

Petroleum Cleanup Program

REMEDIAL ACTION GUIDELINES

BUREAU OF PETROLEUM STORAGE SYSTEMS

History: New 5/8/98

Identification No.: BPSS-11

Topic of Guideline: Natural Attenuation Evaluation Procedures

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Monitoring of natural attenuation is a recognized strategy for the remediation of petroleum contaminated sites. Natural attenuation relies on natural processes including bioremediation, chemical reactions with subsurface materials, sorption, dispersion, diffusion, and volatilization to contain the spread of contamination and reduce the concentrations of contaminants in soil and groundwater. Most chemicals found in petroleum fuels are amenable to these processes and natural attenuation can be expected to be occurring to some degree at most petroleum contaminated sites. Many site-specific variables affect the rates of natural attenuation, including the soil and aquifer physical characteristics, soil and groundwater chemistry, and types of petroleum products in the soil and groundwater. The time frame for a site to achieve cleanup objectives through natural attenuation will depend on these factors plus the initial mass of contamination in different phases at the site. Monitoring of natural attenuation is only appropriate if human health and the environment are adequately protected while monitoring occurs and if the cost of monitoring natural attenuation is less than the cost of other remediation alternatives. Monitoring of natural attenuation may be appropriate after the completion of the site assessment, after a source removal activity following the completion of the site assessment, or after some other short term or longer term remediation strategy, depending on site-specific variables.

The Department has approved natural attenuation monitoring plans in our cleanup programs for several years in the form of Monitoring Only Plan (MOP) approvals. The criteria for MOP approvals was previously set out in a guidance document titled "No Further Action and Monitoring Only Guidelines for Petroleum Contaminated Sites." This guidance allowed for a "Monitoring Only" site remediation strategy for sites that met certain specified requirements. The Department's experience has been

that "Monitoring Only" was successful on the majority of the sites in that monitoring resulted in sites ultimately qualifying for No Further Action.

Revisions to Chapter 62-770, FAC, which became effective September 23, 1997, have incorporated specific requirements into the rule for determining if monitoring of natural attenuation is an acceptable remedial strategy. The revised rule allows the consideration of natural attenuation monitoring for a broader range of site conditions than was possible under the Department's previous guidance. The rule requirements allow for two general procedures to justify natural attenuation as a cleanup remedy.

The first procedure, which is described in Rule 62-770.690(1)(a) through (e) and as "Level 1 Evaluation" in this guidance, allows for a simplified justification that natural attenuation is the appropriate cleanup strategy. This concept is similar to the one followed in the Department's former guidance document. In effect, if certain conservative criteria are met, natural attenuation may be considered a presumptive remedy for the site.

If the criteria for the Level 1 Evaluation are not met, natural attenuation may still be demonstrated to be an appropriate cleanup strategy; however, a more rigorous demonstration is necessary in accordance with the second procedure described in Rule 62-770.690(1)(f), FAC, and referred to as "Level 2 Evaluation" in this guidance.

An important issue when considering monitoring of natural attenuation as a cleanup strategy is the need to achieve cleanup criteria for soil as well as groundwater. Even if the groundwater is ultimately remediated by natural attenuation to the groundwater cleanup target levels in Chapter 62-770, a No Further Action Without Conditions may only be granted if the soil cleanup target levels are also achieved. If soil concentrations exceeding the soil cleanup target levels remain on site, the soil will have to be remediated or, alternately, a No Further Action With Conditions may be granted if the site owner is willing to agree to deed restrictions as assurance that engineering and/or institutional controls will remain in effect. The strategy for dealing with soil contamination exceeding the soil cleanup target levels (remediation or institutional controls) must be considered before embarking on a program of long term monitoring of natural attenuation of groundwater.

Another important consideration is the concentration of MTBE relative to other chemicals of concern. Though natural attenuation relies on physical processes as well as biological processes, the biological processes generally dominate and are necessary for monitoring of natural attenuation to be successful. MTBE does not readily biodegrade. The abundance of MTBE relative to other petroleum hydrocarbons should be given special

consideration because its overall rate of natural attenuation may be lower than other petroleum hydrocarbons.

Once natural attenuation has been determined to be a feasible and cost-effective remediation method by either the Level 1 Evaluation or Level 2 Evaluation process, annual milestones for monitoring well concentration reductions must be established as required by Rule 62-770.690(7)(g), FAC. Monitoring well concentrations can generally be expected to decline in an exponential manner, however, for the purpose of establishing milestones, a straight line reduction based on the projected number of years to attain cleanup completion (5 years or less for Level 1 Evaluation) may be assumed when establishing annual milestone concentrations. It is acceptable to establish an average annual milestone concentration for each year of natural attenuation for the wells monitored rather than individual milestone concentrations for individual wells. However, all monitoring wells must ultimately achieve the groundwater cleanup target levels to qualify for No Further Action with no conditions.

Level 1 Evaluation (from Rule 62-770.690(1)(a) through (e), FAC)

A proposal for natural attenuation monitoring may be submitted to the Department if the following provisions of Rule 62-770.690(1)(a) through (e) are met, which are repeated here in abbreviated form and with some explanation added:

- a. There is no floating phase-separate product with a thickness greater than the thickness specified in the Department's definition of "free product" of .01 feet.
- b. Contaminated soil does not exist to the extent that it may result in increased cleanup cost (time and cost of natural attenuation monitoring). Careful consideration needs to be given to the results of the soil analyses that have been conducted at the site. An NFA without conditions may only be granted at a point in the future if both the soil cleanup criteria of Table IV and the groundwater cleanup criteria of Table V have been achieved. It may do little good to monitor natural attenuation of groundwater while doing nothing to remediate soil with concentrations above the direct exposure criteria of Table IV if the site owner is not willing to agree to engineering and/or institutional controls for the soil contamination that will remain when natural attenuation monitoring has achieved the groundwater cleanup target levels. Some natural attenuation of soil may also be occurring while monitoring of natural attenuation of groundwater is proceeding, but this process is much more problematic to predict or monitor than that of groundwater, and the rate of natural attenuation of soil may be too slow

relative to the soil cleanup target levels that must be achieved. In any case, monitoring of natural attenuation should not proceed if there are concentrations of petroleum chemicals of concern above the Table IV direct exposure criteria in the top two feet of the site unless an engineering control (e.g.-pavement) is present to protect the public from exposure to the soil during natural attenuation monitoring of groundwater.

- c. Groundwater concentrations are not migrating beyond a temporary point of compliance (TPOC), or migrating vertically that may result in increased cleanup costs. The TPOC may be within the property boundary, at the property boundary, or beyond the property boundary. The significance of the TPOC is that it is a downgradient monitoring well that is not currently contaminated and is expected to remain uncontaminated (that is, cleanup target levels are not exceeded) during the monitoring period (stable or shrinking plume). If the TPOC is an off-site monitoring well, it will be necessary to notify the property owner(s) on whose property the contaminant plume extends and any county or municipality having jurisdiction over the area before initiating the monitoring program.
- d. If more than one sampling event has been performed, the available data show an overall decrease in mass. In other words, historical concentrations in monitoring wells indicate an overall declining trend.
- e. The site is anticipated to achieve No Further Action levels as a result of natural attenuation in five years or less and the concentrations of chemicals of concern are less than the Table IX levels (Attachment A). For the purpose of the Level 1 Evaluation, if the current concentrations are less than the Table IX levels in all monitoring wells, in most cases it can be assumed that the site will reach cleanup objectives by monitoring natural attenuation in five years or less.

It should be noted that even though natural attenuation monitoring is expected to be appropriate for most sites that meet the above Level 1 Evaluation criteria, there will be a subset of those sites which will probably not achieve cleanup objectives in a cost effective manner by natural attenuation monitoring alone. Therefore, there may be instances where sites that meet the above criteria should still perform the more rigorous demonstration described below as "Level 2 Evaluation." Some of the circumstances which may call for this are: site assessment information indicates that there is significant source mass on site that will take a substantial time frame to decay, there is previous monitoring data that indicates a less-than-adequate trend of decreasing concentrations in monitoring wells, or that

the primary chemicals of concern on site are the longer chain, less biodegradable compounds. If these circumstances exist, or if monitoring of natural attenuation is initiated on a site that meets the Level 1 Evaluation criteria but monitoring data suggest the site will not achieve cleanup objectives in five years or less, than the more extensive evaluation described below may be appropriate.

Level 2 Evaluation (from Rule 62-770.690(1)(f), FAC)

Natural attenuation monitoring may be proposed as a cleanup strategy at sites that meet the criteria of (a) through (d) above but do not meet item (e) above if the cost-effectiveness of natural attenuation monitoring is demonstrated based on:

- a. A technical evaluation of groundwater and soil characteristics, chemistry, and biological activity.
- b. A scientific evaluation of the plume migration in relation to the TPOC and an estimate of the time needed to achieve the No Further Action Criteria.
- c. A cost analysis of remedial alternatives.

There is potentially a range of levels of effort associated with the demonstration described above. An incremental approach to the evaluation, which depends on site-specific conditions, is appropriate. The following "Procedures for the Verification of Natural Attenuation" were developed by the Technical Advisory Committee, which provided suggestions for program improvements to the Bureau of Petroleum Storage Systems through a series of meetings held between January of 1997 and February of 1998.

PROCEDURES FOR THE VERIFICATION OF NATURAL ATTENUATION

A. EXAMINATION OF HISTORIC DATA

An investigation of the areal and vertical extent of the contaminant plume over time may be performed if sufficient historical data is available. The examination of the data must establish if the plume is expanding, stable or shrinking. An expanding plume may be considered under Section C.

An evaluation must be performed to determine the decay rate kinetics as a function of time (shrinking plume) or distance (stable plume or limited historical data) for all chemicals of concern. These evaluations should utilize applicable reaction order equations to establish decay rates. Attachment B is an excerpt from the ASTM Draft "Standard Guide For Remediation of Ground Water By Natural Attenuation At Petroleum Release Sites" (Reference 4) and may be used to establish decay rates. References 1, 2, 3, and 7 at the end of this guideline also describe the derivation of decay rates.

Any additional rationale for historical concentration variations must be identified (i.e. source removal events or other remedial activities, groundwater table fluctuations, etc.) and only relevant data utilized. The statistical and practical relevance of the attenuation rate determination must be evaluated.

If decay rate kinetics as a function of distance are evaluated, the following information is required:

1. The groundwater flow direction must be defined (if necessary, based on multiple monitoring events covering the tidal cycle).
2. Concentration data must be available from a minimum of three monitoring wells along the direction of groundwater flow.
3. The calculation of K requires an estimate of the groundwater velocity. In the absence of a reliable velocity estimate (no pump test performed), the k/v factor may be useful relative to comparable sites with available data.

B. EVALUATION OF GEOCHEMICAL INDICATORS SUPPORTING NATURAL ATTENUATION

If sufficient historical data is not available to support Natural Attenuation, a more aggressive assessment of the geochemical indicators may be performed to demonstrate the role of intrinsic bioremediation. This additional assessment may also be utilized as further support for the historical data evaluation as referenced above.

Based upon the Site Assessment, representative monitoring wells indicating groundwater contamination, as well as a sufficient number of up gradient and down gradient wells, should be sampled for the chemicals of concern and all appropriate biological indicators. The selection criteria for representative monitoring wells should include concentration distribution, areas of potential aeration such as drainage structures, backfill areas and other heterogeneities, monitoring well construction, etc. The analytical data should be utilized to properly evaluate concentration trends between contaminated and non-contaminated areas.

In background areas where Dissolved Oxygen (DO) concentrations are above 1-2 mg/l, it may be assumed that oxygen is the preferred electron acceptor. Biological indicators for aerobic degradation should include at a minimum:

- DO*
- pH*

In background areas, where DO concentrations are below 1.0 mg/l, biological indicators for anaerobic degradation may be considered and should include, but not be limited to:

- sulfate
- nitrate
- iron
- methane
- Redox potential
- pH

*These parameters must be analyzed in the field utilizing an appropriate sampling procedure that minimizes aeration of the groundwater sample. See Attachment C and References 5, 8, and 9, of this guideline.

Supplemental data such as microbial enumeration and nutrients may be considered for either study.

The significantly slower kinetics associated with biodegradation in an anaerobic environment must be fully evaluated in determining whether Natural Attenuation (without enhancement) is a suitable remedial alternative at sites with low background DO levels. The indicators of biodegradation should be evaluated as described in Attachment D which is an excerpt from the ASTM Draft "Standard Guide For Remediation of Ground Water By Natural Attenuation At Petroleum Release Sites" (Reference 4). The theoretical biodegradation capacity should be calculated as described in the Attachment E table for this evaluation.

C. FATE AND TRANSPORT MODELING

For cases with complex site conditions (expanding plume, multiple sources, preferential pathways/complex hydrology, mixed plumes, deep contamination, continuing source, etc.), a scientific evaluation consisting of a fate and transport model addressing all appropriate attenuation processes may be required. A listing of appropriate models will be maintained by FDEP and updated as necessary.

All input parameters must be fully justified based upon site specific field testing, bio-laboratory verification/studies or sound, technical assumptions. The calculated error must be determined and fall within a scientifically acceptable range. If sufficient data exist, the model or applicable portions of the model must be properly calibrated.

Based upon the results of the above evaluation, the estimated time to achieve NFA criteria may be calculated. Supporting calculations must be submitted confirming that intrinsic remediation is the most cost effective and suitable remedial alternative. The

intrinsic remediation is the most cost effective and suitable remedial alternative. The cost evaluation may consist of a cost comparison with alternative remedial technologies (or a combination of technologies) and may include design, implementation and monitoring costs for the duration of the remedial activities. It may be useful to make note of the estimated cost of site remediation by the most cost-effective alternative other than natural attenuation for future reference. This may be useful later when evaluating natural attenuation monitoring information. If it appears that the timeframe for natural attenuation monitoring may be longer than the original estimate, knowing the approximate cost of active remediation may simplify and expedite the decision of whether to continue monitoring of natural attenuation and establish new annual milestone objectives.

MONITORING

A. Initial year

If sufficient historic data do not exist quarterly sampling shall be performed for the initial year of monitoring. At a minimum, a representative number of source wells and one down gradient well should be included. Parameters should include:

- water table elevation,
- chemicals of concern,
- appropriate biological indicators (these parameters may be eliminated once the Department has determined that sufficient data exist to support natural attenuation).

B. Subsequent years

Semiannual or annual monitoring for the parameters stipulated in the initial year monitoring shall be required. The frequency shall be based upon the results of the initial year data or historic data and upon the estimated time of clean-up.

Monitoring status reports shall be submitted semiannually for the initial year and annually thereafter. An evaluation of the original models or analytical predictions must be performed and submitted within the status reports. All models and original analytical predictions must be properly calibrated or verified once the monitoring data is available. The results of the monitoring and evaluation shall be compared to the established annual milestone reductions of concentrations in monitoring wells. An evaluation may be required to determine whether costs incurred during the remaining monitoring period will exceed costs associated with active remediation.

Based upon the results of the evaluation, it must be determined if the annual rate of expected cleanup has been achieved or if additional assessment or a more aggressive remedial approach is required.

REFERENCES

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5. Wiedemeier, T.H.; Wilson J.T.; Kampbell, D.H.; Miller, R.N.; Hansen, J.E., Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater", Air Force Center for Environmental Excellence, November 11, 1995.
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Attachment A

TABLE IX
Natural Attenuation Default Source Concentrations

Benzene	100 ug/l
Ethylbenzene	300 ug/l
Toluene	400 ug/l
Total Xylenes	200 ug/l
MTBE	350 ug/l
Acenaphthene	200 ug/l
Acenaphthylene	2100 ug/l
Anthracene	21000 ug/l
Benzo(a)anthracene	20 ug/l
Benzo(a)pyrene	20 ug/l
Benzo(b)fluoranthene	20 ug/l
Benzo(g,h,i)perylene	2100 ug/l
Benzo(k)fluoranthene	50 ug/l
Chrysene	500 ug/l
Dibenzo(a,h)anthracene	20 ug/l
Fluoranthene	2800 ug/l
Fluorene	2800 ug/l
Indeno(1,2,3-c,d)pyrene	20 ug/l
Naphthalene	200 ug/l
Phenanthrene	2100 ug/l
Pyrene	2100 ug/l
1,2-dichloroethane	300 ug/l
1,2-dibromoethane (EDB)	2 ug/l
Arsenic	500 ug/l
Barium	20000 ug/l
Cadmium	50 ug/l
Chromium	1000 ug/l
Lead	150 ug/l
Mercury	20 ug/l
Selenium	500 ug/l
Silver	1000 ug/l
TRPHs	50 mg/l
Chloride	2500 mg/l *
Sulfate	2500 mg/l *
Total Dissolved Solids	5000 mg/l *

* Only applicable to sites where the contamination is derived from petroleum as defined in Section 376.301, F.S.

X6.2.1 Concentration versus Time - Shrinking Plume

Dissolved hydrocarbon plumes may decrease in size, as observed by declining contaminant concentrations in monitoring wells. The conditions of a shrinking plume suggest some form of source control or removal, either by engineered remediation or by natural source attenuation (flushing, biodegradation, etc.) A sufficiently deep water table may limit the contaminant mass loading to ground water. Given the conditions of a shrinking plume, the rate of natural attenuation must be greater than the rate of contaminant addition (McAllister and Chiang 1994).

Salanitro (1993) indicates a shrinking plume has significant reinfiltration of oxygenated water into the aquifer (precipitation). Wells on the periphery of these types of plumes have higher dissolved oxygen (DO) and lower BTEX concentrations, consistent with BTEX biodegradation. Analysis of shallow and deep monitoring wells show that the soluble plume "shrinks" in the longitudinal direction with little vertical dispersion (Chiang et al. 1989). In the three examples described by Salanitro (1993), mass balance analysis of the hydrocarbon in the aquifer show that natural biodegradation by soil biota must be responsible for most (80 to 100%) of the apparent reduction and retardation of the BTEX plume.

Exponential regression methods can be used to evaluate whether concentration versus time data fit a first-order decay observed for petroleum hydrocarbons under certain conditions. The solution to the first-order decay is given by the following equation:

$$C(t) = C_i e^{-kt} \quad 1$$

$C(t)$ (M/L³) is concentration as a function of time, t (T).

C_i is the concentration at $t = 0$.

k is the first-order attenuation rate (T⁻¹).

The temporal regression technique is based on equation (1), in which concentration is expressed as a function of time. Contaminant concentration versus time is plotted for a hypothetical monitor well in Figure X6.3. Concentration is plotted on a log scale, consistent with the assumption of first-order degradation. If a first-order decay describes the apparent contaminant concentration decline, the data plot as a straight line. Exponential regression of log concentration versus time yields a value proportional to the slope of the regressed line (k), the y-intercept (C_i), and the goodness of fit (R^2 value).

A more general form of equation (1) may be appropriate to fit late-time data which are asymptotic. This equation is given as follows:

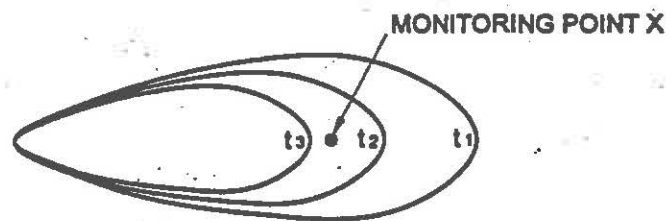
$$C(t) = (C_i - C_a) e^{-kt} + C_a \quad 2$$

C_a is the asymptotic concentration.

As C_a approaches zero, equation (2) reduces to equation (1). Equation (2) is useful to fit data to an asymptotic concentration. It can also be used to confirm the long-term, asymptotic concentration (Chiang et al. 1989, API 1991).

The transport processes contributing to these first-order attenuation rates include volatilization, dispersion, sorption, dilution by recharge, and biological degradation. It is difficult to distinguish these mechanisms using the temporal method. However, as partitioning approaches equilibrium, sorption is less significant in reducing solute concentrations with time. Wilson et al. (1993) suggest the use of a recalcitrant, organic compound, having similar sorptive properties as the biodegradable compound of interest, to serve as a tracer.

PLUME MAP



**CONCENTRATION VERSUS TIME
AT MONITORING POINT X**

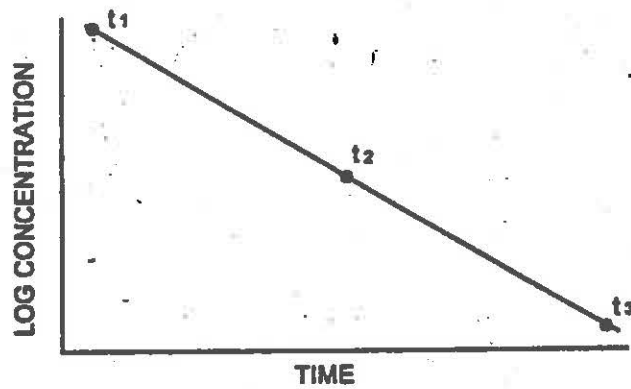


FIGURE X6.3 SHRINKING PLUME

X.6.2.2 Concentration versus Distance - Stable Plume

A stable plume is characterized by dissolved contaminant concentrations remaining constant over time in individual monitoring wells. Short-term variations in monitoring well concentrations due to water table fluctuation, variability in ground water flow direction, sampling variability, and analytical uncertainty should be distinguished from statistically significant concentration changes. In order for a plume to reach stable conditions, the rate of natural attenuation must be equal to the rate of contaminant addition to the aquifer from the source (McAllister and Chiang 1994). The contaminant source or influx rate is limited by the compound's effective solubility and the flow rate of water through the source area (infiltration, fluctuating water table, etc.).

Time, t , can be described in terms of seepage velocity, v (L/T) and distance traveled, x (L).

$$t = \frac{x}{v} \quad 3$$

The term " x/v " is the residence time for ground water to move some distance, x , from the source. Kemblowski et al. (1987) substituted equation (3) into equation (1), and the first-order attenuation rate can be recast for concentration as a function of distance:

$$C(x) = C_0 e^{-k \frac{x}{v}} \quad 4$$

$C(x)$ is concentration as a function of distance, x (L).

C_0 is the concentration at $x = 0$.

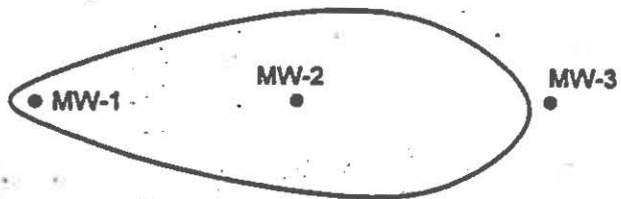
k is the first-order attenuation rate (T^{-1})

The spatial regression technique is based on equation (4). The regression of concentration versus distance is appropriate for the stable plume. It can also be used for a shrinking plume for individual monitoring events. The ground water flow direction is defined based on multiple monitoring events covering the hydrologic cycle. A minimum of three monitoring wells are selected along the ground water trajectory (see Figure X6.4). Figure X6.4 is a plot of compound concentration (log scale) versus distance. If data from multiple sampling events are available for a stable plume, the concentrations plotted should be the average concentration over time for each well. If concentrations decline with time, concentration versus distance can be plotted for individual monitoring events. From the exponent in equation (4), the slope of the line in Figure X6.4 is k/v (L^{-1}), the reciprocal of the attenuation distance. If this slope is multiplied by ground water velocity, v (L/T), we obtain the attenuation rate, k (T^{-1}). In the absence of a reliable estimate of ground water velocity, the k/v term is useful, particularly for selecting the downgradient monitoring well locations.

X.6.2.3 Expanding Plume

The calculation of RNA rate is not as straightforward for an expanding plume as it is for a shrinking or stable plume. It is possible to compare the actual rate of migration to the expected rate of migration, assuming sorption only (contaminant velocity). Using the Mass Balance Approach described in X6.1, it is also possible to estimate the attenuation rate (lbs/day), as less than the contaminant mass loading to the water table. Transient analytical solutions can be used to predict the migration distance of an expanding plume or the time required to reach a particular configuration. These analytical models are presented in X6.4.

WELL LOCATION MAP



CONCENTRATION VERSUS DISTANCE

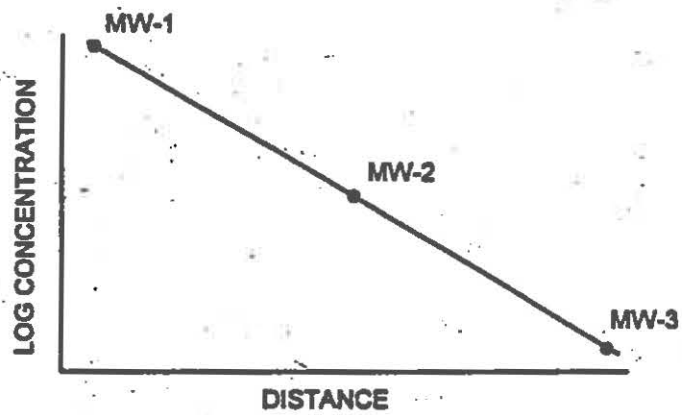


FIGURE X6.4 AVERAGE COMPOUND CONCENTRATION VERSUS DISTANCE FOR A KNOWN STABLE PLUME

X6.3 One-Dimensional Analytical Solution for a Stable Plume

The graphical/regression techniques described in X6.2 yield an attenuation rate which does not distinguish between sorption, dispersion, and biodegradation. The objective of X6.3 is to evaluate the contribution of biodegradation to the overall attenuation rate. This is accomplished by using an analytical solution which includes advection, dispersion, sorption, and decay (biodegradation). The concentration versus distance regression for a stable plume is coupled with this analytical solution for one-dimensional, steady-state contaminant transport. This method, presented in Buscheck and Alcantar (1995) is intended to distinguish those mechanisms which contribute to natural attenuation. Wiedemeier et al. (1996) also demonstrate the use of this method.

The general one-dimensional transport equation, with first-order decay of the contaminant, is given by the following equation:

$$\frac{\partial C}{\partial t} = \frac{1}{R} \left[D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} \right] - \lambda C \quad 1$$

Where D_x (L^2/T) is the dispersion coefficient, v_x (L/T) the seepage velocity in the x direction, R (-) the retardation coefficient and λ (T^{-1}) is the total decay rate. The form of equation (1) assumes D_x is constant and independent of distance, x . While the terms in brackets describe the mass transport by dispersion and advection, respectively, the retardation coefficient characterizes the contribution of sorption. The form of this equation assumes degradation occurs in the aqueous and sorbed phases at the same rate. If biological transformation of the contaminants occurs primarily in the aqueous phase, the term " λC " would also appear inside the brackets.

Dispersion and linear ground water velocity are related by the longitudinal dispersivity, α_x (L), which has been described by empirical expressions:

$$D_x = \alpha_x v_x \quad 2$$

The retardation coefficient (R) accounts for partitioning between the solid and aqueous phases. R describes the relationship between the seepage velocity, v_x and contaminant velocity, v_c (L/T):

$$R = \frac{v_x}{v_c} \quad 3$$

Chiang et al. (1989) demonstrated that the contribution of volatilization to the dissolved contaminant attenuation was only 5% at one site. Except in the case of very shallow ground water, volatilization is not expected to contribute significantly to the overall attenuation. Therefore, volatilization is neglected and the decay rate is assumed to be a measure of biodegradation of BTEX compounds.

Bear (1979) obtained the following solution for one-dimensional transport with a first-order decay:

$$C(x,t) = \left(\frac{C_0}{2}\right) \exp\left[\left(\frac{x}{2\alpha_x}\right)\left[1 - \left(1 + \frac{4\lambda\alpha_x}{v_c}\right)^{\frac{1}{2}}\right]\right] \operatorname{erfc}\left[\frac{x - v_c t \left(1 + \frac{4\lambda\alpha_x}{v_c}\right)^{\frac{1}{2}}}{(4\alpha_x t v_c)^{\frac{1}{2}}}\right] \quad 4$$

This solution is based on the assumptions that the contaminant concentration is initially zero, a continuous dissolved hydrocarbon source exists at C_0 , and the transport is contained within a semi-infinite medium. The respective initial and boundary conditions are as follows:

$$C(x,0) = 0$$

$$C(0,t) = C_0$$

$$C(\infty,t) = 0$$

Equation (4) reflects a steady-state when the complementary error function (erfc) argument approaches +2, such that the point of observation, x , is behind the advective front $vt(1+4\lambda\alpha_x/v_c)^{1/2}$ (Domenico and Schwartz 1990). As such, the steady-state solution is:

$$C(x) = C_0 \exp\left[\left(\frac{x}{2\alpha_x}\right)\left[1 - \left(1 + \frac{4\lambda\alpha_x}{v_c}\right)^{1/2}\right]\right] \quad 5$$

For the case in which decay occurs only in the aqueous phase, the contaminant velocity, v_c , is replaced by the seepage velocity, v_x .

As the decay rate, λ , increases with respect to the other transport mechanisms, the extent of the plume at steady-state will decrease. As decay rate increases relative to the other mechanisms, the concentration away from the source ($x > 0$), approaches zero since the material is decaying at a greater rate than it is being transported through the medium. Similarly, as the contaminant velocity increases, the decay becomes ineffective in reducing concentrations as a function of distance. Retarded contaminants therefore have a greater opportunity to decay because retarded velocities favor biodegradation kinetics over transport (Domenico and Schwartz 1990).

The regression of contaminant concentration versus distance was developed in X6.2.2. This equation yields the reciprocal of the attenuation distance, k/v_x (L^{-1}):

$$C(x) = C_0 e^{-\left(\frac{x}{v_x}\right)} \quad 6$$

Equations (5) and (6) are of the same form:

$$C(x) = C_0 \exp(mx) \quad 7$$

The slope of the log-linear data is given by m . The one-dimensional, steady-state transport solution also describes the slope, m , of the log-linear data:

$$m = \left(\frac{1}{2\alpha_x}\right) \left[1 - \left(1 + \frac{4\lambda\alpha_x}{v_c}\right)^{1/2}\right] \quad 8$$

Therefore, the term k/v_x and equation (8) both describe the slope of the log-linear data and can be equated to solve for the total decay rate, λ , a measure of intrinsic bioremediation of petroleum hydrocarbons. Dispersivity (α_x), contaminant velocity (v_c), and k/v_x are input to following equation to calculate the decay rate (Buscheck and Alcantar 1995).

$$\lambda = \left(\frac{v_c}{4\alpha_x}\right) \left(\left[1 + 2\alpha_x\left(\frac{k}{v_x}\right)^2\right] - 1\right) \quad 9$$

For the case in which decay occurs only in the aqueous phase, v_c is replaced by v_x in equation (9).

Attachment C

Parameter	Field or Lab. Method	Analytical Method(s)	Comments	Use of Data
pH	Field	EPA Method 150.1 or SW-9040 direct reading meter ASTM D 1293-84	Can be analyzed in flow through cell or collect 100-250 mL of water in glass or plastic container and analyze immediately. Calibration should be conducted using manufacturers standard solutions.	Difference in pH between contaminated and uncontaminated groundwater may indicate biological activity is occurring.
Temperature	Field	EPA Method 170.1	Available from some DO, ORP, pH, or EC probes. Can be analyzed in flow through cell or from 100-250 mL of water collected	Oxygen solubility is dependent on groundwater temperature. Biodegradation rates may depend on temperature. An increase in

			and analyzed immediately.	temperature may be seen within the solute plume
Dissolved Oxygen (DO)	Field	<p>Meter and Probe Flow through cell</p> <p>D 888-92(B) 360.1</p> <p>360.1 ASTM D 888-92 (A) Winkler titration</p> <p>Down hole probe</p>	<p>With all DO methods extra care must be taken to avoid aeration during all steps of the analysis including well purging and sample collection. Utilizes a flow thru cell with a dissolved oxygen electrode. Other parameters such as temperature, pH, oxidation reduction potential and conductivity can be measured simultaneously. If an oxygen consuming probe is used, then care must be taken to ensure sufficient and continuous flow from the well through the cell.</p> <p>Field kits for performing Winkler titrations can be used as the primary method of DO measurement or to confirm meter measurements. A combination of both methods can be used to ensure data quality.</p> <p>If an oxygen consuming probe is used down hole, then gentle agitation of the probe is required. Vigorous agitation should be avoided to prevent aeration. This technique is recommended only in low permeability conditions where continuous well purging is not possible.</p>	<p>An inverse correlation of DO to BTEX concentrations indicates aerobic biodegradation is occurring. This relationship may also be expressed as depressed or non-detectable levels of DO throughout the plume.</p>
Ferrous Iron	Field	<p>Colorimetric Std. Methods 18th Edition. Method 3500-Fe D Hach 25140-25</p>	<p>Collect 100 mL of water in glass container. Filter sample with 0.2 μ filter.</p>	<p>Increased concentrations of Fe(II) may indicate Fe(III) is being used as an electron acceptor during anaerobic biodegradation of petroleum hydrocarbons.</p> <p>Also useful in assessing feasibility of other corrective action alternatives.</p>

Total Dissolved Iron	Lab	Atomic adsorption SW-846 Method 7380/7381 ICP SW-846 Method 6010A 200.7	filter, 0.2 μ ; acidify; refrigerate.	Increased dissolved Fe may indicate Fe(III) is being used as an electron acceptor during anaerobic biodegradation of petroleum hydrocarbons. Also useful in assessing feasibility of other corrective action alternatives.
Oxidation Reduction Potential	Field	Ion Selective Electrode direct reading meter 2580 B (SM) ASTM D 1498-93	ORP probe can be inserted into flow thru cell and reading obtained simultaneously with DO, pH, T, and EC. Can be taken downhole if necessary.	Define regions of the plume under oxidizing and reducing conditions. Evaluate potential for biologically mediated redox reactions to occur. Helps validate DO measurements. Determine Eh values.
Nitrate	Field	Colorimetric field kit	Collect 100 mL of water in a glass container.	Decreased nitrate concentrations in anaerobic portion of the plume may indicate use of nitrate as an electron acceptor for anaerobic biodegradation of petroleum hydrocarbons.
	Lab	EPA method 353.2 SW9056 300.0 ASTM D 4327-91	Collect 100 mL of water in a glass or plastic container, cool to 4°C and analyze within 48 hours.	
Sulfate	Field	Colorimetric field kit.	Collect 100 mL of water in a glass or plastic container, cool to 4°C, analyze immediately.	Decreased sulfate concentrations in anaerobic portion of the plume may indicate use of sulfate as an electron acceptor for anaerobic biodegradation of petroleum hydrocarbons.
	Lab	EPA Method 375.4 or SW-9056 ASTM D 4327-91	Collect 100 mL of water in a glass or plastic container, cool to 4°C, analyze within 28 days.	
Manganese	Field	Colorimetric	Collect 100 mL of water in a glass container. Filter sample with 0.2- μ filter.	Increased Mn(II) may indicate Mn(IV) is being used during anaerobic biodegradation as a terminal electron acceptor.
	Lab	EPA Method 6010 3010/200.7		
Alkalinity	Field	Field test kit.	Collect 100 to 250 mL of water in a glass container.	Typically, total alkalinity is primarily due to carbonate alkalinity. Thus, alkalinity is a measure of dissolved
	Lab	310.1 EPA method 310.2	Collect 100 mL of water in a glass	

		Colorimetric	container cool to 4°C	carbonate and bicarbonate. A zone of increased alkalinity indicates biodegradation is either producing organic acids which lower the pH and solubilize carbonate from the soil or CO ₂ is being produced.
<p>Additional Parameters: In some cases, it may be necessary to evaluate additional indicators of biodegradation if the primary indicators are insufficient, or if it is desired to further understand the potential mechanisms of biodegradation. These parameters may increase the complexity of interpretation and/or the analytical effort.</p>				
Parameter	Field or Lab. Method	Analytical Method	Comments	Use of Data
Methane	Field or Lab GC	Head Space; GC/FID. IJEAC 3810 - Screening	Collect water samples in 40 mL VOA vials with butyl gray/Teflon-lined caps. Head space is analyzed by GC equipped with thermal conductivity and/or flame ionization detector.	Elevated concentrations may indicate anaerobic degradation using carbon dioxide as an electron acceptor.
Carbon Dioxide	Lab GC or Field Method	Head Space; GC/TCD. IJEAC Field titration kit 4500	Collect water samples in 40 mL VOA vials with butyl gray/Teflon-lined caps. Head space is analyzed by GC equipped with thermal conductivity and/or flame ionization detector.	Elevated carbon dioxide levels may indicate aerobic biodegradation or depleted levels may indicate methanogenesis is occurring. Carbon dioxide data must be collected and reviewed carefully due to complex geochemical interactions.
Dissolved sulfides	Field	Colorimetric ASTM D 4658-92	Collect 100 mL of water in a glass container and analyze immediately.	Increased levels above background may indicate sulfate-based anaerobic respiration

ASTM - American Society for Testing of Materials, standard methods.

Hach - HACH Company, P.O. Box 389, Loveland Colorado.

IJEAC - Kampbell, D.H., J.T. Wilson, and S. A. Vandegrift, 1989. Dissolved oxygen and methane in water by a gas chromatography headspace equilibrium technique. International Journal of Environmental Analytical Chemistry, 36:249-257.

Std. Methods - Standard Methods for the Examination of Water and Wastewater, 1992. American Public Health Assoc., American Water Works Assoc., Water Environment Assoc., 18th Edition.

EPA, SW-846 - Test Methods for Evaluating Solid Waste, 1992. USEPA, Office of Solid Waste and Emergency Response, Washington D.C., SW-846.

X5.3. Secondary Line of Evidence - Indicators of Biodegradation

Biodegradation is the process in which naturally-occurring subsurface microorganisms biodegrade contaminants, often completely degrading hydrocarbons to carbon dioxide and water. Evaluating indicators specific to the biodegradation process is of critical importance when presenting secondary lines of evidence for natural attenuation. The discussion presented below is confined to an assessment of the biodegradation of benzene, toluene, ethylbenzene and xylenes (BTEX). Because of their toxicity and especially their environmental mobility, these chemicals are typically the constituents of concern in groundwater at petroleum release sites. Other compounds (e.g., oxygenated additives, naphthalene) may be of concern on a site specific basis depending on the age and nature of the petroleum release. A discussion of the bioremediation of such compounds is beyond the scope of the following presentation.

X5.3.1. Introduction to indicators of biodegradation: Microorganisms transform organic molecules, such as benzene, toluene, ethylbenzene and xylenes (BTEX), and obtain carbon and energy from these substrates for survival, growth and reproduction. Initially, the microbes "attack" these hydrocarbons through a series of enzyme-catalyzed oxidative-reduction reactions. The resulting metabolic intermediates are then either diverted to biomass-producing pathways or completely oxidized to carbon dioxide and water. The oxidative reactions yield electrons which through a series of enzyme-catalyzed electron transport steps produce the energy the cell needs for maintenance and growth. In order for the electrons to pass through the energy generating steps, though, an electron sink is required. Typically, this electron acceptor (sink) is molecular oxygen (O_2) and the process is called aerobic respiration. In the absence or near absence of molecular oxygen (O_2) and in the order presented, nitrate (NO_3^-), manganese (Mn^{+4}), ferric iron (Fe^{+3}), sulfate (SO_4^{-2}) or carbon dioxide (CO_2) may serve, if available, as terminal electron acceptors in a process called anaerobic respiration.

The aerobic metabolism of benzene, toluene, ethylbenzene and xylenes has been widely documented in subsurface soils and aquifer materials, both through *ex-situ* microcosm studies and through field studies (Barker et al. 1987; Kemblowski et al. 1987; Chiang 1989; Salanitro 1993). It is likely that microorganisms capable of aerobically degrading BTEX constituents are nearly ubiquitous in subsurface environments.

The anaerobic metabolism of toluene, ethylbenzene and xylenes has been widely demonstrated under nitrate-reducing (Hutchins 1992; Barbaro et al. 1992; Alvarez and Vogel 1994; Ball et al. 1994; Ball and Reinhard 1995), sulfate-reducing (Beller et al. 1992; Edwards et al. 1992; Ball et al. 1994; Ball & Reinhard 1995), iron- and manganese-reducing (Cozzarelli 1990; Baedecker et al. 1993; Cozzarelli et al. 1994; Loveley et al. 1994; Borden et al. 1994) and methanogenic (Wilson et al. 1986; Wilson et al. 1990; Edwards and Grbic-Galic 1994) conditions. The anaerobic metabolism of benzene has not been well documented. Nevertheless, an increasing number of microcosm and field studies are demonstrating the metabolism of benzene under nitrate-, sulfate-, iron-reducing and methanogenic conditions (Major 1988; Wilson et al. 1986; Wilson et al. 1990; Edwards and Grbic-Galic 1992; Baedecker et al. 1993; Lovley et al. 1994; Loveley et al. 1995, Caldwell and Suffita 1995, Newell et al. 1995).

The equations given in Figure X5.1 show the reactants and products involved in the aerobic and anaerobic metabolism of BTEX. The reactions below are balanced based on toluene, but the reactions apply to all BTEX constituents.

AEROBIC RESPIRATION



ANAEROBIC RESPIRATION

Nitrate Reduction



Manganese Reduction



Iron Reduction



Sulfate Reduction



Methanogenesis



Figure X5.1 - Aerobic and anaerobic pathways of BTEX biodegradation [Equations are balanced using toluene and would slightly differ for other BTEX constituents. The equations balanced using benzene can be found in Wiedemeier et al. 1995]

As shown in the above equations, under aerobic conditions, the metabolism of BTEX results in the consumption of oxygen and the production of carbon dioxide and water. Under anaerobic conditions, the metabolism of BTEX consumes the particular electron acceptor and yields the reduced electron acceptor, carbon dioxide and water (water is not produced in methanogenesis). Thus, coupled with BTEX attenuation, the disappearance in ground water of dissolved oxygen and/or anaerobic electron acceptors, or the appearance of electron-acceptor reduction products, (all relative to upgradient concentrations) is clear evidence of biodegradation.

X5.3.2. *A quantitative approach to evaluating indicators of biodegradation:* Quantitatively, the balanced equations given in Figure X5.1 allow a calculation of: (1) the mass of a terminal electron acceptor necessary to completely metabolize a given mass of BTEX; and (2) the yield of reduced electron acceptor per mg of BTEX metabolized. Based on the above equations, 3.1, 4.6 and 4.8 mg/L of oxygen, sulfate and nitrate, respectively, are necessary to completely metabolize 1 mg/L BTEX, while 0.8, 11 and 22 mg/L of methane, Mn^{+2} and Fe^{+2} , respectively, are produced from the complete metabolism of 1 mg/L BTEX (note: these are values specific to toluene, but values for other BTEX constituents will vary only slightly). These are maximum values, since not all of the carbon will be completely oxidized (a significant portion of the carbon will be used for biomass). While a quantitative approach (e.g., a decrease in BTEX concentration of 2 mg/L yielded a decrease in sulfate concentration of 10 mg/L) is valuable and has been

utilized (Wilson 1994a,b), the possible environmental sources and sinks for electron acceptors and metabolites can make quantification very difficult. Therefore, a qualitative approach is usually followed, with a direct or inverse correlation between electron acceptors/reduction products and BTEX concentrations providing clear evidence for biodegradation.

Many of the electron acceptors and their reduction products given in Figure X5.1 can be readily and accurately measured in ground water samples. These include O_2 , Fe(II), Mn(II), NO_3 , SO_4 , CH_4 and CO_2 . Measurement of these parameters is discussed in detail in Appendix X4. Thus, these parameters can be used to evaluate the influence of biodegradation on a solute plume. Other means of assessing biodegradation include measuring oxidation-reduction potentials, microcosm studies and microbial counts. Electron acceptors and their reduction products, as well as other methods for assessing biodegradation, are discussed in more detail below.

X5.3.3. *Electron acceptors and reduction products (secondary lines of evidence):*

X5.3.3.1. Oxygen: In zones of high BTEX concentration, dissolved oxygen is depleted because the naturally-occurring microorganisms have utilized the available oxygen as they biodegrade BTEX and other constituents and any oxygen entering this zone is rapidly depleted (due to the high oxygen demand generated by the high BTEX concentrations and other constituents such as Fe(II), Mn(II), etc). The inverse relationship of high hydrocarbon concentration and low dissolved oxygen concentration can be used as a key indicator of bioremediation.

X5.3.3.2. Nitrate: After dissolved oxygen has been depleted (typically considered <0.5 ppm) in a given ground water zone, nitrate, if available, may be used as an electron acceptor for anaerobic biodegradation. In anaerobic ground water zones with high BTEX concentrations, nitrate demand (by nitrate-reducing microorganisms capable of biodegrading BTEX) may be high and nitrate concentrations may be depleted relative to concentrations upgradient and outside the plume. Overall, an inverse relationship between BTEX concentrations and nitrate concentration should be expected.

X5.3.3.3. Manganese: The use of manganese (Mn^{+4}) as a terminal electron acceptor by microorganisms yields a reduced water-soluble manganese (Mn^{+2}). In anaerobic ground water zones where BTEX and a source of Mn^{+4} (MnO_2) are present, Mn^{+2} can be used as an indicator of biodegradation. Overall, a positive correlation between BTEX concentrations and Mn^{+2} concentration should be expected.

X5.3.3.4. Iron: The use of ferric (Fe^{+3}) iron as a terminal electron acceptor by microorganisms yields water-soluble ferrous (Fe^{+2}) iron. In anaerobic ground water zones where BTEX and a source of ferric iron are present, ferrous iron can be used as an indicator of biodegradation. Overall, a positive correlation between BTEX concentrations and ferrous iron concentration should be expected.

X5.3.3.5. Sulfate: Under strongly reducing conditions, after available oxygen, nitrate and ferric iron have been depleted, sulfate can be used as an electron acceptor for anaerobic biodegradation of BTEX. The process results in the production of sulfide, which may precipitate from solution as ferrous sulfide. Under sulfate-reducing conditions and in the presence of high BTEX concentrations, sulfate demand (by sulfate-reducing BTEX degraders) will be high and sulfate concentrations will be depleted relative to concentrations upgradient and outside the plume. Overall, in these sulfate-reducing

zones, an inverse relationship between BTEX concentrations and sulfate concentration should be expected.

X5.3.3.6. Methane: Methane is produced only under strongly reducing conditions by a group of strict anaerobes. Methanogens either use CO₂ as a terminal electron acceptor, producing methane, or cleave acetate to CO₂ and methane. Because methane is not present in fuels, it can be used as an indicator of biodegradation. Under methanogenic conditions and in the presence of high BTEX concentrations, the rate of methane production can be significant, with the concentration of methane in this zone high relative to areas upgradient and outside the plume (where the methane concentration is typically nondetect). Overall, under methanogenic conditions, a positive correlation between BTEX concentrations and methane concentration should be expected.

X5.3.3.7. Carbon dioxide: Both aerobic and anaerobic biodegradative processes can yield large quantities of CO₂, as the BTEX constituents are completely oxidized. An accurate measurement of the CO₂ produced through biodegradation, though, is difficult because the carbonate-buffering system in ground water (measured as alkalinity) serves as both a sink and source of CO₂. Nevertheless, in many circumstances, a positive correlation between BTEX and CO₂ concentrations can be expected and can be used as a qualitative indicator of biodegradation.

X5.3.4. Summary of the relationship between BTEX and electron acceptor/reduction product concentrations: The expected relationship between BTEX concentration and the concentration of a particular electron acceptor or its reduction product is summarized in Table X5.1.

Table X5.1

Expected Relationship Between BTEX and Electron Acceptor/Reduction Product Concentrations
Within a Plume

BTEX	OXYGEN	NITRATE	Mn (II)	FE(II)	SULFATE	METHANE
HIGH	LOW	LOW	HIGH	HIGH	LOW	HIGH
LOW	HIGH	HIGH	LOW	LOW	HIGH	LOW

X5.3.5. Additional indicators of biodegradation:

X5.3.5.1. Oxidation-reduction (redox) potential: The oxidation-reduction potential of ground water is a measure of the relative tendency of a solution to accept or donate electrons. Importantly, redox reactions in ground water are usually mediated by microorganisms. Therefore, the redox potential can strongly depend on biodegradative processes and, in turn, the redox potential can strongly influence such processes. While the redox potential of ground water can range from -400 to 800 mv, certain biodegradative processes can only operate within a prescribed range of redox conditions (Figure X5.2). By measuring upgradient redox values and values within the plume, zones where biodegradation (especially anaerobic processes) is lowering the redox potential can be identified.

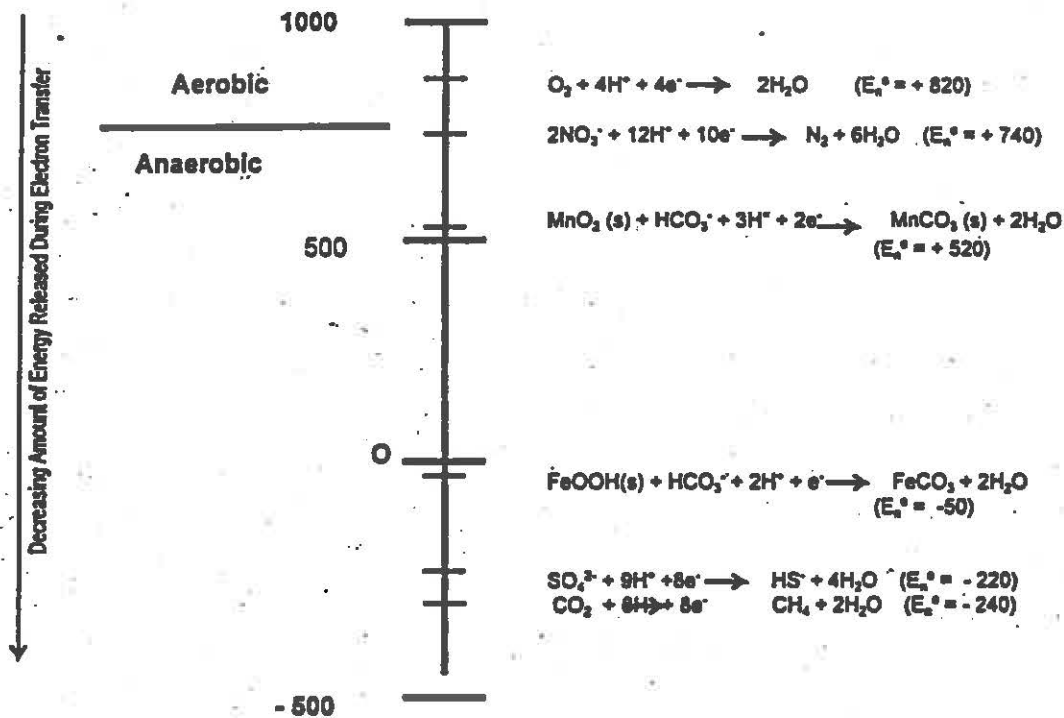


Figure X5.2
Redox Potentials in millivolts, pH 7, 25 °C
 (from Wiedemeier et al. 1995)

X5.3.5.2. Microbial counts: Microbial counts, using both counts of total heterotrophic bacteria and hydrocarbon degraders, can be used as an indicator of biodegradation. The ratio of hydrocarbon degraders to total heterotrophic bacteria should increase in aquifer zones where biodegradation of BTEX is occurring. It should be noted, though, that microbial counts are often unreliable indicators of biodegradation (Salanitro 1993).

X5.3.5.3. Microcosm studies: In microcosms studies, small quantities of ground water and aquifer solids are placed into serum bottles, shake flasks or into columns. The disappearance of a carbon substrate, sometimes along with the disappearance of a terminal electron acceptor or the appearance of the appropriate reduction product, is then measured over time. Microcosm studies are often used to clearly demonstrate the ability of native microorganism to biodegrade a given compound. As discussed above, the biodegradation of BTEX constituents is well documented and, therefore, microcosm studies are not typically necessary. In addition, although microcosms studies can be

used to estimate *in-situ* biodegradation rates, field methods detailed in Appendix 6 are preferred.

X5.4. Measuring Nutrient Levels:

Measuring nutrient levels can provide an optional line of evidence. Measuring the concentration of electron acceptors or their reduction products should not be confused with measuring the level of microbial nutrients. Nutrients are incorporated into microbial biomass and are necessary for the formation of proteins, DNA, cell membranes and other components of microbial cells. Microbial nutrients are usually divided into two categories: macronutrients (i.e., nitrogen and phosphorus), for which microorganisms require relatively large amounts, and micronutrients (i.e., sulfur, manganese, magnesium and many others), for which only a trace amount is required. In contrast to nutrients, electron acceptors and their reduction products are not incorporated into microbial biomass, but the reduced compounds are "excreted" into the environment (e.g., the microbes take in sulfate and release H₂S). Macronutrient (nitrogen and phosphorus) levels are often assessed in surface and subsurface environments by measuring ammonium (NH₄⁺), nitrate (NO₃⁻), organic (Kjeldahl) nitrogen, available phosphorus or phosphate (PO₄⁻³) and total phosphorus (mostly organic phosphorus compounds + phosphate). Certain molecules, such as nitrate and sulfate, can serve either as nutrients or terminal electron acceptors. While the availability of electron acceptors in the subsurface is a critical factor in assessing the rate and extent of biodegradation (McAllister and Chiang 1994), as discussed above, nutrient levels are rarely limiting microbial biodegradation activity in the subsurface, and, thus, measuring subsurface nutrient levels is unnecessary.

X5.5. References

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Attachment E

Biodegradation Capacity

	D.O.	Sulfate	Nitrate	Methane	Ferrous Iron (Fe+2)	Total Biodegradation Capacity
Background Concentrations						
Source Concentrations						
Difference						
Operation Utilization Factor (UF)	divide by UF	divide by UF	divide by UF	divide by UF	divide by UF	
Biodegradation Capacity	3.1	4.6	4.8	0.8	22	
						(mg/L)