Borski, Jennifer - DNR

From: Seely.David@epamail.epa.gov
Sent: Tuesday, June 12, 2007 8:48 AM
To: Borski, Jennifer - DNR
Subject: N.W. Mauthe - Transmittal of National MNA Guidance

Attachments: Monitored Natural Attenuation 9200.4-17P April 1999.pdf

Monitored Natural
Attenuation ...

Jennifer,

Attached is the National Monitored Natural Attenuation Guidance I referenced during our conference call. There are other guidances that discuss monitoring the remedy and data needs that can be found at the following link:

http://www.epa.gov/superfund/resources/gwdocs/monit.htm

I haven't been able to locate the regional guidance as yet. I will send it as soon as I can locate it.

Thanks.

-David Seely-
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(See attached file: Monitored Natural Attenuation 9200.4-17P April
1999.pdf)

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 5

DATE: September 27, 2000

SUBJECT: Transmittal of Monitored Natural Attenuation Framework

FROM: William E. Muno, Director
Superfund Division

TO: Superfund Staff

Attached is the document "Region 5 Framework for Monitored Natural Attenuation Decisions for Ground Water" which I have approved for release in the Region 5 Superfund Program. The Framework provides technical direction in the Region 5 Superfund Program based on the final OSWER Directive on the *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites*. The document is a framework to be used to ensure that the proper data is collected when making monitored natural attenuation remedy decisions. It includes a discussion of the process of making natural attenuation decisions and a brief explanation of the use of the natural attenuation data in the evaluation process.

In order to maximize the sound science represented by the Framework while minimizing decision delays, the Framework is to be implemented in a phased approach with a transition period for full implementation by October 1, 2001.

- For those sites without an approved workplan and where Monitored Natural Attenuation (MNA) is proposed for consideration, the data requirements of the Framework shall be fully implemented now.
- For those sites already considering MNA as a remedial alternative or remedy modification with an approved workplan for data collection, the recommendations of this Framework should be considered. The site's project manager should consult with a Region 5 Superfund geologist to determine what modifications to the existing data collection efforts are required to adequately evaluate MNA consistent with the Framework.
- For those sites where MNA has been selected and/or those sites which are in the process of implementing MNA, the ground-water sampling requirements contained in the Framework should be fulfilled by the MNA monitoring program. In addition, a comprehensive contingency remedy including implementation criteria as discussed in the OSWER Directive should be developed for these sites.

The Framework document includes the Framework text; one figure (a flowchart of the decision-making process); three tables (a table summarizing the various natural attenuation processes, a table listing required indicator parameters and sampling frequencies, and a table summarizing the data uses of each parameter); and a glossary of technical terms.

The Framework was developed by a workgroup composed of the hydrogeological support staff

(Luanne Vanderpool, Doug Yeskis, Gary Cygan) and five RPMs (Brad Bradley, Karen Cibulskis, Ross Del Rosario, Dion Novak and Terese Van Donsel). If you have any questions on the document, please contact the workgroup co-chairs (Luanne Vanderpool at 3-9296 or Doug Yeskis at 6-0408) or any other member of the workgroup.

REGION 5 FRAMEWORK
FOR
MONITORED NATURAL ATTENUATION DECISIONS
FOR GROUND WATER

Introduction - Monitored Natural Attenuation (MNA) is an increasingly utilized remedial option for contaminated ground water. This Framework outlines the types of data that will be used to evaluate MNA. Typically MNA is selected as a remedy in combination with one or more other actions (e.g. source control); or selected as a remedy modification to replace another action. This Framework is not meant to serve as a replacement for proper technical review from a qualified hydrogeologist, but is instead meant to educate Remedial Project Managers (RPMs) on the MNA evaluation process and to provide general direction on the type and amount of information needed for decision-making. The major decisions and actions required to evaluate and implement monitored natural attenuation are summarized in the flowchart in Figure 1. When possible, the specific boxes in Figure 1 are cited in the text of this Framework.

This Framework summarizes the current state-of-the-science and the U.S. EPA policy on the use of monitored natural attenuation in the Superfund program. As additional research, site investigations and remedial actions are completed, this paper should be revised to include new information and concerns. This Framework is applicable to the majority of Superfund sites; however, unusual, site-specific circumstances may require approaches other than those specified in this document. In these instances, the appropriate Regional hydrologists/geologists/technical specialists should be consulted. A reference list for the citations in this Framework, a list of other sources of information, and a glossary for italicized terms is attached.

What is Monitored Natural Attenuation? -Monitored Natural Attenuation is a remedy alternative that relies on natural attenuation processes to achieve site-specific remedial objectives within an acceptable timeframe. Natural attenuation is defined as "naturally occurring processes in the environment that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater". These processes are briefly described in Table 1.

Current U.S. EPA policy concerning the use of MNA for the remediation of ground water is provided in the OSWER Directive, **Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action and Underground Storage Tank Sites** (U.S. EPA, 1999a). When relying on natural attenuation processes for site remediation, the U.S. EPA prefers those processes that are *destructive* (U.S. EPA, 1999a, page 3). Biodegradation (which may be aerobic or anaerobic) is the most important destructive process, although radioactive decay and abiotic degradation of some compounds does occur. The other attenuation processes are *nondestructive*. While natural attenuation of organic compounds (U.S. EPA, 1998, Appendix B) generally means breakdown (biodegradation) by microorganisms, natural attenuation of metals (Waters et al, 1998) often means immobilization or transformation by the soil matrix, geochemical changes and/or dispersion.

When the U.S. EPA implements natural attenuation as a remedy at a Superfund site, the Agency uses a monitored natural attenuation approach. The selection of a MNA remedy assumes that natural attenuation can be documented to be occurring at a site as discussed in this Framework.

The MNA remedy involves establishing a long-term monitoring program (Figure 1, Box 11b) with criteria for evaluating the monitoring data to determine if contaminant levels are decreasing as expected (Figure 1, Box 11a). The use of MNA also has the expectation that it will be used "in conjunction with other active remediation measures (e.g., source control)" (U.S. EPA, 1999a, page 17) and that a contingency remedy (Figure 1, Box 8a) will be developed, which can be implemented if MNA fails to perform as anticipated or required (U.S. EPA, 1999a, page 24). This Framework does not address the issues of source control (Figure 1, Box 1c) or contingency remedies (Figure 1, Box 8a) that are part of the MNA decision.

What Information is Needed? - A detailed site characterization is required to evaluate the possible implementation of MNA as a remedial alternative. The characterization should include collecting data to define (vertically and horizontally over time) the nature and distribution of the contaminants of concern and contaminant sources, as well as the potential impacts on receptors as listed below (U.S. EPA, 1998, page 34)(Figure 1, Box 1b):

- data on the location, nature, and extent of contaminant sources
- data on the location, nature, extent, and concentrations of dissolved contamination
- chemical properties of the contaminants and the subsurface materials which the contaminants migrate through
- contaminant phase distribution and partitioning (such as presence of *NAPL*, gaseous phases, dissolved phases)
- rates of biological and non-biological transformation
- ground-water geochemical data (major anions and cations, organic carbon, pH, etc.)
- geologic information on the type and distribution of subsurface materials (transmissive vs. non-transmissive materials, thicknesses and horizontal extent)
- aquifer hydraulics and characteristics, including *hydraulic conductivity* and *hydraulic gradients*, particularly preferred flow pathways
- location of areas of recharge and discharge and rates
- potential contaminant migration pathways to points of exposure to human or ecological receptors
- flux of water through areas of recharge and discharge
- toxicity versus carcinogenicity (risk, concentration limits, etc.)
- an understanding of how all of these factors are likely to vary with time

A conceptual site model should be developed to integrate site characterization data and guide both investigative and remedial actions. The conceptual model provides the basis for assessing all potential remedial technologies including MNA at the site. A site-specific conceptual model is a three-dimensional representation of the ground-water flow and *solute* transport system. This model conveys what is known or suspected about contamination sources, release mechanisms, and the transport and fate of those contaminants and includes the site's geochemical and biochemical conditions. The conceptual model should indicate ORP *(oxidation-reduction potential)* conditions at the site and identify any zonation of ORP conditions along contaminant flowpaths since many degradation and transformation processes are controlled by ORP conditions. The conceptual model should also indicate whether conditions exist to support the biological activity necessary for biodegradation and biotransformation processes. "Conceptual site model" is not synonymous with "computer model" or "simulation model"; however, a computer/simulation model may be helpful for understanding and visualizing current site conditions or for predictive simulations of potential future conditions. The conceptual site model should be constantly evaluated during the site characterization process against all possible remedial alternatives. As the model is evaluated, additional site characterization data may be necessary to complete the MNA evaluation.

All potential exposure pathways to contaminants should be identified during site characterization. If currents threats to human health or the environment are identified (Figure 1, Box 4b), remedial measures should be evaluated, selected and implemented prior to further consideration of MNA (Figure 1, Box 1c). MNA should not be considered as a possible remedial method until current, unacceptable exposure pathways have been eliminated. To ensure protectiveness, site risks should be thoroughly evaluated and all pathways of exposure should be considered (including commonly overlooked pathways such as volatilization into basements, migration into sewer systems, etc.) as well as the extent of <u>all</u> chemical contamination. When considering MNA, the evaluation of the extent of contamination may be broader than the original delineation of contaminants of concern in order to include less obvious compounds as described in detail in the OSWER Directive (U.S. EPA, 1999a, page 5) and to quantify degradation by-products (i.e., daughter products) of the contaminants of concern (which may be more toxic and/or mobile than the parent compounds).

MNA should be considered an unlikely remedy to be considered for compounds that have a high degree of persistence and toxicity.

Should I consider MNA for my site? - Once site characterization data has been collected and a conceptual model is developed, the next step is to evaluate the potential effectiveness of MNA as a remedial alternative. It must be recognized that demonstrating MNA may not be easy and that MNA is not always an effective remedial alternative. The National Research Council (2000) cautions:

> Although natural attenuation has been well documented as a method for treating the fuel components benzene, toluene, ethyl benzene, xylene (BTEX); currently it is not well established as a treatment for most other common classes of groundwater contaminants. Under limited circumstances, it can be applied at sites contaminated with other types of compounds, such as chlorinated solvents and metals, but its successful use will depend on attenuation rates, site conditions, and the level of scientific understanding of processes that affect the contaminant. In some cases, natural attenuation will be effective only at sites with special environmental conditions conducive to attenuation of the contaminants in question. In other cases, the use of natural attenuation is problematic because scientific understanding is too limited to predict with sufficient confidence whether this strategy will protect public health and the environment.

Analyzing the data generated by site monitoring is the next step in evaluating MNA. Although the evaluation process is the same for all sites, the level of effort needed to carry it out varies substantially with the complexity of the site and the likelihood that the contaminant is controlled by a natural attenuation process. While natural attenuation may be a feasible alternative in many cases, it must be understood that a higher level of data gathering and analysis is required to demonstrate MNA when the contaminant is likely to be persistent, is likely to be mobile, the controlling attenuation mechanisms are uncertain, and/or the hydrogeology is complex.

The demonstration of MNA should follow a three-tiered approach. In this approach, successively more detailed information is collected as required to establish a net loss of contaminants and the processes responsible for this loss. All data (including hydraulic conductivity data and water- level measurements) used for this evaluation should be collected, handled and analyzed consistent with the U.S. EPA requirements for quality assurance/quality control. These three categories of supporting site-specific information are commonly referred to (U.S. EPA, 1999a, page 15) as "lines of evidence" (Figure 1, Boxes 5b and 6c).

1. **Primary Category of Information**
   Historical ground-water and/or soil-chemistry data that demonstrate a clear and meaningful trend of decreasing contaminant mass and/or concentration. Data should include analytical results for the contaminants of concern and their degradation by-products from nine or more rounds of samples collected under non-pumping conditions over a period of three to five years. There should be at least two years of quarterly sampling to evaluate seasonal effects on the contaminant concentrations. This data should be collected from appropriately located sampling points, including within the plume source area, within the center of the plume and at the leading edges of the plume. In addition, samples should be collected from points located vertically (above and below) and horizontally (upgradient and downgradient) outside the area of ground-water contamination. The most recent analytical data on ground water should be no more than two years old at the time of the evaluation. Demonstrating that a trend of decreasing contaminant concentration is clear and meaningful should be based on statistical tests which indicate a high degree of confidence in the apparent trend line. Additional rounds of samples may be required to demonstrate this trend.

2. **Secondary Category of Information**
   Hydrogeologic and geochemical data that can be used to demonstrate indirectly the type(s) of natural attenuation processes and the rate at which such processes will reduce contaminant concentrations. This data should be collected from appropriate locations that are distributed both vertically and horizontally throughout the plume. Sample locations should consider heterogeneities in geologic structures and in the spatial distribution of contaminants. Ground-water flow paths and rates should be fully and accurately defined, as this is one of the most important factors in evaluating the applicability of natural attenuation. The locations should be sampled under non-pumping conditions and should include, at a minimum:

   a. Contaminants of concern and their potential degradation by-products as determined from literature searches (Fetter, 1993, Chapelle, 1993, U.S. EPA, 1998).
   b. Routine Indicator Parameters, including pH, dissolved oxygen, ORP (a.k.a.: Redox, Eh or *Oxidation/Reduction Potential*), temperature, and specific electrical conductance (a.k.a.: SEC) (see Table 2 and Table 3 for details).
   c. Indicator Parameters which can be used to support MNA decisions, such as: alkalinity, chloride, nitrite, nitrate, dissolved methane, iron (II) and iron (III), chloride, sulfate, sulfide, total organic carbon, etc. (see Table 2 and Table 3 for details).
   d. Vertical and horizontal characterization of the distribution of *hydraulic conductivity*

and its effect on contaminant concentrations. Most of the field methods used to determine hydraulic conductivity represent horizontal hydraulic conductivity. For sites where vertical components of ground-water flow and/or contaminant transport are present, the vertical hydraulic-conductivity component should also be determined. Hydraulic conductivity estimates should be based on:

- Single and multiple-well aquifer tests (at least 25% of wells single-well tested and one or more multiple-well aquifer tests).
- Single-well aquifer tests (at least 50% of wells tested, or all wells if fewer than 10 wells present). Note: These may under-estimate hydraulic conductivity if large-scale heterogeneties are present.
- Other field characterization methods (e.g., flowmeters, tracer tests) may be appropriate under certain site conditions, which can be evaluated by the appropriate Regional hydrologists/geologists/technical specialists. Tracer tests can be especially helpful in determining contaminant transport properties, especially since these are performed at the field scale.

Note: Laboratory permeability tests should be performed on low permeability soils (clays, silty clays, marls, etc.) only.

e. Water levels should be measured to determine ground-water-flow directions. These water levels should be taken from possible receptors, including surface-water bodies and pumping wells.

f. Seasonal variations and trends should be evaluated by obtaining data from different times of the year to determine if changes in contaminant concentrations, indicator parameters or *water types* are caused by natural attenuation or may be attributed to seasonal variability. To determine seasonal variations, the effects of different, potential influences on water quality (such as recharge events, pumping effects, etc.) need to be evaluated and documented. In most cases, this will require quarterly water-quality samples, with more frequent water-level measuring events during the period of evaluation of the applicability of natural attenuation. These water-level measuring events usually are monthly, but continuous monitoring (e.g. use of data loggers) of water levels is needed to assess high frequency events, such as pumping or tidal cycles.

The information (a. thru f.) listed above should be incorporated in a detailed site-specific conceptual model that describes the contaminant migration pathways and the natural-attenuation processes involved, as well as estimates of travel times of contaminants from sources to receptors. The conceptual model should also include degradation by-products, degradation rates and potential future receptors. Consideration should be given to all applicable processes that may affect the contaminant concentrations as listed in Table 2, when determining the list of field and indicator parameters to be analyzed at a site.

3. Supplemental Category of Information

Data from field or *microcosm* studies which directly demonstrate the occurrence of a particular natural attenuation process at the site. In microcosm studies ground-water and aquifer materials are collected and studied in the laboratory in small containers (microcosms) The disappearance of the contaminant, along with the disappearance of terminal electron acceptors or the appearance of appropriate reduction products, is measured over time to demonstrate the ability of native microorganisms to degrade given compounds. Like any bench-scale testing done as part of treatability studies, care should be taken to ensure the transferability of the results from the laboratory to field conditions. Microcosm studies can also be used to estimate biodegradation rates; however, field-derived values are preferred due to uncertainty about the representiveness of the microcosm results for actual field conditions. Microcosm studies are time-consuming and expensive; they should only be undertaken at sites where there is considerable uncertainty concerning the biodegradation potential of the contaminants.

How is the MNA Decision Made? - The primary category of information uses historical contaminant data to determine if the contaminant plume is shrinking, stable, or expanding (Figure 1, Box 6b). This first category of information can be used to show that a contaminant plume is being attenuated; it does not necessarily show that contaminant mass is being destroyed nor does it provide the information necessary to evaluate the applicable attenuation process(es). For sites which have sufficient historical monitoring data, the primary category of information may be adequate to demonstrate remediation by MNA. In the absence of historical evidence for reductions in contaminant concentrations (i.e. the plume is expanding), the argument for natural attenuation probably cannot be made. If the primary category of information is inconclusive or inadequate, it is necessary to obtain the secondary category of information (Figure 1, Box 6c). Even when the secondary category of information is available, field monitoring and contaminant data collection should continue in order to ultimately substantiate the primary category of information. For sites with insufficient historical monitoring data, the collection and evaluation of geochemical data (secondary category of information) should be used to expedite the demonstration of remediation by MNA rather than waiting to develop a longer historical record. When data from the secondary category of information are inadequate or inconclusive, data from the supplemental category of information may be used to help support information from the primary and secondary categories. The supplemental category of information, by itself, is not sufficient to support a MNA decision.

Although not a category of information, solute fate and transport simulation models may be valuable when evaluating natural attenuation when properly chosen and implemented. Such models can be used to evaluate the relative importance of natural attenuation mechanisms, to predict the migration and attenuation of the dissolved contaminant plume through time, to predict cleanup timeframes, or to provide an estimate of time required to reach a receptor well. The use of solute fate and transport modeling in the natural attenuation evaluation is described by Wiedemeier, et al., 1999.

Even when the primary category of information is conclusive, further effort should still be made to develop the secondary category of information. The challenge in evaluating MNA is not only demonstrating that natural attenuation is occurring. This can be a relatively easy task. Rather, the appropriate evaluation of MNA as a remedial alternative requires making the determination that the natural attenuation processes are taking place at a rate that is protective of human health and the environment (Figure 1, Box 7b), that there is a reasonable expectation that these processes will continue at acceptable rates for an acceptable period of time (Figure 1, Box 8b), and that the MNA remedy is capable of achieving the site specific remediation objectives within a timeframe that is reasonable compared to other remedial alternatives (Figure 1, Box 9b).

Tables: Table 1. Summary of Major Processes Affecting Contaminant Concentrations
Table 2. Required Indicator Parameters and Sampling Frequency
Table 3. Uses of Indicator Parameters

Figure 1. Monitored Natural Attenuation Flow Chart for Decision-Making

References

Additional Sources of Information

Glossary of Terms

Table 1
Summary of Major Processes Affecting Contaminant Concentrations

(Italicized words are defined in glossary)

Processes	**Relevance**	**Description**	**Dependencies**	**Effect**
Destructive				
Abiotic Degradation	Organic	A variety of chemical transformation mechanisms (e.g., hydrolysis, *redox* reactions, elimination reactions, etc.) that degrade contaminants without microbial facilitation, commonly significant for *halogenated compounds*.[1]	Dependent on contaminant properties and ground-water geochemistry.	Can result in partial or complete degradation of contaminants. Rates typically much slower than for biodegradation. May result in more toxic by-products than parent compound.
Biodegradation	Organic & Inorganic	Microbially mediated *oxidation-reduction* reactions that degrade contaminants. Oxygen consumption, *denitrification*, sulfate reduction, iron reduction, methanogenesis and *reductive dehalogenation* are among the more common processes.	Dependent on ground-water geochemistry, microbial population and contaminant properties. Biodegradation can occur under aerobic and/or anaerobic conditions, however, the kinetics of aerobic reactions are generally more rapid.	May ultimately result in complete degradation of contaminants. Typically the most important process acting to reduce contaminant mass. May result in more toxic by-products than parent compound. May mobilize certain inorganics such as As, Mn and Fe.

Table 1

Summary of Major Processes Affecting Contaminant Concentrations

(Italicized words are defined in glossary)

Processes	**Relevance**	**Description**	**Dependencies**	**Effect**
Radioactive Decay	Inorganic	A process by which the nucleus of a radioactive atom undergoes spontaneous decay into one or more nuclei with a different number of protons. The process continues until a stable nucleus (nuclei) is/are produced. Usually assumed to be controlled by first order kinetics. Relevant only to radiogenic elements.	No dependencies on environmental parameters. Decay will occur until a stable nucleus (nuclei) is produced. For example, radioactive decay rates exhibit no relationship to temperature, pressure or concentrations, or any other characteristic of the local environment.	Decay can result in partial or complete *transmutation* of the radionuclide(s) of concern. However, the production of *daughter nuclides* may represent an enhanced hazard that could outweigh the benefit due to loss of the parent nuclide. Special consideration should be given to the time frames required for sufficient decay.
Nondestructive				
Advection [2]	Organic & Inorganic	Movement of solute by bulk (flowing) ground-water movement. This first order control on flow is described by *Darcy's Law*.	Dependent on physical aquifer properties, mainly *hydraulic conductivity*, effective *porosity*, and *hydraulic gradient*. Independent of contaminant properties.	Most important control on the movement of contaminants in the subsurface.

Table 1
Summary of Major Processes Affecting Contaminant Concentrations

(Italicized words are defined in glossary)

Processes	Relevance	Description	Dependencies	Effect
Dispersion [2,3]	Organic & Inorganic	Mechanical fluid mixing due to ground-water movement and aquifer (pore space) heterogeneities.	Dependent on aquifer properties and scale of observation. Independent of contaminant properties.	Causes longitudinal, transverse, and vertical spreading of the plume. Reduces *solute* concentration.
Diffusion	Organic & Inorganic	Spreading and dilution of contaminant in response to a concentration gradient. Usually operates on a scale extending from a few centimeters to, at most, a few hundreds of centimeters.	Dependent on contaminant properties and concentration gradients. Described by *Fick's Laws*.	Diffusion of contaminant from areas of high concentration to areas of low concentration. Generally unimportant relative to dispersion at most ground-water flow velocities. May become important in low permeability formations or at very low hydraulic gradients.

Table 1
Summary of Major Processes Affecting Contaminant Concentrations
(Italicized words are defined in glossary)

Processes	Relevance	Description	Dependencies	Effect
Sorption	Organic & Inorganic	Reaction between aquifer materials and *solute* whereby compounds become attached to formation materials (e.g., organic carbon or clay minerals) as commonly described by the partition coefficient.	Dependant on aquifer material properties (e.g., organic carbon and clay mineral content, sulfide content, electrical conductance, *bulk density*, specific surface area, and porosity) and contaminant properties (e.g., water *solubility values*, *hydrophobicity*, *octanol-water partitioning coefficient*, *charge balance* considerations).	Tends to reduce apparent *solute transport velocity* and removes *solutes* from the ground water via sorption to the formation material.
Biotransformation	Inorganics & Organics	Microbially mediated *oxidation-reduction* reactions that transform contaminants, making them less soluble or more soluble in water. Alternatively, sulfide or iron (II) produced by biological activity may precipitate metals.	Dependent on ground-water geochemistry, microbial population and contaminant properties. Biotransformation can occur under aerobic and/or anaerobic conditions.	Does not result in the complete destruction of contaminants. The reactions may be reversible.

Table 1
Summary of Major Processes Affecting Contaminant Concentrations

(Italicized words are defined in glossary)

Processes	Relevance	Description	Dependencies	Effect
Oxidation-Reduction (Redox) [4]	Organic & Inorganic	A reaction couple producing a change in *valence* state (e.g., H_2S, HSO_4^-, SO_4^{2-}). For every oxidation reaction, there exists an accompanying reduction. Only inert gases, halogens, alkali metals and earths are relatively immune to redox. Although seldom reaching equilibrium, redox rates of reaction are usually kinetically slow. Organic examples may be: $\frac{1}{2} CH_2O + H^+ = \frac{1}{2} CH_3OH$	Function of aqueous pH, DO, TOC, and microbial character(s). Accurate measurements of redox potentials are difficult to make in the field mostly due to slow kinetics. If the Fe^{2+}/Fe^{3+} couple predominates, the accuracy of field measurements increases.	Produces an oxidized contaminant with accompanying change in solubility characteristics, along with a chemically reduced couple, or visa versa. Redox reactions may exert major influence on ground-water quality because of the large number of possible redox reactions and the frequency of redox changes. A common example of redox behavior is the reduction of Mn(IV) in minerals to the more soluble and toxic Mn^{+2}.
Partitioning from *NAPL*	Organic	Partitioning from *NAPL* into ground water. *NAPL* plumes, whether mobile or residual, tend to act as a continuing source of ground-water contamination.	Dependent on aquifer materials and contaminant properties, as well as ground-water flux through or past *NAPL* plume.	Dissolution of contaminants from *NAPL* represents the primary source of dissolved contamination in ground water.

Table 1
Summary of Major Processes Affecting Contaminant Concentrations

(Italicized words are defined in glossary)

Processes	**Relevance**	**Description**	**Dependencies**	**Effect**
Volatilization	Organic [5]	Release of dissolved contaminants from the ground-water into the vapor phase (soil gas).	Dependent on the chemical's vapor pressure, *Henry's Law* constant, and, to a lesser extent, temperature.	Removes contaminants from ground water and transfers them to soil gas or the atmosphere.
Precipitation	Inorganic	Occurs when contaminant concentration exceeds its maximum solubility at equilibrium resulting in a transfer from the aqueous phase to the solid phase.	Dependent on contaminant properties, especially solubility product constants, and ground-water geochemistry.	Can result in transformation of soluble contaminant into solid phase product thereby reducing aqueous contaminant concentration in ground water.

[1] Because industrial organic compounds that contain chlorine have only recently been introduced to the environment in large quantities (since the late 1940's), the indigenous microorganisms are not fully adapted to them, and their degradation is generally slow compared to degradation of naturally occurring compounds.

[2] Recharge processes are responsible for driving advection and mechanical dispersion.

[3] In most situation the effects of dispersion are difficult to isolate from the effects of diffusion. The effects of dispersion and diffusion are combined in the term hydrodynamic dispersion (Freeze and Cherry, 1979).

[4] Included as "non-destructive" since process is reversible in nature.

[5] To be accurate, some inorganic compounds with high vapor pressures also volatilize such as mercury or methyl-mercuric chloride (e.g., CH_3HgCl).

Table 2
Required Field and Laboratory Indicator Parameters

Process [1]	Required Parameter [2]	Frequency
Abiotic Degradation	Chloride, Specific Electrical Conductance, Oxidation-Reduction Potential, Dissolved Oxygen, pH, Temperature, Turbidity	every sampling round
Biodegradation or Biotransformation	Alkalinity, Calcium, Carbon Dioxide, Chloride, Specific Electrical Conductance, Iron (II), Magnesium, Methane, Nitrate, Nitrite, Oxidation-Reduction Potential, Dissolved Oxygen, pH, Potassium, Sodium, Sulfate, Sulfide, Temperature, Turbidity, Dissolved Organic Carbon	every sampling round
	Arsenic, Manganese, Iron (III), Total Organic Carbon	first sampling round [3,4]
	Dissolved Hydrogen	only if other data is inconclusive [5]
Radioactive Decay	Alkalinity, Specific Electrical Conductance, Oxidation-Reduction Potential, Dissolved Oxygen, pH, Temperature, Turbidity, Total Dissolved Solids, Dissolved Organic Carbon, Total Suspended Solids	every sampling round
	Cation Exchange Capacity, Clay Content, Total Organic Carbon, Sulfide	first sampling round [3,4]
	Partitioning Coefficient	site-specific conditions determine necessity [6]
Advection	Specific Electrical Conductance, Oxidation-Reduction Potential, Dissolved Oxygen, pH, Temperature, Turbidity [7]	every sampling round
Dispersion	Specific Electrical Conductance, Oxidation-Reduction Potential, Dissolved Oxygen, pH, Temperature, Turbidity [7]	every sampling round
Diffusion	Specific Electrical Conductance, Oxidation-Reduction Potential, Dissolved Oxygen, pH, Temperature, Turbidity [7]	every sampling round
Sorption	Alkalinity, Specific Electrical Conductance, Oxidation-Reduction Potential, Dissolved Oxygen, pH, Sulfides, Sulfates, Temperature, Turbidity, Dissolved Organic Carbon	every sampling round
	Cation Exchange Capacity, Clay Content, Grain Size, Total Organic Carbon	first sampling round [3,4]
	Partitioning Coefficient	site-specific conditions determine necessity [6]
Oxidation-Reduction	Specific Electrical Conductance, Oxidation-Reduction Potential, Dissolved Oxygen, pH, Temperature, Turbidity, Sulfide, Iron (II)	every sampling round
	Partitioning Coefficient	site-specific conditions determine necessity [6]

Table 2
Required Field and Laboratory Indicator Parameters

Process [1]	Required Parameter [2]	Frequency
Partitioning from NAPL	Specific Electrical Conductance, Oxidation-Reduction Potential, Dissolved Oxygen, pH, Temperature, Turbidity, Iron (II)	every sampling round
	Clay Content, Grain Size, Total Organic Carbon	first sampling round [3,4]
Volatilization	Specific Electrical Conductance, Oxidation-Reduction Potential, Dissolved Oxygen, pH, Temperature, Turbidity, Iron (II)	every sampling round
	Grain Size	first sampling round [3,4]
Precipitation	Specific Electrical Conductance, Oxidation-Reduction Potential, Dissolved Oxygen, pH, Temperature, Turbidity, Iron (II)	every sampling round
	Cation Exchange Capacity, Clay Content, Grain Size, Total Organic Carbon	first sampling round [3,4]
	Partitioning Coefficient	site-specific conditions determine necessity [6]

[1] All applicable processes should be considered and discussed, with supporting information, prior to a decision of the required parameters to be analyzed.

[2] A summary of the data uses of the required parameters are provided in Table 3.

[3] A single round of samples will be needed for this parameter, unless later investigation/site characterization activities indicate that the ground-water contamination plume(s) have varying *oxidation/reduction potentials* and/or dissolved oxygen levels (variations of more than instrument error, which is commonly 5% to 10%).

[4] A single round of samples will be needed for this parameter. However, if the plume(s) is found in other area(s) than first investigated, or in additional aquifers, or found in different types of aquifer materials than first sampled, then additional samples should be collected and analyzed from these locations.

[5] Dissolved Hydrogen may be necessary if the other data is inconclusive or contradictory. Until such time that the Dissolved Hydrogen procedure is more routine and easily implemented in the field, it should only be analyzed when necessary.

[6] USEPA, 1998 (for organics) and USEPA, 1999b (for inorganics) provide information on the necessity of determining site-specific partition coefficients.

[7] These parameters are analyzed for stabilization parameter during ground-water sampling.

Table 3
Data Uses of Indicator Parameters

Parameter	Data Use	References
GROUND WATER		
Alkalinity (CO_2, HCO_3^-, CO_3^{-2})	Used for *charge balance* during major ion analysis	b, c
	Changes in alkalinity can result from biological activity in ground water through production of carbon dioxide (CO_2).	a, h
	A measure of the *buffering capacity* of ground water to pH changes.	a, b, d
Arsenic (As^{+3}, As^{+5})	To determine if anaerobic microbiological activity is dissolving arsenic from aquifer matrix material. May require determination of the *speciation* of arsenic.	a
Calcium (Ca^{+2})	Used for *charge balance* during major ion analysis	b, c
Carbon Dioxide (CO_2)	Can act as an electron acceptor for anaerobic microorganisms.	a
	By-product of some degradation pathways.	a
Chloride (Cl^-)	Used for *charge balance* during major ion analysis.	b, c
	Chloride can be from other sources such as road salt, general waste, etc.	b
	Dechlorination processes (see *reductive dehalogenation)* from chlorinated compounds may result in increases in chloride.	a, h
	Can be used as a conservative tracer to determine ground-water flow rates.	a
Iron (II) (Fe^{+2})	May indicate an anaerobic degradation process that transforms vinyl chloride, or BTEX compounds.	a, d, h
Hydrogen, Dissolved (H_2)	Dissolved hydrogen is an electron donor. May indicate the potential for reductive dechlorination to occur. Dissolved hydrogen concentrations indicate ambient redox conditions.	a, h

Table 3
Data Uses of Indicator Parameters

Parameter	Data Use	References
Magnesium (Mg^{+2})	Used for *charge balance* during major ion analysis.	b, c
Manganese (Mn^{+2}, Mn^{+3}, Mn^{+4})	To determine if anaerobic biological activity is dissolving manganese from aquifer matrix material. May require determination of *speciation.*	a, d, h
Methane (CH_4)	Methane is a by-product of methanogenesis. Associated with conditions that promote reductive dechlorination.	a, h
Nitrate (NO_3^-)	Nitrate may act as a medium for growth of microorganisms for anaerobic degradation, if oxygen is depleted. Nitrate inhibits reductive dechlorination.	a, h
Nitrites (NO_2^-)	Is an intermediate during the denitrification processes. Product of ammonia oxidation by aerobic microorganisms. Toxic by-product of denitrification of nitrate.	d
Oxidation-Reduction Potential (ORP or sometimes Eh)	Used as stabilization parameter during ground-water sampling. Used for determining the presence of oxygen in ground water (Oxidation state). Frequently, the electrode potentials measured in the field must be corrected to standard conditions.	f b, h a
Oxygen, Dissolved (O_2)	Used as stabilization parameter during ground-water sampling and aids in determining the redox regime. Used for determining the concentration of oxygen in ground water.	f a, h
Partition Coefficient (also known as a Distribution Coefficient or K_d) [1]	Used for determining the relative mobility of contaminant. Direct measure of the partitioning of a contaminant between the formation materials and ground water.	g

Table 3
Data Uses of Indicator Parameters

Parameter	Data Use	References
pH	Used for *charge balance* during major ion analysis.	b, c
	Used as stabilization parameter during ground-water sampling.	f
	Chemical and biological reactions are pH dependent.	h
Potassium (K^+)	Used for *charge balance* during major ion analysis.	b, c
Specific Electrical Conductance (SEC) (also commonly referred to as Conductivity or Specific Conductance)	Used for *charge balance* during major ion analysis.	b, c
	Used as an estimate of Total Dissolved Solids	c
	Used as a stabilization parameter during ground-water sampling.	f
	Directly related to ion concentration in solution and therefore may indicate total number of ions.	a
Sodium (Na^+)	Used for *charge balance* during major ion analysis.	b, c
Sulfate (SO_4^{-2})	Used for *charge balance* during major ion analysis.	b, c
	Sulfate may act as an electron acceptor for anaerobic degradation.	a, h
Sulfide (S^{-2})	Sulfide may be produced by sulfate reduction by sulfate-reducing bacteria, primarily in the form of hydrogen sulfide (H_2S). Tests are typically for H_2S. The presence of sulfide is a good indication that sulfate reduction is on-going.	d, h

Table 3
Data Uses of Indicator Parameters

Parameter	Data Use	References
Temperature	Used to support the evaluation of *charge balance* during major ion analysis.	b, c
	Used as stabilization parameter during ground-water sampling.	f
	Chemical and biological reactions are temperature dependent.	a, h
	Affects the solubility of dissolved gases.	a
Total Dissolved Solids (TDS)	Used with Total Suspended Solids to determine fraction of particulates that are able to pass a specified filter size. The particulates can be mobile in ground water and may provide a mechanism for facilitated transport for compounds that otherwise would not be mobile.	
Total Inorganic Carbon (CO_2, HCO_3^-, CO_3^{-2}) ^{2}	Used for *charge balance* during major ion analysis	b, c
	Changes in alkalinity can result from biological activity in ground water through production of carbon dioxide (CO_2).	a, h
	A measure of the *buffering capacity* of ground water to pH changes.	a, b, d
Total Organic Carbon (TOC)	Used to classify plume and to determine if reductive dechlorination is possible in the absence of anthropogenic carbon.	a
Total Suspended Solids (TSS)	Used with Total Dissolved Solids. TSS is the total fraction of particulates.	
Turbidity	Used as stabilization parameter during ground-water sampling.	f
	Represents fine particles suspended in water, which can be correlated to TDS and TSS.	

Table 3
Data Uses of Indicator Parameters

Parameter	Data Use	References
FORMATION MATERIALS		
Biologically Available Iron (III) (Fe^{+3})	Iron (III) may serve as the terminal electron acceptor for the destruction of fuel hydrocarbons and vinyl chloride.	a
Cation Exchange Capacity (CEC)	Measure of the capacity of formation materials to sorb metals. Composed of sorption sites on both clay and organic matter.	d, g
Grain Size	Size of grains controls some sorption and precipitation properties.	h, i
Clay Content	Clay provides sorptive sites for metals, organics and radio-nuclides. Different clay mineralogical types may also affect sorption. May be completed via x-ray analysis for mineralogy determination, via sieve analysis, or via natural-gamma geophysical logs for relative differences in clay content. Also, sorption is pH dependent.	d, g, i
Total Organic Carbon (TOC)	The rate of migration of various contaminants in ground water is dependent upon the amount of TOC in the aquifer matrix.	a, d
	May also preferentially sorb some metals, organics and radio-nuclides.	d, g, h
	TOC may reduce Chromium (VI) to Chromium (III), making it less mobile and less toxic.	j

For information on analytical procedures/methods/references, see Table 2.1 in U.S. EPA, 1998 and/or the Standard Methods for the Examination of Water and Wastewater, 18th edition, 1992.

[1] Methods for determining partition coefficients are presented in USEPA, 1999b, with the general recommendation that in-situ tests be performed.

[2] Total Inorganic Carbon can be determined by calculation or by modification of TOC method.

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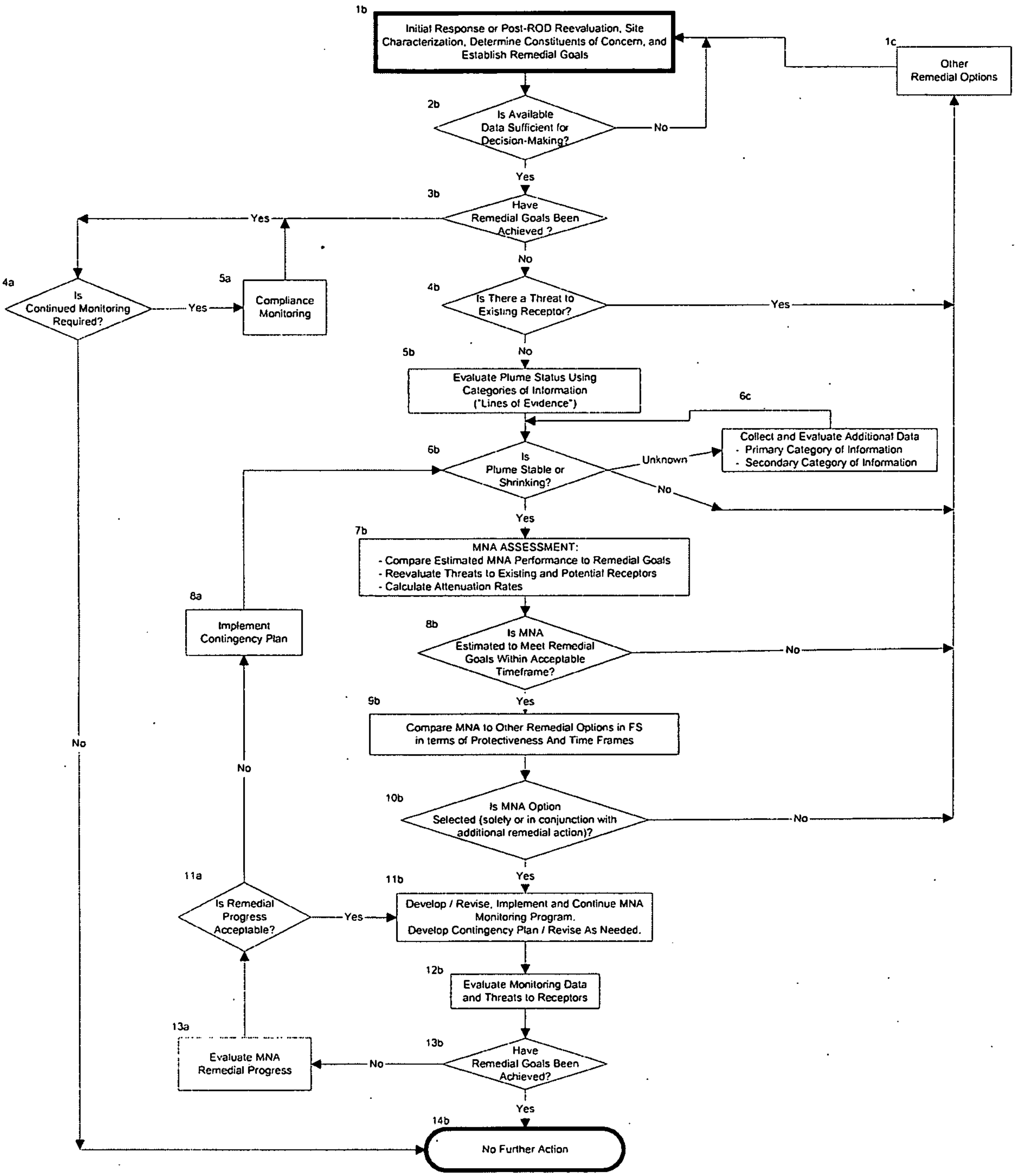
a) United States Environmental Protection Agency, 1998
b) Hem, 1985
c) Hounslow, 1995
d) Deutsch, 1997
e) Wiedemeier, Rifai, Newell and Wilson, 1999
f) Puls and Barcelona, 1996
g) United States Environmental Protection Agency, 1999b
h) Azadpour-Keeley, Russell and Sewell, 1999
i) Piwoni and Keeley, 1990
j) Palmer and Puls, 1994

FIGURE 1

Monitored Natural Attenuation Flowchart for Decision-Making



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Glossary of Terms

Abiotic	A process occurring without the involvement of microorganisms.
Buffering Capacity	The ability of either water or a water-rock (aquifer) system to resist pH change when mixed with a more acid or alkaline water or rock. This concept is particularly useful in understanding what reactions may influence the pH of natural waters.
Bulk Density	Total mass of aquifer solids and enclosed fluid(s), per unit volume.
Charge Balance	Refers to the need for electrical neutrality in flowing ground water. In essence, the total charge of the positive ions (cations) per unit volume generally must equal the total charge of the negative ions (anions), per unit volume. The charge difference between anions and cations can be used to determine the relative accuracy of the alkalinity, chloride, and sulfate analytical results, and generally should be within 5% of each other. If the charge is out of balance by more than 5%, the analysis may be inaccurate and should be re-examined. The charges may not be balanced if other constituents are present (including significant quantities of organics) or the water is very acid (with significant H^+ ions). The more common cations and anions are calcium, magnesium, potassium, sodium, carbonate, chloride and sulfate.
Darcy's Law	The principle relationship controlling ground-water movement, $Q = KA\,(dh/dl)$ where Q is the quantity of water per unit time, A is the cross-sectional area perpendicular to flow, K is *hydraulic conductivity* and (dh/dl) is the *hydraulic gradient*. Units are volume/time.
Daughter Nuclides	The nuclides formed from a parent nucleus, for example ^{238}U producing ^{234}Th, through radioactive decay. These nuclides usually have half-lives many orders of magnitude shorter than the parent nucleid e.g., ^{238}U or ^{232}Th.
Denitrification	Process whereby compounds containing nitrogen and oxygen act as an electron acceptor allowing biodegradation of the electron donor, e.g. a hydrocarbon contaminant.
Destructive Processes	A process that either chemically transforms a compound into another, or *transmutes* an atom (as in the radiogenic process). These reactions usually proceed in one direction only (irreversible). See *nondestructive* process.

Electrical Surface Charge	Electrical charges associated with unbalanced ions in crystal structure and/or ions attached to a surface through sorption which produce a net positive or negative charge per unit surface area. These localized areas may form adsorption sites for dissolved compounds in groundwater. Particularly relevant in fine-grained materials such as clays.
Electron Acceptors	Something for microorganisms to "breathe". In order for complete oxidation of an organic compound to occur, these compounds must be available to accept the electrons generated from the food source. The most common, in the preferred order are: oxygen (O_2), nitrate (NO_3^-), manganese IV (Mn^{4+}), ferric iron (Fe^{3+}), sulfate (SO_4^{-2}), CO_2, organic carbon, and chlorinated solvents. The coupled process of oxidation of organic compounds with the reduction of electron acceptors is termed respiration. Electron acceptors are reduced during the reaction.
Electron Donors	The "food" for oxidizing microorganisms e.g., simple molecules like sugars, organic acids, fulvic and humic acids, and petroleum-derived hydrocarbons. Need to be present for biodegradation to proceed. Electron donors are oxidized during the reaction.
Fick's Laws	Relationships governing the mass of a diffusing substance per unit time. The rate of contaminant transport through diffusion is proportional to the contaminant's concentration gradient or the change in concentration with distance.
Halogenated Compounds	Organic compounds containing any member of the non-metallic group VIIA in the periodic chart (F, Cl, Br, I, or At). Compounds containing chlorine are most common, for example TCE (trichloroethylene), TCA (1,1,1-trichloroethane) and vinyl chloride.
Henry's Law	A linear relationship describing the dissolved concentration in solution in water versus the partial pressure of the constituent in a vapor (air) above the fluid at equilibrium. At equilibrium the dissolved concentration and the partial pressure are related through Henry's constant.
Hydraulic Conductivity	The coefficient in Darcy's Law which equates the hydraulic gradient to the rate of ground-water flow. It describes the water transmission (flow) properties of geologic materials. Values are usually high for sand and gravel and low for clay and most rocks. Units are length/time and typically range from 10^{-11} cm/s to 10^2 cm/s for unfractured rock and gravel, respectively.

Hydraulic Gradient	A quantity, $(\Delta h_L / L)$, describing the difference in water head measurements (elevations) (Δh_L), divided by the distance between the wells being measured (L). A measure of the driving force for ground-water flow. Units are dimensionless length/length. See hydraulic conductivity.
Hydrophobic	Tendency of covalently bonded, non-polar compounds to avoid dissolution in the polar solvent, water. See *hydrophilic*.
Hydrophilic	Tendency of a compound to favor dissolution in water rather than being sorbed onto sediments or organic layers, for example. See *hydrophobic*.
Microcosm	A laboratory experiment set up to resemble as closely as possible the conditions of the natural environment under consideration.
NAPL	Non-Aqueous Phase Liquid, or an immiscible liquid in water. NAPL's tend to be formed by hydrophobic chlorinated organic compounds and may have densities either greater than or less than that of ground water, causing the NAPL to sink or float.
Nondestructive Processes	Processes that maintain a state of chemical or physical equilibrium and are capable of reversing themselves given the appropriate conditions. See *destructive* processes.
Octanol-Water Partitioning Coefficient	The unit-less ratio of the equilibrium concentration of a constituent in an organic solvent (octanol) versus that in pure water. Used as a measure of the hydrophobic tendencies (insoluble in water) of a compound.
Oxidation-Reduction Potential	The loss or gain of electrons among reactive elements or compounds, also termed '*Redox*', ORP or Eh. The loss of electrons by the electron donor is called oxidation while the gain of electrons is termed reduction. Oxidation must be accompanied by reduction since the electron exchange between the *electron acceptor* and *donor* must balance. The same is true for the inverse case, reduction processes. See electron donors/acceptors, valence.
Porosity	The ratio of openings (voids) to the total volume of a soil or rock, expressed as percentage or decimal fraction.
Redox	See Oxidation-Reduction Potential
Reductive dehalogenation	Process whereby a halogen (I, Br, Cl, F) atom is replaced with a hydrogen atom; e.g. PCE → TCE → DCE → vinyl chloride → ethane. This progression results in a successively lower number of

	halogens (chlorine, in the above case, and termed "dechlorination") attached to the compound structure.
Solubility Value	Maximum constituent concentration in solution at a given temperature and pressure at equilibrium. Common units are mass per volume, mass/unit weight, and weight/unit weight.
Solute	The dissolved inorganic or organic constituent.
Solute Transport Velocity	Average velocity of a given dissolved chemical constituent in ground water. In ground water, solute transport velocities range from the average ground-water velocity to a small fraction of the ground-water velocity.
Speciation	The chemical species corresponding to a particular oxidation state of an element. For instance, ferrous iron, Fe^{2+} versus ferric iron, Fe^{3+}. May be important in understanding the chemical conditions of ground water with respect to ORP and pH conditions. Especially important to distinguish toxicity potential when considering Cr^{3+}versus Cr^{6+}.
Transmutation	Indicates a spontaneous change in the number of neutrons and/or protons in a nucleus due to radioactive decay, resulting in the transformation to a different element such as ^{238}U (uranium) transmuting to ^{234}Th (thorium).
Valence	Electrical charge an atom would acquire if it would form ions in aqueous solution. Controls the chemical character of an ion, for example, Cr^{3+} , with a valence of +3, while that of Cr^{6+} is +6. Also known as the oxidation number.
Water Type	A convenient method of describing the variation in chemical composition between natural waters. Different styles of plots and diagrams are available to present variations in composition (e.g. Piper Diagram, Stiff Pattern, or a Trilinear Diagram). These plots are used to distinguish between different waters in the same aquifer based on their chemical characteristics, which reflect their sources and interactions between the ground water, the rock in the aquifer and geochemical/biochemical reactions taking place in ground water.

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Superfund

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Guidance:

"Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites," April 1999.
Final OSWER Directive, Publication EPA/540/R-99/009. NTIS Order Number PB99 963 315, 41p.
Available on-line from OSWER [HTML, PDF 278K]

> This directive clarifies EPA's policy regarding the use of monitored natural attenuation (MNA) for the remediation of contaminated soil and ground water. It defines the term "monitored natural attenuation" and explains that EPA considers it a remedy, not a "no action" alternative. The directive outlines potential advantages and disadvantages of this remedy, under what conditions it should be selected, the type of site most suitable for this remedy choice, the site data required to support the decision, performance monitoring considerations, and the use of contingency remedies. The directive also has a lengthy bibliography, including EPA web sites with information on monitored natural attenuation.

Other Reports:

"Performance Monitoring of MNA Remedies for VOCs in Ground Water"
April 2004.
National Risk Management Research Laboratory (NRMRL), Ada, Oklahoma, Publication EPA/600/R-04/027, 92p.
Available on-line from ORD.
Document in Sections PDF 415K, 13p]
Abstract Only: [HTML]

> This report identifies data needs and evaluation methods useful for monitoring the performance of MNA remedies selected for VOCs in ground water. The document discusses the design considerations for monitoring networks and methods for determining remedy effectiveness. Effective monitoring of natural attenuation processes involves a three-dimensional approach to network design and clearly defined performance criteria based on site-specific remedial action objectives. Objectives for the monitoring program will be met through routine evaluations of institutional controls and measurements of contaminant, geochemical, and hydrologic

parameters. These data are used to evaluate changes in three-dimensional plume boundaries, contaminant mass and concentration, and hydrological and geochemical changes that may indicate changes in remedy performance.

"Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water" October 1998.
National Risk Management Research Laboratory (NRMRL), Ada, Oklahoma, Publication EPA/600/R-98/128, NTIS Order Number PB99-130023, 214p.
Available on-line from OSWER [HTML]

This protocol provides guidance for environmental managers on the steps that must be taken to understand the rate and extent to which natural processes are reducing contaminant concentrations at sites that are contaminated by chlorinated solvents. The document identifies parameters that are useful in the evaluation of natural attenuation of chlorinated solvents (chlorinated aliphatic hydrocarbons and/or fuel hydrocarbons) and provides recommendations to analyze and interpret the data collected from the site characterization process. It also provides suggestions for integrating monitored natural attenuation (MNA) into an integrated approach to remediation that also includes an active remedy. It includes a useful list of definitions of terms related to the topic. It is a technical, not a policy, document. Data gathered using this protocol can be used to evaluate whether MNA by itself or in conjunction with other technologies is sufficient to achieve site remedial objectives, and to compare the relative effectiveness of MNA and other remedial methods. This protocol is the result of a collaborative field and laboratory research effort involving researchers from EPA's Office of Research and Development, the U.S. Air Force, and the U.S. Geological Survey.

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URL: http://www.epa.gov/superfund/resources/gwdocs/monit.htm

United States
Environmental Protection
Agency

Office of
Solid Waste and
Emergency Response

EPA

DIRECTIVE NUMBER: 9200.4-17P

TITLE: Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites

APPROVAL DATE: April 21, 1999

EFFECTIVE DATE: April 21, 1999

ORIGINATING OFFICE: OSWER

☒ **FINAL**

☐ **DRAFT**

STATUS:

REFERENCE (other documents):

OSWER OSWER OSWER
DIRECTIVE DIRECTIVE DIRECTIVE

EPA	United States Environmental Protection Agency Washington, DC 20460 **OSWER Directive Initiation Request**		1. Directive Number 9200.4-17P
2. Originator Information			
Name of Contact Person Hal White	Mail Code 5403G	Office OUST	Telephone Code (703)-603-7177

3. Title
Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites

4. Summary of Directive (include brief statement of purpose)
The purpose of this Directive is to clarify EPA's policy regarding the use of monitored natural attenuation (MNA) for the remediation of contaminated soil and groundwater at sites administered by EPA's Office of Solid Waste and Emergency Response (OSWER).

5. Keywords
natural attenuation, remediation, soil, groundwater, contamination

6a. Does This Directive Supersede Previous Directive(s)?
☒ No ☐ Yes What Directive (number, title)

b. Does It Supplement Previous Directive(s)?
☒ No ☐ Yes What Directive (number, title)

7. Draft Level
☒ A - Signed by AA/DAA ☐ B - Signed by Office Director ☐ C -For Review and Comment ☐ D - In Development

8. Document to be distributed to States by Headquarters? ☒ Yes ☐ No

This Requests Meets OSWER Directives System Format Standards	
9. Signature of Lead Office Directives Coordinator Shushona Clark	Date 3/29/99
10. Name and Title of Approving Official Timothy Fields, Jr., Acting AA/OSWER	Date 4/21/99

EPA Form 1315-17 (Rev 5-87) Previous editions are obsolete

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

APR 21 1999

OFFICE OF
SOLID WASTE AND EMERGENCY
RESPONSE

MEMORANDUM

SUBJECT: Final OSWER Directive "Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites" (OSWER Directive Number 9200.4-17P)

FROM:
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TO: Addressees

Purpose

This memorandum accompanies a copy of the Final OSWER Directive regarding the use of monitored natural attenuation for the remediation of contaminated soil and groundwater at sites regulated under all Office of Solid Waste and Emergency Response (OSWER) programs. A draft Interim Final version of this Directive was released on December 1, 1997 for use, and for general public review and comment. In response to comments received on that draft, EPA has incorporated several changes in this final version dealing with topics such as contaminants of concern, cross-media transfer, plume migration, and remediation time frame.

Implementation

This Directive is being issued in Final form and should be used immediately as guidance for proposing, evaluating, and approving Monitored Natural Attenuation remedies. This Final Directive will be available from the Superfund, RCRA, and OUST dockets and through the RCRA, Superfund & EPCRA Hotline (800-424-9346 or 703-412-9810). The directive will also be available in electronic format from EPA's home page on the Internet (the address is http://www.epa.gov/swerust1/directiv/d9200417.htm).

Questions/Comments

If you need more information about the Directive please feel free to contact any of the appropriate EPA staff listed on the attachment.

Addressees: Federal Facility Forum
Federal Facilities Leadership Council
Other Federal Facility Contacts
OSWER Natural Attenuation Workgroup
RCRA Corrective Action EPA Regional and State Program Managers
State LUST Fund Administrators
State LUST Program Managers
UST/LUST Regional Program Managers
UST/LUST Regional Branch Chiefs
State Superfund Program Managers
Superfund Regional Policy Managers

attachment

Attachment
EPA Contacts

January 1999

If you have any questions regarding this policy, please first call the RCRA/Superfund Hotline at (800) 424-9346. If you require further assistance, please contact the appropriate staff from the list below:

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USE OF MONITORED NATURAL ATTENUATION AT SUPERFUND, RCRA CORRECTIVE ACTION, AND UNDERGROUND STORAGE TANK SITES

U.S. Environmental Protection Agency
Office of Solid Waste and Emergency Response
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USE OF MONITORED NATURAL ATTENUATION AT SUPERFUND, RCRA CORRECTIVE ACTION, AND UNDERGROUND STORAGE TANK SITES

Contents

NOTICE: This document provides guidance to EPA and state staff. It also provides guidance to the public and to the regulated community on how EPA intends to exercise its discretion in implementing its regulations. The guidance is designed to implement national policy on these issues. The document does not, however, substitute for EPA's statutes or regulations, nor is it a regulation itself. Thus, it does not impose legally-binding requirements on EPA, States, or the regulated community, and may not apply to a particular situation based upon the circumstances. EPA may change this guidance in the future, as appropriate.

PURPOSE AND OVERVIEW

The purpose of this Directive is to clarify EPA's policy regarding the use of monitored natural attenuation (MNA) for the cleanup of contaminated soil and groundwater[1] in the Superfund, RCRA Corrective Action, and Underground Storage Tank programs. These programs are administered by EPA's Office of Solid Waste and Emergency Response (OSWER) which include the Office of Emergency and Remedial Response (OERR), Office of Solid Waste (OSW), Office of Underground Storage Tanks (OUST), and the Federal Facilities Restoration and Reuse Office (FFRRO). Statutory authority for these remediation programs is provided under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the Resource Conservation and Recovery Act (RCRA).

EPA remains fully committed to its goals of protecting human health and the environment by remediating contaminated soils, restoring contaminated groundwaters to their beneficial uses, preventing migration of contaminant plumes[2], and protecting groundwaters and other environmental resources[3]. EPA advocates using the most appropriate technology for a given site. EPA does not consider MNA to be a "presumptive" or "default" remedy—it is merely one option that should be evaluated with other applicable remedies. EPA does not view MNA to be a "no action[4]" or "walk-away" approach, but rather

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[1] Although this Directive does not address remediation of contaminated sediments, many of the same principles would be applicable. Fundamental issues such as having source control, developing lines of evidence, monitoring and contingency plans are also appropriate for sediments. However, the Agency is developing the policy and technical aspects for sediments, specifically.

[2] The outer limits of contaminant plumes are typically defined for each contaminant of concern based on chemical concentrations above which the overseeing regulatory authority has determined represent an actual or potential threat to human health or the environment.

[3] Environmental resources to be protected include groundwater, drinking water supplies, surface waters, ecosystems and other media (air, soil and sediments) that could be impacted by site contamination.

[4] For the Superfund program, Section 300.430(e)(6) of the National Contingency Plan (NCP) directs that a "no action alternative" (or no further action) "shall be developed" for all feasibility studies (USEPA, 1990a, p. 8849). The "no action" alternative can include monitoring but generally not other remedial actions, where such actions are defined in Section 300.5 of the NCP. In general, the "no action" alternative is selected when there is no current or potential threat to human health or the environment or when CERCLA exclusions preclude taking an action (USEPA, 1991a). As explained in this Directive, a remedial alternative that relies on monitored natural attenuation to attain site-specific remediation objectives is **not** the same as the "no action" alternative.

considers it to be an alternative means of achieving remediation objectives[5] that may be appropriate for specific, well-documented site circumstances where its use meets the applicable statutory and regulatory requirements. As there is often a variety of methods available for achieving remediation objectives at any given site, MNA may be evaluated and compared to other viable remediation methods (including innovative technologies) during the study phases leading to the selection of a remedy. As with any other remedial alternative, MNA should be selected only where it meets all relevant remedy selection criteria, and where it will meet site remediation objectives within a timeframe that is reasonable compared to that offered by other methods. In the majority of cases where MNA is proposed as a remedy, its use may be appropriate as one component of the total remedy, that is, either in conjunction with active remediation or as a follow-up measure. MNA should be used very cautiously as the sole remedy at contaminated sites. Furthermore, the availability of MNA as a potential remediation tool does not imply any lessening of EPA's longstanding commitment to pollution prevention. Waste minimization, pollution prevention programs, and minimal technical requirements to prevent and detect releases remain fundamental parts of EPA waste management and remediation programs.

Use of MNA does not signify a change in OSWER's remediation objectives. These objectives (discussed in greater detail under the heading "Implementation") include control of source materials[6], prevention of plume migration, and restoration of contaminated groundwaters, where appropriate. Thus, EPA expects that source control measures (see section on "Remediation of Sources") will be evaluated for all sites under consideration for any proposed remedy. As with other remediation methods, selection of MNA as a remediation method should be supported by detailed site-specific information that demonstrates the efficacy of this remediation approach. In addition, the progress of MNA toward a site's remediation objectives should be carefully monitored and compared with expectations. Where MNA's ability to meet these expectations is uncertain and based predominantly on predictive analyses, decision makers should incorporate contingency measures into the remedy.

The scientific understanding of natural attenuation processes continues to evolve. EPA recognizes that significant advances have been made in recent years, but there is still a great deal to be learned regarding the mechanisms governing natural attenuation processes and their ability to address different types of contamination problems. Therefore, while EPA believes MNA may

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[5] In this Directive, remediation objectives are the overall objectives that remedial actions are intended to accomplish and are not the same as chemical-specific cleanup levels. Remediation objectives could include preventing exposure to contaminants, preventing further migration of contaminants from source areas, preventing further migration of the groundwater contaminant plume, reducing contamination in soil or groundwater to specified cleanup levels appropriate for current or potential future uses, or other objectives. The term "remediation" as used in this Directive is not limited to "remedial actions" defined in CERCLA §101(24), and includes CERCLA "removal actions", for example.

[6] "**Source material** is defined as material that includes or contains hazardous substances, pollutants or contaminants that act as a reservoir [either stationary or mobile] for migration of contamination to the ground water, to surface water, to air, [or other environmental media,] or acts as a source for direct exposure. Contaminated ground water generally is not considered to be a source material although non-aqueous phase liquids (NAPLS [occurring either as residual- or free-phase]) may be viewed as source materials." (USEPA, 1991b).

be used where circumstances are appropriate, it should be used with caution commensurate with the uncertainties associated with the particular application. Furthermore, largely due to the uncertainty associated with the potential effectiveness of MNA to meet remediation objectives that are protective of human health and the environment, EPA expects that **source control and long-term performance monitoring will be fundamental components of any MNA remedy**.

This Directive is a policy document and as such is not intended to provide detailed technical guidance on evaluating MNA remedies. EPA recognizes that at present there are relatively few EPA guidance documents concerning appropriate implementation of MNA remedies. Chapter IX of OUST's alternative cleanup technologies manual (USEPA, 1995a) addresses the use of natural attenuation at leaking UST sites. The Office of Research and Development (ORD) has recently published a protocol for evaluating MNA at chlorinated solvent sites (USEPA, 1998a). Additional technical resource documents for evaluating MNA in groundwater, soils, and sediments are being developed by ORD. Supporting technical information regarding the evaluation of MNA as a remediation alternative is available from a variety of other sources, including those listed at the end of this Directive. "References Cited" lists those EPA documents that were specifically cited within this Directive. The list of "Additional References" includes documents produced by EPA as well as non-EPA entities. Finally, "Other Sources of Information" lists sites on the World Wide Web (Internet) where additional information can be obtained. Non-EPA documents may provide regional and state site managers, as well as the regulated community, with useful technical information. However, these non-EPA guidances are not officially endorsed by EPA, EPA does not necessarily agree with all their conclusions, and all parties involved should clearly understand that such guidances do not in any way replace current EPA or OSWER guidances or policies addressing the remedy selection process in the Superfund, RCRA, or UST programs.

BACKGROUND

The term "monitored natural attenuation", as used in this Directive, refers to the reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods. The "natural attenuation processes" that are at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. These *in-situ* processes include biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants. When relying on natural attenuation processes for site remediation, EPA prefers those processes that degrade or destroy contaminants. Also, EPA generally expects that MNA will only be appropriate for sites that have a low potential for contaminant migration. Additional discussion of criteria for "Sites Where Monitored Natural Attenuation May Be Appropriate" may be found later in this Directive. Other terms associated with natural attenuation in the literature include "intrinsic remediation", "intrinsic bioremediation", "passive bioremediation", "natural recovery", and "natural assimilation". While some of these terms are synonymous with "natural attenuation," others refer strictly to biological processes, excluding chemical and physical processes. Therefore, it is recommended that for clarity and consistency, the term "monitored natural attenuation" be used throughout OSWER remediation programs unless a specific process (*e.g.*, reductive dehalogenation) is being referenced.

Natural attenuation processes are typically occurring at all sites, but to varying degrees of effectiveness depending on the types and concentrations of contaminants present and the physical, chemical, and biological characteristics of the soil and groundwater. Natural attenuation processes may reduce the potential risk posed by site contaminants in three ways:

(1) Transformation of contaminant(s) to a less toxic form through destructive processes such as biodegradation or abiotic transformations;

(2) Reduction of contaminant concentrations whereby potential exposure levels may be reduced; and

(3) Reduction of contaminant mobility and bioavailability through sorption onto the soil or rock matrix.

Where conditions are favorable, natural attenuation processes may reduce contaminant mass or concentration at sufficiently rapid rates to be integrated into a site's soil or groundwater remedy. Following source control measures, natural attenuation may be sufficiently effective to achieve remediation objectives at some sites without the aid of other (active) remedial measures. Typically, however, MNA will be used in conjunction with active remediation measures. For example, active remedial measures could be applied in areas with high concentrations of contaminants while MNA is used for low concentration areas; or MNA could be used as a follow-up to active remedial measures. EPA also encourages the consideration of innovative technologies for source control or "active" components of the remedy, which may offer greater confidence and reduced remediation time frames at modest additional cost.

While MNA is often dubbed "passive" remediation because natural attenuation processes occur without human intervention, its use at a site does **not** preclude the use of "active" remediation or the application of enhancers of biological activity (*e.g.*, electron acceptors, nutrients, and electron donors). However, by definition, a remedy that includes the introduction of an enhancer of any type is no longer considered to be "natural" attenuation. Use of MNA does not imply that activities (and costs) associated with investigating the site or selecting the remedy (*e.g.*, site characterization, risk assessment, comparison of remedial alternatives, performance monitoring, and contingency measures) have been eliminated. These elements of the investigation and cleanup must still be addressed as required under the particular OSWER program, regardless of the remedial approach selected.

Contaminants of Concern

It is common practice in conducting remedial actions to focus on the most obvious contaminants of concern, but other contaminants may also be of significant concern in the context of MNA remedies. In general, since engineering controls are not used to control plume migration in an MNA remedy, decision makers need to ensure that MNA is appropriate to address **all contaminants** that represent an actual or potential threat to human health or the environment. Several examples are provided below to illustrate the need to assess both the obvious as well as the less obvious contaminants of concern when evaluating an MNA remedial option.

- Mixtures of contaminants released into the environment often include some which may be amenable to MNA, and others which are not addressed sufficiently by natural attenuation processes to achieve remediation objectives. For example, Benzene, Toluene, Ethylbenzene and Xylenes (BTEX) associated with gasoline have been shown in many circumstances to be effectively remediated by natural attenuation processes. However, a common additive to gasoline (*i.e.*, methyl tertiary-butyl ether [MTBE]) has been found to migrate large distances and threaten downgradient water supplies at the same sites where the BTEX component of a plume has either stabilized or diminished due to natural attenuation. In general, compounds that tend not to degrade readily in the subsurface (*e.g.*, MTBE and 1,4-dioxane) and that represent an actual or potential threat should be assessed when evaluating the appropriateness of MNA remedies.

- Analyses of contaminated media often report chemicals which are identified with a high degree of certainty, as well other chemicals labeled as "tentatively identified compounds" (TICs). It is often assumed that TICs will be addressed by a remedial action along with the primary contaminants of concern. This may be a reasonable assumption for an active remediation system (*e.g.*, pump and treat) which is capturing all contaminated groundwater, but might not be acceptable for an MNA remedy that is relying on natural processes to prevent contaminant migration. Where MNA is being proposed for sites with TICs, it may be prudent to identify the TICs and evaluate whether they too will be sufficiently mitigated by MNA.

- At some sites the same geochemical conditions and processes that lead to biodegradation of chlorinated solvents and petroleum hydrocarbons can chemically transform naturally occurring minerals (*e.g.*, arsenic and manganese compounds) in the aquifer matrix to forms that are more mobile and/or more toxic than the original materials (USEPA, 1998). A comprehensive assessment of an MNA remedial option should include evaluation of whether naturally occurring metals will become contaminants of concern.

Addressing the above concerns does not necessarily require sampling and analysis of extensive lists of parameters at every monitoring location in all situations. The location and number of samples collected and analyzed for this purpose should be determined on a site-specific basis to ensure adequate characterization and protection of human health and the environment.

Transformation Products

It also should be noted that some natural attenuation processes may result in the creation of transformation products[7] that are more toxic and/or mobile than the parent contaminant (*e.g.*, degradation of trichloroethylene to vinyl chloride). The potential for creation of toxic transformation products is more likely to occur at non-petroleum release sites (*e.g.*, chlorinated solvents or other volatile organic spill sites) and should be evaluated to determine if implementation of a MNA remedy is appropriate and protective in the long term.

Cross-Media Transfer

Natural attenuation processes may often result in transfer of some contaminants from one medium to another (*e.g.*, from soil to groundwater, from soil to air or surface water, and from groundwater to surface water). Processes that result in degradation of contaminants are preferable to those which rely predominantly on the transfer of contamination from one medium to another. MNA remedies involving cross-media transfer of contamination should include a site-specific evaluation of the potential risk posed by the contaminant(s) once transferred to a particular medium. Additionally, long-term monitoring should address the media to which contaminants are being transferred.

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[7] The term "transformation products" in the Directive includes intermediate products resulting from biotic or abiotic processes (*e.g.*, TCE, DCE, vinyl chloride), decay chain daughter products from radioactive decay, and inorganic elements that become methylated compounds (*e.g.*, methyl mercury) in soil or sediment. Some transformation products are quickly transformed to other products while others are longer lived.

Petroleum-Related Contaminants

Natural attenuation processes, particularly biological degradation, are currently best documented at petroleum fuel spill sites. Under appropriate field conditions, the regulated compounds benzene, toluene, ethylbenzene, and xylene (BTEX) may naturally degrade through microbial activity and ultimately produce non-toxic end products (*e.g.*, carbon dioxide and water). Where microbial activity is sufficiently rapid, the dissolved BTEX contaminant plume may stabilize (*i.e.*, stop expanding), and contaminant concentrations in both groundwater and soil may eventually decrease to levels below regulatory standards. Following degradation of a dissolved BTEX plume, a residue consisting of heavier petroleum hydrocarbons of relatively low solubility and volatility will typically be left behind in the original source (spill) area. Although this residual contamination may have relatively low potential for further migration, it still may pose a threat to human health or the environment either from direct contact with soils in the source area or by continuing to slowly leach contaminants to groundwater. For these reasons, MNA alone is generally not sufficient to remediate petroleum release sites. Implementation of source control measures in conjunction with MNA is almost always necessary. Other controls (*e.g.*, institutional controls[8]), in accordance with applicable state and federal requirements, may also be necessary to ensure protection of human health and the environment.

Chlorinated Solvents

Chlorinated solvents[9], such as trichloroethylene, represent another class of common contaminants. These compounds are more dense than water and are referred to as DNAPLs (dense-non-aqueous phase liquids). Recent research has identified some of the mechanisms potentially responsible for degrading these solvents, furthering the development of methods for estimating biodegradation rates of these chlorinated compounds. However, the hydrologic and geochemical conditions favoring significant biodegradation of chlorinated solvents sufficient to achieve remediation objectives within a reasonable timeframe are anticipated to occur only in limited circumstances. DNAPLs tend to sink through the groundwater column toward the bottom of the aquifer. However, they can also occur as mixtures with other less dense contaminants. Because of the varied nature and distribution of chlorinated compounds, they are typically difficult to locate, delineate, and remediate even with active measures. In the subsurface, chlorinated solvents represent source materials that can continue to contaminate groundwater for decades or longer. Cleanup of solvent spills is also complicated by the fact that a typical spill includes

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[8] The term "institutional controls" refers to non-engineering measures—usually, but not always, legal controls—intended to affect human activities in such a way as to prevent or reduce exposure to hazardous substances. Examples of institutional controls cited in the National Contingency Plan (USEPA, 1990a, p.8706) include land and resource (*e.g.*, water) use and deed restrictions, well-drilling prohibitions, building permits, well use advisories, and deed notices.

[9] Chlorinated solvents are only one type of halogenated compound. Chlorinated solvents are specifically referenced in this Directive because they are commonly found at contaminated sites. The discussion in this Directive regarding chlorinated solvents may also apply to other halogenated compounds to be remediated.

multiple contaminants, including some that tend not to degrade readily in the subsurface.[10] Extremely long dissolved solvent plumes have been documented that may be due to the existence of subsurface conditions that are not conducive to natural attenuation.

Inorganics

MNA may, under certain conditions (*e.g.*, through sorption or oxidation-reduction reactions), effectively reduce the dissolved concentrations and/or toxic forms of inorganic contaminants in groundwater and soil. Both metals and non-metals (including radionuclides) may be attenuated by sorption[11] reactions such as precipitation, adsorption on the surfaces of soil minerals, absorption into the matrix of soil minerals, or partitioning into organic matter. Oxidation-reduction (redox) reactions can transform the valence states of some inorganic contaminants to less soluble and thus less mobile forms (*e.g.*, hexavalent uranium to tetravalent uranium) and/or to less toxic forms (*e.g.*, hexavalent chromium to trivalent chromium). Sorption and redox reactions are the dominant mechanisms responsible for the reduction of mobility, toxicity, or bioavailability of inorganic contaminants. It is necessary to know what specific mechanism (type of sorption or redox reaction) is responsible for the attenuation of inorganics so that the stability of the mechanism can be evaluated. For example, precipitation reactions and absorption into a soil's solid structure (*e.g.*, cesium into specific clay minerals) are generally stable, whereas surface adsorption (*e.g.*, uranium on iron-oxide minerals) and organic partitioning (complexation reactions) are more reversible. Complexation of metals or radionuclides with carrier (chelating) agents (*e.g.*, trivalent chromium with EDTA) may increase their concentrations in water and thus enhance their mobility. Changes in a contaminant's concentration, pH, redox potential, and chemical speciation may reduce a contaminant's stability at a site and release it into the environment. Determining the existence, and demonstrating the irreversibility, of these mechanisms is important to show that a MNA remedy is sufficiently protective.

In addition to sorption and redox reactions, radionuclides exhibit radioactive decay and, for some, a parent-daughter radioactive decay series. For example, the dominant attenuating mechanism of tritium (a radioactive isotopic form of hydrogen with a short half-life) is radioactive decay rather than sorption. Although tritium does not generate radioactive daughter products, those generated by some radionulides (*e.g.*, Am-241 and Np-237 from Pu-241) may be more toxic, have longer half-lives, and/or be more mobile than the parent in the decay series. Also, it is

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[10] For example, 1,4-dioxane, which is used as a stabilizer for some chlorinated solvents, is more highly toxic, less likely to sorb to aquifer solids, and less biodegradable than some other solvent constituents under the same environmental conditions.

[11] When a contaminant is associated with a solid phase, it is usually not known if the contaminant is precipitated as a three-dimensional molécular coating on the surface of the solid, adsorbed onto the surface of the solid, absorbed into the structure of the solid, or partitioned into organic matter. "Sorption" will be used in this Directive to describe, in a generic sense (*i.e.*, without regard to the precise mechanism) the partitioning of aqueous phase constituents to a solid phase.

important that the near surface or surface soil pathways be carefully evaluated and eliminated as potential sources of external direct radiation exposure[12].

Inorganic contaminants persist in the subsurface because, except for radioactive decay, they are not degraded by the other natural attenuation processes. Often, however, they may exist in forms that have low mobility, toxicity, or bioavailability such that they pose a relatively low level of risk. Therefore, natural attenuation of inorganic contaminants is most applicable to sites where immobilization or radioactive decay is demonstrated to be in effect and the process/mechanism is irreversible.

Advantages and Disadvantages of Monitored Natural Attenuation

MNA has several potential advantages and disadvantages, and the factors listed below should be carefully considered during site characterization and evaluation of remediation alternatives before selecting MNA as the remedial alternative. **Potential advantages** of MNA include:

- As with any *in situ* process, generation of lesser volume of remediation wastes, reduced potential for cross-media transfer of contaminants commonly associated with *ex situ* treatment, and reduced risk of human exposure to contaminants, contaminated media, and other hazards, and reduced disturbances to ecological receptors;

- Some natural attenuation processes may result in *in-situ* destruction of contaminants;

- Less intrusion as few surface structures are required;

- Potential for application to all or part of a given site, depending on site conditions and remediation objectives;

- Use in conjunction with, or as a follow-up to, other (active) remedial measures; and

- Potentially lower overall remediation costs than those associated with active remediation.

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[12] External direct radiation exposure refers to the penetrating radiation (*i.e.,* primarily gamma radiation and x-rays) that may be an important exposure pathway for certain radionuclides in near surface soils. Unlike chemicals, radionuclides can have deleterious effects on humans without being taken into or brought in contact with the body due to high energy particles emitted from near surface soils. Even though the radionuclides that emit penetrating radiation may be immobilized due to sorption or redox reactions, the resulting contaminated near surface soil may not be a candidate for a MNA remedy as a result of this exposure risk.

The **potential disadvantages** of MNA include:

- Longer time frames may be required to achieve remediation objectives, compared to active remediation measures at a given site;
- Site characterization is expected to be more complex and costly;
- Toxicity and/or mobility of transformation products may exceed that of the parent compound;
- Long-term performance monitoring will generally be more extensive and for a longer time;
- Institutional controls may be necessary to ensure long term protectiveness;
- Potential exists for continued contamination migration, and/or cross-media transfer of contaminants;
- Hydrologic and geochemical conditions amenable to natural attenuation may change over time and could result in renewed mobility of previously stabilized contaminants (or naturally occurring metals), adversely impacting remedial effectiveness; and
- More extensive education and outreach efforts may be required in order to gain public acceptance of MNA.

IMPLEMENTATION

The use of MNA is not new in OSWER programs. For example, in the Superfund program, use of natural attenuation as an element in a site's groundwater remedy is discussed in "Guidance on Remedial Actions for Contaminated Groundwater at Superfund Sites" (USEPA, 1988a). Use of MNA in OSWER programs has slowly increased over time with greater program experience and scientific understanding of the processes involved. Recent advances in the scientific understanding of the processes contributing to natural attenuation have resulted in a heightened interest in this approach as a potential means of achieving remediation objectives for soil and groundwater. However, EPA expects that reliance on MNA as the sole remedy will only be appropriate at relatively few contaminated sites. This Directive is intended to clarify OSWER program policies regarding the use of MNA and ensure that MNA remedies are selected and implemented appropriately. Topics addressed include the role of MNA in OSWER remediation programs, site characterization, the types of sites where MNA may be appropriate, reasonable remediation timeframes, source control, performance monitoring, and contingency remedies where MNA will be employed.

Role of Monitored Natural Attenuation in OSWER Remediation Programs

Under OSWER programs, remedies selected for contaminated media (such as contaminated soil and groundwater) must protect human health and the environment. Remedies may achieve this level of protection using a variety of methods, including treatment, containment, engineering controls, and other means identified during the remedy selection process.

The regulatory and policy frameworks for corrective actions under the UST, RCRA, and Superfund programs have been established to implement their respective statutory mandates and to promote the selection of technically defensible, nationally consistent, and cost effective solutions for the cleanup of contaminated media. EPA recognizes that MNA may be an appropriate remediation option for contaminated soil and groundwater under certain circumstances. However, determining the appropriate mix of remediation methods at a given site, including when and how to use MNA, can be a complex process. Therefore, MNA should be carefully evaluated along with other viable remedial approaches or technologies (including innovative technologies) within the applicable remedy selection framework. **MNA should not be considered a default or presumptive remedy at any contaminated site.**

Each OSWER program has developed regulations and policies to address the particular types of contaminants and facilities within its purview[13]. Although there are differences among

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[13] Existing program guidance and policy regarding MNA can be obtained from the following sources: For Superfund, see "Guidance on Remedial Actions for Contaminated Groundwater at Superfund Sites," (USEPA, 1988a; pp. 5-7 and 5-8); the Preamble to the 1990 National Contingency Plan (USEPA, 1990a, pp.8733-34); and "Presumptive Response Strategy and Ex-Situ Treatment Technologies for Contaminated Ground Water at CERCLA Sites, Final Guidance" (USEPA, 1996a; p. 18). For the RCRA program, see the Subpart S Proposed Rule (USEPA, 1990b, pp.30825 and 30829), and the Advance Notice of Proposed Rulemaking (USEPA, 1996b, pp.19451-52). For the UST program, refer to Chapter IX in "How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers;" (USEPA, 1995a).

these programs, they share several key principles that should generally be considered during selection of remedial measures, including:

- Source control measures should use treatment to address "principal threat" wastes (or products) wherever practicable, and engineering controls such as containment for waste (or products) that pose a relatively low long-term threat, or where treatment is impracticable.[14]

- Contaminated groundwaters should be returned to "their beneficial uses[15] wherever practicable, within a timeframe that is reasonable given the particular circumstances of the site." When restoration of groundwater is not practicable, EPA "expects to prevent further migration of the plume, prevent exposure to the contaminated groundwater, and evaluate further risk reduction."[16]

- Contaminated soil should be remediated to achieve an acceptable level of risk to human and environmental receptors, and to prevent any transfer of contaminants to other media (*e.g.*, surface or groundwater, air, sediments) that would result in an unacceptable risk or exceed required cleanup levels.

- Remedial actions in general should include opportunity(ies) for public involvement that serve to both educate interested parties and to solicit feedback concerning the decision making process.

Consideration or selection of MNA as a remedy or remedy component does not in any way change or displace these (or other) remedy selection principles. Nor does use of MNA

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[14] Principal threat wastes are those **source materials** that are "highly toxic or highly mobile that generally cannot be reliably contained or would present a significant risk to human health or the environment should exposure occur. They include liquids and other highly mobile materials (*e.g.*, solvents) or materials having high concentrations of toxic compounds." (USEPA, 1991b). Low level threat wastes are "source materials that generally can be reliably contained and that would present only a low risk in the event of release." (USEPA, 1991b). Since contaminated groundwater is not source material, it is neither a principal nor a low-level threat waste.

[15] **Beneficial uses** of groundwater could include uses for which water quality standards have been promulgated, (*e.g.*, drinking water supply, discharge to surface water), or where groundwater serves as a source of recharge to either surface water or adjacent aquifers, or other uses. These or other types of beneficial uses may be identified as part of a Comprehensive State Groundwater Protection Program (CSGWPP). For more information on CSGWPPs, see USEPA, 1992a and USEPA, 1997b, or contact your state implementing agency.

[16] This is a general expectation for remedy selection in the Superfund program, as stated in §300.430 (a)(1)(iii)(F) of the National Contingency Plan (USEPA, 1990a, p.8846). The NCP Preamble also specifies that cleanup levels appropriate for the expected beneficial use (*e.g.*, MCLs for drinking water) "should generally be attained throughout the contaminated plume, or at and beyond the edge of the waste management area when waste is left in place" (USEPA, 1990a, p.8713). The RCRA Corrective Action program has similar expectations (see USEPA, 1996b, pp.19448-19450).

diminish EPA's or the regulated party's responsibility to achieve protectiveness or to satisfy long-term site remediation objectives. EPA expects that **MNA will be an appropriate remediation method only where its use will be protective of human health and the environment and it will be capable of achieving site-specific remediation objectives within a timeframe that is reasonable compared to other alternatives.** The effectiveness of MNA in both near-term and long-term timeframes should be demonstrated to EPA (or other overseeing regulatory authority) through: 1) sound technical analyses which provide confidence in natural attenuation's ability to achieve remediation objectives; 2) performance monitoring; and 3) contingency (or backup) remedies where appropriate. **In summary, use of MNA does not imply that EPA or the responsible parties are "walking away" from the cleanup or financial responsibility at a site.**

It also should be emphasized that the selection of MNA as a remedy does **not** imply that active remediation measures are infeasible, or are "technically impracticable" from an engineering perspective. Technical impracticability (TI) determinations are used to justify a departure from cleanup levels that would otherwise be required at a Superfund site or RCRA facility based on the inability to achieve such cleanup levels using available remedial technologies (USEPA, 1993a). Such a TI determination does not imply that there will be no active remediation at the site, nor that MNA will be used at the site. Rather, such a TI determination simply indicates that the cleanup levels and objectives which would otherwise be required cannot practicably be attained using available remediation technologies. In such cases, an alternative cleanup strategy that is fully protective of human health and the environment must be identified. Such an alternative strategy may still include engineered remediation components, such as recovery of free phase NAPLs and containment of residual contaminants, in addition to approaches intended to restore some portion of the contaminated groundwater to beneficial uses. Several remedial approaches could be appropriate to address the dissolved plume, one of which could be MNA under suitable conditions. However, the evaluation of natural attenuation processes and the decision to rely upon MNA for the dissolved plume should be distinct from the recognition that restoration of a portion of the plume is technically impracticable (*i.e.*, MNA should **not** be viewed as a direct or presumptive outcome of a technical impracticability determination.)

Demonstrating the Efficacy of Natural Attenuation Through Site Characterization

Decisions to employ MNA as a remedy or remedy component should be thoroughly and adequately supported with site-specific characterization data and analysis. In general, the level of site characterization necessary to support a comprehensive evaluation of MNA is more detailed than that needed to support active remediation. Site characterizations for natural attenuation generally warrant a quantitative understanding of source mass; groundwater flow (including preferential pathways); contaminant phase distribution and partitioning between soil, groundwater, and soil gas; rates of biological and non-biological transformation; and an understanding of how all of these factors are likely to vary with time. This information is generally necessary since contaminant behavior is governed by dynamic processes which must be well understood before MNA can be appropriately applied at a site. Demonstrating the efficacy of

MNA may require analytical or numerical simulation of complex attenuation processes. Such analyses, which are critical to demonstrate natural attenuation's ability to meet remediation objectives, generally require a detailed conceptual site model[17] as a foundation.

EPA recommends the use of conceptual site models to integrate data and guide both investigative and remedial actions. However, program implementors should be cautious and collect sufficient field data to test conceptual hypotheses and not "force-fit" site data into a pre-conceived, and possibly inaccurate, conceptual representation. For example, a common mechanism for transport of contaminants is advection-dispersion, by which contaminants dissolved in groundwater migrate away from a source area. An alternative mechanism of contaminant transport (*i.e.*, NAPL migration) could be associated with a relatively large release of NAPL into the subsurface such that the NAPL itself has the potential to migrate significant distances along preferential pathways. Since NAPL migration pathways are often difficult to locate in the subsurface, one may incorrectly conclude that only the dissolved transport model applies to a site, when a combined NAPL and dissolved phase migration model would be more accurate. Applying a wrong conceptual model, in the context of evaluating an MNA (or any other) remedy, could result in a deficient site characterization (*e.g.*, did not use tools and approaches designed to find NAPLs or NAPL migration pathways), and inappropriate selection of an MNA remedy where long-term sources were not identified nor considered during remedy selection. NAPL present as either free- or residual phase represents a significant mass of contamination that will serve as a long-term source. Sources of contamination are more appropriately addressed by engineered removal, treatment or containment technologies, as discussed later in this Directive. Where the sources of contamination have been controlled, dissolved plumes may be amenable to MNA because of the relatively small mass of contaminants present in the plume.

Site characterization should include collecting data to define (in three spatial dimensions over time) the nature and distribution of contaminants of concern and contaminant sources as well as potential impacts on receptors (see "Background" section for further discussion pertaining to "Contaminants of Concern"). However, where MNA will be considered as a remedial approach, certain aspects of site characterization may require more detail or additional elements. For

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[17] A conceptual site model (CSM) is a three-dimensional representation that conveys what is known or suspected about contamination sources, release mechanisms, and the transport and fate of those contaminants. The conceptual model provides the basis for assessing potential remedial technologies at the site. "Conceptual site model" is **not** synonymous with "computer model"; however, a computer model may be helpful for understanding and visualizing current site conditions or for predictive simulations of potential future conditions. Computer models, which simulate site processes mathematically, should in turn be based upon sound conceptual site models to provide meaningful information. Computer models typically require a lot of data, and the quality of the output from computer models is directly related to the quality of the input data. Because of the complexity of natural systems, models necessarily rely on simplifying assumptions that may or may not accurately represent the dynamics of the natural system. Calibration and sensitivity analyses are important steps in appropriate use of models. Even so, the results of computer models should be carefully interpreted and continuously verified with adequate field data. Numerous EPA references on models are listed in the "Additional References" section at the end of this Directive.

example, to assess the contributions of sorption, dilution, and dispersion to natural attenuation of contaminated groundwater, a very detailed understanding of aquifer hydraulics, recharge and discharge areas and volumes, and chemical properties is necessary. Where biodegradation will be assessed, characterization also should include evaluation of the nutrients and electron donors and acceptors present in the groundwater, the concentrations of co-metabolites and metabolic by-products, and perhaps specific analyses to identify the microbial populations present. The findings of these, and any other analyses pertinent to characterizing natural attenuation processes, should be incorporated into the conceptual model of contaminant fate and transport developed for the site.

MNA may not be appropriate as a remedial option at many sites for technological or economic reasons. For example, in some complex geologic systems, technological limitations may preclude adequate monitoring of a natural attenuation remedy to ensure with a high degree of confidence that potential receptors will not be impacted. This situation typically occurs in many karstic, structured, and/or fractured rock aquifers where groundwater moves preferentially through discrete pathways (*e.g.*, solution channels, fractures, joints, foliations). The direction of groundwater flow through such heterogeneous (and often anisotropic) materials can not be predicted directly from the hydraulic gradient, and existing techniques may not be capable of identifying the pathway along which contaminated groundwater moves through the subsurface. MNA will not generally be appropriate where site complexities preclude adequate monitoring. In some other situations where it may be technically feasible to monitor the progress of natural attenuation, the cost of site characterization and long-term monitoring required for the implementation of MNA may be higher than the cost of other remedial alternatives. Under such circumstances, MNA may not be less costly than other alternatives.

A related consideration for site characterization is how other remedial activities at the site could affect natural attenuation. For example, the capping of contaminated soil could alter both the type of contaminants leached to groundwater, as well as their rate of transport and degradation. Another example could be where there is co-mingled petroleum and chlorinated solvent contamination. In such cases, degradation of the chlorinated solvents is achieved, in part, through the action of microbes that derive their energy from the carbon in the petroleum. Recovery of thc petroleum removes some of the source of food for these microbes and the rate of degradation of the chlorinated solvents is decreased. Therefore, the impacts of any ongoing or proposed remedial actions should be factored into the analysis of the effectiveness of MNA.

Once site characterization data have been collected and a conceptual model developed, the next step is to evaluate the potential efficacy of MNA as a remedial alternative. This involves collection of site-specific data sufficient to estimate with an acceptable level of confidence both the rate of attenuation processes and the anticipated time required to achieve remediation objectives. A three-tiered approach to such an evaluation is becoming more widely practiced and accepted. In this approach, successively more detailed information is collected as necessary to provide a specified level of confidence on the estimates of attenuation rates and remediation timeframe. These three tiers of site-specific information, or "lines of evidence", are:

(1) Historical groundwater and/or soil chemistry data that demonstrate a clear and meaningful trend[18] of decreasing contaminant mass and/or concentration over time at appropriate monitoring or sampling points. (In the case of a groundwater plume, decreasing concentrations should not be solely the result of plume migration. In the case of inorganic contaminants, the primary attenuating mechanism should also be understood.)

(2) Hydrogeologic and geochemical data that can be used to demonstrate **indirectly** the type(s) of natural attenuation processes active at the site, and the rate at which such processes will reduce contaminant concentrations to required levels. For example, characterization data may be used to quantify the rates of contaminant sorption, dilution, or volatilization, or to demonstrate and quantify the rates of biological degradation processes occurring at the site.

(3) Data from field or microcosm studies (conducted in or with actual contaminated site media) which **directly** demonstrate the occurrence of a particular natural attenuation process at the site and its ability to degrade the contaminants of concern (typically used to demonstrate biological degradation processes only).

Unless EPA or the overseeing regulatory authority determines that historical data (Number 1 above) are of sufficient quality and duration to support a decision to use MNA, data characterizing the nature and rates of natural attenuation processes at the site (Number 2 above) should be provided. Where the latter are also inadequate or inconclusive, data from microcosm studies (Number 3 above) may also be necessary. In general, more supporting information may be required to demonstrate the efficacy of MNA at those sites with contaminants which do not readily degrade through biological processes (*e.g.*, most non-petroleum compounds, inorganics), or that transform into more toxic and/or mobile forms than the parent contaminant, or where monitoring has been performed for a relatively short period of time. The amount and type of information needed for such a demonstration will depend upon a number of site-specific factors, such as the size and nature of the contamination problem, the proximity of receptors and the potential risk to those receptors, and other characteristics of the environmental setting (*e.g.*, hydrogeology, ground cover, climatic conditions).

Note that those parties responsible for site characterization and remediation should ensure that all data and analyses needed to demonstrate the efficacy of MNA are collected and evaluated by capable technical specialists with expertise in the relevant sciences. Furthermore, EPA expects that documenting the level of confidence on attenuation rates will provide more technically defensible predictions of remedial timeframes and form the basis for more effective performance monitoring programs.

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[18] For guidance on statistical analysis of environmental data, please see USEPA, 1989, USEPA, 1993b, USEPA, 1993d, and Gilbert, 1987, listed in the "References Cited" section at the end of this Directive.

Sites Where Monitored Natural Attenuation May Be Appropriate

MNA is appropriate as a remedial approach where it can be demonstrated capable of achieving a site's remediation objectives within a timeframe that is reasonable compared to that offered by other methods and where it meets the applicable remedy selection criteria (if any) for the particular OSWER program. **EPA expects that MNA will be most appropriate when used in conjunction with other remediation measures (*e.g.*, source control, groundwater extraction), or as a follow-up to active remediation measures that have already been implemented.**

In determining whether MNA is an appropriate remedy for soil or groundwater at a given site, EPA or other regulatory authorities should consider the following:

- Whether the contaminants present in soil or groundwater can be effectively remediated by natural attenuation processes;
- Whether or not the contaminant plume is stable and the potential for the environmental conditions that influence plume stability to change over time;
- Whether human health, drinking water supplies, other groundwaters, surface waters, ecosystems, sediments, air, or other environmental resources could be adversely impacted as a consequence of selecting MNA as the remediation option;
- Current and projected demand for the affected resource over the time period that the remedy will remain in effect;
- Whether the contamination, either by itself or as an accumulation with other nearby sources (on-site or off-site), will exert a long-term detrimental impact on available water supplies or other environmental resources;
- Whether the estimated timeframe of remediation is reasonable (see section on "Reasonable Timeframe for Remediation") compared to timeframes required for other more active methods (including the anticipated

effectiveness of various remedial approaches on different portions of the contaminated soil and/or groundwater);

- The nature and distribution of sources of contamination and whether these sources have been, or can be, adequately controlled;
- Whether the resulting transformation products present a greater risk, due to increased toxicity and/or mobility, than do the parent contaminants;
- The impact of existing and proposed active remediation measures upon the MNA component of the remedy, or the impact of remediation measures or other operations/activities (*e.g.*, pumping wells) in close proximity to the site; and
- Whether reliable site-specific mechanisms for implementing institutional controls (*e.g.*, zoning ordinances) are available, and if an institution responsible for their monitoring and enforcement can be identified.

Of the above factors, the most important considerations regarding the suitability of MNA as a remedy include: whether the contaminants are likely to be effectively addressed by natural attenuation processes, the stability of the groundwater contaminant plume and its potential for migration, and the potential for unacceptable risks to human health or environmental resources by the contamination. MNA should not be used where such an approach would result in either plume migration[19] or impacts to environmental resources that would be unacceptable to the overseeing regulatory authority. **Therefore, sites where the contaminant plumes are no longer increasing in extent, or are shrinking, would be the most appropriate candidates for MNA remedies.**

An example of a situation where MNA may be appropriate is a remedy that includes source control, a pump-and-treat system to mitigate the highly-contaminated plume areas, and MNA in the lower concentration portions of the plume. In combination, these methods would maximize groundwater restored to beneficial use in a timeframe consistent with future demand on the aquifer, while utilizing natural attenuation processes to reduce the reliance on active remediation methods and reduce remedy cost. If, at such a site, the plume was either expanding

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[19] In determining whether a plume is stable or migrating, users of this Directive should consider the **uncertainty** associated with defining the limits of contaminant plumes. For example, a plume is typically delineated for each contaminant of concern as a 2- or 3-dimensional feature. Plumes are commonly drawn by computer contouring programs which estimate concentrations between actual data points. EPA recognizes that a plume boundary is more realistically defined by a zone rather than a line. Fluctuations within this zone are likely to occur due to a number of factors (*e.g.*, analytical, seasonal, spatial, etc.) which may or may not be indicative of a trend in plume migration. Therefore, site characterization activities and performance monitoring should focus on collection of data of sufficient quality to enable decisions to be made with a high level of confidence. See USEPA, 1993b, USEPA, 1993c, USEPA, 1994b, and USEPA, 1998b, for additional guidance.

or threatening downgradient wells or other environmental resources, then MNA would **not** be an appropriate remedy.

Reasonable Timeframe for Remediation

EPA recognizes that determination of what timeframe is "reasonable" for **attaining remediation objectives** is a site-specific determination. The NCP preamble suggests that a "reasonable" timeframe for a remedy relying on natural attenuation is generally a "...timeframe **comparable** to that which could be achieved through active restoration" (USEPA, 1990a, p.8734; emphasis added). The NCP preamble further states that "[t]he most appropriate timeframe must, however, be determined through an analysis of alternatives" (USEPA, 1990a, p.8732). To ensure that these estimates are comparable, assumptions should be consistently applied for each alternative considered. Thus, determination of the most appropriate timeframe is achieved through a comparison of estimates of remediation timeframe for **all** appropriate remedy alternatives.

If **restoring groundwaters to beneficial uses** is a remediation objective, a comparison of restoration alternatives from most aggressive to passive (*i.e.*, MNA) will provide information concerning the approximate range of time periods needed to attain groundwater cleanup levels. An excessively long restoration timeframe, using the most aggressive restoration method, **may** indicate that groundwater restoration is technically impracticable from an engineering perspective (USEPA, 1993a). Where restoration **is** technically **practicable** using either aggressive or passive methods, the longer restoration timeframe required by the passive alternative may be reasonable in comparison with the timeframe needed for more aggressive restoration alternatives (USEPA, 1996a).

The advantages and disadvantages of each remedy alternative, including the timeframe, should be evaluated in accordance with the remedy selection criteria used by each OSWER program. Whether a particular remediation timeframe is appropriate and reasonable for a given site is determined by balancing tradeoffs among many factors which include:

- Classification of the affected resource (*e.g.*, drinking water source, agricultural water source) and value of the resource[20];

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[20] In determining whether an extended remediation timeframe may be appropriate for the site, EPA and other regulatory authorities should consider state groundwater resource classifications, priorities and/or valuations where available, in addition to relevant federal guidelines. Individual states may provide information and guidance relevant to groundwater classifications or use designations as part of a Comprehensive State Groundwater Protection Program (CSGWPP). (See USEPA, 1992a and USEPA, 1997b).

- Relative timeframe in which the affected portions of the aquifer might be needed for future water supply (including the availability of alternate supplies);
- Subsurface conditions and plume stability which can change over an extended timeframe;
- Whether the contamination, either by itself or as an accumulation with other nearby sources (on-site or off-site), will exert a long-term detrimental impact on available water supplies or other environmental resources;
- **Uncertainties** regarding the mass of contaminants in the subsurface and predictive analyses (*e.g.*, remediation timeframe, timing of future demand, and travel time for contaminants to reach points of exposure appropriate for the site);
- Reliability of monitoring and of institutional controls over long time periods;
- Public acceptance of the timeframe required to reach remediation objectives; and
- Provisions by the responsible party for adequate funding of monitoring and performance evaluation over the time period required for remediation.

It should be noted that the timeframe required for MNA remedies is often longer than that required for more active remedies. **As a consequence, the uncertainty associated with the above factors increases dramatically. Adequate performance monitoring and contingency remedies (both discussed in later sections of this Directive) should be utilized because of this higher level of uncertainty.** When determining reasonable timeframes, the uncertainty in estimated timeframes should be considered, as well as the ability to establish performance monitoring programs capable of verifying the performance expected from natural attenuation in a timely manner (*e.g.*, as would be required in a Superfund five-year remedy review).

A decision on whether or not MNA is an appropriate remedy for a given site is usually based on estimates of the rates of natural attenuation processes. Site characterization (and monitoring) data are typically used for estimating attenuation rates. These calculated rates may be expressed with respect to either time or distance from the source. Time-based estimates are used to predict the time required for MNA to achieve remediation objectives and distance-based estimates provide an evaluation of whether a plume will expand, remain stable, or shrink. For environmental decision-making, EPA requires that the data used be of "adequate quality and usability for their intended purpose." (USEPA, 1998b). Therefore, where these rates are used to evaluate MNA, or predict the future behavior of contamination, they must also be of "adequate quality and usability." Statistical confidence intervals should be estimated for calculated attenuation rate constants (including those based on methods such as historical trend data analysis, analysis of attenuation along a flow path in groundwater, and microcosm studies). When predicting remedial timeframes, sensitivity analyses should also be performed to indicate the dependence of the calculated remedial timeframes on uncertainties in rate constants and other factors (McNab and Dooher, 1998). A statistical evaluation of the rate constants estimated from site characterization studies of natural attenuation of groundwater contamination often reveals that the estimated rate constants contain considerable uncertainty. For additional guidance on data quality, see USEPA, 1993c, 1994c, 1995b, and 1995c.

As an example, analysis of natural attenuation rates from many sites indicates that a measured decrease in contaminant concentrations of at least one order of magnitude is necessary to determine the appropriate rate law to describe the rate of attenuation, and to demonstrate that the estimated rate is statistically different from zero at a 95% level of confidence (Wilson, 1998). Due to variability resulting from sampling and analysis, as well as plume variability over time, smaller apparent reductions are often insufficient to demonstrate (with 95% level of confidence) that attenuation has in fact occurred at all.

Thus, EPA or other regulatory authorities should consider a number of factors when evaluating reasonable timeframes for MNA at a given site. These factors, on the whole, should allow the overseeing regulatory authority to determine whether a natural attenuation remedy (including institutional controls where applicable) will fully protect potential human and environmental receptors, and whether the site remediation objectives and the time needed to meet them are consistent with the regulatory expectation that contaminated groundwaters will be restored to beneficial uses within a reasonable timeframe. **When these conditions cannot be met using MNA, a remedial alternative that more likely would meet these expectations should be selected.**

Remediation of Sources

Source control measures should be evaluated as part of the remedy decision process at **all** sites, particularly where MNA is under consideration as the remedy or as a remedy component. Source control measures include removal, treatment, or containment, or a combination of these approaches. EPA prefers remedial options which remove free-phase NAPLs and treat those source materials determined to constitute "principal threat wastes" (see Footnote 13).

Contaminant sources that are not adequately addressed complicate the long-term cleanup effort. For example, following free product recovery, residual contamination from a petroleum fuel release may continue to leach significant quantities of contaminants into the groundwater as well as itself posing unacceptable risks to humans or environmental resources. Such a lingering source often unacceptably extends the time necessary to reach remediation objectives. This leaching can occur even while contaminants are being naturally attenuated in other parts of the plume. If the rate of attenuation is lower than the rate of replenishment of contaminants to the groundwater, the plume can continue to expand thus contaminating additional groundwater and potentially posing a threat to downgradient receptors.

Control of source materials is the most effective means of ensuring the timely attainment of remediation objectives. **EPA, therefore, expects that source control measures will be evaluated for all contaminated sites and that source control measures will be taken at most sites where practicable.** At many sites it will be appropriate to implement source control measures during the initial stages of site remediation ("phased remedial approach"), while collecting additional data to determine the most appropriate groundwater remedy.

Performance Monitoring and Evaluation

Performance monitoring to evaluate remedy effectiveness and to ensure protection of human health and the environment is a critical element of all response actions. Performance monitoring is of even greater importance for MNA than for other types of remedies due to the potentially longer remediation timeframes, potential for ongoing contaminant migration, and other uncertainties associated with using MNA. This emphasis is underscored by EPA's reference to "monitored natural attenuation".

The monitoring program developed for each site should specify the location, frequency, and type of samples and measurements necessary to evaluate whether the remedy is performing as expected and is capable of attaining remediation objectives. In addition, all monitoring programs should be designed to accomplish the following:

- Demonstrate that natural attenuation is occurring according to expectations;
- Detect changes in environmental conditions (*e.g.*, hydrogeologic, geochemical, microbiological, or other changes) that may reduce the efficacy of any of the natural attenuation processes[21];
- Identify any potentially toxic and/or mobile transformation products;
- Verify that the plume(s) is not expanding (either downgradient, laterally or vertically);

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[21] Detection of changes will depend on the proper siting and construction of monitoring wells/points. Although the siting of monitoring wells is a concern for any remediation technology, it is of even greater concern with MNA because of the lack of engineering controls to control contaminant migration.

- Verify no unacceptable impact to downgradient receptors;
- Detect new releases of contaminants to the environment that could impact the effectiveness of the natural attenuation remedy;
- Demonstrate the efficacy of institutional controls that were put in place to protect potential receptors; and
- Verify attainment of remediation objectives.

The frequency of monitoring should be adequate to detect, in a timely manner, the potential changes in site conditions listed above. At a minimum, the monitoring program should be sufficient to enable a determination of the rate(s) of attenuation and how that rate is changing with time. When determining attenuation rates, the uncertainty in these estimates and the associated implications should be evaluated (see McNab and Dooher, 1998). Flexibility for adjusting the monitoring frequency over the life of the remedy should also be included in the monitoring plan. For example, it may be appropriate to decrease the monitoring frequency at some point in time, once it has been determined that natural attenuation is progressing as expected and very little change is observed from one sampling round to the next. In contrast, the monitoring frequency may need to be increased if unexpected conditions (*e.g.*, plume migration) are observed.

Performance monitoring should continue until remediation objectives have been achieved, and longer if necessary to verify that the site no longer poses a threat to human health or the environment. Typically, monitoring is continued for a specified period (*e.g.*, one to three years) after remediation objectives have been achieved to ensure that concentration levels are stable and remain below target levels. The institutional and financial mechanisms for maintaining the monitoring program should be clearly established in the remedy decision or other site documents, as appropriate.

Details of the monitoring program should be provided to EPA or the overseeing regulatory authority as part of any proposed MNA remedy. Further information on the types of data useful for monitoring natural attenuation performance can be found in the ORD publications (*e.g.*, USEPA, 1997a, USEPA, 1994a) listed in the "References Cited" section of this Directive. Also, USEPA (1994b) published a detailed document on collection and evaluation of performance monitoring data for pump-and-treat remediation systems.

Contingency Remedies

A contingency remedy is a cleanup technology or approach specified in the site remedy decision document that functions as a "backup" remedy in the event that the "selected" remedy fails to perform as anticipated. A contingency remedy may specify a technology (or technologies) that is (are) different from the selected remedy, or it may simply call for modification of the selected technology, if needed. Contingency remedies should generally be flexible—allowing for the incorporation of new information about site risks and technologies.

Contingency remedies are not new to OSWER programs. Contingency remedies should be included in the decision document where the selected technology is not proven for the specific site application, where there is significant uncertainty regarding the nature and extent of contamination at the time the remedy is selected, or where there is uncertainty regarding whether a proven technology will perform as anticipated under the particular circumstances of the site (USEPA, 1990c).

It is also recommended that one or more criteria ("triggers") be established, as appropriate, in the remedy decision document that will signal unacceptable performance of the selected remedy and indicate when to implement contingency remedies. Such criteria should generally include, but not be limited to, the following:

- Contaminant concentrations in soil or groundwater at specified locations exhibit an increasing trend not originally predicted during remedy selection;
- Near-source wells exhibit large concentration increases indicative of a new or renewed release;
- Contaminants are identified in monitoring wells located outside of the original plume boundary;
- Contaminant concentrations are not decreasing at a sufficiently rapid rate to meet the remediation objectives; and
- Changes in land and/or groundwater use will adversely affect the protectiveness of the MNA remedy.

In establishing triggers or contingency remedies, however, care is needed to ensure that sampling variability or seasonal fluctuations do not unnecessarily trigger a contingency. For example, an anomalous spike in dissolved concentration(s) at a well(s) might not be a true indication of a change in trend.

EPA recommends that remedies employing MNA be evaluated to determine the need for including one or more contingency measures that would be capable of achieving remediation objectives. EPA believes that contingency remedies should generally be included as part of a MNA remedy which has been selected based primarily on predictive analyses rather than documented trends of decreasing contaminant concentrations.

SUMMARY

EPA remains fully committed to its goals of protecting human health and the environment by remediating contaminated soils, restoring contaminated groundwaters to their beneficial uses, preventing migration of contaminant plumes, and protecting groundwaters and other environmental resources. EPA does not view MNA to be a "no action" remedy, but rather considers it to be a means of addressing contamination under a limited set of site circumstances where its use meets the applicable statutory and regulatory requirements. MNA is not a "presumptive" or "default" remediation alternative, but rather should be evaluated and compared to other viable remediation methods (including innovative technologies) during the study phases leading to the selection of a remedy. The decision to implement MNA should include a comprehensive site characterization, risk assessment where appropriate, and measures to control sources. In addition, the progress of natural attenuation towards a site's remediation objectives should be carefully monitored and compared with expectations to ensure that it will meet site remediation objectives within a timeframe that is reasonable compared to timeframes associated with other methods. Where MNA's ability to meet these expectations is uncertain and based predominantly on predictive analyses, decision-makers should incorporate contingency measures into the remedy.

EPA is confident that MNA will be, at many sites, a reasonable and protective component of a broader remediation strategy. However, EPA believes that there will be many other sites where either the uncertainties are too great or there is a need for a more rapid remediation that will preclude the use of MNA as a stand-alone remedy. This Directive should help promote consistency in how MNA remedies are proposed, evaluated, and approved.

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