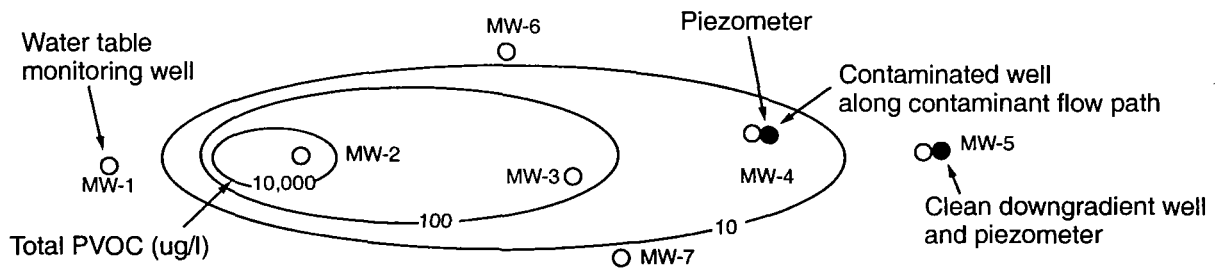
Figure 1. Example well locations for determining plume behavior

  c. Based on groundwater and contaminant flow velocities, determine the time frame that contaminant movement is likely to be detected between these two monitoring wells. Monitor contaminants and natural attenuation parameters for that time period. This monitoring period should not be less than the groundwater travel time between these two monitoring wells.

  d. If the calculated monitoring period is longer than desired to establish plume behavior, consider installing at least one additional monitoring well closer to the edge of the plume (the new monitoring well could be placed either upgradient or downgradient of the leading edge of the plume). Generally, monitoring wells should be spaced more than 20 feet apart.

2. Graphical Analysis to Determine Plume Behavior

  a. Plot contaminant concentration versus distance downgradient for monitoring wells located along or near the plume centerline for several sampling events. The plots should include monitoring results from a monitoring well at or very near the source zone and a

monitoring well at or very near the downgradient edge of the contaminant plume. (These plots can be semi-logarithmic.)

b. If possible, compare data from the same season, to help eliminate the impacts of seasonal water level variation on the contaminant concentrations.

c. Compare the concentration vs. distance plots. Plume behavior along the contaminant flowpath is:

    i. Receding if the concentration in plume trends decrease over time and a sentinel well beyond the plume front remains clean. (see Figure 2)

    ii. Stable if the concentration in plume trends remain the same overtime and a sentinel well beyond the plume front remains clean.

    iii. Advancing if the plume trends increase in concentration over time OR a sentinel well beyond the plume becomes contaminated.

Temporal Trends along Plume Centerline
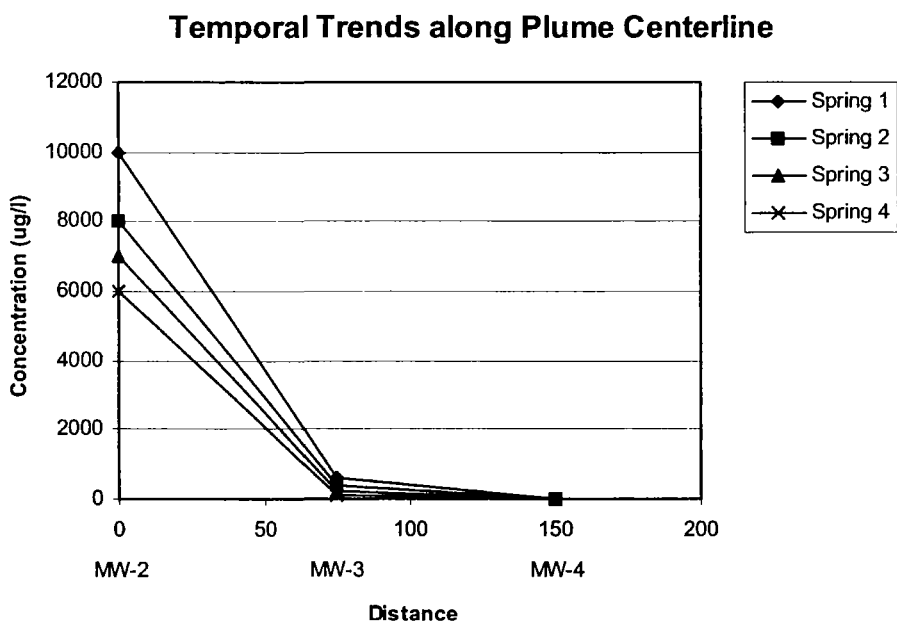
Figure 2. Example of a Receding Plume.
Contaminant concentrations along the plume centerline are decreasing with time at all monitoring points.

3. Statistical Test of Plume Behavior

There are several statistical methods available to evaluate contaminant trends in groundwater. These include Wilcoxon rank sum test (also known as the Mann-Whitney U test), Sen's test, and the Seasonal Kendall test (Gilbert, 1987). The Mann-Kendall Test, described in Appendix A, is a simple test for trend. Mann-Kendall is a non-parametric test and as such, it is not dependent upon the magnitude of data, assumptions of distribution, missing data or irregularly spaced monitoring periods. Mann-Kendall assesses whether a time-ordered data set exhibits an increasing or decreasing trend, within a predetermined level of significance. While it is expected that a stable plume will pass the no-trend null hypothesis of the Mann-Kendall test, this alone does not necessarily mean the plume is stable. This is because the Mann-Kendall test does not take into account magnitude or

variation of the data. Therefore, data sets that exhibit no trend in the Mann-Kendall analysis should also test for data variability by assessing the coefficient of variation, or a similar assessment tool.

The Mann-Kendall test has several limitations and should be used with caution. The following should be considered before relying on results of the Mann-Kendall test to determine trends in contaminant data:

a. The Mann-Kendall test requires 4 to 10 rounds of data that are <u>NOT</u> influenced by seasonal effects. This means the investigator must either determine that the data is not influenced seasonally or collect data from the same season of the year for at least 4 years. Another option is to use the Seasonal Kendall test (Gibbons, 1994) which includes seasonal variability in the analysis.

b. Statistical confidence increases with the number of data points available. The more data there are, the more likely that the Mann-Kendall test will discern a trend. While the test can use as few as 4 data points, often these are not enough data to detect a trend. A "no trend" finding with few data points does not always indicate a stable plume. This situation more likely indicates there are too few data to determine a trend. Therefore, it is highly recommended that at least 6 or more data rounds be collected before using the Mann-Kendall test to assess data trends.

4. <u>Determining Plume Behavior in Low Permeability Materials</u>

It is difficult to determine plume behavior in low permeable saturated materials (defined as K ≤ 10^{-5} cm/sec) because preferential flow pathways primarily control plume movement. These preferential flow pathways include interbedded permeable units, gravel backfilled utility trenches below the water table, fractures in overconsolidated glacial tills, building foundations, etc. Determining plume behavior at these sites may include:

a. Survey the site for preferential contaminant flow pathways. If a contaminant flow pathway exists, monitor the pathway and determine if action needs to be taken to limit contaminant movement within the pathway.

b. Install and monitor a water table well and piezometer immediately downgradient of the source zone. Fractures can channel contaminants vertically to deeper, more permeable units.

c. Identifying the location of nearby utilities. Does the plume intersect a gravel-filled utility trench? Could vapors or contaminated groundwater flow along the trench? If the plume intersects a utility trench, monitoring within the trench should be conducted to ensure that vapors and/or groundwater are not migrating and posing a threat to receptors. See "Guidance for Documenting the Investigation of Utility Corridors for Petroleum Releases", currently under development by the Department.

d. Identifying whether fracture flow controls plume movement. Consider the possibility of plume movement along fractures if the plume shape or extent is not explainable through other characteristics of the saturated material.

e. Statistical analysis or graphic analysis of the groundwater data may produce a trend in the contaminant plume. See discussion above for details on these methods.

f. Compare expected groundwater flow velocity with contaminant velocity. If contaminants are moving faster than predicted, preferential flow paths likely exist.

g. If there are no preferential flow pathways, groundwater movement is usually very slow in these systems, therefore consider sampling groundwater annually (at the same season

each year) for several years to determine if significant changes occur in the plume. If changes are not detected, the plume can be considered to be stable.

B.   Interpretations of Plume Behavior

Criteria for interpreting plume behavior follow. These definitions cannot be applied to contaminant migration along anthropological pathways (e.g., contaminant plumes migrating along sewer lines).

1. Receding Plume. A receding plume indicates that natural attenuation rates are greater than source zone contaminant releases to groundwater. A receding plume indicates source zone contaminants are nearly depleted. A receding plume is characterized by a:
    a. Receding plume margin and decreasing contaminant concentration trends within the source zone and plume; or
    b. Decreasing contaminant concentration trends within the plume and a stable plume margin; or
    c. Negative Mann-Kendall statistics of S, with $S \leq S_{max}$ occurring at an α level of significance of 0.20 or less. (See Appendix A for a discussion of the Mann-Kendall Test.)

2. Stable Plume. A stable plume indicates that natural attenuation rates are equal to the source zone contaminant releases to groundwater. A stable plume is characterized by the following conditions:
    a. Stable plume margin, stable contaminant concentration trends within the source zone and within the plume or
    b. Mann-Kendall statistics of S = 0 or near zero means that the no-trend hypothesis cannot be rejected at an α level of significance. Estimate the coefficient of variation to assess whether more data collection is necessary.

3. Advancing Plume. An advancing groundwater plume indicates that natural attenuation rates are less than the source zone contaminant releases to groundwater. In this case, natural attenuation cannot be relied upon as the sole remedy for groundwater and additional remedial actions are necessary. A plume is considered to be advancing if any of the following occurs:
    a. A monitoring well installed at or near the leading edge of the plume demonstrates increasing contaminant levels for any single contaminant over three or more consecutive rounds of sampling.
    b. A private or public water supply well within the plume demonstrates detectable, increasing contaminant levels for any single contaminant over two or more consecutive rounds of sampling. Contaminant levels may be lower than the preventive action limit (PAL) and meet this criterion.
    c. Wells within the source zone or plume demonstrate increasing contaminant trends over 3 or more consecutive rounds.
    d. Statistical analysis produces a positive Mann-Kendall statistic of S, with $S \geq |S_{max}|$ at an α level of significance of 0.20 or more.

4. Additional Considerations for Plume Behavior.

   a. Variation in groundwater gradients or infiltration rates can cause the plume centerline to shift away from the established monitoring well network. Under these conditions, it may be necessary to perform additional site investigation to determine plume behavior.
   b. Declining contaminant trends in the source zone alone are not sufficient to establish that a plume is stable or receding. Contaminant mass can migrate from the source zone with little retardation or degradation downgradient. For example, methyl tertiary butyl-ether (MTBE) can exhibit this behavior.
   c. Significant changes in the source zone may cause contaminant trends to reverse. Pavement removal or a rising water table can cause increased leaching from contaminated soils. A plume that was formerly stable or receding may begin to advance under these or other changing site conditions.

V. Conditions Where Natural Attenuation Should Not Be Used as a Sole Remedy for Groundwater Contamination

There are conditions where natural attenuation should not be the sole remedy to address groundwater contamination. These conditions include:

1. Advancing Groundwater Plume. An advancing groundwater plume indicates that contaminant release exceeds the natural attenuation capacity of the system to control the contaminants. Natural attenuation cannot be applied as the sole remedy at a site with an expanding contaminant plume. Subsections NR 140.24(2) and 140.26(2), Wis. Adm. Code, state in part that responses shall be implemented to prevent any new releases of substances from traveling beyond the applicable point of standards application. For a spill site (which includes all petroleum releases), the "point of standards application" to determine if a PAL or ES has been exceeded is every point at which groundwater is monitored. If a contaminant plume advances and causes PAL or ES exceedances in a new area, that advance constitutes a "new release" into a formerly uncontaminated portion of groundwater. Therefore, one or more feasible remedies should be implemented until the plume is no longer advancing and until natural attenuation processes by themselves will prevent further plume migration, i.e., the plume margin is stable or receding.

2. Bedrock Contamination. The efficacy of natural attenuation in bedrock is unknown at this time. Natural attenuation processes, including sorption, cation exchange, biodegradation, hydrolysis, etc., are not as effective in bedrock, particularly fractured bedrock, environments. (Some bedrock groundwater systems are so weathered and fractured that they behave as porous media, however this is not common.) The microbes involved in contaminant degradation are usually attached to soil surfaces and fractured bedrock has little surface area for microbe attachment. Groundwater flow through fractures allows minimal contact between microbes and dissolved contaminants.

   Fractured bedrock presents a very complicated geologic and hydrogeologic setting for monitoring contaminant movement and natural attenuation processes. Groundwater flow in fractures can be several orders of magnitude faster than in porous media, allowing

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contaminants to spread farther and faster. In general, natural attenuation cannot be applied as the sole remedy at a site with bedrock contamination.

3. Contaminated Receptors. Natural attenuation will usually not be the sole remedy for contaminant plumes that are intercepted by potable groundwater wells, surface water bodies, or other anthropologic or environmental receptors. Anthropological pathways (e.g., utility trenches) have the potential to spread contaminants far beyond the site. The degree and extent of contaminant movement along anthropological pathways should be identified before the effectiveness of natural attenuation can be assessed.

4. Presence of Liquid Petroleum Product. Natural attenuation cannot be used to remediate free product, unless free product removal has been conducted to the maximum extent practicable, in accordance with ss. NR 708.13, NR 722.09(2), Wis. Adm. Code, and federal regulations (40 CFR 280.64).

VI.   Site Investigation Report (NR 716.15)

In addition to the report contents listed in s. NR 716.15, Wis. Adm. Code, the following information should be included in the site investigation report when natural attenuation is being considered as a remedy for the site, in order to provide sufficient information to permit evaluation of natural attenuation, as required by s. 716.11(3)(b), Wis. Adm. Code.

1. Assess the contaminants of concern and evidence that these contaminants are naturally attenuating. Determine if natural attenuation can serve as a remedy for all contaminants at the site or if there are contaminants that may be recalcitrant to natural attenuation, such as MTBE, TMB, chlorinated compounds, etc.

2. Delineate the contaminant concentrations in the source zone, including the unsaturated soils, saturated materials, and dissolved in groundwater. Where necessary, estimate the contaminant mass in the source zone.

3. Assess the potential for the plume to dive within the aquifer and for seasonal shifts in groundwater flow direction.

4. Assess the adequacy of the monitoring well network to provide information on natural attenuation of the plume. Determine plume behavior.

5. Perform an initial assessment of natural attenuation processes, including an evaluation of geochemical data and determine the presence of appropriate site conditions for natural attenuation. This assessment is often best presented through maps, cross-sections and data plots.
   a. Water table/piezometric maps. Prepare a water table map(s) and a piezometric surface map if there are 3 or more piezometers screened at similar depths in the same geologic unit.
   b. Contaminated plume map. On the water table map, document the extent and concentration of dissolved hydrocarbons, labeling each monitoring point with the contaminant concentration for each compound. Plume maps can be used to assess

plume changes over time, thereby providing the primary evidence for the effectiveness of natural attenuation.

c. Plot of water level variation. Prepare a set of hydrographs for at least 3 monitoring wells along the centerline of the plume: an upgradient, source zone, and downgradient well. Include a piezometer on the hydrograph, if available. Note on the hydrograph any point in time when a water table well screen is completely submerged. Use the same scales for all hydrographs.

d. Geologic cross-sections. Where possible, include at least two geologic cross-sections:
   i. parallel to the centerline (flowline) of the plume, and
   ii. perpendicular to the center flowline **through the source zone**. Include the vertical extent of contaminants in the source zone.

e. Map the extent of subsurface contamination. The following can be compiled onto one map or mapped separately: extent of free product; extent of residual phase product; the horizontal and vertical distribution of contaminants in the unsaturated source zone; and extent of smear zone below the water table.

SECTION 2

DATA ANALYSIS FOR NATURAL ATTENUATION

This section outlines the analyses available to assess the effectiveness of natural attenuation processes. The effectiveness of natural attenuation as an acceptable remedial measure is based upon decreasing contaminant concentrations in groundwater together with a stable or receding contaminant plume. For sites where data are not sufficient to demonstrate reduction in contaminant concentrations in groundwater, other evidence can be used to demonstrate the potential for natural attenuation to serve as a remedial action. These second and third lines of evidence provide support for showing natural attenuation is an effective remedy, but are not sufficient evidence on their own to demonstrate the effectiveness of natural attenuation.

Demonstrate the effectiveness of natural attenuation by analyzing and integrating site characterization data into the conceptual model. A number of assessment tools are recommended in this section. Sections NR 716.15, NR 722.13, and NR 726.05, Wis. Adm. Code, list requirements for data analysis and submittal. It is not necessary to use all of the assessment tools discussed in this section at every site. The choice of which calculations, trend analyses, etc. to prepare should be based upon administrative code requirements, the complexity of the site and the usefulness of the assessment tool in understanding site geology, contaminant distribution and movement, and natural attenuation processes.

I.   Lines of Evidence Supporting Natural Attenuation

In 1993, the National Research Council proposed three lines of evidence to assess natural attenuation processes. The three part strategy includes:

- Decreasing trends in groundwater quality data for the contaminants of concern, using historical data.
- Geochemical data indicative of biodegradative processes in the groundwater.
- Microcosm studies to demonstrate degradation within the contaminated soil and groundwater system.

Analyses of the primary and secondary lines of evidence are emphasized in this guidance. The third line of evidence, microbial studies, and other supporting data, such as fate & transport models and tracer studies, are most useful for recalcitrant contaminants or at sites in complex geologic settings.

A.   Primary Line of Evidence – Decreasing Contaminant Trends

Decreasing contaminant concentrations with time in conjunction with a stable or receding contaminant plume are primary evidence that natural attenuation processes are effective.

Procedures for assessing declining trends are discussed in this section and in Appendix B. Be aware that results of initial investigations do not usually contain enough data to assess contaminant trends with time. Long-term monitoring is usually needed to assess data trends. If data trends cannot be assessed, or are inconclusive, secondary lines of evidence can be used to support the assertion that natural attenuation processes have a potential to remediate the groundwater.

B.   Secondary Line of Evidence – Trends in Geochemical Parameters

Natural attenuation depends upon both the contaminant's reactivity and the site's geologic and chemical characteristics. Assessment of the changes in a site's geochemical environment constitutes a secondary line of evidence. Geochemical parameters for petroleum contaminants typically include dissolved oxygen, nitrate, dissolved manganese, ferrous iron, sulfate, methane, alkalinity, oxidation-reduction potential, pH, temperature and conductivity. Section 3 describes sampling and analysis of the geochemical parameters. This section and Appendix B describe methods to assess the results of geochemical analysis.

C.   Third Line of Evidence – Microbial Studies and Other Analysis

The National Research Council originally proposed the use of laboratory assays showing that microorganisms from a contaminated site had the potential to degrade the contaminants of concern. Petroleum degrading microorganisms are found to be ubiquitous in soil and groundwater. However, microbes at a given site may not be able to degrade certain petroleum additives, such as MTBE. The third line of evidence is expanded here to include all other assessments not included in the first two lines of evidence. In general, it is not necessary to perform any evaluation included under the third line of evidence unless the first two lines of evidence do not support the use of natural attenuation as a remedy.

II.   Data Requirements

Basic data, collected during the site investigation, are necessary to quantitatively assess natural attenuation processes. Hydraulic parameters and contaminant velocity are critical to site assessment and contaminant movement. Equations and examples of the assessment methods listed in this section can be found in Appendix B.

The following data are needed to complete the assessments presented in this section. The investigator should determine which assessments to use for a specific site. This will govern the actual data needs for each site.

1. Groundwater elevation for all sampling rounds, for each monitoring well.
2. Contaminant concentration for all sampling rounds, for each monitoring well.
3. Concentration or measurement of geochemical parameters for all wells.
4. Hydraulic conductivity (K) for the primary contaminant flow paths.
5. Horizontal hydraulic gradient ($\Delta h/\Delta l$) and vertical gradient ($\Delta h/\Delta z$) for the primary contaminant flow paths.
6. Effective porosity (n_e) for the primary contaminant flow paths.

7. Bulk density (ρ_b) of aquifer solids.
8. Organic carbon/water partition coefficient (K_{oc}) for each contaminant.
9. Fraction of organic carbon content (f_{oc}) for the aquifer material along the primary contaminant flow paths.
10. Location and horizontal and vertical dimensions of contaminant source area.
11. Estimate of contaminant mass in source area, including soils (M_s), saturated zone material (M_{sz}) and dissolved phase (M_{gw}).

III. Primary Line of Evidence – Contaminant Trend Analysis

Most trend analyses require at least 4 rounds of monitoring. More data is often necessary, especially if the groundwater level or flow direction fluctuates seasonally. The analytical techniques included here are examples of approaches that may be used to show that contaminant mass and concentration is decreasing in groundwater.

A.   Estimates of Contaminant Decay Rate in Groundwater

Several methods exist to estimate contaminant decay rate. Several approaches are presented here and in Appendix B. Other approaches may be acceptable. **These analyses apply only to the reduction of contaminant mass in the groundwater. They do not apply to reduction of contaminant mass in the source area. If free product or residual product is present, much longer time frames will be required to degrade contaminants than indicated by the calculations below.**

1. Batch Flushing. The rate of removal of contaminants remaining in the groundwater may be estimated as clean water flushes through the contamination. This approach should only be used where the contaminant source has been completely removed. See Appendix B for an example calculation.

2. Concentration - time plot for each contaminated well. Prepare a semi-logarithm plot of concentration versus time for every contaminated monitoring well at the site. Evaluate the data to determine if a trend exists. Appendix B contains an example of assessing concentration-time plots. The hydrograph for a well can be combined with the concentration-time plot for the same well to produce a single graph. If this data is plotted separately, use the same time scale to present the information, so that variation in water level can be directly compared to variation in concentration.

3. Concentration - distance plot along the centerline of the plume. Prepare a semi-logarithm plot of concentration versus distance that includes all monitoring wells (water table and piezometers) located along the plume centerline. Appendix B contains an example of a concentration – distance plot. Concentrations of contaminants will decrease with distance from a source area due merely to dispersion. To demonstrate that natural attenuation is an effective remedy, a series of these plots should show decreasing contaminant concentrations through time and the sentinel monitoring wells should remain uncontaminated.

4. Concentration vs. Travel Time Plot. An alternative to the Concentration vs. Distance Plot is a Concentration vs. Travel Time Plot. This analysis may be preferred in where hydraulic conductivity changes along a flow path. Just as with the concentration – distance plots, these plots should be compared in a time series to show natural attenuation is an effective remedy. See Appendix B for an example calculation.

5. Mann-Kendall Analysis for Trend. Contaminant trends can be analyzed using the Mann-Kendall statistical test, described in Appendix A. The Mann-Kendall test can help determine data trends but will not provide estimates of contaminant decay rates, as the above approaches do.

B.   Estimates of Contaminant Decay Rate in the Source Zone

Estimates of contaminant decay in the source zone may be necessary if monitoring of the contaminant plume does not demonstrate reduction in contaminant mass and concentration in groundwater. If significant contaminant mass remains in the source area (as free or residual product) and continues to enter the groundwater, groundwater contaminant concentrations may remain high and not demonstrate a downward trend. Under these conditions, an estimate of contaminant source lifetime is needed to determine how long groundwater will remain contaminated. The examples presented in Appendix B are intended to serve as tools to understanding natural attenuation at a given site. Estimates of mass loss using these tools do not represent actual subsurface reactions. Gross simplifications of the subsurface are required in these estimates. Due to the lack of knowledge of actual reaction kinetics in the subsurface and other simplifications, monitoring must be relied upon to observe contaminant degradation and mass reduction.

1. Mass Flux Method. This method assumes that decay of contaminant mass in the source occurs only through dissolution into the groundwater. It is a conservative estimate of the source lifetime and is applied where source area groundwater well(s) exhibit constant contaminant levels.

2. First Order Decay of Contaminant Source. If the contaminant source is decreasing, as evidenced by a source area groundwater monitoring well and if the observed decay fits a first order decay rate, then this approach can be applied to estimate how quickly natural attenuation processes will reduce the contaminant mass in the source area. **This calculation is not applicable to non-first order decay rates or in cases where there is no observed decrease in source area concentrations.**

IV. Secondary Line of Evidence – Trends in Geochemical Parameters

Changes in electron acceptors and metabolic byproducts can be easily assessed through mapping. However, it is difficult to map these changes at some sites. Tables or plots presenting concentrations of electron acceptors, metabolic byproducts and alkalinity upgradient, in the source zone and downgradient can be substituted for the isoconcentration maps. All geochemical parameters do not need to be analyzed during all sampling rounds. Site specific data will determine which electron acceptors and metabolic byproducts are most useful for assessing natural attenuation processes. Prepare plots or tables for those geochemical parameters measured at a site.

A. Assessing Geochemical Trends

1. <u>Electron Acceptors</u>. Plot isoconcentration maps or a distribution plot (using the water table map as a base map) for dissolved oxygen, nitrate, and sulfate for at least one round of data. During biodegradation microbes directly utilize these compounds. If biodegradation is occurring, it is expected that oxygen, and perhaps nitrate and/or sulfate will be depleted within the dissolved plume.

2. <u>Metabolic Byproducts</u>. Plot isoconcentration maps or a distribution plot (using the water table map as a base map) for dissolved manganese (Mn^{2+}), dissolved iron (Fe^{2+}), and methane (if methane is analyzed) for at least one round of data. These compounds are byproducts of microbial metabolism and may increase within the dissolved plume.

3. <u>Alkalinity</u>. Prepare a isoconcentration map for alkalinity concentrations using the water table map as a base map, for at least one round of data, if alkalinity is measured. Alkalinity is expected to increase within the plume.

B. Assimilative Capacity

Assimilative capacity is the sum of all the electron acceptor mass utilized in the biodegradation of contaminant mass at the site. The example calculations of assimilative capacity in Appendix B are based upon accepted chemical relationships between electron acceptors and BETX metabolism.

These calculations assume that BETX are the only contaminants providing a demand for electron acceptors. In actuality, the entire mass of organic compounds in the subsurface contributes to the electron acceptor demand. Mass flux of available electron acceptors through the source zone provides an estimate of total mass of organic material (natural and contaminant) degraded rather than total BETX degraded. Therefore, caution should be exercised when using assimilative capacity to estimate length of time for degradation of contaminants of concern.

C.   Screening Models

For most petroleum contaminated sites, sophisticated fate and transport modeling is not necessary to demonstrate the effectiveness of natural attenuation. Screening models, such as BIOSCREEN, can be a useful tool for assessing natural attenuation, if site-specific data for the model are available. It is not appropriate to assume degradation rates or to use literature values for basic model inputs (such as hydraulic conductivity, mass in contaminant source, etc.).

V.   Third Line of Evidence – Microbial and Other Studies

A third line of evidence for natural attenuation is rarely needed at petroleum release sites. These evaluations, however, can support a natural attenuation remedy if groundwater monitoring alone does not establish that contaminant concentrations are decreasing.

1. Laboratory Assays of Microorganism Numbers and Degradative Capacity. Microorganisms adapted to degrade most petroleum contaminants appear to be ubiquitous in soil and groundwater environments. For petroleum releases, microbial assays may be necessary when contaminants appear to be recalcitrant to biodegradation.

2. Conservative Tracers. Wiedemeyer, et.al., present a method to estimate biodegradation using a conservative tracer to correct for dispersion, dilution and sorption of the contaminant. The conservative tracer should be biologically recalcitrant and have chemical properties similar to the contaminant of concern. Often the tracer is itself an existing contaminant (Wiedemeyer, et. al., use trimethylbenzene). Injection of groundwater tracers requires the approval of the Department's Bureau of Drinking Water and Groundwater.

3. Groundwater Fate & Transport Models. Numerical fate and transport models can be useful for large, complicated contaminated groundwater sites. Most petroleum sites do not warrant the use of fate and transport models; however, at sites that warrant this level of effort, these models can be very helpful to guiding the site remediation.

4. Groundwater Sampling for Metabolites of Biodegradation. BETX microbially degrades into a variety of compounds, such as methylbenzylsuccinic acid isomers, and other aromatic compounds (Gieg, et.al., 1999). Other contaminants also have signature degradation products. Detection of metabolites strongly indicates degradation of contaminants.

5. Soil testing through time. Contaminated soil and saturated material in the source zone can be sampled over time to determine whether residual contaminant mass is decreasing, even if dissolved contaminant concentrations remain constant.

VI. Progress Reports

Submit the appropriate pages of Department of Natural Resources Form 4400-194 (Operation, Maintenance, Monitoring and Optimization Reporting of Soil and Groundwater Remediation Systems) for on-going natural attenuation monitoring after submittal of the site investigation report. Section NR 724.13(3), Wis. Adm. Code, provides that, unless otherwise directed by the Department, progress reports are to be submitted quarterly. However, in most case where monitoring is being conducted to assess natural attenuation processes, the Department directs responsible parties to submit annual progress reports.

VII. Remedial Action Options Report or Closure Report

Site data, including a demonstration of the effectiveness of natural attenuation, should be summarized and submitted to the Department in either a Remedial Action Options Report (in accordance with the requirements of s. NR 722.13, Wis. Adm. Code) or in a Closure Report (under s. NR 726.05, Wis. Adm. Code). A Remedial Action Options Report allows the investigator to evaluate the remedial actions most appropriate and cost effective for site cleanup and document the choice of remedial action for the site. These are especially useful at sites where a "treatment train" of remedies, including both active remediation and natural attenuation, are the most cost-effective approach to cleaning up the contaminated site.

When natural attenuation constitutes part or all of the selected remedy, the following information should be included in the Remedial Action Options Report. When a RAOR is not submitted, this information should be submitted in the Closure Report or closure request.

1. Proposed or completed source control action.

2. Trend analysis of contaminant data, which can include such things as concentration vs. distance along the plume centerline, concentration vs. time in the source zone wells and for wells within the contaminant plume, and comparison of isoconcentration maps of contaminants.

3. Analysis of water level changes with time and effect of water level on contaminant trends.

4. Spatial trends of electron acceptors in the groundwater.

5. Actions proposed to address recalcitrant contaminants, if these contaminants are present at the site.

SECTION 3

NATURAL ATTENUATION MONITORING RECOMMENDATIONS

I.   Geochemical Parameters as Indicators of Natural Attenuation

A.   Introduction

Geochemical indicators are secondary support for demonstrating that natural attenuation processes can control contaminant movement and ultimately remediate groundwater contamination. Geochemical parameters can be used to:

1. indicate the presence of appropriate site conditions for natural attenuation;
2. indicate subsurface biological activity;
3. estimate aquifer capacity to degrade contaminant mass;
4. aid in determining monitoring well placement;
5. assess field sampling techniques; and
6. determine constancy of groundwater quality conditions.

The geochemical parameters selected for monitoring are based upon the sequential use of terminal electron acceptors as microorganisms consume petroleum contaminants. Terminal electron acceptors (TEA) and the sequence of use are:

$$\text{dissolved oxygen (DO)} > \text{nitrate (NO}_3^-\text{)} > \text{manganese (Mn}^{+4}\text{)} > \text{ferric iron (Fe}^{+3}\text{)} >$$
$$\text{sulfate (SO}_4^{-2}\text{)} > \text{carbon}$$

The use of a specific TEA is closely related to the oxidation-reduction potential (ORP) of the groundwater. The more reducing the groundwater conditions, the greater the depletion of the available electron acceptors. Source zone groundwater usually exhibits the greatest depletion of TEA.

Geochemical parameters monitor TEA directly (e.g., DO, NO_3^- and SO_4^{-2}) or monitor the byproduct of the metabolized TEA (e.g., Mn^{+2}, Fe^{+2}, and methane). Other geochemical parameters include oxidation-reduction potential (ORP), pH, alkalinity, temperature and specific conductivity. Table C-1 (in Appendix C) lists the geochemical parameters, their use and changes expected with biological activity.

B.   Data Quality

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

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

The goals of the monitoring program will determine the level of precision and sensitivity needed for the geochemical indicators. <u>Base the choice of sampling and analytical methodologies on the goals of the monitoring program</u>. Often, geochemical parameters are used in a more qualitative fashion to determine changes within the groundwater plume over time and/or compared to upgradient, uncontaminated groundwater. Therefore, there is no standard or "correct" concentration for geochemical parameters. For on-going, natural attenuation assessment, the monitoring philosophy should be "use whatever works". This includes the use of field or laboratory methods that give an accurate representation of site conditions. Because many geochemical parameters are sensitive to redox conditions, field generated data will often produce better quality data than laboratory analysis. For instance, levels of dissolved oxygen, ORP, dissolved manganese, and ferrous iron rapidly change upon exposure to the atmosphere. Field analytical methods for these compounds will likely produce data that is more representative of actual site condtions.

If a round of geochemical data is to be used in a quantitative manner (for instance, to determine assimilative capacity of the groundwater) then select field or laboratory methods which will give data the highest known quality that is practical. Recognize that the sampling and analysis decisions should take into account the assumptions and limitations of calculating total assimilative capacity (discussed in Appendix B).

II.   Methods of Collecting & Analyzing Samples for Geochemical Parameters

The objective of groundwater data collection methods is to collect data representative of groundwater quality in the vicinity of the monitoring well. Close attention must be paid to the following aspects of sample collection and analysis: well purging, sampling methodology, and

choice of analytical technique. Contaminated groundwater is often in dramatic non-equilibrium with atmospheric conditions (API, 1997). Exposure of the groundwater sample to the atmosphere can cause significant and instantaneous shifts in sample geochemistry. In addition, sample turbidity can also bias the geochemistry of the sample. Table C-2 in Appendix C lists the potential effects of aeration and turbidity on sample integrity. Limiting sample aeration and turbidity to the extent practical will help ensure good quality groundwater data and will improve assessment of natural attenuation processes at a site.

In choosing methodology for well purging, sampling and analytical methods, consider the use of the data. If the geochemical parameters are used to assess data trends across a site, lessor quality data may be acceptable. If the geochemical parameter data is used quantitatively to assess degradation capacity, then higher quality sample collection and methodology is necessary. Refer to the Department's Groundwater Sampling Desk Reference and Groundwater Sampling Field Manual for a detailed discussion of pump types, sampling methodology, etc.

A.   Well Purging

1. Low Flow Purging/Sampling. Low flow purging with closed flow-through cell for parameter measurement (e.g., DO, pH, ORP, Temperature, Specific Conductance) will produce data of highest quality. In addition, samples for iron and manganese collected with low flow methods do not require field filtering. Low flow purging is a method to achieve equilibrium levels for all parameters quickly while generating very little purge water. For wells in permeable formations, low flow purging is defined as < 1 L/min (0.26 gpm) and low flow sampling is defined as < 300 ml/min (0.1 gpm). The following techniques should be used:

   a. Water level in the well should not decrease significantly. If the water level declines, reduce the pumping rate to the extent possible.
   b. Purge groundwater until measurement of flow-through cell parameters has stabilized.
   c. Record parameter values from the flow-through cell and collect groundwater samples.

2. Bailer Purging/Sampling. The bailer method tends to aerate groundwater within the well, stir up sediment from the bottom of the well, and result in aeration above ground when the sample is transferred into sample bottles. If a bailer is used to purge/sample wells, use the following technique:

   a. Measure DO and ORP at the well screen with a downhole probe before and after purging. Use the lowest DO and ORP reading as representative of the formation water. Avoid measuring DO and ORP on a water sample taken from a bailer.
   b. Mark the bailer line at a length a few inches shorter than the depth of the well to avoid suspending sediment from the well bottom.
   c. Slowly lower and raise the bailer in the well water to avoid a surge effect within the well.
   d. Collect samples using a bottom emptying bailer attachment. Fill sample bottles completely. Sample bottles containing a head space aerate groundwater samples, thereby changing water quality.

3. Standard Pump Purging/Bailer Sampling. Purging groundwater from a well at a high rate and subsequently bailing the well to obtain samples can significantly bias sample results, particularly for DO, ORP, dissolved manganese, ferrous iron and methane. Significant

water draw down in a well results in water cascading down the well screen and equilibrating with the atmosphere. For this reason, this method of sample collection should be avoided. However, if it is used, then the following techniques will help minimize sample disturbance:

a. Measure DO and ORP at the well screen with a downhole probe before and after purging. Use the lowest DO and ORP reading as representative of the formation water. Avoid measuring DO and ORP on a water sample taken from a bailer.
b. Turn down the purge rate on the pump. Try to avoid drawdown in the well screen of more than 5%.
c. Use a bottom emptying bailer to collect samples into bottles. Fill sample bottles completely. Sample bottles containing a headspace aerate groundwater samples.

B. Sample Methodology for Geochemical Parameters

For field generated data, document the field methodology and quality control procedures used to generate data. It is preferable to have laboratory samples analyzed in a NR 149 certified laboratory. However, certification is not required. If a non-NR 149 certified laboratory is used for analysis of geochemical parameters, document the quality control and quality assurance procedures used for the analyses.

Consult the Department's Groundwater Sampling Desk Reference and Groundwater Sampling Field Manual for information on sample collection, sample container, holding times, preservation methods, etc. This discussion focuses on the impact of sampling methodology on accuracy of selected natural attenuation parameters.

The following provides general information on each TEA and suggests sample monitoring guidelines.

1. Dissolved Oxygen (DO)

    Oxygen consumption provides the greatest amount of energy to microbes during metabolism. Typically, oxygen will be absent throughout the plume and an "oxygen sag" zone (zone of lower oxygen compared to uncontaminated background levels) will be present beyond the front of the plume, because oxygen-depleted groundwater moves faster than groundwater contaminants. A properly designed monitoring program will include a monitoring well at the far downgradient edge of the plume in the "oxygen sag" zone. The oxygen sag precedes the plume, so placement of a well screen in this zone allows detection of an advancing plume. In addition, a monitoring well in the oxygen sag zone gives the investigator confidence that the contaminant flow pathway has been identified.

    It is recommended that DO be measured at every well during every sampling round conducted at a site to:

    a. identify potential changes in plume configuration;
    b. confirm consistency of upgradient water quality;
    c. confirm the quality of groundwater sampling techniques at the site (see sample collection methods below); and
    d. confirm the presence of aerobic degradation processes at the site.

Analyze DO in the field with an oxygen probe, field test kit, or other method sensitive to dissolved oxygen concentrations between 0 and 10 ppm. Accurate DO measurements require the use of purging, sampling, and analytical techniques that do not introduce air to the water column or sample. Assess DO before and after purging each well and use the lowest DO reading obtained as being representative of the groundwater conditions. In some cases, purging may not be necessary to obtain accurate DO measurements; however this should be confirmed by comparing non-purged and purged DO readings. Use consistent sampling and analytical methodologies on all monitoring wells to ensure comparability of the data.

2. Nitrate (NO_3^-)

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

Nitrate is often analyzed by methods that measure nitrate (NO_3^-) + nitrite (NO_2^-). It is acceptable to use nitrate+nitrite as a measure of nitrate because nitrite makes up a small percentage of total nitrogen at the vast majority of sites. As noted above, only a portion of nitrate utilization will generate nitrite. In addition, nitrite is not stable under most environmental conditions and will quickly convert to ammonia. Nitrate specific analysis is also acceptable. However, because nitrate-only samples are not preserved, it is important that the samples be analyzed within 48 hours. Otherwise, bacterial action will convert the nitrate and bias the sample.

It is recommended that nitrate be measured at least twice to determine if it is a TEA at the specific site. If nitrate is acting as a TEA, sampling should occur at least once a year thereafter. At this time, laboratory measurement of nitrate is preferred over field techniques. Field methods may evolve to provide accurate nitrate data. The use of the brucine sulfate method to measure nitrate is not recommended because of high variability in the sample results.

3. Manganese (Mn^{+2})

Manganese (+4) is reduced to soluble manganese (+2) by microbial activity. Midwestern soils often contain manganese (+4) and this TEA can contribute significantly to the contaminant degradation capacity of an aquifer. It is recommended that dissolved manganese (Mn^{+2}) be monitored at least twice to determine if manganese is present as an electron acceptor. If manganese is acting as a TEA, sampling should occur at least once a year thereafter.

Dissolved manganese (Mn^{+2}) is very sensitive to oxidation. Therefore, in-line filtering of manganese is recommended with subsequent field or laboratory analysis for total manganese. (Field filtering will remove insoluble Mn^{+4}, so that a total manganese analysis should reflect Mn^{+2} in the sample.) Field test kits are available for total (not soluble) manganese. However, manganese dioxide, the typical form of Mn^{+4}, is relatively insoluble, therefore the test kits may be fairly accurate for dissolved manganese (Mn^{+2}). Field test kits may be biased high by turbid samples, so in-line filtering or low-flow sampling is important in obtaining an accurate manganese concentration. If turbid samples are analyzed using a colorimetric method, determine how much "color" the turbidity contributes to the sample before determining the manganese concentration.

4. Ferrous Iron (Fe^{+2})

Available ferric iron (Fe^{+3}) on soil surfaces can serve as a TEA and be reduced to soluble ferrous iron (Fe^{+2}). Not all ferric iron can be utilized by microbes as a TEA and measurement of total iron or ferric iron is of little use in understanding subsurface biological processes at a site. Ferrous iron is an indication of reducing conditions and microbial activity, but is very sensitive to the presence of oxygen and readily oxidizes to the ferric form. Therefore, great care must be used in sampling and analyzing ferrous iron if this parameter is to be of any value in assessing biodegradation capacity at a site. It is recommended that ferrous iron (Fe^{+2}) be monitored at least twice to determine if iron is serving as a TEA. If iron is acting as a TEA, sampling for Fe^{+2} should occur at least once a year thereafter.

Ferrous iron is generally measured by one of two methods:

a. Immediate field filtering of samples for removal of insoluble ferric iron followed by laboratory analysis for total iron. This method actually measures dissolved iron rather than ferrous iron, with the assumption that soluble ferric iron is negligible in the groundwater. At neutral pH and with exposure to air, almost all soluble ferrous iron will precipitate out of solution within 1 minute or less. Therefore, filtering of iron samples should be done with cartridge-style filters, in-line filters or other systems that exclude contact with the atmosphere.
b. Field methods for ferrous iron analysis. Because field test kits are specific for ferrous iron, field filtering is not necessary. However, the instability of ferrous iron in the presence of oxygen and sunlight can severely limit the usefulness of the test kit data. Samples must be analyzed immediately after collection.

If a colorimetric method is used to determine ferrous iron, determine if the sample is turbid. Determine how much "color" the turbidity contributes to the sample before determining the iron concentration.

5. Sulfate (SO_4^{-2})

During microbial metabolism, sulfate (SO_4^{-2}) is reduced to sulfide (S^{-2}), which subsequently forms metal sulfide precipitates. Sulfate can be readily analyzed by laboratory methods and is not particularly sensitive to oxidation changes in the sample. It is recommended that sulfate be monitored at least twice to determine if it is serving as a TEA at the site. If sulfate is acting as a TEA, sampling for sulfate should occur at least once a year thereafter.

Sulfate can be analyzed in the field or laboratory. However, automated methods of sulfate analysis are preferred to turbidimetric methods.

6. Methane (CH_4)

Methanogenesis is most likely to occur in the source area due to the high organic carbon content. Detection of methane in groundwater is an indication of very low redox potential of groundwater. It is difficult to establish in the field mass balance relationships between methane production and contaminant degradation (Norris, et. al., 1994).

Methane in water is a more difficult and expensive analysis than the other geochemical parameters. There is no standard U.S. EPA laboratory method for measuring methane in water. In addition, because methane is a gas, it is readily lost from groundwater samples. Methane data can be of little value unless extreme caution is exercised in sample handling. It is recommended that sample collection and handling procedures be carefully documented to determine whether data are comparable to previous sampling events.

These problems create difficulties for establishing the precision and sensitivity of methane data. Therefore, when determining whether to analyze for methane, the investigator should assess the site data needs and the ability to produce methane data that accurately represent site conditions.

7. Alkalinity

Alkalinity is not a TEA. Changes in alkalinity are an indication of microbial activity. Alkalinity reflects the buffering capacity of groundwater and is most influenced by CO_2 content. Carbon dioxide originates from dissolution of carbonates in the aquifer, atmospheric CO_2, and the respiration of microbes. As the sequential TEA are utilized, CO_2 is produced at each metabolic step. Therefore, alkalinity can be expected to increase across a site where biological activity is occurring. Alkalinity titration can be performed in the laboratory or field. It is recommended that alkalinity be measured twice in monitoring wells and at least once a year thereafter.

8. Oxidation-Reduction Potential (ORP)

Oxidation-reduction potential (ORP) changes in groundwater are usually mediated by biological activity, therefore, ORP can be a valuable geochemical indicator. ORP is readily measured with a pair of electrodes and is an easy parameter to incorporate into a monitoring program. As with DO, ORP is extremely sensitive to sample aeration and all air must be excluded during sampling.

ORP data can be difficult to interpret. The ORP reading reflects many chemical reactions within the groundwater, so it is not possible to associate the ORP reading with a specific chemical condition in the groundwater. Data comparability is an issue for ORP measurements because different electrodes (platinum, O_2/H_2O, Fe^{+2}, SO_4^{-2}/H_2S, CO_2/CH_4, etc.) show little agreement with each other. Therefore, if ORP measurements are to be comparable, measurements must be made using the same electrode type throughout the monitoring life of the site. In addition, ORP electrodes tend to exhibit "drift" and become "poisoned" (due to accumulation of oxidation products on the electrode). If these limitations are addressed, ORP can be useful as a qualitative indicator of groundwater geochemistry.

C.   Quality Control Checks for Field Measurements

Perform the following field checks to ensure that the groundwater samples are representative of the formation water (see API Publ. No. 4658).

1. DO and ORP readings should be in agreement. DO should be less than 1 ppm when ORP is negative. If this is not the case, at least one of the measurements is in error.
2. Ferrous iron should be present only if DO is less than 1 ppm and ORP is negative.
3. Compare DO and ORP values in the well water before and after purging. The DO and ORP of the well water after purging should be equal to or lower than the readings prior to purging. An increase of DO and ORP after purging indicates the well water has been artificially aerated by the purging process.

A water sample may have "incompatible" water chemistry, such as the presence of ferrous iron and DO, because of sampling technique (such as artificial aeration) or because of mixed water chemistry. Mixed water chemistry occurs when a well screen intersects both contaminated and uncontaminated groundwater and the water sample exhibits characteristics of both of these zones. When field measurements are not in agreement, effort should be made to achieve measurements that are in agreement by repeated sampling and, if necessary, by using alternative techniques for field purging, sampling and analytical methods. If anomalies persist, it may be useful to consult an analytical chemist to help resolve the inconsistencies. If the chemical anomalies can not be resolved through changes in field technique, the possibility of mixed water chemistry within the well screen should be considered.

III.   Monitoring for Contaminants of Concern

A.   Data Quality

Methods used to sample and analyze groundwater for contaminants of concern should be chosen to generate data with the highest possible certainty. For this reason, sampling

methodology, sample handling, and analytical methods (performed by certified laboratories) must follow administrative rule requirements of the Department. Groundwater sampling and analytical requirements are contained in s. NR 700.13, chs. NR 716, NR 724, and NR 149, Wis. Adm. Code, and other rules, where applicable.

B.   Parameters & Methodology for Petroleum Contaminants

Tables C-3 through C-7 in Appendix C are updated from the Leaking Underground Storage Tank (LUST) Analytical and Quality Assurance Guidance, WI DNR, July 1993. The tables are intended to provide guidance on contaminant characterization and methodology for assessing petroleum releases. For guidance on sample collection and analysis, refer to the Department's Groundwater Sampling Field Manual (Karklins, 1996).

IV.   Monitoring Schedule

A.   Recommended Monitoring Schedule

Table 3-1

Recommended Site Monitoring Schedule

PARAMETER	MONITORING FREQUENCY	SELECTED WELLS
PVOCs and Contaminants of Concern	2 years[1], Quarterly (8 rounds); annually thereafter	All site monitoring wells for 1st 2 years[1]; selected wells thereafter.
Water table elevation	All monitoring rounds	All site monitoring wells
DO, ORP	All monitoring rounds	All site monitoring wells
pH, Temperature, Specific Conductivity	All monitoring rounds	All site monitoring wells
Nitrate, Manganese[3], Ferrous Iron[3], Sulfate, Methane[2], Alkalinity	2 rounds, quarterly; thereafter, analyze those parameters of benefit to assessing NA at specific site on an annual basis[4].	All site monitoring wells for the first 2 rounds. Other rounds: wells along the centerline of the plume.

[1] 2 years quarterly monitoring is recommended. The actual monitoring time frame may be longer or shorter, depending on the ability to demonstrate contaminant trends and plume behavior.
[2] No standard method for analysis.
[3] Sample for iron and manganese the last round before closure to determine if these parameters are above site background levels and exceed NR 140 Table 2, Public Welfare Groundwater Quality Standards.

[4] Collect annual groundwater samples during the same season of the year.

B.   Long Term Monitoring

Consider site setting, hydrogeology, and the ability to gather data on contaminant trends and plume migration when developing a long term monitoring schedule.

1. Monitoring wells to include in monitoring plan. If the plume behavior is stable and predictable, monitoring can be limited to wells along the centerline of the plume. If the groundwater flow direction fluctuates, or if plume behavior is not known, or if the plume is suspected to be advancing, all site monitoring wells should be monitored each round.

   If sample results demonstrate a diving plume where an uncontaminated water table well is nested with a contaminated piezometer, contaminant monitoring of the water table well can be reduced or eliminated. However, continue monitoring water elevation in the water table well.

2. Frequency of monitoring. Section NR 724.17, Wis. Adm. Code, requires that monitoring be conducted at a frequency appropriate to detect any changes in the contaminant plume, especially changes in contaminant concentrations over time and distance. Frequency of monitoring should not be less than once per year, preferably carried out during the same season each year. Annual monitoring for contaminants should be performed during the season that gives the highest contaminant concentrations, based on the results from the first two years of monitoring.

3. Parameters to be monitored. In most situations, PVOCs , contaminants of concern, water table elevation and DO should be monitored at a minimum at the selected wells each monitoring period. Selection and frequency of monitoring other geochemical parameters should be based on the results of the initial site monitoring.

V.   Data Reporting

Data may be reported in any format that is determined appropriate. The following should be included when reporting groundwater monitoring data:

1. Field sampling methodology, including well purging and sample collection methods, pumping rate if pumps are used to purge or sample wells, methods used to collect samples, methods used to field filter, etc. Note sample turbidity on filtered and unfiltered samples. Document the time of day when purging is completed and the time of day when field analysis is completed on each well sampled.

2. Field analytical methods, including use of field instruments and field test kits, instrument calibration, downhole vs. above ground analysis, use of flow through cells, etc. Include quality control and quality assurance methods used, such as duplicate analysis, calibration, etc. Include expected sensitivity and precision of field methods. Report the criteria used for accepting calibration checks and duplicates. (For example: the calibration check sample

must be within ±10% of the expected value, otherwise recalibration takes place. Duplicates must have a relative percent difference (RPD) of ≤ 20%, or additional analysis is performed. Note that these are examples, not requirements for the criteria.)

3. Laboratory analysis, including analytical methods, holding time from sample collection to analysis and quality control and quality assurance checks for the specific analyses.

SECTION 4

REGULATORY REQUIREMENTS FOR SITE CLOSURE WHEN USING NATURAL ATTENUATION AS A REMEDIAL ACTION

The effectiveness of natural attenuation as a remedial action is determined in the context of the conceptual model for the site, the supporting site data and the regulatory requirements. This section summarizes the regulatory requirements for demonstrating to the Department that natural attenuation is an effective remedy and a site may be closed using natural attenuation as the selected remedy. It should be noted this is a summary and should not be used as a "checklist" for closure requests. Please refer to the actual administrative code language for a complete list of requirements.

I. Site Closure Criteria

In accordance with s. NR 726.05(2)(b), when the following criteria are met, a site that has groundwater contaminant levels exceeding the PAL or ES may use natural attenuation as a remedial option and can be considered for closure.

A. Summary of NR 726.05(2)(b)1.a. to e. Requirements, Source Zone & Interim Actions Completed

1. Complete source zone actions, including removal, closure, upgrading or containment of all tanks, pipes, barrels or containers that may discharge petroleum product to the environment. Take additional source control measures to reduce contaminant mass and concentration in the subsurface, where necessary. (NR 726.05(2)(b) 1. a. to c.)

2. Address impacts to receptors, including threatened or impacted drinking water wells; odors in basements; discharge to surface water; etc. (NR 726.05(2)(b) 1. d.)

3. Remove free product to the maximum extent practicable (that is, in accordance with the criteria in NR 708.13 and the requirements of NR 722.09(2), Wis. Adm. Code). (NR 726.05(2)(b) 1. e.)

B. Satisfying the Requirements of NR 726.05(2)(b)1.f. and 2. Related to Demonstrating Effectiveness of Natural Attenuation Processes

The following criteria demonstrate that adequate source control has been achieved and that natural attenuation is reducing the remaining contaminant mass and concentration such that site cleanup goals will be met. Specifically, criteria 1 and 3 or 2 and 3 below should be met.

1. Groundwater monitoring data establishes that the contaminant plume is receding, defined as:
   a. Receding plume margin and decreasing contaminant concentration trends within both the source zone and plume;
   b. Receding plume margin, stable contaminant concentration trends within the source zone and decreasing trends within the plume; or
   c. Receding plume margin and stable contaminant concentration trends within the source zone and plume.

2. Groundwater monitoring data establishes a stable plume, defined as:
   a. Stable plume margin, stable groundwater concentrations and decreasing contaminant trends in source zone;
   b. Stable plume margin, stable contaminant concentration trends in the source zone and decreasing trends in the groundwater plume; or
   c. Stable plume margin and stable contaminant trends within the source and the plume and all of the following conditions exist:
      i.   Source zone actions have been completed to the extent technically and economically feasible.
      ii.   Other supporting data indicates contaminant mass reduction is taking place, such as geochemical indicators, mass loss from the source zone, presence of biodegradation products, etc.

3. Downgradient sentinel well (the monitoring well placed beyond the plume boundary) remains free of contamination.

C.   Satisfying the Requirements of NR 726.05(2)(b)1.f. and 2. Related to Meeting NR 140 Standards Within a Reasonable Period of Time

Section NR 722.07(4)(a)4, "Restoration time frame", outlines eight qualitative criteria to consider whether the site cleanup time frame is "reasonable".

Using the tools provided in this guidance, or other appropriate methods, make an estimate of site cleanup time frame. These estimates may have a significant range between the upper and lower time estimates. Most sites will meet the standard of restoring the groundwater in a reasonable period of time if the following criteria are satisfied:

1. Source zone and interim actions are adequate to achieve site cleanup goals (see 1.A. above).

2. Natural attenuation has been demonstrated to be effective (see 1.B. above).

3. There are no receptors affected or threatened. Establish that existing and probable future receptors are fully protected through the use of the selected remedy. Document pathways of contaminant movement and the location of existing receptors. Land use plans and professional judgment should be used to determine whether future receptors will be affected by the contaminated site.

4. Land use is unlikely to change significantly within the site cleanup time frame.

a. Any existing zoning restrictions and land use plans should be referred to when determining if land use is likely to change, and the existence of zoning restrictions and land use plans that are applicable to the site should be documented as part of the case close out report. However, most land use plans will typically have a limited planning time frame, often 20 years. Professional judgment and knowledge of current land use and feasible future development in an area should be used to determine if land use may change.

b. If no land use changes are planned or expected within the restoration time frame that would adversely impact the effectiveness of the natural attenuation remedy, then, under most circumstances, the estimated site cleanup time frame can be considered "reasonable". If land use changes are anticipated, then more assessment is needed to determine:

   ii.   If the land use changes will affect groundwater use, contaminant pathways, or geochemical inputs needed for the continued effectiveness of natural attenuation;

   iii. If natural attenuation will cleanup the site before the land use changes occur; or

   iv.   If the estimated cleanup time is "reasonable" compared to alternate cleanup remedies that could be implemented at the site.

In addition, for sites contaminated with petroleum products discharged from petroleum storage tanks, Chapter NR 746 sets forth risk screening and closure criteria, which when used to make closure decisions, defines on a site-by-site basis when natural attenuation will achieve groundwater enforcement standards within a reasonable period of time.

D.   Institutional Controls and Notices

Institutional controls and notices, including, in the appropriate case, deed notices, deed restrictions and placement on the DNR's Geographic Information System (GIS) Registry, may be necessary prior to, or at the time of, requesting case closure.

1. GIS Registry of Closed Remediation Sites.   If groundwater contamination above NR 140 Enforcement Standards (ESs) or soil contamination above ss. NR 720.09 or NR 720.19 applicable RCLs exists on a source property or on any off source property within the contaminated site boundaries, the site will be put onto an Internet accessible database, called the GIS Registry of Closed Remediation Sites (GIS Registry), after a complete closure request is submitted and approved.   Rule revisions in 2001 provided for entry of sites with ES exceedances onto the GIS Registry. This replaced the requirement for a groundwater use restriction on properties with residual groundwater contamination exceeding an ES. These rule revisions also require that the responsible party (RP) send a letter to all owners of properties with ES exceedances, offering them the opportunity to provide technical information supporting any argument that they may want to make as to why closure may not be appropriate, as well as informing them that their property will be included on the GIS Registry. Sites formerly closed with a groundwater use restriction have also been included on the GIS Registry.

Rule revisions that went into effect on August 1, 2002, provide for the entry of sites with residual soil contamination exceeding generic or site-specific soil standards developed under

NR 720 onto the GIS Registry. Sites closing with residual soil contamination above applicable RCLs need to be put on the GIS Registry for all conditions requiring a deed restriction except the use of industrial RCLs for closure. Sites with residual soil contamination above applicable standards in the smear zone are also required to be included on the GIS Registry.

Sites can be removed from the GIS Registry if information demonstrating that the applicable standards have been met is provided to the Department with a complete request for revising the Registry. Options include 1) requesting a general liability clarification letter if splitting a property and removing the unaffected portion from the GIS Registry, or 2) submitting a new closure request for the entire site once standards are met, or 3) requesting technical assistance to have a property that is not the source property removed from the GIS Registry if applicable standards are met.

2. Deed Restrictions. Rule revisions that went into effect on August 1, 2002, specify the situations in which deed restrictions are required for case closure of sites with residual soil contamination above either generic or site-specific residual contaminant levels developed in accordance with ch. NR 720. Conditions where deed restrictions are required for case closure are set forth in section NR726.05(8)(b). Specific conditions include where a site is to be closed after soils have been remediated based on industrial RCLs, where a building prevents access and therefore prevents completion of a site investigation to determine the degree and extent of residual contamination, where some type of soil cover, cap or other engineered structure is used to contain soil RCLs based on protection of groundwater, and where maintenance of a cover or cap is necessary to prevent direct exposure to residual soil contamination.

Where closure is conditioned on the recording of a deed instrument, the RP is required to record the deed instrument within 90 days after conditional closure is granted, and provide documentation to the Department that the deed instrument has been recorded within 120 days after conditional closure is granted. A deed restriction or deed notice may be required in limited situations other than those described above if there are site specific circumstances for which a deed notice or restriction would be necessary to adequately protect human health, safety or the environment. Refer to "Close Out Guidance on the Use of Deed Restrictions, Deed Notices and the Geographic Information System Registry of Closed Remediation Sites", PUBL-RR-606, for more information.

Sites closed with a deed instrument (including the formerly employed groundwater use restriction) still have the option of later requesting unconditional closure from the Department, and responsible persons or other interested parties may request that the Department issue an affidavit that can be recorded at the county register of deeds office to give notice that the recorded deed instrument is no longer needed, under the following conditions:
a. If the levels of groundwater contamination fall below the ES, the RP or person requesting unconditional closure will need to provide information that shows that (i) the contamination has fallen below the ch. NR 140 preventive action limits (PALs), or (ii) the site qualifies for an NR 140.28 PAL exemption.
b. For soils, contamination would have to be below the generic or site-specific RCLs from NR 720, as applicable.

3. Soil Performance Standards. The rule revisions that became effective on August 1, 2002, repealed sec. NR 714.05 and amended sec. NR 722.09(2)(a), removing the requirement for publishing a notice when an RP proposes to use a soil performance standard to complete the cleanup of the site. The rule revisions provide instead for notification of affected property

owners by letter, and inclusion of sites with residual soil and/or groundwater contamination above standards to be included on the GIS Registry, which is publicly accessible. Further information can be found in "Interim Guidance on Soil Performance Standards", WDNR PUBL RR-528-97.

II.   Case Closure for Contaminated Clay Sites

Contaminated sites located in geologic environments with low hydraulic conductivity (such as overconsolidated glacial tills, silty clay soil, etc.) present unique problems for case closure because it can be difficult to establish contaminant trends due to slow groundwater movement. Comm 46/NR 746 assumes that natural attenuation is an effective remedy at sites with low hydraulic conductivity, when certain criteria are met. Comm 46/NR 746 and associated guidance documents should be referred to for sites contaminated with petroleum products discharged from petroleum storage tanks.

III.   NR 726.05, Case Closure Request & Report

Section NR 726.05 lists the requirements for case closure at complex sites. The closure request must be submitted on a close out form supplied by the Department in accordance with NR 726.05(2)(a) (Wisconsin DNR Form 4400-202, "Case Summary and Close Out Form) and must be accompanied by the appropriate fee.

Sites requesting closure which need to be added to the GIS Registry due to either exceedances of soil RCLs or groundwater enforcement standards have specific submittal requirements as part of the closure request. Specific information and the required order of submittal are found at http://dnr.state.wi.us/org/aw/rr/archives/pubs/4400-202.pdf.

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APPENDIX A

SITE CHARACTERIZATION GUIDELINES

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APPENDIX A

SITE CHARACTERIZATION GUIDELINES

A-1   Location of Monitoring Wells and Hydraulic Conductivity

A.   Hydraulic Gradient and Diving Plumes

The movement of <u>dissolved petroleum</u> contaminants is controlled by the hydraulic properties of the groundwater system. Frequently, water table monitoring wells are relied upon to define the degree and extent of groundwater contamination at petroleum release sites because <u>petroleum product</u> is less dense than water and floats on the water table. This practice, of relying on shallow water table wells alone to characterize the groundwater plume, may result in partially or completely missing a dissolved plume that moves to deeper levels in the groundwater flow system.

Near the source of release, petroleum contaminants will be found at the water table. As dissolved contaminants move away from the source area, the contaminants will move with the groundwater flow field. Freeze and Witherspoon (1967) demonstrated several conditions under which groundwater contamination moves to deeper aquifer units.
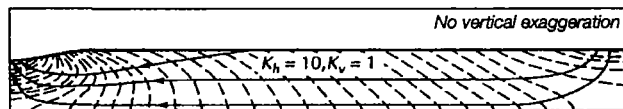
Figure A-1. Flow in an anisotropic aquifer with horizontal hydraulic conductivity ten times the vertical.
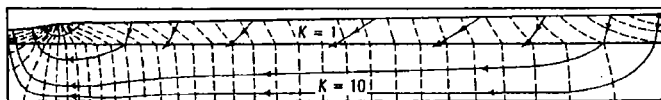
Figure A-2. Regional groundwater flow in layered aquifers. The greater proportion of the flow occurs in the layer with higher hydraulic conductivity.
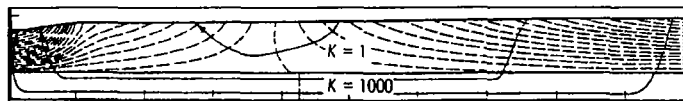
Figure A-3. Aquifer confined by a flat-lying confining layer. Source for
Fig. A -1 through A-3 :   R.A. Freeze and P.A. Witherspoon, Water
Resources Research, No. 3 (1967), © 1967 American Geophysical
Union.

These figures demonstrate that downward vertical gradients can be expected based on location
within the regional groundwater flow system and differences between hydraulic conductivity of
the units. When downward vertical gradients are present, plumes can usually be expected to
dive. Therefore, a site investigation should include an assessment of vertical gradients by
assessing location of the contaminated site within the regional groundwater flow regime, by
installing at least one piezometer nested with a water table well downgradient of the
contaminant source, or by some other method.

Even in cases where vertical gradients are not measurable, plumes can be expected to dive
when there is significant surface recharge. Surface recharge essentially accumulates above
the shallow plume, causing the plume to dive at a shallow angle as the plume moves
downgradient. An estimate of the expected depth of the plume centerline due to surface
infiltration can be made as follows:

Depth of infiltrated water overlying plume at distance (d): $D=(t)\left(\dfrac{I}{n}\right)$

Distance of plume travel from the point source in t years: $d=(v)(t)$

where: v = horizontal component of groundwater velocity
          n = porosity
          I = annual recharge rate
          t = length of time of infiltration/plume travel
          d = distance of plume from point source
          D = depth of infiltrated water over plume at distance (d)
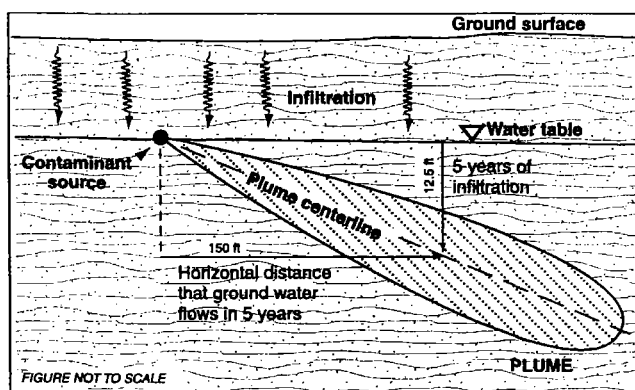
Figure A-4. Shallow diving plume from a point source. This example includes the following assumptions: 1) Single point source. 2) Infiltration rate = 1.0 ft/yr. 3) porosity = 40 percent. 4) groundwater average linear velocity = 30 ft/yr. and 5) time is 5 years. In this example, at 5 years the plume has traveled 150 feet [30 ft/yr x 5 yrs = 150 ft] and infiltration constitutes the upper 12.5 feet of the aquifer [5 yrs x 1 ft/yr /0.40 = 12.5 ft]. (Source for Fig. A-4: UTTU, Vol 12, No. 2, 1998)

While the conditions for diving plumes exist at many petroleum release sites, not all petroleum plumes will exhibit this characteristic. This is particularly true of sites with very recent releases where the plume has not traveled far, sites where there is limited infiltration due to surface seals such as pavement, sites with very low permeability, or where rates of natural attenuation significantly limit the extent of plume movement. However, it is important that all sites be evaluated for the possibility of a diving plume. Options for this evaluation include direct push sampling techniques, screened augers, installation of piezometers or other techniques, such as those described by Robbins (1997).

<u>Recommendations:</u>

- **Consider the use of vertical profiling and accelerated site characterization techniques, including direct push or other discrete zone sampling technologies and field laboratories, to define site stratigraphy and soil and groundwater quality prior to placing permanent monitoring wells and piezometer nests.**
- **Install at least one (or more) downgradient piezometer nests to evaluate vertical gradients and plume depth.**

B. Placement of Monitoring Wells

The proper placement of borings and monitoring wells will help define the hydrostratigraphic controls on the contaminant plume and the mass of contaminants that must be degraded by natural attenuation processes (primarily biodegradation). Monitoring wells should be placed to define the horizontal and vertical gradients, distribution of contaminants and the discharge location of the plume (if the plume is discharging to the surface).

After groundwater flow direction and plume shape and depth are determined, monitoring wells should be placed to monitor plume behavior and natural attenuation within the plume over time. These well locations should include:

a. *Upgradient of the Plume.* Place one monitoring well upgradient of the plume and on the axis of the center flowline. This well provides information on the water quality entering the contaminated area.

b. *Source Area Well.* Place one or more monitoring wells within the "source area" of contamination to determine if the source is decaying, increasing or remaining stable over time.

c. *Center Flowline of the Plume.* Place one or more, depending on plume length, monitoring wells within the plume, along the center flowline. Standard hydrogeologic textbooks contain information on determining flowlines (for instance, Fetter, 1994). It will be more difficult to assess the ability of natural attenuation processes to control and remediate the contaminants if wells are not or cannot be placed along the same flowline.

d. *Downgradient of the Plume.* Place one or more wells beyond the leading front of the plume and within a one to two year groundwater flow distance of the plume. This well should lie along the center flow line to detect migration of the plume.

e. *Sidegradient of the Plume.* Place one well on either side of the dissolved plume to define the width of the plume, define fluctuations in groundwater flow direction and to detect plume expansion.

f. *Piezometer Placement.* Locate one piezometer with the water table well placed beyond the leading front of the plume (well discussed in paragraph d). When necessary (based on plume length, groundwater gradients and surface water infiltration), locate a piezometer beside one or more water table wells within the downgradient plume (wells discussed in paragraph c).

An idealized groundwater monitoring system for monitoring natural attenuation within the plume over time is illustrated in Fig. A-5. Well screens should target the location of the plume and the stratigraphic units in which the plume moves, including downward movement.

Plan view
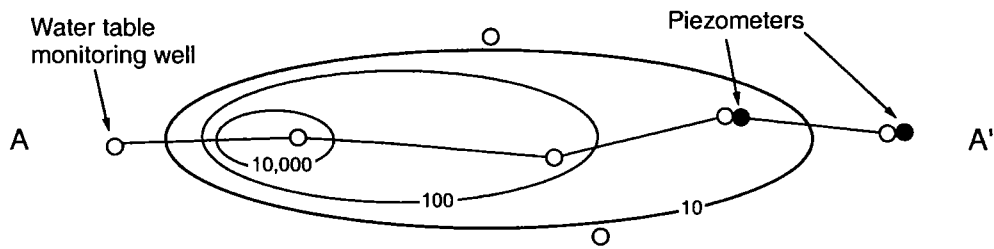
Cross-section through center flow line

NOT TO SCALE

Monitoring well detail
(water table well or piezometer)
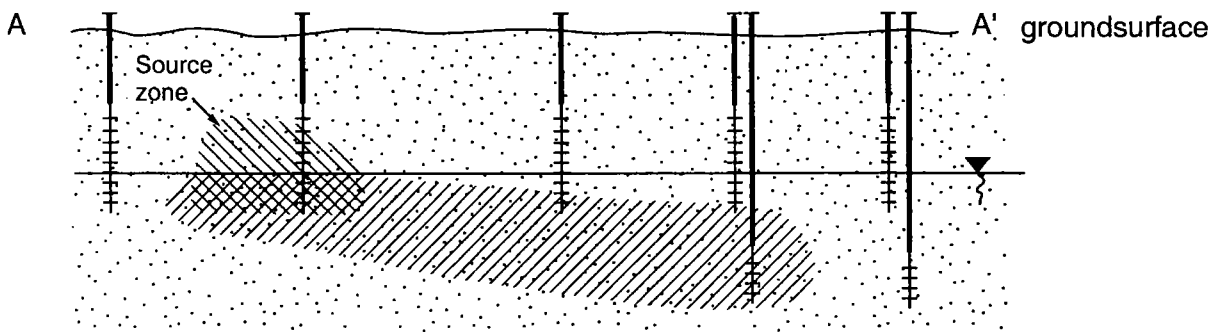
⧎ Source zone of petroleum contamination

⧄ Area of contaminated groundwater

○ Monitoring well

● Piezometer

100 = Total PVOC (ug/l)
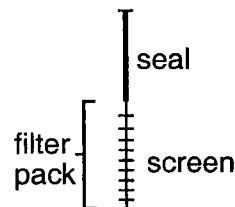
Figure A-5.
Idealized Natural Attenuation Monitoring Scheme

If monitoring wells cannot be placed along a contaminant flow line, then it will be necessary to assess natural attenuation processes on a well by well basis (e.g., changes in concentration over time) rather than concentration changes with distance. See appendix B for discussion of various methods for assessing natural attenuation processes.

C. Spacing of Monitoring Wells

Spatial trends in contaminant concentration data are determined by factors such as the source width perpendicular to groundwater flow, age of the plume, groundwater flow velocity,

dispersivity, and the rate of natural attenuation processes. Monitoring well spacing along a flow path should reflect plume dynamics. Monitoring well spacing will, in part, determine the length of time a plume must be monitored before natural attenuation as a remedy can be established. The more slowly groundwater flows, the longer monitoring may be necessary to establish plume behavior. Ultimately, there is a trade off between well spacing and length of time monitoring is necessary to establish that natural attenuation is an effective remedy.

For sites with fairly rapid groundwater velocity, well spacing can be based upon the distance groundwater will flow between wells along a flowline. The investigator should determine the travel time (which is essentially the minimum time over which monitoring will take place) that is acceptable:

$$d = (v)(t)$$

where: d = distance between wells
        v = horizontal linear groundwater velocity
        t = time for groundwater to flow between monitoring wells

For sites with low groundwater flow velocities, wells should not be placed closer than 20 feet apart, primarily to avoid an unreasonable number of monitoring wells at a site. Sites with slow groundwater flow may require longer periods of monitoring to establish contaminant plume behavior and the effectiveness of natural attenuation than sites with faster groundwater movement.

Recommendations:

- **Install monitoring wells as necessary to reflect the dynamics of plume movement.**
- **More closely spaced monitoring wells (but generally no closer together than 20 feet apart) may allow for more rapid assessment of natural attenuation processes.**

D.   Placement of Monitoring Well Screens

Monitoring well screens at petroleum contaminated sites are often installed in pre-determined lengths and placed at the water table. The well screen should be placed to bracket the most contaminated groundwater unit[4]. Consider the following when determining placement of well screens:

a. Hydraulic conductivity measurements are most critical in the zone of primary contaminant movement. Well screens targeted to the contaminated zone will better ensure the accuracy of these tests.
b. Limit piezometer well screens to the contaminated groundwater zone so that groundwater quality will be accurately defined. Well screens that bracket zones of contaminated and uncontaminated water result in mixed water chemistry and misleading results. For example, high dissolved oxygen and high dissolved iron can result from a monitoring well screen intersecting uncontaminated and contaminated groundwater. Review water quality results for indication of mixed water chemistry.

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[4] Where necessary, distinct hydrogeologic zones (e.g., sand units within silty clay formations or top of weathered bedrock) should be evaluated as pathways for contaminant movement.

c. Recognize the possibility of a diving plume. As a plume dives, a water table well may only partially intersect the contaminant plume or miss the plume entirely. This results in underestimating contaminant levels and possibly misinterpreting plume behavior. A series of water table wells along the plume centerline may give results that look like an attenuating plume, when in fact most of the plume has moved below the wells and only a small portion of the plume is being sampled. (See Figure A-6)
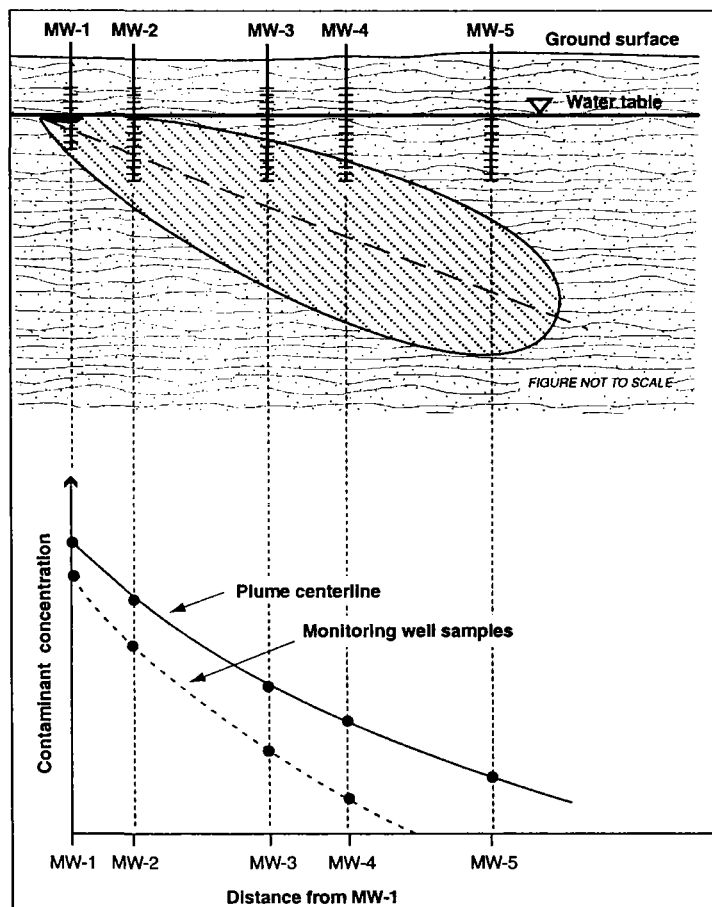
Figure A-6. Cross section of a plume with conventional water table monitoring wells for sampling. Graph shows distance verses concentration for the plume centerline and for the monitoring well sample results. (Source for Fig. A-7: UTTU, Vol 12, No. 2)

Recommendations:

- **Place monitoring wells and piezometer nests along the horizontal and vertical plume centerline to allow proper assessment of contaminant movement between well points.**
- **Place one or more monitoring wells within the source area to assess decay of the source.**
- **Assess water quality results to determine if a monitoring well is sampling water from contaminated and uncontaminated groundwater.**

E.   Hydraulic Conductivity

The calculation of contaminant movement is based on estimates of hydraulic conductivity (K), effective porosity (n), horizontal groundwater gradient (I), and retardation (R). (Appendix B contains an example calculation.)

$$v = \frac{\left(\dfrac{KI}{n}\right)}{R}$$

Hydraulic conductivity is one of the most critical parameters in assessing the ability of natural attenuation to prevent plume migration. Therefore, it is important that site hydraulic conductivity estimates are accurate. Hydraulic conductivity may be estimated from observation of lithologic samples, grain size analysis, or in-situ tests such as slug or bail down tests. Observation of lithologic samples and grain size analysis are indirect means of estimating hydraulic conductivity and rely on the experience of the site investigator and standard tables correlating grain size with hydraulic conductivity.

Slug and bail down tests provide a direct measure of subsurface hydraulic conductivity. Site investigators must recognize possible errors when interpreting the results of slug or bail down tests. Slug or bail down tests can underestimate or overestimate hydraulic conductivity. Water table wells (partially submerged screens) present significant challenges in interpreting data (Binkhorst & Robbins, 1998). The most common errors in slug or bail down tests result from improperly developed wells, well screens that intersect multiple geologic units, improperly placed well screens, procedural errors in conducting the tests and analyzing the data, and filter packs that may be more or less permeable than the aquifer.

The practice of averaging high and low hydraulic conductivity values from different wells across the site can introduce error when estimating contaminant movement. At sites where laterally extensive, high permeability zones exist between layers of lower conductive material, use of an averaging technique (such as the geometric mean) will not reflect groundwater flow velocity within the most conductive portions of the aquifer. In heterogeneous geologic settings, high permeability materials may not be laterally extensive and contaminant movement may be overestimated in these settings. In all cases the estimated hydraulic conductivity should be based upon the saturated materials controlling overall plume movement.

In very heterogeneous geologic settings where hydraulic conductivity is difficult to estimate or where existing slug/bail down tests do not appear to give adequate results, the use of alternative hydraulic conductivity test methods may be warranted. These methods may include pumping tests or methods that measure hydraulic conductivity at discreet depth intervals, such as borehole flow meters. (UTTU vol. 12, no. 2, 1998; and Molz, F and Boman, G, 1996).

Recommendations:

- Determine hydraulic conductivity from existing data, such as observation of lithologic samples or grain size analysis. Where necessary, conduct field tests at the site, including bail down or slug tests on at least a portion of site monitoring wells.
- Where laterally extensive permeable material exists at a site, use the highest hydraulic conductivity measured at a site to calculate groundwater and contaminant velocities.
- If necessary, use alternative methods to determine hydraulic conductivity in order to obtain an accurate measurement of groundwater velocity, such as borehole flow meters, etc.

A-2   Mann-Kendall Statistical Test for Plume Behavior

A.   Calculating Mann-Kendall Statistic

Mann-Kendall is one of several available non-parametric statistical tests. The test presented here should only be used for data that is not affected by seasonality. The data (4 to 10 rounds) should be collected from the same season of the year or the investigator should determine that seasonality has no effect on site groundwater data. Data variability can result in misinterpretation of the test results, so it is recommended that the coefficient of variation, explained at the end of this section, be assessed for the data set. Proper interpretation of the Mann-Kendall test requires an understanding of the limitations of this test. It is recommended that a text book on non-parametric statistics (e.g., Gibbons, 1994) be consulted prior to using this method.

Because the Mann-Kendall test is a simple test, it can be used to screen data sets prior to performing a regression analysis. If a decreasing contaminant trend is determined by the Mann-Kendall test, the rate of decrease can be further quantified through a regression analysis (see Appendix B for examples). If the Mann-Kendall test demonstrates a no-trend or an increasing trend, then a regression analysis may not provide any significant insight into contaminant degradation rates.

The basic approach of Mann-Kendall Test is:

1. Assemble well data for each contaminant for each sampling event in the order in which the data was collected. At a minimum, assess data from one or more contaminated wells near the margin of the contaminant plume (including piezometers) and a well near the source zone.

   For purposes of the Mann-Kendall test, all non-detect data values should be assigned a value that is less than the detection limit. If the detection limit varies over time, select a single value to represent all non-detection values.

Mann-Kendall Statistic

	Sampling Event 1	Sampling Event 2	Sampling Event 3	Sampling Event 4	Sampling Event 5	Sum Rows
Contaminant concentration →	100	50	85	75	50	
Compare to Event 1	→	-1	-1	-1	-1	- 4
Compare to Event 2		→	+1	+1	0	+ 2
Compare to Event 3			→	-1	-1	- 2
Compare to Event 4					-1	- 1
				Mann Kendall Statistic (Total) =		- 5

Figure A-7
Mann-Kendall Analysis of Plume
(see Gilbert, 1987, and Wiedemeier, et. al., 1999)

2. Compare data sequentially, comparing sampling event 1 to sampling events 2 through n, then sampling event 2 to sampling events 3 through n, etc. Each row is filled in with a 1, 0 or –1, as follows:

Along row 2, if:
- Concentration of event x_i > event 1:   Enter +1
- Concentration of event x_i = event 1:   Enter 0
- Concentration of event x_i < event 1:   Enter - 1

Where: n = total number of sampling events
         x_i = value of given sample event, with i = 2 to n

Continue for the remaining rows.

Sum each row and enter result at the end of the row. Add the sum of each row down to obtain the Mann-Kendall Statistic (S). If S is positive, then later measurements tend to be bigger than earlier measurements, pointing to an increasing trend in that well. If S is negative, then a declining trend in that well may be indicated.

3. Test for a declining trend. Evaluate data trends for each contaminant identified in the plume. Evaluate the null hypothesis of no trend against the alternative of a decreasing trend. The null hypothesis can be rejected in favor of a decreasing trend if the following conditions are met:

a. S is a large negative number (see lookup table below for magnitude of S)
b. The probability value (from Table A18, Gilbert, 1987), given n (number of data) and the absolute value of S, is LESS than the a priori significance level, α, of the test. An α = 0.2 is acceptable.

Example
For example, if there are 6 data (n = 6) and a Mann-Kendall statistic, S, of –1, can a declining trend be concluded?

Table A18 of Gilbert (1987) gives the probability for this example (n=6, $|S| \geq 1$) at 0.5. Therefore, one can conclude that there is a declining trend only at the $\alpha > 0.5$ level of significance. However, a 50% probability (or more) is too large to confidently conclude the data exhibit a trend. Therefore, one can not reject the hypothesis that the data exhibit no trend. The significance level (α) can be pre-specified (e.g., that $\alpha = 0.2$ is an acceptable significance level). In this example, at $\alpha = 0.2$, S needs to be -6 or better (i.e., -6 to -15) to conclude that a declining trend exists.

For the example data given in Figure A-7 (n = 5 and S = - 5), we can reject the no trend hypothesis at the $\alpha = 0.2$ significance level and accept the alternative hypothesis that the data for this well and this contaminant indicate a declining trend (see Table 1 below).

Look up Table

The following table was developed using Table A18 of Gilbert (1987). The table gives the maximum S statistic (S_{max}) to accept a declining trend alternative at an α level of significance. If the computed S is greater than S_{max} (or S is a smaller negative number than S_{max}), then we need to accept either a no-trend or an increasing trend in the data.

Table A-1
Mann-Kendall Statistic Look Up Table

n	Range of S	S_{max} $\alpha = 0.1$*	S_{max} $\alpha = 0.2$*
4	- 6 to + 6	- 6	- 4
5	- 10 to + 10	- 7	- 5
6	- 15 to + 15	- 8	- 6
7	- 21 to + 21	-10	- 7
8	- 28 to + 28	-11	- 8
9	- 36 to + 36	-14	-10
10	- 45 to +45	-16	-11

* The probability that the computed Mann-Kendall statistic $S \leq S_{max}$ is at most α.

4. Test for an increasing trend. An increasing trend alternative (i.e., an advancing plume) is accepted if:
   a. S is positive
   b. $S \geq |S_{max}|$ at a given α level of significance (see Look up Table above). If the computed S is equal to or greater than the absolute value of S_{max}, then it can be concluded the plume is advancing at an α level of significance. An $\alpha=0.2$ is acceptable for this test.

5. Additional analysis when the Mann-Kendall Test indicates no-trend is present. The results of the Mann-Kendall Test do not take into account the scatter of the data. A data set with a great deal of scatter may return a Mann-Kendall test indicating there is no trend, when, in fact, no conclusion can be drawn regarding trend because of data variability. In this case, additional data collection may be necessary to determine that the plume is stable, declining or advancing. As a simple test, the coefficient of variation can assess the scatter in the data:

$$CV = \frac{\text{standard deviation}}{\text{arithmetic mean}}$$

Where: CV = coefficient of variation

CV should be ≤ 1 to say that the no-trend hypothesis also indicates a stable plume configuration.

B. Spreadsheet of Mann-Kendall Statistic & Coefficient of Variation

An Excel spreadsheet has been developed to calculate the Mann-Kendall Statistic and coefficient of variation. The spreadsheet file name is **RR614_A.xls** and the file for the spreadsheet instructions is named **RR614_A.rtf**. The spreadsheet and instructions can be downloaded as a zip file from the Department's web site or the Department will provide the zip file on a floppy disk (for more information, see Other Relevant Guidance Documents at the beginning of the Interim Guidance on Natural Attenuation for Petroleum Releases). The spreadsheet below shows the summary statistics for an example site.

Microsoft Excel - Rr614_a.xls

Mann-Kendall Analysis Spreadsheet, Wisconsin DNR Remediation and Redevelopment Program

This spreadsheet is used to test for increasing, decreasing or stable trends, based on the Mann-Kendall statistical test. Refer to guidance titled *Natural Attenuation of Petroleum Contaminants in Groundwater* dated _____ for more information about the Mann-Kendall test. Spreadsheet version 1.0 prepared by George Mickelson, June 9, 1999. Spreadsheet QA/QC check by Resty Pelayo, June and July 1999.

Site Name =	Joe's Gas and Croisants	Anytown	Wisconsin	BRRTS No. =	03-72-0000001	Well Number =	MW-09
Compound		Benzene Concentration (leave blank if no data)	Toluene Concentration (leave blank if no data)	Ethylbenzene Concentration (leave blank if no data)	Total Xylenes Concentration (leave blank if no data)	Total TMB Concentration (leave blank if no data)	MTBE Concentration (leave blank if no data)
Event Number	Sampling Date (most recent last)						
1	10-Aug-94	150.00	38.00	1.30	4.40	24.50	55.00
2	03-Nov-94	140.00	18.00	3.00	17.00	65.00	2.00
3	17-Feb-95	270.00	16.00	5.30	11.00	15.70	2.00
4	18-May-95	740.00	33.00	8.80	16.00	28.90	2.00
5	28-Sep-95	290.00	28.00	3.30	8.20	16.20	2.00
6	04-Jan-96	92.00	7.80	1.60	7.50	5.30	2.00
7	04-Apr-96	25.00	3.60	0.50	1.00	2.90	2.00
8	11-Jun-96	890.00	20.00	8.00	20.00	57.00	2.00
9	22-Oct-96	450.00	21.00	12.00	15.00	33.30	52.00
10	24-Apr-97	480.00	19.00	6.60	6.70	18.30	37.00
	S =	11	-11	13	-5	-5	4
	n =	10	10	10	10	10	10
	Average =	352.7	20.44	5.04	10.68	26.71	15.8
	St. Dev. =	286.1266425	10.51382159	3.763331857	6.138367499	20.45164758	22.680388
	CV =	0.811246506	0.514374833	0.746692829	0.574753511	0.765692534	1.435467595
Increasing Trend (80% Confidence)		YES	NO	YES	NO	NO	NO
Decreasing Trend (80% Confidence)		NO	YES	NO	NO	NO	NO
Undetermined Stable Trend, CV<=1		NO	NO	NO	YES	YES	NO
Undetermined Non-Stable Trend, CV>1		NO	NO	NO	NO	NO	YES
Error Check, OK if Blank							
Stable or Decreasing Trend at 80% Confidence Level		NO	YES	NO	YES	YES	NO
Data Entry By =	A.A.		Date =	01-Jul-99	Checked By =		

Figure A-8
Excel Spreadsheet of Mann-Kendall Test

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:

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

where: $\bar{c}_v$ = 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).

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

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.

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

where: i = number of soil intervals (soil layers), where i =1 to ℓ
A_n^i = area represented by n^{th} sample in the ith layer (L^2)
d^i = thickness of the ith 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.

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

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 ($A_1, A_2, ... A_n$), by the depth of groundwater contamination at the source, by the porosity of the geologic media to obtain dissolved contaminant mass.

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

where: $\bar{c}_{gw}$ = area weighted concentration for groundwater in the source zone groundwater (M/L^3)
$A_1, A_2, ... A_n$ = 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:

Depth (m)

	Depth
Soil Depth Interval 1	$d_{L1} = 1$
Soil Depth Interval 2	$d_{L2} = 1$
Soil Depth Interval 3	$d_{L3} = 2$
Saturated Source Zone (Smear Zone below the water table)	$d_{SZ} = 1$
Groundwater Source Zone	$d_{GW} = 2$

∇
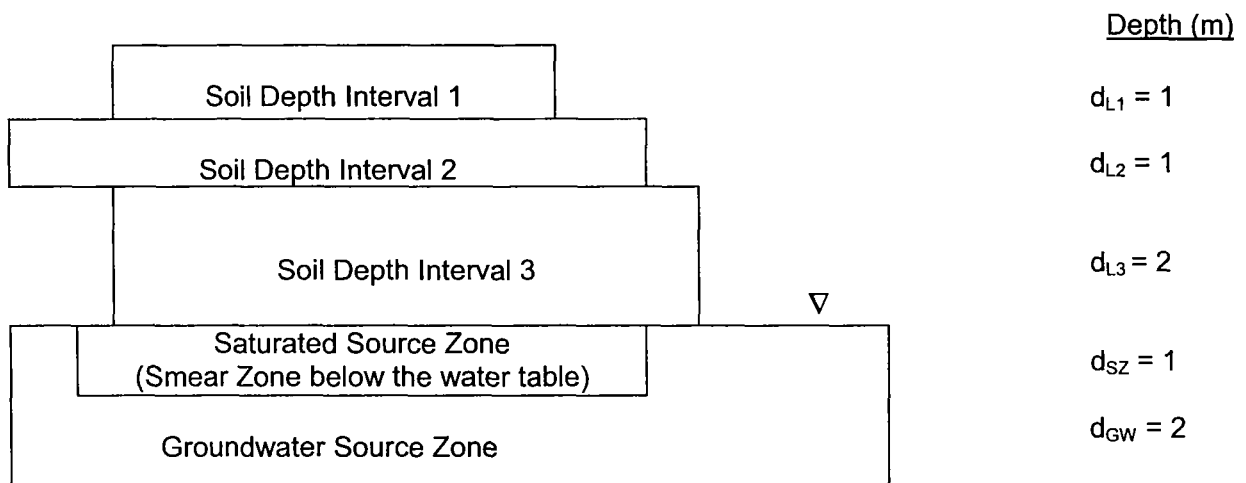
Plan View of Contaminant Source: Thiessen Polygon Network

Boundaries of each soil area are formed by the perpendicular bisectors of lines connecting adjacent points.

Boundary of outermost areas is formed by the no detect isocontour line for each soil layer.

Area = A_1 Area = A_2

C_1 C_2

Area = A_4

Area = A_3 C_4

C_3

(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:

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

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

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

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 $\bullet$ Area-Weighted Ave. Conc. ($m^3 \bullet$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).

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

Example calculation:

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

soil zone

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

Given Data Set:
    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

$$8000\frac{mg}{Kg} \times 95m^2 \times 1m \times 1650\frac{Kg}{m^3} \times \frac{Kg}{1 \times 10^6 mg} = 1254 \ Kg \ \text{of total BETX in}$$

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.

Example:
Wetted screen length: 3 meters
Vertical extent of groundwater contamination: 2 meters
Contaminant concentration (total BETX):   20,000 ug/l

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

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:

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

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

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

Example:
Area weighted mean: 30,000 ug/l = 30 g/m³

$$30,000\frac{ug}{l} \times \frac{g}{1\times10^6\ ug} \times \frac{l}{1\times10^{-3}\ m} = 30\frac{g}{m^3}$$

Area of source: 135 m²
Depth of groundwater contamination in source area: 2 m
Porosity: 35%

$$30\frac{g}{m^3} \times 135m^2 \times 2m \times .35 \times \frac{Kg}{1\times10^3\ g} = 2.8\,Kg \approx 3\,Kg$$

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%

APPENDIX B

DATA ANALYSIS FOR NATURAL ATTENUATION

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APPENDIX B

DATA ANALYSIS FOR NATURAL ATTENUATION

B-1   Data Requirements

The following data are needed to complete the assessment presented in this section:

1. Groundwater elevation for all sampling rounds, for each monitoring well.
2. Contaminant concentration for all sampling rounds, for each monitoring well.
3. Concentration or measurement of geochemical parameters for all wells.
4. Hydraulic conductivity (K) for the primary contaminant flow paths.
5. Horizontal hydraulic gradient ($\Delta h/\Delta l$) and vertical gradient ($\Delta h/\Delta z$) for the primary contaminant flow paths.
6. Effective porosity (n_e) for the primary contaminant flow paths.
7. Bulk density (ρ_b) of aquifer solids.
8. Organic carbon/water partition coefficient (K_{oc}) for each contaminant.
9. Fraction of organic carbon content (f_{oc}) for the aquifer material along the primary contaminant flow paths.
10. Location and horizontal and vertical dimensions of contaminant source area.
11. Estimate of contaminant mass in source area, including soils (M_s), saturated zone material (M_{sz}) and dissolved phase (M_{gw}).

B-2   Hydraulic Parameters & Contaminant Velocity

1. <u>Hydraulic Conductivity (K)</u>. Calculate a range of values for site hydraulic conductivity (K) from in-situ well tests, grain size analysis or observation of lithologic samples for each saturated geologic unit that conducts contaminants.

2. <u>Horizontal and Vertical Hydraulic Gradients ($\Delta h/\Delta l$ and $\Delta h/\Delta z$)</u>. Calculate horizontal and vertical gradients across the site using the on-site water table wells and piezometer(s).

3. <u>Groundwater Velocity</u>. Calculate the range for groundwater velocity (v) using the range of K values for the site and the estimated values of effective porosity from standard textbooks for the soil types present at the site. Evaluate the effects of secondary porosity on groundwater velocity, if present.

$$v = \frac{K}{n_e} \frac{\Delta h}{\Delta l}$$

where: v = groundwater velocity (L/T)
K = hydraulic conductivity (L/T)
n_e = effective porosity
$\dfrac{\Delta h}{\Delta l}$ = hydraulic gradient

4. <u>Contaminant Velocity</u>. Most, but not all, petroleum contaminants will attach to the surface of soil and saturated materials. This process, referred to as sorption, has the effect of slowing down or retarding contaminant movement relative to groundwater movement. Calculate the retardation of each contaminant in order to estimate contaminant velocity.

a. Estimate the retardation[5] of the contaminant(s).

$$R = 1 + (\frac{\rho_b}{n_e})(K_{oc})(f_{oc})$$

where: R = retardation factor (unitless). This factor will vary for different compounds
ρ_b = bulk density of aquifer solids (M/L^3)
K_{oc} = organic carbon/water partition coefficient (L^3/M)
f_{oc} = fraction of the organic carbon content of aquifer material. (Samples for organic carbon content should be taken from areas along primary contaminant flow paths that are not affected by the petroleum release, such as upgradient of the release.)

Appendix D contains tables of selected physical and chemical properties. Bulk density usually ranges between 1.4 and 2.0 g/cm^3; effective porosity in soil, between 0.3 and 0.4. The partition coefficient between organic carbon and water, K_{oc}, is chemical specific.

NOTE: Soil types with secondary porosity, such as over-consolidated glacial tills usually have a lower effective porosity.

b. Calculate contaminant velocity (v_c).

$$v_c = \frac{v}{R}$$

where: v_c = velocity of the contaminant (L/T)
v = groundwater velocity (L/T)
R = retardation factor (unitless)

---

[5] Equation for calculating retardation taken from Wiedemeier, et.al., 1999. This equation may underestimate retardation in soils with high clay content and low organic content. In these soils, clay minerals may serve as the dominant sorptive sites.

B-3   Estimates of Contaminant Decay Rate in Groundwater

Several methods exist to estimate contaminant decay rate. Several approaches are presented here. Other approaches may be acceptable. **These analyses apply only to the reduction of contaminant mass in the groundwater. They do not apply to reduction of contaminant mass in the source area.** If free product or residual phase product is present, much longer time frames will be required than indicated by these calculations.

A.   Batch Flushing

The rate of removal of contaminants remaining in the groundwater may be estimated as clean water flushes through the contamination.

Assumptions of this calculation include:

- **The contaminant source has been completely removed and all contaminants are in the dissolved phase.**
- **Incoming groundwater (free of contaminant) has sufficient time to mix completely within the aquifer.**
- **All contaminant concentration reduction occurs because of dilution alone.**

1. Calculate the number of pore volumes to flush the contaminant. From Zheng et al. (*Ground Water 29*, p. 838-848, 1991), US NRC (*Alternatives for Groundwater Cleanup*, 1994) and Brusseau (*Ground Water 34*, p. 19-22, 1996), the number of pore volumes (PV) needed to reach cleanup concentration (C_s) given an initial contaminant concentration (C_i) is given by:

$$PV = -R \; \ln(C_s / C_i) = 2.303 \; R \; \log(C_i / C_s)$$

   where: R = retardation factor (unitless)
   C_s = cleanup concentration (M/L^3)
   C_i = initial contaminant concentration (M/L^3)

2. Calculate time for groundwater to flow through plume. Given the groundwater velocity, v, and the downgradient length of contamination L, the time (τ) it would take for groundwater to traverse this length is:
$$\tau = L/v$$

   The time (T) it will take to reduce the contaminant level from C_i to C_s due to flushing alone is:

$$T = (PV)\tau$$

   The first order decay rate, k, from this 1-dimensional model is given by:

$$k = 1 / (R \tau)$$

Example, given the following:

K = hydraulic conductivity = 0.001 cm/s
$i = \Delta h/\Delta l$ = hydraulic gradient = 0.02
n_e = effective porosity = 0.4
f_{oc} = fraction of organic carbon = 0.001
ρ_b = bulk density = 1.65 g/cm3
L = downgradient length of contamination = 100 m
K_{oc} for benzene = 59 ml/g
C_i = initial benzene level = 20,000 ug/l
C_s = ES for benzene = 5 ug/l

The following can then be calculated:

v= groundwater velocity = $K\,i\,/\,n_e$
v=(0.001 cm/s) (0.02) / 0.4 = 5×10^{-5} cm/s = 15.8 m/yr

$$R = 1+(\frac{\rho_b}{n_e})(K_{oc})(f_{oc}) \; ; \; R_{benzene} = 1+(1.65/0.4)(59)(0.001) = 1.243$$

PV =2.303 R log(C_i/C_s)= 2.303 x 1.243 x log(20,000./5.) =10.3
τ = L/v = 100 m / (15.8 m/yr) = 6.3 yr
k = 1/($R\,\tau$) = 1/[(1.243) (6.3 yr) (365 d / yr)] = 0.0003 / day

This k can be interpreted as the contribution to the total contaminant decay due merely to the influx of clean water through the contamination. The time it will take to reduce the initial benzene level of 20,000 ug/l in groundwater to its enforcement standard of 5 ug/l through "flushing" is:

$$T = (PV)\,\tau\ = 10.3 \times 6.3\ yr = 65\ yr$$

[An Excel spreadsheet is provided for this one-dimensional batch flushing calculation. See Figure B-1 for the input/output of the above example.]

Figure B-1[6]
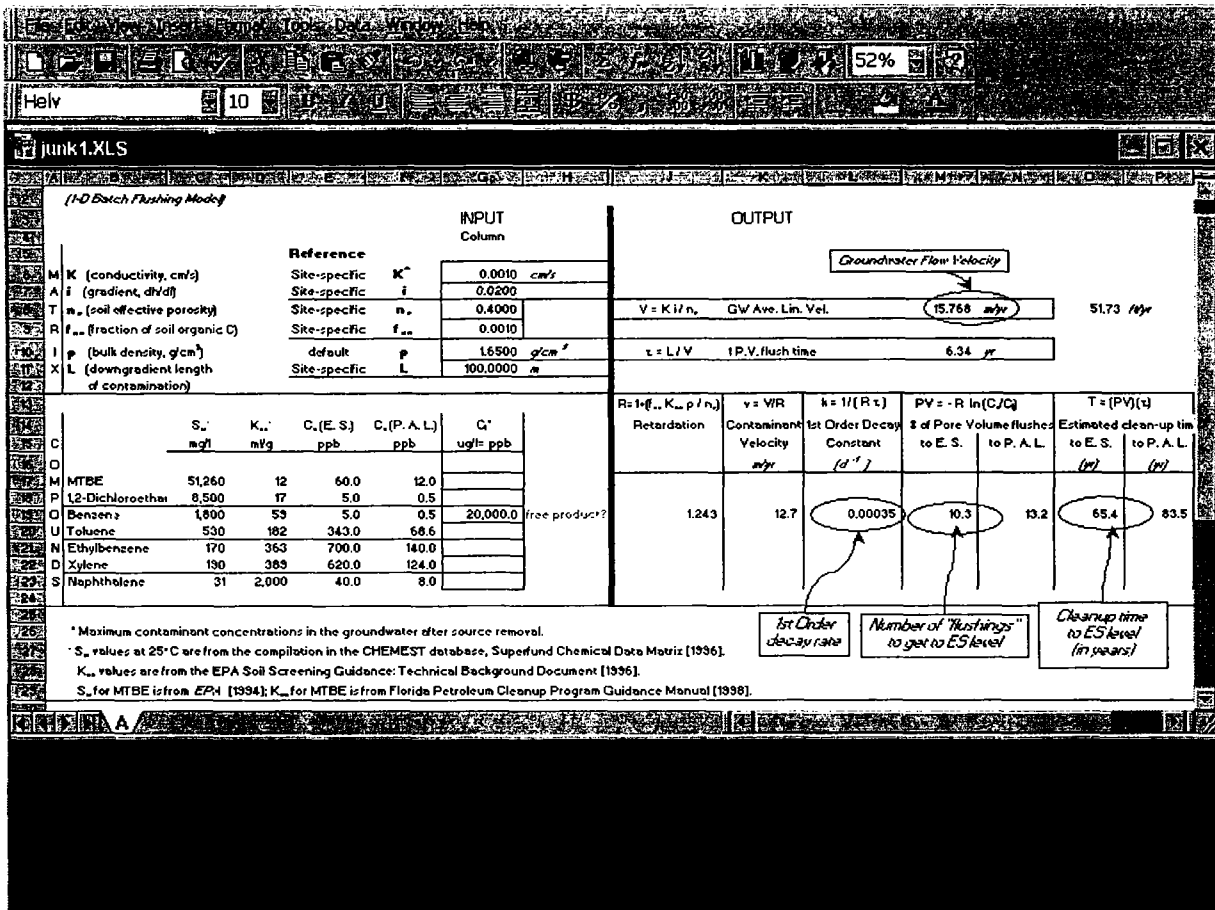
Figure B-1. Calculation of time to cleanup using the batch flushing method.

B.   Concentration vs. Time Plot

Prepare a semi-logarithm plot of the concentration of each BETX compound versus time for a source area well and a downgradient well, at a minimum. Prepare semi-logarithm vs. time plots of all other contaminants of concern, such as detected VOCs, MTBE, TMB, PAHs, lead, etc., if applicable. See Figure B-2 for an example. Assess these plots to determine that contaminant trends are stable or decreasing. If the trends are increasing, contaminants are entering groundwater faster than the capacity of natural attenuation processes to reduce contaminant

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[6] *This spreadsheet can be downloaded as a zip file from the DNR's web site or the DNR will provide the zip file on a floppy disk (for more information, see Other Relevant Guidance Documents at the beginning of the Interim Guidance on Natural Attenuation for Petroleum Releases). The spreadsheet file name is RR614_B.xls.*

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levels. Increasing contaminant levels over time indicate that natural attenuation processes need to be supplemented by other remedial actions to control contaminant release to the groundwater.

Table B-1

Example of Observed Groundwater Elevation and Concentration Variations
vs. Time Trend in a Single Well

Date	Benzene (ug/l)	Groundwater Elevation (ft)	Date	Benzene (ug/L)	Groundwater Elevation (ft)
1/26/94	5600	716.34	10/26/95	2	713.86
4/12/94	3900	716.19	1/9/96	25	714.02
7/20/94	200	715.9	4/11/96	50	714.17
10/18/94	100	715.29	8/28/96	11	715.06
1/18/95	610	714.52	12/3/96	2	713.68
4/18/95	110	715.13	3/5/97	6	714.1
7/12/95	3500	714.76	6/18/97	6	714.73

Figure B-2[7]
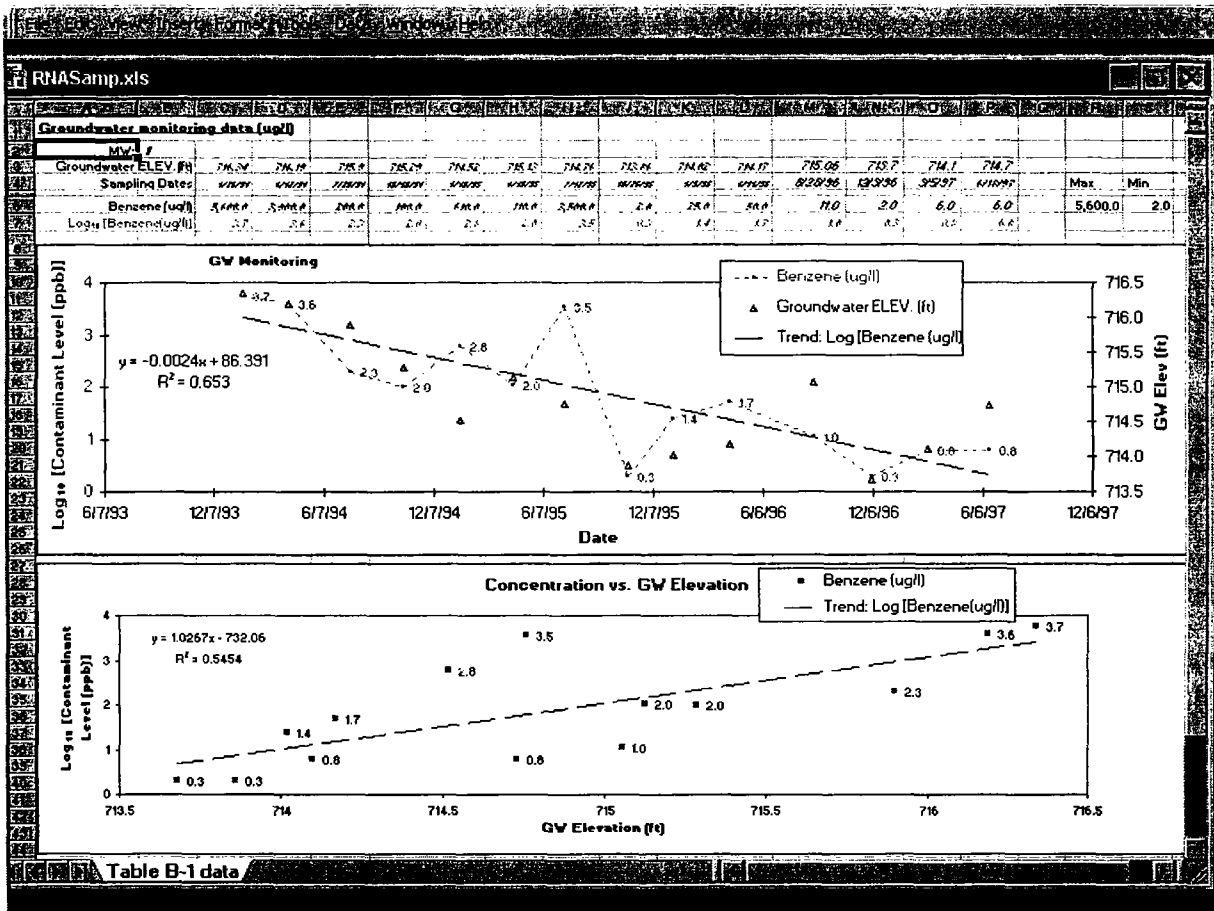
Figure B-2.
Semi-log plot of concentration vs. time (above) and concentration vs. groundwater elevation (below).

1. <u>Time Analysis</u>. Take the logarithm (to the base 10) of the benzene concentration data (see Fig. B-2, labeled symbols connected by small dash line in the upper plot) and plot them as a function of time (in days) and establish a trend. This trend line (long-dashed line in the upper plot of Fig. B-2) is the semi-log$_{10}$-transformed regression line. In addition, plot the groundwater elevation data (triangles connected by dashed lines in Fig. B-2) superimposed on the concentration data. For this well illustrated in Fig. B-2, overall benzene concentrations appear to be declining, and there seem to be a declining water level with time.

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[7] *This spreadsheet can be downloaded as a zip file from the DNR's web site or the DNR will provide the zip file on a floppy disk (for more information, see Other Relevant Guidance Documents at the beginning of the Interim Guidance on Natural Attenuation for Petroleum Releases). The spreadsheet file name is **RR614_C.xls**.*

Assume a first-order time decay for the benzene concentration. This first-order decay can be expressed as:

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

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

The term k' is the slope of the $\log_{10}$-transformed concentration data as a function of time. [Note that had the concentration data been transformed via natural log ($\log_e$ or simply, ln), the regression line would have a slope of k (not k'). Likewise, the standard MS Excel exponential fitting of the form: $y = b\, e^{mx}$ would give k (not k') = -m. The ASTM RBCA standard guide lists the degradation rate k (not k') for several petroleum compounds. It may be worthwhile to compare the site-specific k with the range for k given in the ASTM compilation.]

The trend line for the Table B-1 data gives a slope of k'=0.0024/day, so the first-order decay rate is equal to: $k = k' \times \ln(10) = 0.0055$/day, which is relatively fast for the degradation of benzene. The R^2 in the figure is the result of fitting a line to the log-transformed data. R^2 (=0.65) is termed the coefficient of determination. As R^2 approaches 1, the higher the proportion of the variation in the benzene concentration that can be attributed to its approximate log-linear relationship with time. For the above example, we can say that 65% of the variation in the log-transformed concentration data can be associated with the passage of time.

2. <u>Elevation analysis</u>. After the above analysis, an obvious question would be, are there other explanations for the decreasing benzene levels? Can the declining benzene levels be attributed to groundwater not coming in contact with contamination in the soil zone? In the upper plot in Fig. B-2, the groundwater elevation seems to exhibit a downward trend with time, and the variation in benzene concentration seem to be, more or less, "in-sync" with water elevation variation. Examining the extreme data points, observe that: 1.) benzene level was at a low of 2 ppb on 10/26/95 and on 12/3/96 when, at both times, the groundwater elevations were also the lowest; 2.) benzene levels were highest when the groundwater elevations were highest in 1994. Benzene levels seem to increase with the rising groundwater elevation, then fall when the groundwater elevation declined. The lower plot in Fig. B-2 is a plot of concentration levels vs. groundwater elevation with a trend line analysis. This analysis shows that benzene and water elevation are correlated with R^2 = 0.55. By projecting the trend line, we can predict that when the groundwater elevation drops below 712.7 ft, the benzene level is predicted to be below its PAL of 0.5 ug/l! Can the effects of benzene decay with time be sorted from the effects of groundwater elevation? Unfortunately, no. Additional data showing low benzene concentration when the groundwater elevation rises should confirm that the downward trend in benzene level is not merely an artifact of the groundwater elevation.

3. <u>Coefficient of determination (R^2)</u>. The R^2 value tells how well the regression line estimates the data. The square root of R^2 is the correlation coefficient, R. Generally, values of R greater than 0.80 (or $R^2 > 0.64$) indicate the data can easily fit a first order regression model. Correlation coefficients R less than 0.60 (or $R^2 < 0.36$) indicate that the data may not be a

good fit for a first order regression analysis. Note that R^2 is always 1 when we only have 2 data pairs, so the significance of R^2 is tied to the number of data. For instance, the typical statistical t-test (2-tail, $\alpha=0.01$ level of significance), given 5 data pairs, would need a minimum R^2 of 0.92 to conclude that a significant linear correlation exists in the data. If the number of data were increased to 10 pairs, the test would only need an R^2 of 0.58 to conclude that a significant correlation exists in the data.

C.   Concentration versus Distance Plot

Determine that the plume is at steady state by using any of the methods discussed in Section 1 of this guidance. If the plume is at steady state, prepare a semi-logarithm plot of BETX contaminant concentrations versus distance including all wells along the plume centerline. Prepare concentration vs. distance plots of all other contaminants of concern, such as detected VOCs, MTBE, TMB, PAHs, lead, etc., if applicable. See Table B-2 and Figure B-3 for examples.

Table B-2
Benzene concentration vs. Distance

Distance (m)	Benzene (ug/l)
0	4411
210	207
360	10
550	< 0.5

Figure B-3
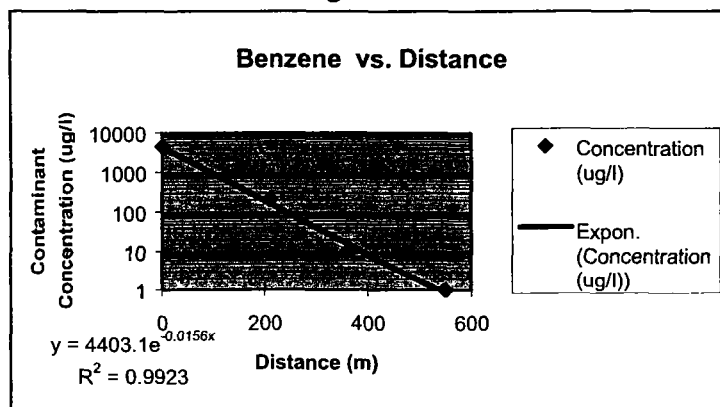
NOTE:
- The high correlation of the data (with coefficient of determination, $R^2 = 0.9923$) indicates that first order decay rate is applicable to this data. [The standard MS Excel exponential trendline calculates the R^2 using a log-transformed regression model as presented above in Figure B-2.]

- The decay constant of the exponential regression line is equal to k/v$_c$ (= 0.0156); this, however, is <u>not</u> just the biodegradation rate. It is the exponential reduction rate of the contaminant concentration in groundwater associated with distance from the source. This decay rate may be due to the combined processes of advection, dispersion, sorption and biodegradation.

1. <u>Estimating Decay Rate of Contaminant in Groundwater</u>. Exponential regression analysis of a log-linear plot results in an equation of the form:

$$y = be^{-mx}$$

where: y = y axis value
              b = y intercept
              m = decay constant with distance (L^{-1})
              x = x -axis value (L)

From the regression line:

$$m = \frac{k}{v_c}$$

Therefore,

$$k = (m)\left(v_c\right)$$

For the data presented above, if the contaminant velocity is 0.4 m/day:

$$k = (0.0156/m) \times (0.4m/d) = 0.006/d$$

Therefore, the estimated decay rate, k, is less than a percent of the contaminant decaying per day (0.6% per day). <u>This is the degradation rate of the contaminant in the groundwater, not the source area.</u>

2. <u>Estimate the half-life of the contaminant in groundwater</u>. The half-life (HL) is defined by:

$$HL = \frac{\ln(2)}{k} = 2.303 \frac{\log(2)}{k} = \frac{0.693}{k}$$

In this example, the half life of the benzene is:

$$HL = \frac{0.693}{0.006/day} = 115 days$$

Therefore, we expect half of the benzene mass <u>in the groundwater</u> to be reduced every 115 days.

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3. <u>R^2 value</u>. Examine the R^2 value and the number of data points. If the data do not fit a straight line, contaminant decay can not be assumed to be first order, therefore, the approach presented here may not be appropriate to determine contaminant decay rate and half life.

D.   Concentration vs. Travel Time Plot

An alternative to the Concentration vs. Distance Plot is a Concentration vs. Travel Time Plot. This analysis may be preferred in where hydraulic conductivity changes along a flow path. In this analysis, the travel time between each point along a flow path is calculated:

$$t = \frac{x}{v_c}$$

where: t = travel time between two points (T)
x = distance between two points (L)
v_c = contaminant velocity (L/T)

<u>Example:</u>

distance from source to downgradient well (x) = 210 m

contaminant velocity (v_c) = 0.4 m/d

$$t = \frac{210m}{0.4m/d} = 525days$$

Table B-3

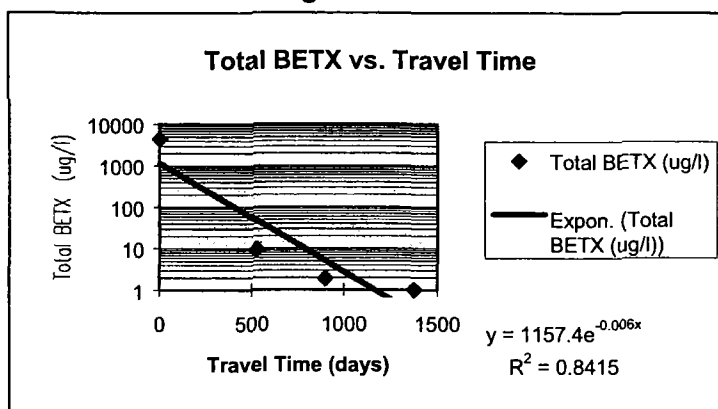Total BETX vs. Travel Time

Travel Time (d)	Benzene (ug/l)
1	4411
525	9.5
900	1.9
1375	1

Prepare a log-linear plot of concentration versus travel time and perform an exponential regression analysis of the plotted data.

Figure B-4

Total BETX vs. Travel Time

$$y = 1157.4e^{-0.006x}$$
$$R^2 = 0.8415$$

The decay rate from the concentration vs. travel time log-linear plot is the contaminant degradation rate, k.

$$y = be^{-kx}$$

where: y = y axis value
   b = y intercept
   k = degradation rate (T^{-1})
   x = x -axis value (T)

The same data set is used in the concentration vs. distance and concentration vs. travel time analysis above. Both analyses yield the same decay rate, k = 0.006/day.

B-4   Estimate of Contaminant Decay Rate in Source Area

If soluble contaminant mass remains in the source area and continues to enter the groundwater, then an estimate of contaminant source lifetime is needed to determine how long groundwater will remain contaminated. The examples presented here are intended to serve as tools to understanding natural attenuation at a given site. Estimates of mass loss do not represent actual subsurface reactions. Gross simplifications of the subsurface are required in these estimates. Due to the lack of knowledge of actual reaction kinetics in the subsurface and other simplifications, long term monitoring must be relied upon to observe contaminant degradation and mass reduction.

A.   Mass Flux Method

This method assumes that decay of contaminant mass in the source occurs only through dissolution into the groundwater. It is a conservative estimate of the source lifetime and should be applied where source area groundwater well(s) exhibit constant contaminant levels.

$$Mass\, Flux = K \frac{\Delta h}{\Delta l} A C_o$$

where: *Mass Flux* = mass movement from source into groundwater (M/T)
K = hydraulic conductivity (L/T)

$\dfrac{\Delta h}{\Delta l}$ = hydraulic gradient

A = cross-sectional area of groundwater flow through source, (L^2)
C$_o$ = concentration in groundwater at the source area, (M/L^3)

Mass flux, divided into total soluble mass in the source area, will give an estimate of the source lifetime:

$$Source\ Lifetime = \frac{M_s + M_{sz} + M_{gw}}{Mass\ Flux}$$

where: M_s = soluble mass in soil in source area
M_{sz} = soluble mass in smear zone in source area
M_{gw} = soluble mass in dissolved phase in source area

Assumptions:

- All soluble contaminant mass in unsaturated soils leaches into saturated zone.
- Cross sectional area of groundwater flow is equal to the depth of the contaminated saturated zone (smear zone below the water table) and groundwater contaminated source area multiplied by the width of the source area perpendicular to groundwater flow. Water table fluctuation is not taken in to account in this example.
- Hydraulic conductivity measured in source area represents actual permeability of smear zone. Trapped residual product can reduce permeability by 20 to 70 percent.
- Contaminant concentration in groundwater (C$_o$) in the source area is the highest concentration measured within the source area.
- No retardation.

Example:

$K = 1 \times 10^{-3}$ cm/sec = 0.86 m/d

$\dfrac{\Delta h}{\Delta l}$ = 0.01

$A = 3$ m (depth) x 16.6 m (width) = 50 m^2
$C_o = 30,000$ ug/l = 30 g/m^3

Mass Flux out of Source Area: $0.86\dfrac{m}{d} \times 0.01 \times 50 m^2 \times 30\dfrac{g}{m^3} = 12.9\ \dfrac{g}{d} \approx 13\dfrac{g}{d}$

Total Mass in Source Area = 2,230 Kg (see calculation in Appendix A-3)

$$\text{Convert Mass Flux Rate: } 13\ \frac{g}{d} \times \frac{Kg}{1000\,g} = 0.013\ \frac{Kg}{d}$$

$$\text{Source Life Time: } \quad \frac{2{,}230\,Kg}{0.013\dfrac{Kg}{d}} = 171{,}500\,days \approx 470\,years$$

B.   First Order Decay of Contaminant Source

If the contaminant source is decreasing, as evidenced by a source area groundwater monitoring well and if the observed decay fits a first order decay rate, then the following calculations can be applied to estimate how quickly natural attenuation processes will reduce the contaminant mass in the source area. **This calculation is not applicable to non-first order decay rates or in cases where there is no observed decrease in source area concentrations.**

1. Determine a first order decay rate for the source area. Prepare a concentration vs. time log-linear plot for one or more source area groundwater wells. Determine if the data fits a first order decay rate. If a first order decay rate does represent the data, then determine the slope (m) from the exponential regression of the data. The slope (m) equals the observed decay rate for the source (k_s).

Example:

Table B-4
Total Benzene vs. Date for Source Area Well

Date	Benzene
4/12/94	16000
7/20/94	13000
10/18/94	12000
1/18/95	10000
4/18/95	9000
7/12/95	12000
10/26/95	11000
1/9/96	8000
4/11/96	6500
8/28/96	7000
12/3/96	5500

Figure B-5
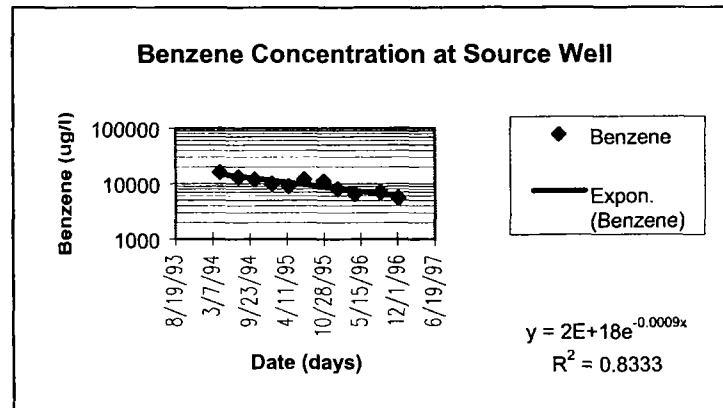
Benzene degradation rate of source (k_s) = 0.0009/day

2. Calculate final contaminant mass to be reached after remediation.

$$M = ES \times (K_{oc} f_{oc}) \times \rho \times (V_s + V_{sz})$$

where: M = final mass to be reached at end of source life (M)
ES = enforcement standard from NR 140 (M/L^3)
K_{oc} = organic carbon/water partition coefficient (L^3/M)
f_{oc} = fraction of organic carbon content of aquifer material (M/M)
V_s = volume of source area unsaturated soils (L^3)
V_{sz} = volume of source area saturated soils (smear zone) (L^3)
ρ = soil bulk density (M/L^3)

Example:

ES = 5 ug/l for Benzene
K_{oc} = 59 l/Kg for Benzene = 59 cm^3/g
f_{oc} = 0.001 g/g
V_s = 1300 m^3
V_{sz} = 95 m^3
ρ = 1.65 g/cm^3

$$M = \left(5.0\frac{ug}{l}\right) \times \left(59\frac{cm^3}{g}\right) \times \left(0.001\frac{g}{g}\right) \times 1.65\frac{g}{cm^3} \times \left(1300m^3 + 95m^3\right) \times \left(10^3\frac{l}{m^3}\right) \times \left(10^{-6}\frac{g}{ug}\right) = 0.7\,g$$

3. Calculate the source lifetime.

$$SourceLifetime = \frac{-\ln\left[\frac{M}{(M_S + M_{SZ} + M_D)}\right]}{k_s} = 2.303\frac{-\log\left[\frac{M}{(M_S + M_{SZ} + M_D)}\right]}{k_s}$$

where: M = final mass to be reached at end of source life (M)
          M_S = soluble mass in soil in source area (M)
          M_{SZ} = soluble mass in smear zone in source area (M)
          M_D = soluble mass in dissolved phase in source area (M)

Example:

Mass to be reached after remediation = 0.7 g = 0.7 x 10^{-3} Kg
Mass of Benzene in source area $\cong$ 1,000 Kg
k_s = 0.0009/d

$$\frac{\ln\left(\frac{0.7\times10^{-3}Kg}{1,000Kg}\right)}{-0.0009/day} = 2.303\frac{\log\left(\frac{0.7\times10^{-3}Kg}{1,000Kg}\right)}{-0.0009/day} = \frac{-14.2}{-0.0009/day} = 15,800 days \approx 43 years$$

B-5   Assimilative Capacity Calculations

Expressed assimilative capacity (EAC) is used to estimate the capacity of the aquifer to degrade BETX. Screening models, such as Bioscreen[8] or GNAM[9], use an electron acceptor limited kinetic model as one approach to calculating decay of the contaminant source. EAC can aid in demonstrating mass loss of contaminant from the aquifer. As with all estimates of mass loss, EAC does not represent actual subsurface reactions. **Because of the simplifications of these estimates, only empirical field data can be relied upon to reflect contaminant degradation and mass reduction.**

A.   Utilization Factors

The utilization factor is the ratio of the mass of biodegraded contaminant to the mass of electron acceptor utilized (or metabolic byproduct produced).

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[8] BIOSCREEN Natural Attenuation Decision Support System - developed by Groundwater Services, Inc. for the Air Force Center for Environmental Excellence.
[9] Groundwater Natural Attenuation Model (GNAM), in the RNA Tool Kit, Florida Petroleum Cleanup Program, developed by Groundwater Services, Inc.

Table B-5
Utilization Factors[*]

Electron Acceptor/ Metabolic Byproduct	Utilization Factor
Oxygen utilized	0.32
Nitrite utilized	0.21
Manganese produced	0.06
Ferrous iron produced	0.05
Sulfate utilized	0.21
Methane produced	1.28

[*]   from Wiedemeier, et. al., 1996

B.   Expressed Assimilative Capacity (EAC)

Calculate an EAC using the difference in concentration between a background well and a well in the area of highest BETX contamination. (from Wiedemeier, et.al., 1996)

$$EAC = 0.32\ (O_B - O_M) + 0.21\ (N_B - N_M) + 0.06\ (Mg_M - Mg_B) + 0.05\ (Fe_M - Fe_B)$$
$$+ 0.21\ (S_B - S_M) + 1.28\ (M_M - M_B)$$

where: O_B = Oxygen concentration in background
O_M = Oxygen concentration in area of highest BETX
N_B = Nitrate concentration in background
N_M = Nitrate concentration in area of highest BETX
Mg_B = Manganese concentration in background
Mg_M = Manganese concentration in area of highest BETX
Fe_B = Ferrous iron concentration in background
Fe_M = Ferrous iron concentration in area of highest BETX
S_B = Sulfate concentration in background
S_M = Sulfate concentration in area of highest BETX
M_B = Methane concentration in background
M_M = Methane concentration in area of highest BETX

The expressed assimilative capacity approximately equals the equivalent BETX biodegraded.

Table B-6
Example of Expressed Assimilative Capacity*

Geochemical Parameter	Utilization Factor	Concentration of Geochemical Parameters (mg/l)			Equivalent BETX Degradation
		Background	Zone of Highest BETX	Difference	
DO	0.32	7.0	<0.1	7.0	2.2
NO_3	0.21	21	<0.1	21	4.4
Mg^{+2}	0.06	<0.025	<0.025	-	-
Fe^{+2}	0.05	<0.025	36	36	1.8
SO_4^{-2}	0.21	1575	42	1533	321.9
CH_4	1.28	0.0005	11.0	11.0	14.1
Total Expressed Assimilative Capacity (mg/l)					344.4

* from API Publication #4658

The assimilative capacity assumes instantaneous degradation of BETX once the contaminant is in contact with the electron acceptors. In the above example, approximately 345 mg of BETX is degraded for every liter of groundwater that flows through the source area. **It is important to note that other organic compounds also exert an electron acceptor demand and this calculation likely overestimates the mass of BETX degraded by the available mass of electron acceptors.**

C. EAC to Estimate Source Lifetime

An estimate of the life of the contaminant source can be made using expressed assimilative capacity. Note that **this method assumes that BETX are the only compounds exerting an electron acceptor demand.**

Groundwater flow through a perpendicular cross-section of the source area:

$$Q = K \frac{\Delta h}{\Delta l} A$$

where: Q = groundwater volume flowing through perpendicular cross-section of the source area (L^3/T)
K = hydraulic conductivity, measured on a source well (L/T)
$\dfrac{\Delta h}{\Delta l}$ = hydraulic gradient (L/L)
A = area of groundwater flow through the source area, perpendicular to groundwater flow (L^2)

Example:

$K = 1 \times 10^{-3}$ cm/sec = 0.86 m/d

$\dfrac{\Delta h}{\Delta l} = 0.01$

$A = 50$ m^2

EAC = 345 mg/l = 3.45×10^{-4} Kg/l

Flow through source area : $Q = \dfrac{0.86\,m}{d} \times 0.01 \times 50\,m^2 \times \dfrac{l}{1 \times 10^{-3}\,m^3} = 430\dfrac{l}{d}$

Assimilative Capacity per day : $430\dfrac{l}{d} \times 3.45 \times 10^{-4}\dfrac{Kg}{l} = 0.148\dfrac{Kg}{d}$ *EAC*

Estimate of Source Lifetime from EAC, where
      total BETX mass in source = 1000 Kg
      assume all EAC consumed solely for BETX degradation

$1000\,Kg$ total BETX $\times \dfrac{d}{0.148\,Kg} = 6760\,days \approx 18\,years$

APPENDIX C

NATURAL ATTENUATION MONITORING TABLES

Table of Contents

Table C-1

Geochemical Parameters for Assessing Natural Attenuation at Petroleum Contaminated Sites

Analyte	Use	Change with Biological Activity*
Oxygen (DO)	Terminal electron acceptor. At most sites, <1ppm indicates anaerobic conditions.	↓
Nitrate (NO_3)	Terminal electron acceptor when O_2 depleted.	↓
Manganese (Mn^{+2})	Metabolic byproduct of Mn^{+4} reduction.	↑
Ferrous Iron (Fe^{+2})	Metabolic byproduct of Fe^{+3} reduction.	↑
Sulfate (SO_4)	Terminal electron acceptor.	↓
Methane (CH_4)	Metabolic byproduct of methanogenesis.	↑
Alkalinity	Measures buffering capacity of groundwater. Affected by CO_2 producted from biodegradation.	↑
Redox Potential (ORP)	Important control on biological activity in subsurface.	↓
pH	Biological activities are pH sensitive.	→ or ↓
Temperature	Helps determine representative groundwater when purging a well.	→
Conductivity	Helps determine representative groundwater when purging a well.	→

Ref: based on API Publication #4658 and Air Force Technical Protocol for Implementing Natural Attenuation
*Note: all sites will not exhibit these parameters or necessarily exhibit the changes indicated.

Table C-2

Potential Effects of Sampling Protocol on Select Intrinsic Bioremediation Parameters[1]

PARAMETER	ARTIFICIAL AERATION	TURBIDITY[2]
Oxidation/reduction potential (ORP or Eh)	Introduction of oxygen raises Eh through oxidation of reduced species.	Solids in bottom of well may be a different geochemical state than formation; introduction of these solids into groundwater may alter Eh in resulting groundwater sample.
Dissolved Oxygen (D.O.)	May increase D.O. of sample.	May lower D.O. of sample through oxygen demand exerted by geochemically reduced solids.
Nitrate (NO_3)	Aeration is not likely to affect nitrate concentration.	Nitrate may be lowered through electron acceptor demand exerted by geochemically reduced species associated with solids.
Manganese	Oxidation/precipitation of manganese will decrease concentration of dissolved manganese.	Analysis may yield concentration greater than in formation groundwater because of manganese associated with solids. In addition, turbidity itself may contribute to color in colorimetric analyses.
Iron	Oxidation/precipitation of iron will decrease concentration of ferrous iron.	Analysis may yield iron concentration greater than in formation groundwater because of iron associated with solids. In addition, turbidity itself may contribute to color in colorimetric analyses.
Sulfate	Aeration is not likely to affect sulfate concentration.	Analysis may yield sulfate concentration greater than in formation groundwater because of sulfate associated with solids.
Methane	Will reduce concentration through loss to atmosphere.	Turbidity not likely to affect methane concentration.
Alkalinity	May reduce concentration due to loss of CO_2 to the atmosphere.	May increase alkalinity concentration if carbonates are in solids.
Note: Turbidity may also adversely impact field and laboratory measurements based on colorimetric and turbidimetric methods.		

[1] Ref: based on API Publication #4658, p. A-6, Nov. 1997

[2] Field filter dissolved iron and dissolved manganese if these parameters are to be analyzed in the laboratory. If the water sample is exposed to air while field filtering, the results for these metals will be significantly affected.

Table C-3

Contaminant Characterization of Groundwater for Types and Location of Petroleum Discharges

PETROLEUM SUBSTANCE DISCHARGED	FIELD INVESTIGATIONS AND CHARACTERIZATION FOR TREATMENT[1]	GROUNDWATER CHARACTERIZATION FOR SURFACE WATER DISCHARGE
Regular and Unleaded Gasoline; Grades 80, 100, and 100 LL (low lead) Aviation Fuel	GRO VOC/PVOC[2] Pb[3]	individual BETX components Total Suspended Solids
Diesel; Jet Fuels; and No's 1, 2, and 4 Fuel Oil	DRO VOC/PVOC[2] PAH[4]	individual BETX components PAH Oil & Grease as HEM[5] Total Suspended Solids
Crude Oil; Lubricating Oils; No. 6 Fuel Oil	DRO PAH[4]	Oil & Grease as HEM[5] PAH Total Suspended Solids
Unknown Petroleum	GRO and DRO VOC/PVOC[2] PAH[4] Pb, Cd[3]	individual BETX components PAH Oil & Grease as HEM[5] Total Suspended Solids
Waste Oil	DRO VOC/PVOC[2] PAH[4] PCBs[6] Pb, Cd[3]	individual BETX components PAH Oil & Grease as HEM[5] Total Suspended Solids

Abbreviations:
GRO = Gasoline Range Organics, determined by Wisconsin DNR Modified GRO Method
DRO = Diesel Range Organics, determined by Wisconsin DNR Modified DRO Method
VOC = Volatile Organic Compounds
PVOC = Petroleum Volatile Organic Compounds
PAH = Polynuclear Aromatic Hydrocarbons
PCBs = Polychlorinated Biphenyls
BETX = benzene, ethylbenzene, toluene, and xylenes (o-,m- and p- isomers)
[1] These are minimum requirements. Other parameters or compounds may need to be assessed for effectiveness of groundwater treatment.
[2] Sample for the full list of VOCs in at least one round of samples at all groundwater wells. Subsequent rounds of analysis can be limited to the PVOC compounds and any other VOCs detected in the first sampling round or as requested by the DNR project manager.
[3] Sample for Pb and/or Cd in at least one round of samples at all groundwater wells. Subsequent rounds of analysis may drop the Pb and/or Cd parameters if these compounds are not detected in the first sampling round, unless specified by the DNR project manager.
[4] Polynuclear aromatic hydrocarbons (PAH) analysis in groundwater may be requested by DNR project managers at some sites, when: 1) the petroleum is weathered; 2) DRO is >1000 ppm but PVOCs are absent or very low; 3) groundwater is <25 feet below ground surface and soil permeability is > 1x10^{-3} cm/sec; 4) groundwater is <10 feet below the base of the spill regardless of permeability; 5) soils are low organic matter; 6) private drinking water wells are within 500 feet or public wells are within 1,500 feet of the site.
[5] HEM = hexane extractable material
[6] Sample for PCBs only if PCBs have been found in surrounding soils.

Table C-4

Analytical Methods[1] for Petroleum Contaminants in Groundwater

ANALYTE	DESCRIPTION	APPROVED METHOD
GRO	Gasoline Range Organics	WI DNR Modified GRO Method
DRO	Diesel Range Organics	WI DNR Modified DRO Method
VOC	Volatile Organic Compounds	EPA Method 5030/8021 or 5030/8260
PVOC	Petroleum Volatile Organic Compounds	EPA Method 5030/8021 or 5030/8260
PAH	Polynuclear Aromatic Hydrocarbons	EPA Method 8310 (HPLC)
PCBs	Polychlorinated Biphenyls	EPA Method 3510/8082 or 3520/8082
Pb	Dissolved Lead[2]	EPA Method 3020/7421 or 3020/6020
Cd	Dissolved Cadmium[2]	EPA Method 3020/7131 or 3020/7130
Oil & Grease	Gravimetric Method for Determining Heavy Hydrocarbons	EPA Method 1664
TSS	Total Suspended Solids	EPA Method 160.2

[1] Unless an analytical method is specified by the WI DNR's RR program (such as GRO/DRO), any method from the NR 149 "Authoritative Sources" may be used provided it is appropriate for the media and concentration of the sample, and has an LOD and LOQ below the PAL or produces the lowest available LOD and LOQ if the LOD and LOQ are above the PAL.

[2] Groundwater to be analyzed for the inorganic contaminant parameters of total lead or total cadmium should be filtered through a 0.45 micron filter (for more details see SW-846 chapter 3 or EPA method 3005).

Table C-5

NR 140 Public Health Related Groundwater Standards
Metals

METAL	ENFORCEMENT STANDARD (UG/L)	PREVENTIVE ACTION LIMIT (UG/L)
Lead	15	1.5
Cadmium	5	0.5

Table C-6

NR 140 Public Health Related Groundwater Standards

Petroleum Volatile Organic Compounds (PVOCs)

PVOC	ENFORCEMENT STANDARD (UG/L)	PREVENTIVE ACTION LIMIT (UG/L)
Benzene	5	0.5
1,2-Dichloroethane	5	0.5
1,2-Dibromoethane (EDB)	0.05	0.005
Ethylbenzene	700	140
Methyl tertiary-butyl ether	60	12
Toluene	343	68.6
1,2,4-Trimethylbenzene+ 1,3,5-Trimethylbenzene	480	96
Total Xylene (m-,o-,p- isomers combined)	620	124

Table C-7

NR 140 Public Health Related Groundwater Standards

Polycyclic Aromatic Hydrocarbons (PAHs)

PAH	ENFORCEMENT STANDARD (UG/L)	PREVENTIVE ACTION LIMIT (UG/L)
Acenaphthene		
Acenaphthylene		
Anthracene	3000	600
Benzo(a) Anthracene		
Benzo(a) Pyrene	0.2	0.02
Benzo (b) Fluoranthene	0.2	0.02
Benzo (g,h,i) Perylene		
Benzo (k) Fluoranthene		
Chrysene	0.2	0.02
Dibenzo (a,h) Anthracene		
Fluoranthene	400	80
Fluorene	400	80
Indeno (1,2,3,c,d) Pyrene		
Naphthalene	40	8
Phenanthrene		
Pyrene	250	50

APPENDIX D

SELECTED PHYSICAL/CHEMICAL PARAMETERS FOR ASSESSMENT OF NATURAL ATTENUATION PROCESSES

Table D-1

Bulk Density and Porosity Based on Soil Texture

SOIL TYPE	BULK DENSITY (g/cm^3) [a]		POROSITY [b]	
	Water-saturated	Above Groundwater surface	Total Porosity	Effective Porosity
Peat	1.0 – 1.1	Often water-saturated		
Clay and Silt	1.4 – 2.0	Often water-saturated	0.4 – 0.5	0.4
Sand and Gravel	2.0 – 2.3	1.6 – 2.0	0.4 – 0.5	0.4
Glacial Till	2.1 – 2.4	1.8 – 2.3	0.4	0.3

[a] From S. Hansbo, *Foundation Engineering, Developments in Geotechnical Engineering 75*, Elsevier, 1994.

[b] Based on M. N. Sara, *Standard Handbook for Solid and Hazardous Waste Facility Assessments*, CRC/Lewis Publishers, 1994. From the compilation of the analyses of 1,323 (clayey to sandy) soils, the smallest effective porosity (of 0.2) is associated with sandy clay soils. The values for effective porosity in this table should be used with care, particularly those for clay soils. Effective porosity in clay soils may be much less than indicated here. These effective porosity values should not be used if fractures exist, such as in clay tills.

Table D-2

Chemical-Specific Properties for Selected Petroleum VOC Contaminants

COMPOUND	SOLUBILITY IN WATER (mg/L)[a]	HENRY'S LAW CONSTANT (unitless)	K_{OC} (L/Kg)
Benzene	1,800.[b]	0.228[e]	59.[e]
Ethyl Benzene	170.[b]	0.323[e]	363.[e]
Dibromoethane, 1,2 (EDB)	4,200.[f]	0.013[g]	28.[g]
Dichloroethane, 1,2	8,500.[f]	0.040[g]	17.[e]
Toluene	530.[b]	0.272[e]	182.[e]
Xylene, m	160.[b]	0.301[e]	407.[e]
Xylene, o	180.[b]	0.213[e]	363.[e]
Xylene, p	190.[b]	0.314[e]	389.[e]
Trimethylbenzene, 1,2,4	57.[c]	0.230[g]	3,700.[g]
Trimethylbenzene, 1,3,5	48.[c]	0.320[g]	820.[g]
Methyl-tert-butyl ether (MTBE)	51,260.[d]		12.[f]

[a] Solubilities are at 25° C. Groundwater temperatures are much lower than 25° C, so a compound's solubility may be significantly different from that listed here.

[b] Ref: Superfund Chemical Data Matrix, 1996, CHEMEST Data Base.

[c] Ref: Literature Survey: Hydrocarbon Solubilities and Attenuation Mechanisms API Publication No. 4414, August, 1985.

[d] Ref: Chemical Summary for MTBE, U.S. EPA, Office of Pollution Prevention and Toxics, August 1994.

[e] Ref: Soil Screening Guidance, Technical Background Document, U.S. EPA Doc. # EPA/5401R-95/128, July 1996.

[f] Ref: RNA Tool Kit, Florida Petroleum Cleanup Program Guidance Manual, Groundwater Services, Inc., 1998.

[g] Ref: U.S. EPA Region 9, Table of Preliminary Remediation Goals: Physical and Chemical Values. http://www.epa.gov/region09/waste/sfund/prg

Table D-3

Chemical-Specific Properties for Selected Polycyclic Aromatic Hydrocarbons (PAHs)

COMPOUND	SOLUBILITY IN WATER (mg/L) [b]	HENRY'S LAW CONSTANT (unitless)	K_{OC} (L/Kg)
Acenaphthene	3.93	0.00636 [b]	7,080. [a]
Acenaphthylene	16.		4,786. [b]
Anthracene	0.043	0.00267 [b]	29,500. [a]
Benzo(a) Anthracene	0.0094	0.000137 [b]	398,000. [a]
Benzo(a) Pyrene	0.0016	0.0000463 [b]	1,020,000. [a]
Benzo (b) Fluoranthene	0.0015	0.00455 [b]	1,230,000. [a]
Benzo (g,h,i) Perylene	0.00026		7,760,000. [b]
Benzo (k) Fluoranthene	0.0008	0.0000340 [b]	1,230,000. [a]
Chrysene	0.0016	0.00388 [b]	398,000. [a]
Dibenzo (a,h) Anthracene	0.0025	0.000000603 [b]	3,800,000. [a]
Fluoranthene	0.21	0.000660 [b]	107,000. [a]
Fluorene	2.	0.00261 [b]	13,800. [a]
Indeno (1,2,3,c,d) Pyrene	0.000022	0.0000656 [b]	3,470,000. [a]
Naphthalene	31.	0.0198 [b]	2,000. [a]
Phenanthrene	1.2		5,248. [b]
Pyrene	0.14	0.000451 [b]	105,000. [a]

[a] Ref: Calculated K_{OC} tabulated in Soil Screening Guidance, Technical Background Document, U.S. EPA Doc. # EPA/5401R-95/128, July 1996

[b] Ref: RNA Tool Kit, Florida Petroleum Cleanup Program Guidance Manual, Groundwater Services, Inc.