REMEDIATION DIVISION
Petroleum Cleanup Section

Evaluation of Monitored Natural Attenuation at Petroleum Release Sites
Technical Guidance Document

This guidance was developed to assist with remediation and cleanup actions at petroleum releases overseen by the Petroleum Tank Cleanup section.

OVERVIEW OF MONITORED NATURAL ATTENUATION

This guidance closely follows **the USEPA document entitled "Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites", published in 1997 by the Office of Solid Waste and Emergency Response (OSWER Directive 9200.4-17**). This guidance is available at the Office of Underground Storage Tank's (OUST) website (http/www.epa.gov/OUST).

Monitored natural attenuation (MNA) differs slightly from remediation by natural attenuation (RNA). RNA is defined in the American Society of Testing Materials (ASTM) standard of practice entitled "Guide for Remediation of Groundwater by Natural Attenuation at Petroleum Release Sites". The most significant differences between MNA and RNA are that RNA strongly emphasizes the need for source control and free product removal, the need for thorough and detailed site characterization for sites proposing natural attenuation, and extends the natural attenuation approach to cover chemicals other than petroleum hydrocarbons. MNA stresses that source control is critical, and that the failure to adequately address source control may lengthen monitoring by many years. In addition, the RNA guidance recognizes that sites proposing natural attenuation should be more detailed than sites where active remediation technologies are proposed. Finally, the RNA guidance differs from the MNA guidance by recognizing that secondary lines of evidence, such as microcosm studies, may be necessary to verify that natural attenuation is occurring. An excellent comparison of both guidances can be found in the February 1998 issue of "LUSTline".

Natural attenuation is one of many remedial options which may be effective, by itself or in combination with other remedies, to restore groundwater if restoration will occur within a reasonable period of time, and if new releases to groundwater exceeding WQB-7 standards will be prevented. Natural attenuation is defined as the *"reduction in the concentration and mass of a substance and its breakdown products in groundwater, due to naturally occurring physical, chemical, and biological processes without human intervention or enhancement. These processes include, but are not limited to, dispersion, diffusion, sorption and retardation, and degradation processes such as biodegradation, and abiotic degradation."*

Natural attenuation has been demonstrated to be effective in reducing mass and concentration of many petroleum hydrocarbons due primarily to natural biodegradation processes by indigenous microbes in soil and groundwater which ultimately transform contaminants to carbon dioxide and water. Generally for petroleum compounds, in comparison to more aggressive remedies, natural attenuation may be less intrusive and disruptive of the site and its infrastructure. Furthermore, the natural attenuation remedy may produce less waste, use less energy, may require less operation and maintenance costs, and therefore overall costs may be less.

Evaluation of a site for natural attenuation potential involves gathering appropriate hydrogeological data relative to the fate and transport of contaminants in the aquifer, and assessing the rate of contaminant degradation. An adequate understanding of a site's hydrogeology is critical to estimating the magnitude of natural attenuation's contribution to the reduction of contaminant mass. It is important to emphasize that a thorough evaluation of groundwater flow velocities and direction, vertical and horizontal gradients, and lithologic characteristics of the site must be obtained <u>before</u> further consideration is given to natural attenuation as a potential remedy. Furthermore, the type, location, concentration and <u>quantity</u> of the contaminant source(s) need to be identified for all affected areas and media. This site-specific information is essential for the assessment of the magnitude of the physical, chemical, and biological processes contributing to natural attenuation. The physical processes of dispersion and diffusion primarily reduce the concentration of contaminants, while the chemical processes of sorption and retardation primarily slow the migration of contaminants. The contribution of the biological processes of aerobic and anaerobic biodegradation by indigenous microbes, which is the <u>primary mechanism of contaminant degradation</u>, can only be evaluated when overlain on the aforementioned data set.

There are, of course, non-technical considerations to implementing natural attenuation as a final remedy, given that a certain level of risk is associated with this alternative. Generally, potential future liability associated with using natural attenuation can be minimized by fully characterizing the site, demonstrating the long term effectiveness of natural attenuation via a stable or receding plume, and adequately treating or removing source areas so residual contaminants and groundwater contamination will be cleaned up within a relatively short period of time. There should also be convincing evidence that current and anticipated land use and aquifer use will not change to the extent that human health or the environment are jeopardized. Current and anticipated land use should also support that there are not upgradient sources of contamination which may rob electron acceptors in groundwater and that this condition is not likely to change.

FEASIBILITY STUDY

Evaluation of the effectiveness of natural attenuation requires an adequate assessment of hydrogeologic characteristics. The following information must be obtained in order to evaluate natural attenuation feasibility:

<u>Hydraulic conductivity</u> is a critical parameter that influences fate and transport of contaminants, and should be assessed at each site by slug, bail-down, or pump tests. If slug tests or baildown tests are used, a minimum of four wells should be evaluated across the site.

<u>Hydraulic gradient</u> is inferred from static water levels in monitoring wells screened at an appropriate depth.

<u>Effective porosity</u> can be estimated from literature values for the types of materials making up the aquifer matrix (Table 1).

These three values are used to calculate the Linear groundwater flow velocity (or see page velocity). See equation 1.a.

At sites where soil borings are planned, fraction organic carbon (*foc*) can be obtained from a clean soil boring within either the vadose or saturated zones. This parameter can also be estimated from literature values.

In addition to the hydrogeologic parameters, an estimate of the Soluble mass of contamination in the soil and as NAPL must be provided. This should be reported in terms of total BTEX mass (Kg), not as GRO. If free product is present, see Wiedemeier et al., 1995, for an appropriate methodolgy of determining the soluble mass component of the particular NAPL.

Conducting a feasibility study to evaluate natural attenuation as a remedy also requires an adequate long-term site-specific monitoring plan. The monitoring plan for natural attenuation must include sufficient groundwater monitoring wells, both in number and location, to measure groundwater flow direction(s), horizontal (and vertical) gradients and velocities, trends in contaminant concentrations within the plume and source areas, and whether the plume is migrating or presenting a threat to human health or the environment. If an adequate number of monitoring wells cannot be placed to fully define and monitor the plume, then natural attenuation is not a viable remedial option.

A monitoring plan typically includes:

1) Upgradient well(s) located outside the plume that are used to evaluate background water quality. These wells should be sampled for contaminant concentrations and geochemical indicator parameters in the first round. Subsequent rounds may be limited to contaminants. For sites with upgradient plumes or multiple source areas (both on site and off site), it is important that upgradient geochemical information be assessed annually to determine if electron acceptors are being depleted prior to reaching the downgradient plume(s).

2) More than one monitoring well should be located within the plume to provide data on trends in contaminant concentrations over time and distance. Ideally, the wells should more or less be aligned along the centerline of the plume. However, complex plume configurations and complex groundwater flow gradients and directions may preclude such a simple monitoring well alignment scheme. After the initial round of sampling for geochemical parameters, annual sampling events are likely adequate. Sites with very coarse soils may have a rapid response from natural attenuation and therefore, inclusion of geochemical parameters in monitoring events may be scheduled approximately every 3rd or 4th round (if site is in a quarterly monitoring mode). Finer grained soils will likely show a slower response, and monitoring of geochemical indicators may be scheduled much less frequently (once per year or more).

3) Down-gradient "sentinel" wells (clean) located outside but *directly* downgradient of the plume, that are capable of detecting further migration of the contamination. In some cases (e.g., no nearby downgradient receptors), these wells could be monitored only for indirect indicators of plume migration, such as dissolved oxygen. The number and location of down-gradient wells will depend on the number and distance to potential downgradient receptors, the site's geology and hydrogeology, and the plume(s) complexity and configuration.

4) The primary geochemical indicators for measuring natural attenuation of petroleum

compounds in groundwater monitoring wells include: dissolved oxygen (DO_2), nitrate (NO_3), sulfate (SO_4), soluble (ferrous) iron (Fe_2), and in some cases manganese (Mn). Field analysis of dissolved oxygen and ferrous iron will yield more accurate results. Either laboratory or field analysis of nitrate, sulfate, and manganese is generally acceptable. Samples for all geochemical constituents that are brought to a lab must be properly preserved and stored to ensure accuracy of data. The Air Force Protocol document titled "Soil, Soil Gas, and Groundwater Analytical Protocol/Standard" discusses appropriate methodologies for each matrix. Which wells are sampled for geochemical parameters depends upon the specifics of the site, but in general, if there are 6 or less wells, sample all wells. For sites with 6 to 12 wells, sample 6 to 8 wells, and for sites with more than 12 wells, sample 8 to 10 wells.

5) At new sites, quarterly monitoring of contaminant levels should be maintained for at least one year, and thereafter the frequency of monitoring should take into consideration the geology, hydrogeology and the ability to gather statistically significant information on contaminant trends and plume migration. In addition, seasonal fluctuations in contaminant concentrations, water table elevations, and hydraulic gradients must be adequately defined during the feasibility study. Insufficient data will preclude an adequate evaluation of trends in contaminant concentrations and a determination of whether the plume is stable, receding or advancing.

Subsequent monitoring must be conducted at a frequency appropriate to detect any changes in the contaminant plume. The monitoring plan should be tailored for site conditions. For example, frequency may vary from 1 monitoring event per year for coarse soils to 1 per five years for fine grained soils. If contaminant concentrations remain stable over time, it generally means that the plume is stable and natural attenuation rates equal the contribution of contaminants from the source area(s). If concentrations decrease over distance from the source it indicates that natural attenuation processes may be effectively reducing contamination. A check on the geochemical indicators will indicate whether natural attenuation processes are actively reducing contamination mass. A receding plume indicates natural attenuation rates exceed source area or mass inputs.

REFERENCES

American Society of Testing Materials (ASTM) standard of practice "Guide for Remediation of Groundwater by Natural Attenuation at Petroleum Release Sites**.**

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MONITORED NATURAL ATTENUATION
REPORTING REQUIRMENTS

1) Quarterly or Semi-annual Monitoring Report including results of all natural attenuation monitoring

2) Annual report that includes the following a brief discussion of the following:
   - Plume dynamics
   - Natural attenuation effectiveness to this point

Attachments to the annual report must include the following:

- Groundwater contour map
- Groundwater contaminant distribution map (BTEX constituents, *not* GRO)
- Dissolved oxygen in groundwater map (may be combined with contaminant data in single map)
- Historical groundwater contaminant table
- Graph of contaminant concentrations versus groundwater level (if answer to 7 below is "yes")
- Groundwater geochemical parameter table (i.e., DO, Fe, NO_3, SO_4)
- Groundwater elevations table
- Estimate of soluble contaminant mass in soils and as NAPL (include methodology for estimate)

MONTANA DEQ PETROLEUM RELEASE SECTION
MONITORED NATURAL ATTENUATION EVALUATION FORM

SITE NAME AND REPORTING PERIOD:

Site name: ____Facility ID

Reporting period from: ________________ To: _________________ Days in period:

EFFECTIVENESS EVALUATION:

1. If free product is not present, determine the single contaminant that requires the greatest percent reduction to achieve WQB-7 standards. Perform this calculation for all contaminants that were present at the site that have a WQB-7 standard. Use the highest concentration measured for any sampling point during the reporting period. If free product is present, write "FREE PRODUCT" on line 1.a below.

a. Contaminant:

b. Percent reduction necessary to achieve WQB-7 standards:

c. Maximum concentration in any well (ug/L):

2. Aquifer parameters:

a. Hydraulic conductivity (cm/sec):

b. Groundwater average linear velocity (ft/yr):

3. Is there a downgradient well that meets MT ARM 36.21.801-810 standards?

4. Based on water chemistry results, is the plume expanding, stabilized or contracting?

5. If the answer in 4 above is "expanding", is Natural Attenuation still the best option? Explain:

6. Geochemical parameters:

a. Upgradient (site-specific background) DO level (mg/L):

b. DO levels in most heavily contaminated area of plume (mg/L):

7. Have contaminant levels changed with groundwater table fluctuations over time?

8. Has the direction of groundwater flow changed during the reporting period (how many degrees)?

ATTACHMENTS: Attach the following to this form:

- Groundwater contour map
- Groundwater contaminant distribution map (BTEX constiuents, ***not*** GRO)
- Dissolved oxygen in groundwater map (may be combined with contaminant data in single map)
- Historical groundwater contaminant table
- Graph of contaminant concentrations versus groundwater level (if answer to 7 above was "yes")
- Groundwater geochemical parameter table (i.e., DO, Fe, NO3, SO4)
- Groundwater elevations table
- Estimate of soluble contaminant mass in soils and as NAPL (include methodology for estimate)

MONITORED NATURAL ATTENUATION PARAMETERS

Geochemical parameters:

DO	Dissolved oxygen, measured with probe, in-situ
Ferrous Iron	Dissolved iron concentrations provide appropriate results, field test
NO_3	Nitrates, test must distinguish between nitrate and nitrite(NO2)
SO_4	Sulfate test, lab samples preserved with H_2SO_4, or field test

Hydrogeological parameters:

foc	Fraction organic carbon, from clean soil sample or estimated
K	Hydraulic conductivity, from slug test, bail-down test or pump test. Values $<5x10^5$ cm/s are marginal, $<1x10^6$ cm/s not eligible for NA. Thickness of zone and homogeneity over screened interval are extremely important to consider
Hyd. Gradient	Static water levels from appropriately screened wells
$N_{(e)}$	Effective porosity, estimate from literature value

Contaminant information:

Source mass	Estimate of source mass as BTEX, not GRO (in Kg)

Updated on March 10, 2015.