

**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 current 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 all 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 heterogeneities 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, <i>redox</i> reactions, elimination reactions, etc.) that degrade contaminants without microbial facilitation, commonly significant for <i>halogenated compounds</i> . 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 <i>oxidation-reduction</i> reactions that degrade contaminants. Oxygen consumption, <i>denitrification</i> , sulfate reduction, iron reduction, methanogenesis and <i>reductive dehalogenation</i> 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 <i>transmutation</i> of the radionuclide(s) of concern. However, the production of <i>daughter nuclides</i> 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 <i>Darcy's Law</i> .	Dependent on physical aquifer properties, mainly <i>hydraulic conductivity</i> , <i>effective porosity</i> , and <i>hydraulic gradient</i> . 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 <i>solute</i> 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 <i>Fick's Laws</i> .	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 <i>solute</i> 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, <i>bulk density</i> , specific surface area, and porosity) and contaminant properties (e.g., water <i>solubility values</i> , <i>hydrophobicity</i> , <i>octanol-water partitioning coefficient</i> , <i>charge balance</i> considerations).	Tends to reduce apparent <i>solute transport velocity</i> and removes <i>solutes</i> from the ground water via sorption to the formation material.
Biotransformation ⁴	Inorganics & Organics	Microbially mediated <i>oxidation-reduction</i> 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	<p>A reaction couple producing a change in <i>valence</i> state (e.g., H₂S, HSO₄⁻, SO₄²⁻). 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:</p> $\frac{1}{2} \text{CH}_2\text{O} + \text{H}^+ = \frac{1}{2} \text{CH}_3\text{OH}$	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 <i>visa versa</i> . 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 <i>NAPL</i>	Organic	Partitioning from <i>NAPL</i> into ground water. <i>NAPL</i> 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 <i>NAPL</i> plume.	Dissolution of contaminants from <i>NAPL</i> 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, <i>Henry's Law</i> 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., CH₃HgCl).

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 (CO₂, HCO₃⁻, CO₃⁻²)	<p>Used for <i>charge balance</i> during major ion analysis</p> <p>Changes in alkalinity can result from biological activity in ground water through production of carbon dioxide (CO₂).</p> <p>A measure of the <i>buffering capacity</i> of ground water to pH changes.</p>	<p>b, c</p> <p>a, h</p> <p>a, b, d</p>
Arsenic (As⁺³, As⁺⁵)	To determine if anaerobic microbiological activity is dissolving arsenic from aquifer matrix material. May require determination of the <i>speciation</i> of arsenic.	a
Calcium (Ca⁺²)	Used for <i>charge balance</i> during major ion analysis	b, c
Carbon Dioxide (CO₂)	<p>Can act as an electron acceptor for anaerobic microorganisms.</p> <p>By-product of some degradation pathways.</p>	<p>a</p> <p>a</p>
Chloride (Cl⁻)	<p>Used for <i>charge balance</i> during major ion analysis.</p> <p>Chloride can be from other sources such as road salt, general waste, etc.</p> <p>Dechlorination processes (see <i>reductive dehalogenation</i>) from chlorinated compounds may result in increases in chloride.</p> <p>Can be used as a conservative tracer to determine ground-water flow rates.</p>	<p>b, c</p> <p>b</p> <p>a, h</p> <p>a</p>
Iron (II) (Fe⁺²)	May indicate an anaerobic degradation process that transforms vinyl chloride, or BTEX compounds.	a, d, h
Hydrogen, Dissolved (H₂)	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 <i>charge balance</i> 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 <i>speciation</i> .	a, d, h
Methane (CH₄)	Methane is a by-product of methanogenesis. Associated with conditions that promote reductive dechlorination.	a, h
Nitrate (NO₃⁻)	Nitrate may act as a medium for growth of microorganisms for anaerobic degradation, if oxygen is depleted. Nitrate inhibits reductive dechlorination.	a, h
Nitrites (NO₂⁻)	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 (O₂)	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 <i>charge balance</i> 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 <i>charge balance</i> during major ion analysis.	b, c
Specific Electrical Conductance (SEC) (also commonly referred to as Conductivity or Specific Conductance)	Used for <i>charge balance</i> 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 <i>charge balance</i> during major ion analysis.	b, c
Sulfate (SO₄⁻²)	Used for <i>charge balance</i> 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 ₂ S). Tests are typically for H ₂ S. 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 <i>charge balance</i> 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 (CO₂, HCO₃⁻, CO₃⁻²)²	Used for <i>charge balance</i> 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 <i>buffering capacity</i> 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.

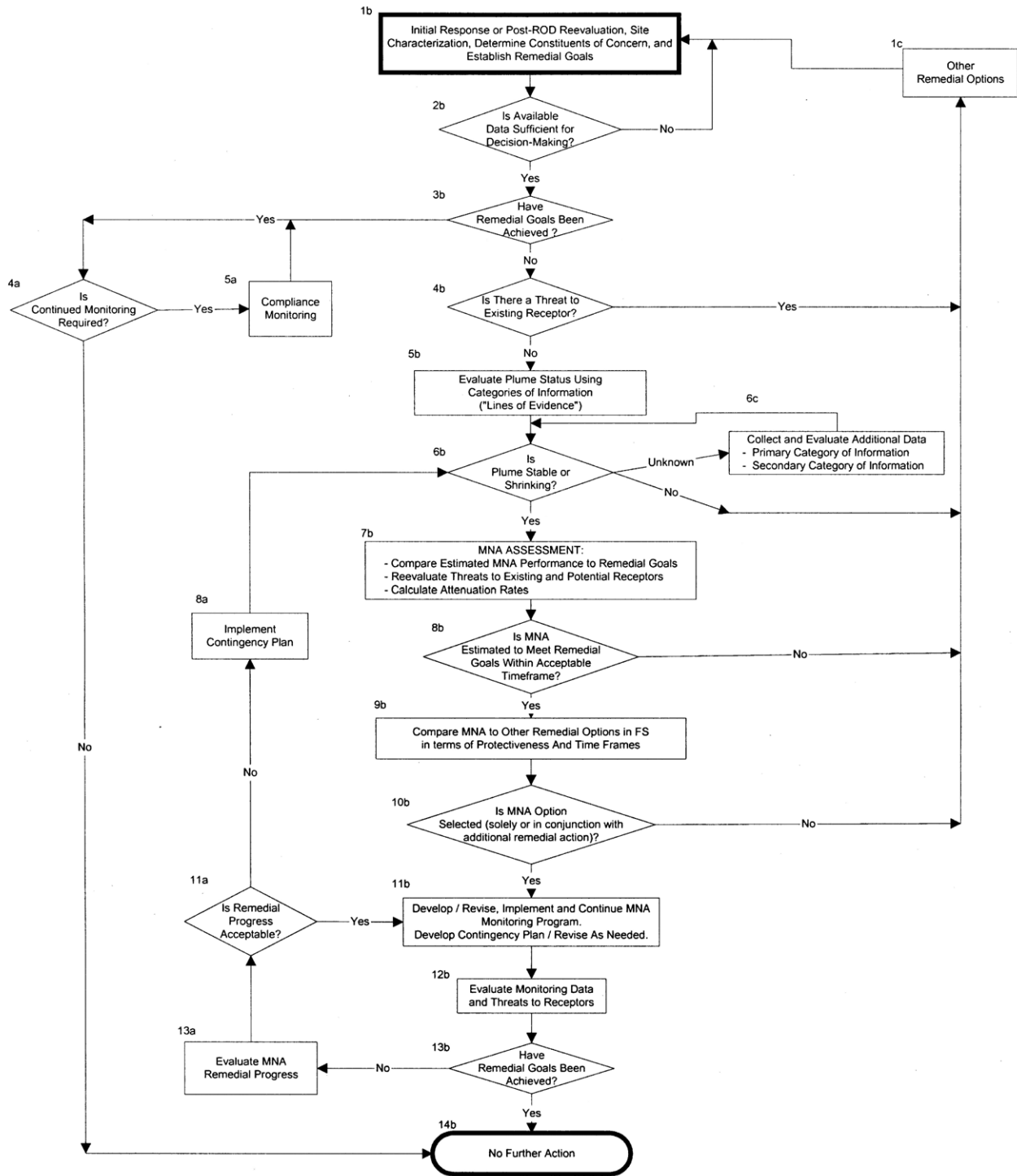
² Total Inorganic Carbon can be determined by calculation or by modification of TOC method.

References:

- 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 <i>hydraulic conductivity</i> and (dh/dl) is the <i>hydraulic gradient</i> . 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 <i>transmutes</i> an atom (as in the radiogenic process). These reactions usually proceed in one direction only (irreversible). See <i>nondestructive</i> 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 <i>hydrophilic</i> .
Hydrophilic	Tendency of a compound to favor dissolution in water rather than being sorbed onto sediments or organic layers, for example. See <i>hydrophobic</i> .
Microcosm	A laboratory experiment set up to resemble as closely as possible the conditions of the natural environment under consideration.
NAPL	<u>N</u> on- <u>A</u> queous <u>P</u> hase <u>L</u> iquid, 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 <i>destructive</i> 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 ' <i>Redox</i> ', 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 <i>electron acceptor</i> and <i>donor</i> 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 \rightarrow TCE \rightarrow DCE \rightarrow vinyl chloride \rightarrow 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.