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Site Screening and Technical Guidance for Monitored Natural Attenuation at DOE Sites

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Site Screening and Technical Guidance for Monitored Natural Attenuation at DOE Sites

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Abstract

Site Screening and Technical Guidance for Monitored Natural Attenuation at DOE Sites briefly outlines the biological and geochemical origins of natural attenuation, the tendency for natural processes in soils to mitigate contaminant transport and availability, and the means for relying on monitored natural attenuation (MNA) for remediation of contaminated soils and groundwaters. This report contains a step-by-step guide for (1) screening contaminated soils and groundwaters on the basis of their potential for remediation by natural attenuation and (2) implementing MNA consistent with EPA OSWER Directive 9200.4-17. The screening and implementation procedures are set up as a web-based tool (http://www.sandia.gov/eesector/gs/gc/na/mnahome.html) to assist U.S. Department of Energy (DOE) site environmental managers and their staff and contractors to adhere to EPA guidelines for implementing MNA. This document is intended to support the Decision Maker's Framework Guide and Monitoring Guide both to be issued from DOE EM-40. Further technical advances may cause some of the approach outlined in this document to change over time.

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Nomenclature

[>-i]	sorbed concentration of contaminant i
AFCEE	U. S. Air Force Center for Environmental Excellence
BF	biodegradation/chemical transformation Factor
BTEX	benzene toluene ethylbenzene xylene
CERCLA	Comprehensive Environmental Response Compensation and Liability Act
C	contaminant concentration
C_{max}	maximum contaminant concentration measured in the soil
C_o	initial concentration of contaminant
C_s	contaminant sorption capacity
C_{sx}	contaminant sorption capacity for weak (reversible) sites
C_{sy}	contaminant sorption capacity for strong (irreversible) sites
C_t	contaminant concentration as a function of time
CT	carbon tetrachloride
d	mixing zone depth (m)
d_a	aquifer depth (m)
DCA	dichloroethane
DCE	dichloroethylene
DCF	dose conversion factor
DL	dose limit from SDWA
DNAPL	dense nonaqueous phase liquid
DOE	U.S. Department of Energy
DTPA	diethylenediaminepentaacetic acid
EDTA	ethylenedinitrilotetraacetic acid
EPA	U.S. Environmental Protection Agency
f	fraction of the irreversible compartment (organics) that is filled at the time of exposure
HDF	hydrologic dilution factor
i	hydraulic gradient (m/m)
i^{aq}	the dissolved concentration of contaminant i
i^{tot}	total amount of contaminant in rock or soil
k	degradation rate constant (yr^{-1})
k_l	Langmuir constant – proportional to the binding strength of a contaminant
K_d	sorption coefficient (ml/g)
K_h	hydrologic conductivity (m/yr)
$K^{irv}{}_{oc}$	organic carbon-normalized partition coefficient
K_{oc}	soil adsorption coefficient normalized to organic carbon content (L/kg)
K_{om}	soil adsorption coefficient normalized to OC organic matter (L/kg)
K_{ow}	octanol water partition coefficient (L/kg)
K_p	predicted equilibrium partition constant
K_x	binding constant for weak sites
K_y	binding constant for strong sites
l	recharge rate (m/yr)
L	length of source parallel to flow (m)
LC	limiting concentration
M_i	molar concentration (mol/L)
MCL	maximum contaminant level
MNA	monitored natural attenuation
Na	Avogadro's number
NAF	natural attenuation factor
n_e	effective aquifer porosity
NTA	nitrilotriacetic acid
OC	organic carbon
om	soil organic matter content (kg/kg)
OSWER	Office of Solid Waste and Emergency Response

PCA	tetrachloroethane
PCE	perchloroethylene
q	total adsorption (organics)(μg/g)
q_{irv}	Irreversible adsorption (organics)(μg/g)
q^{irv}_{max}	maximum irreversible adsorption level (organics) (μg/g)
q_{rev}	reversible adsorption (organics)(μg/g)
R_{irv}	irreversible uptake factor
RCRA	Resource Conservation and Recovery Act
ROD	Record of Decision
RTDF	Remediation Technologies Development Forum
SDWA	Safe Drinking Water Act
SEP	Sequential Extraction Procedure
SF	sorption factor
$t_{1/2}$	radioactive half-life (yr)
TCA	tricholoroethane
TCE	trichloroethylene
TCLP	toxicity characteristic leaching procedure
VC	vinyl chloride
VOL	volume of water or leachate in equilibrium
Vol_{rock}	volume of soil estimated to be encountered by a plume (L)
v	subsurface velocity of dissolved contaminant
V_s	horizontal seepage velocity
WC	water consumption rate (L/yr)
WT	weight of soil or rock in equilibrium
x	distance the contaminant travels in groundwater (m)
X	reversible – weak sites
X_{irv}	irreversible uptake fraction
X_t	a known or measurable amount of contaminant
Y	irreversible – strong sites
α_v	vertical dispersivity (m)
ρ	bulk density (kg/L)
ρ_b	bulk rock density

1.0 Introduction

According to the Environmental Protection Agency's (EPA's) Office of Solid Waste and Emergency Response (OSWER) Directive 9200.4-17, natural attenuation is defined as "the naturally occurring processes in soils and groundwaters that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in those media." These in situ processes include biodegradation, dispersion, dilution, sorption, precipitation, volatilization, and/or chemical and biochemical stabilization of contaminants (U.S. Environmental Protection Agency, 1997).

This document outlines a site-screening procedure for assessing the importance of natural attenuation and provides technical guidance for relying on natural attenuation at contaminated soils and groundwaters at Department of Energy (DOE) sites. The object of this document is to provide site managers, the target audience, the general technical background needed to consider remediation by natural attenuation. The sections that follow define natural attenuation, broadly outline how conceptual models are used to address and implement monitored natural attenuation (MNA) and then link the achievement of cleanup goals with natural attenuation processes.

Specific questions that must be answered for successful reliance on MNA at sites include:

1. Is natural attenuation occurring?
2. If so, are reductions in potential contaminant impacts decreasing rapidly enough to achieve regulatory compliance in an acceptable time frame?
3. Is natural attenuation sufficiently widespread and reliable to assure remedial goals are achieved?
4. How much long-term monitoring is required?
5. What is the cost of MNA in comparison to other remediation techniques?

Development of site-specific conceptual models describing contaminant transport in the subsurface is meant to answer each of these questions.

Given observed evidence of decreases in contaminant mass at a site, formulation of a conceptual model requires that the responsible mechanism(s) be identified, and their absolute capacity and efficiency quantified. This effort will, by necessity, be both contaminant and site-specific, but may draw on regional or historical information from similar sites. A wealth of evidence suggests that most contaminants are affected by a limited number of subsurface geochemical and biological processes. Site-specific conceptual models for contaminant attenuation are therefore reasonably attainable, given the collection of key site-specific hydrological and geochemical parameters. Once developed, conceptual models are useful for assessing the likelihood of natural attenuation achieving regulatory cleanup goals.

Monitored natural attenuation, to be successful, must result in the achievement of cleanup goals. Typically, cleanup goals are based on an estimated level of risk, and removal of contaminants to achieve this goal is argued to reflect a certain reduction of risk. The estimated risk posed by soil contaminants depends on a number of factors such as the details of exposure scenarios involving volumes of contaminated soil or water ingested and/or inhaled or absorbed by a hypothetical receptor. Ultimately the actual risk posed depends on the bioavailability of the contaminant(s), which in turn often depends on the extent of natural attenuation that has occurred since a contaminant has been introduced into the environment. The nature and extent of natural attenuation can vary widely, depending on the specific contaminant and the site.

Biodegradation by indigenous microorganisms often causes fuel hydrocarbon plumes to stabilize and then contract even in the absence of active remediation under certain conditions (Rice et al., 1995). Many chlorinated organic contaminants resist rapid biodegradation unless reducing conditions prevail near the source, but oxidizing conditions exist further away (Chapelle, 1996). Radioactive decay may cause radionuclides with sufficiently short half-lives to vanish rapidly on an environmental time scale. Nevertheless, time often leaves inorganics and long-lived radionuclides in the subsurface where they may also become unavailable for biologic uptake (and hence pose less of a risk) due to sequestration at mineral surfaces or formation of solids. The long-term transport of contaminants that can form solids or species sorbed (reversibly or irreversibly) to mineral surfaces may, because of the ambient geochemistry, be severely limited (colloidal transport of contaminants may occur particularly in aquifers with unusually high groundwater velocities or unusually large pores). Dilution may lower dissolved organic and inorganic contaminant concentrations to the point where remedial goals are met, although there has been no net reduction in contaminant mass.

2.0 The EPA MNA Guidelines

This section briefly describes the EPA's MNA interim guidelines issued on November 22, 1997, for relying on MNA at Superfund, Resource Conservation and Recovery Act (RCRA) corrective action, and underground storage tank sites (U.S. Environmental Protection Agency, 1997). The full document is given in Appendix A and serves as an outline of the EPA's general guidelines for natural attenuation. However, there is only minimal discussion of site-specific data needs for individual contaminants. The EPA views MNA as a remedial alternative that should be evaluated during the site characterization and remedy selection phase. The use of MNA should be supported by site-specific information that demonstrates the efficacy of the method, much like any other remedial approach. EPA does not view natural attenuation as a presumptive remedy or as the default outcome of a technical impracticability determination. MNA, as a remediation alternative for a site, will by its very nature be a significant effort and an improvement over the no-action alternative. The no-action alternative invariably requires very conservative assumptions about contaminant performance and site characteristics, often precipitated by a lack of detailed knowledge about a site. For example, distribution coefficients of contaminants are often assumed to be the lowest credible values (sometimes zero) and groundwater velocities are assumed to their maximum credible values to estimate a worst-case scenario for contaminant migration. If this worst-case scenario shows no impact or no unacceptable risk, then no remediation (including MNA) would be required or justified. Often, however, the no-action alternative shows a significant impact or an unacceptable risk and thus is used to argue for selection of some proactive alternative. In contrast, MNA requires the development of a site-specific conceptual model, and the measurement and demonstration of remediation performance. Unlike the no-action alternative, both groundwater velocities and distribution coefficients would have to be measured and incorporated into a site conceptual model, and a monitoring plan must be implemented. Thus, MNA becomes a significant effort compared to the no-action alternative and possibly provides a means for scaling back and ultimately ceasing monitoring once the uncertainty in the process is sufficiently reduced.

Objectives of OSWER Directive

In the OSWER Directive, emphasis is placed on the use of MNA in conjunction with active remediation rather than natural attenuation as the sole remedy. As such, the EPA suggests that:

1. Source control actions should use active treatment to address principal threat wastes (or products) where practicable and use engineering controls, such as containment, for source waste (or products) that pose a relatively low, long-term threat, or where treatment is impracticable.
2. Contaminated groundwaters should be returned to their beneficial uses where practicable, within a time frame that is reasonable given the particular circumstances of the site. When restoration of groundwater is not practicable, EPA expects site owners "to prevent further migration of the plume, prevent exposure to the contaminated groundwater, and evaluate further risk reduction."
3. 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, sediments, air) that would result in an unacceptable risk or exceed required cleanup goals.

The OSWER Directive recommends that the implementing agency consider:

1. Whether the contaminants present in soil or groundwater can be effectively removed.

2. Whether the resulting transformation products present a greater risk than do the parent contaminants. In the case of chlorinated solvents, the creation of transformation products that are more toxic than the parent contaminant may be a concern. Vinyl chloride (VC), produced by the breakdown of tetrachloroethylene (PCE), trichloroethylene (TCE), and dichloroethylene (DCE), is an example. For petroleum hydrocarbons, the occurrence of heavier compounds remaining in the original (spill) area may be a potential long-term problem for taste and odor. For inorganic contaminants, the uncertainty associated with irreversibility of attenuation mechanism(s), such as sorption and precipitation, is critical.

3. Based on the nature and distribution of sources of contamination, whether these sources have been, or can be, adequately controlled;

4. Whether the plume is relatively stable or is still migrating and the potential for environmental conditions to change over time;

5. The impact of existing and proposed active remediation measures on the MNA component of the remedy;

6. Whether 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;

7. Whether the estimated time frame of remediation is reasonable compared to time frames required for other more active methods (including the anticipated effectiveness of various remedial approaches on different portions of the contaminated soil and/or groundwater);

8. Current and projected demand for the affected groundwater over the time period that the remedy will remain in effect (including the availability of other water supplies and the loss of availability of other groundwater resources due to contamination from other sources); and

9. Whether reliable site-specific vehicles for implementing institutional controls (i.e., zoning ordinances or deed restrictions) are available, and if an institution responsible for their monitoring and enforcement can be identified.

Data Needs

The OSWER Directive cites three distinct types of data necessary for providing clear evidence to implementing agencies that natural attenuation is effectively lowering contaminant concentrations on a site-specific basis. They are, in order of importance:

1. Historical groundwater and/or soil chemistry data that demonstrate a clear and meaningful trend 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);

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 concentrations. 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; and

3. Data from field or microcosm studies (conducted in or with actual contaminated site media) that 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).

The implementing agency has the responsibility to determine if one or more types of the aforementioned information are sufficient to characterize the efficacy of natural attenuation at specific sites. If not, the agency can therefore require more supporting evidence based on the nature and extent of the contamination, proximity of receptors, and other physical characteristics of the site.

If natural attenuation has been accepted by the regulatory agency as part of the remediation option, performance monitoring and contingency remedies will be required to evaluate the long-term effectiveness of the method and provide a backup remedy if natural attenuation fails, respectively. The OSWER Directive requires that monitoring programs accomplish the following:

1. Demonstrate that natural attenuation is occurring according to expectations;

2. Identify any potentially toxic transformation products resulting from biodegradation;

3. Determine if a plume is expanding (either downgradient, laterally, or vertically) and ensure that there will be no impact to downgradient receptors;

4. Detect new releases of contaminants to the environment that could impact the effectiveness of the natural attenuation remedy;

5. Demonstrate the efficacy of institutional controls that were put in place to protect potential receptors;

6. 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; and
7. Verify attainment of cleanup objectives.

Although the EPA MNA guidelines provide clear objectives for any implementation of MNA, much of the guidance is general. Substantial additional technical guidance will be needed for implementation at DOE sites.

3.0 Site Screening

This document provides a technical protocol for selecting an MNA remedy for inorganic contaminants that is consistent with the MNA guidelines developed by EPA and described above, and presents a methodology for doing MNA screening of sites contaminated with either organics or inorganics. The technical protocol for inorganic contaminants is meant to supplement protocols that already exist for organic contaminants. Technical protocols for natural attenuation condense the scientific understanding of chemical pathways for contaminant uptake, or breakdown, into decision-guiding procedures which site-managers can use to initially assess, and ultimately to predict, the extent of natural attenuation. Technical protocols also provide a platform for engaging regulators from the earliest stages of the cleanup process.

Technical protocols have been developed (or are being developed) by the Air Force and a number of industrial groups (often with some collaborative input from the EPA - (Remediation Technologies Development Forum, 1996; Wiedemeier et al., 1996; Wiedemeier et al., 1995b)) to achieve closure of fuel hydrocarbon and chlorinated solvent sites by MNA. These protocols guide site screening, site characterization, monitoring and consideration of future land use.

Site Screening

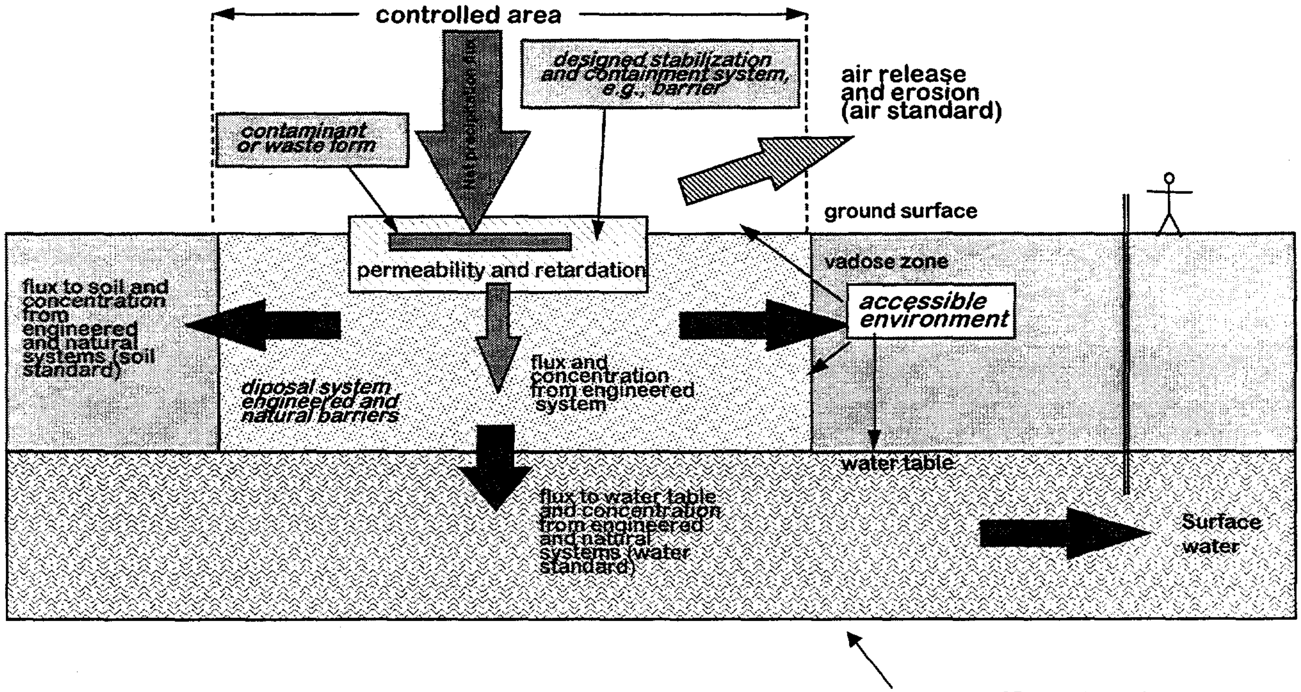
Site screening is a precursor to implementing an MNA remedial alternative. Screening of DOE sites for potential success of MNA involves a first order examination of the geochemical and hydrogeologic basis for successful implementation of MNA. Site screening typically uses existing site characterization and groundwater monitoring data, or regional historical case data, to achieve one of the following situations:

1. Select sites where further study is likely to lead to a full MNA implementation,
2. Identify sites where MNA is clearly inappropriate, or
3. For those sites which fall into neither category, identify the needed information that, once obtained, would allow for a determination of whether or not to pursue MNA.

The ultimate objective of the initial screening step is to achieve efficiencies in effort and expenditure when implementing MNA throughout the DOE complex. Standardization of the steps in the process is therefore important. Critical to the site screening effort is a clear understanding of contaminant-specific and site-specific natural attenuation processes.

Site Characterization

Figure 3.1 depicts the processes and characteristics that need to be characterized prior to, during, and after site remediation. Basically, site characterization gathers the information needed to make a determination of contaminant fluxes to groundwater, soil, and air (large dark arrows in the figure) relative to the accessible environment or points of compliance, as determined by interagency agreement or by the regional administrator.



Examples of Parameter and Model Needs:
- *performance standards including time period*
- *climate*
- *waste characteristics*
- *vadose zone flow model*
- *spatial and time distribution of flux, permeability and retardation in disposal system*

Figure 3.1 Conceptual model of site processes and characteristics required to describe contaminant transport.

The basic and traditional components of the characterization effort include:

1. Water balance of precipitation, evapotranspiration, runoff, and infiltration;
2. Unsaturated zone characteristics (e.g., geological materials, hydrologic conductivities, water content, and depth to groundwater);
3. Background water quality;
4. Waste inventories (if possible);
5. The potential for hazardous waste or hazardous waste constituents, which enter the uppermost aquifer, to migrate to a water supply well or to surface water; and
6. The concentration of contaminants in the soil at the site (these affect exposures on site) and their potential for release to air.

The characterization necessary to consider remediation by MNA requires a change in philosophy regarding the understanding of processes and characteristics at a specific site. Consideration of remediation by natural attenuation requires some specific characterization information not necessarily included in the traditional set of parameters and processes as listed above. For MNA by biodegradation, one needs to determine the rate(s) of transformation, what daughter products are being formed, and how complete the transformation processes are for the life of the plume. For MNA by sorption/solubility, one should identify whether certain adsorption or precipitation processes are active and whether other contaminants, or constituents, may be present that affect adsorption. Contaminants that are originally sorbed to mineral surfaces may become irreversibly bound through some combination of occlusion through continued mineral formation or collapse of clay structures. Contaminants may also diffuse into dead-end pores. Irreversibly bound contaminants, and contaminants in dead-end pores, may have a smaller potential for environmental transport because they may be non-bioavailable. This assumes that ingestion is a minor pathway. At the same time, slow desorption of rapidly degradable contaminants can severely limit their potential dose to the biosphere.

A technically defensible argument for MNA by phase transfer builds on the following four site-specific characterization activities (in addition to a clear definition of the hydrologic regime):

1. Identifying soil-specific contaminant uptake mechanisms,
2. Quantifying phase transfer mechanisms,
3. Constraining contaminant liberation from the soil matrix, and
4. Assessing long-term stability of phase transfer mechanism(s).

Monitoring

As with any other remedial approach, monitoring is a significant and essential component of any attempt to implement MNA. Progressive steps for a monitoring program are shown in Table 3.1. In all steps, the parties involved include the Regional Administrator (from the EPA or state implementing agency) and a Site Operator. In Step VI, the Site Operator will provide details of the monitoring program to EPA or the state implementing agency as part of any proposed MNA remedy.

The establishment, operation, and completion of a monitoring programs must address the basic questions: *Where, What, When, How* and *What-if?*

Where? addresses the location where monitoring of both a process and some standard is to be made. These locations are negotiated with the Regional Administrator based on the characterization of the site and the site-specific conceptual model (understanding) for contaminant fate and transport. One location is often called *the point of compliance* and is chosen as a location where natural attenuation can be verified by observation of a process or attainment of a standard. There is a presumption that any operative natural attenuation process will be verified more extensively closer to the source or at the source. The location is also chosen so that human and environmental safety is maintained by contingency action in case an action level is exceeded (the question *What-if?*). This attempt to allow for contingency actions may direct monitoring approaches and cause the point of compliance to move outwards in the future towards a location between the contaminant source and the groundwater or where the groundwater passes through a zone of administrative control. This direction in future monitoring trends may place more emphasis, for example, on vadose zone monitoring. However, in many humid regions where annual precipitation greatly exceeds potential evapotranspiration, the vadose zone is probably too small and seasonally ephemeral and thus, may be considered unmonitorable by any fixed position monitoring devices or techniques.

What? addresses the identification of the processes, the contaminant, or the possible surrogates for contaminants that are to be monitored in order to verify natural attenuation or to trigger a contingency plan. For example, soil pH, E_H, and carbonate levels may be monitored to provide indirect information about the efficacy of natural attenuation.

How? addresses the techniques used in monitoring, the time scales, and the frequency of the monitoring. This question also includes the demonstration that the monitoring approach is appropriate and verifiable.

What-if? addresses the process of reporting and invoking contingency actions that will take place if action levels or other process are observed.

Table 3.1 Progressive Monitoring Steps for Remediation By MNA

	Step		Description
Where?	I.	Establish Points of Compliance	Specify points of compliance and the points at which monitoring must be conducted.
What?	II.	Define What is to be Monitored	1. Demonstrate that natural attenuation is occurring according to expectations; 2. Identify any potentially toxic transformation products; 3. Determine if a plume is expanding (either downgradient, laterally, or vertically) and ensure no impact to downgradient receptors; 4. Detect new releases of contaminants to the environment that could impact the effectiveness of the natural attenuation remedy and trigger a contingency plan; 5. Demonstrate the efficacy of institutional controls that were put in place to protect potential receptors; 6. Detect changes in environmental conditions (hydrogeologic, geochemical, microbiological, or other changes such as pH, alkalinity) that may reduce the efficacy of any of the natural attenuation processes and trigger a contingency plan; and 7. Verify attainment of cleanup objectives.
When?	III.	Establish the Time Period for Monitoring	Monitoring should continue as long as contamination remains above required cleanup levels and for a specified period after cleanup levels have been achieved to ensure that concentrations are stable and remain below target levels.
How?	IV.	Define How Monitoring is to be Done	Demonstrate that the monitoring approach is appropriate and verifiable by including steps to: 1. Specify methods for statistical analysis of data, e.g., established tolerances, seasonal and spatial variability; 2. Establish performance standards; • *Information on the types of data useful for monitoring natural attenuation performance in the ORD publications (EPA/540/R-97/504, EPA/600/R-94/162)* • *EPA/600/R-94/123: a detailed document on collection and evaluation of performance monitoring data for pump-and-treat remediation systems* • *Standard test methods such as described in EPA SW-846, Test Methods for Evaluating Solid Waste - Physical/Chemical Methods or EPA publication, Methods of Chemical Analysis for Water and Wastes* 3. Establish a time interval agreed upon by Regional Administrator or agency; and 4. Include reporting maps, tabulation of data and statistical analysis, identification of trends, recommendations for changes in approach, evaluations of whether contaminants behave as predicted and whether other contingency remedies are required.
How?	V.	Define Action Levels or Process to Observe Monitoring	Interpret validity of the monitoring system by steps to: 1. Establish background concentrations; 2. Define criteria which show that a plume is expanding or diminishing; 3. Define criteria which shows that the conceptual model is applicable to a site; and 4. Establish how measurement of cleanup objectives and effectiveness will be determined.
What if's	VI.	Define Actions to be Accomplished When Action Levels or Processes are Observed	If monitoring system action criteria measurements are exceeded, establish a contingency plan by steps to: 1. Report to responsible party or agency statistically significant variance compared to background; 2. Identify extent and nature of non-predicted behavior (e.g., release); 3. Reevaluate conceptual model; and 4. Evaluate feasible corrective actions from previous and evolving contingency plan.

Future Use Considerations

The EPA guidelines require an explicit consideration of future use of a site, including an assessment of the time frame in which an aquifer might be needed for use. For organic contaminants that naturally attenuate primarily through biodegradation and dilution, the time frame of future use is important because it is the target against which the predicted efficacy of MNA must be assessed. The success of the natural attenuation of organic contaminants depends on extensive breakdown occurring before previously contaminated groundwaters reach a point of compliance. It also depends on there being no secondary accumulation of contaminants, or daughter products, down the flow path. Future use considerations thus revolve around making certain that natural attenuation proceeds as expected and that new receptors are not established between the initial point of compliance and the source. The first assumes that no large-scale changes in redox state, or nutrient availability, occur over the time required for attenuation. For example, reductive dechlorination of TCE might cease if reducing conditions abate due to depletion of electron donors (reductants) and a shift to aerobic conditions. Alternatively, microbiologic breakdown of fuel hydrocarbons might slow greatly in the face of a shift from aerobic to anaerobic conditions attendant with prolonged saturation of the soil. The second assumes that institutional controls are effective.

For inorganics in particular, an assessment must consider the effect of future use on previously immobilized contaminants. It is not hard to imagine scenarios leading to the remobilization of most, if not all, of the inorganic contaminants of concern. Inorganic contaminants are often present at trace concentrations, even in non-impacted soils, and the major element chemical composition of soils and groundwaters determines their transport characteristics. Large-scale changes in major element chemistry in the distant future can conceivably cause very drastic changes in the transport of trace inorganic contaminants. For example, plutonium bound up in iron hydroxides under initially oxidizing conditions at the Rocky Flats Plant in Colorado was remobilized when high rainfall raised the water table, causing more reducing conditions and the subsequent dissolution of the original host (Litaor and Ibrahim, 1996). A natural attenuation remedy that relies on limited infiltration may be invalidated by subsequent irrigation for agricultural development. In humid areas, natural plant succession from the managed grass cover of most present waste areas to a forest vegetation could significantly alter contaminant mobilization. The contaminants could be brought to the ground surface by the deeper rooted trees and subsequently released to surface waters. On the other hand, if remobilization of ^{90}Sr or ^{137}Cs (half-lives ~ 30 yrs) occurs over time spans much greater than a hundred years, a very significant fraction (approximately 90%) of the radioactivity will have decayed away. For inorganics and longer-lived radionuclides, dilution may be the only process mitigating any potential release that might occur with remobilization.

Clearly, a fundamental understanding of the likely range of groundwater compositions over time and their effect on contaminant transport in the future is needed to estimate the ultimate efficacy of MNA, particularly because longer time frames are typically required for MNA. Groundwater compositions are, to a large extent, determined by: (1) chemical equilibrium with soil CO_2; (2) weathering of soil minerals; (3) atmospheric inputs; (4) organic activity; and (5) adsorption and ion exchange reactions. Often, the composition ranges of soil and groundwaters are somewhat limited, primarily because there are a host of biological and geochemical processes that tend to control the pH, redox state, alkalinity, and mineralogic composition of soils. Although drastic changes in the compositions of natural waters are more the exception than the rule, it may be difficult for site owners to demonstrate that the factors favoring attenuation will be maintained far into the future. This is a critical obstacle to implementing natural attenuation for organics, and in particular, inorganics. If frequent monitoring is required for decades to guard against remobilization of inorganics, natural attenuation may be uneconomic in its application as a remedy, although it may be chosen for radionuclides possessing sufficiently short half-lives.

Technical Approaches

Technical approaches to implementing natural attenuation follow a strategy that includes the actions summarized below. Before MNA is considered, however, any site-specific, nontechnical objections to reliance on MNA must be considered. Are there cultural or natural resources that must be protected? Are there economic or land use changes that affect cleanup levels and times? Are stakeholders likely to accept MNA as a remediation option? Do pre-existing third party agreements prevent implementing MNA? If needed, can institutional controls be maintained at a site undergoing MNA? Regulators should be brought into the process at the earliest stages. Approaches to implementing MNA include:

1. Review available site and regional historical case data. This should provide a conceptual or semiquantitative hydrologic model, or at least interpreted hydrologic data, and roughly locate receptors and pathways. This effort should also indicate whether or not natural attenuation is a possibility, based on the distance and proportional time lag between the present contaminant distribution and potential receptors. Specifically, it should be determined whether existing data suggest a decrease in contaminant bioavailability over time. At this point an explicit consideration of potentially disqualifying characteristics (e.g., immediate proximity of a contaminant plume to a public drinking water supply) should be made.

2. Develop a preliminary set of conceptual model hypotheses and assess the potential for natural attenuation. If contaminant concentrations in soil or groundwaters have decreased or if the geochemical conditions appear to be favorable for natural attenuation, a conceptual model that incorporates natural attenuation hypotheses should be developed.

3. If needed, perform additional site characterization to support natural attenuation. Very rarely will the data required to test and calibrate a

conceptual model be available at the outset. Instead, additional data gathering will be required, particularly to support Step 5 below. Uncertainty in data and the conceptual model must be explicitly recognized. The object of additional site characterization is to decrease uncertainty in an effective fashion.

4. Update the conceptual model. Newly obtained site characteristics or information should be used to improve the site conceptual model.

5. Simulate long-term site behavior (with explicit treatment of uncertainty). Obviously, this will require some estimate of the rate at which natural attenuation is occurring and the capacity of the soil relative to the total mass of contaminants. Whereas biodegradation of organic contaminants can be fit to first order rate laws relatively simply, there is less of an established technical basis to predict rates of the nonbiodegradation natural attenuation processes (e.g., irreversible sorption, solid formation, etc.). This is covered in later sections of this chapter.

6. Perform an exposure pathways analysis. Identify all potential receptors and exposure pathways.

7. If natural attenuation is recommended, prepare long-term monitoring and contingency plan.

The various steps of this process are summarized in Figure 3.2

The flow diagram in Figure 3.2 can be broken down into two procedures: site screening and implementation. Steps 1 and 2 constitute the site screening. Steps 3 through 8 make up the implementation procedure. *MNAtoolbox,* an interactive software package that was developed by Sandia National Laboratories, is used to guide site managers through the site-screening phase. A companion program, *MNAimplement,* that covers the implementation phase is being developed.

MNAtoolbox

The object of this section is to describe how to use *MNAtoolbox* to screen sites for MNA and to establish the framework for developing conceptual models for MNA. Considerable attention is, by necessity, devoted to outlining the controls on attenuation of specific contaminants. Utilization of *MNAtoolbox,* by design, leads to the development of a conceptual model for natural attenuation. Such models are most effectively outlined separately for organic and inorganic contaminants. The broad technical basis for natural attenuation will be covered for each contaminant type, followed by secondary descriptions of natural attenuation, how *MNAtoolbox* screens for attenuation characteristics, and a summary of the state of implementation of MNA.

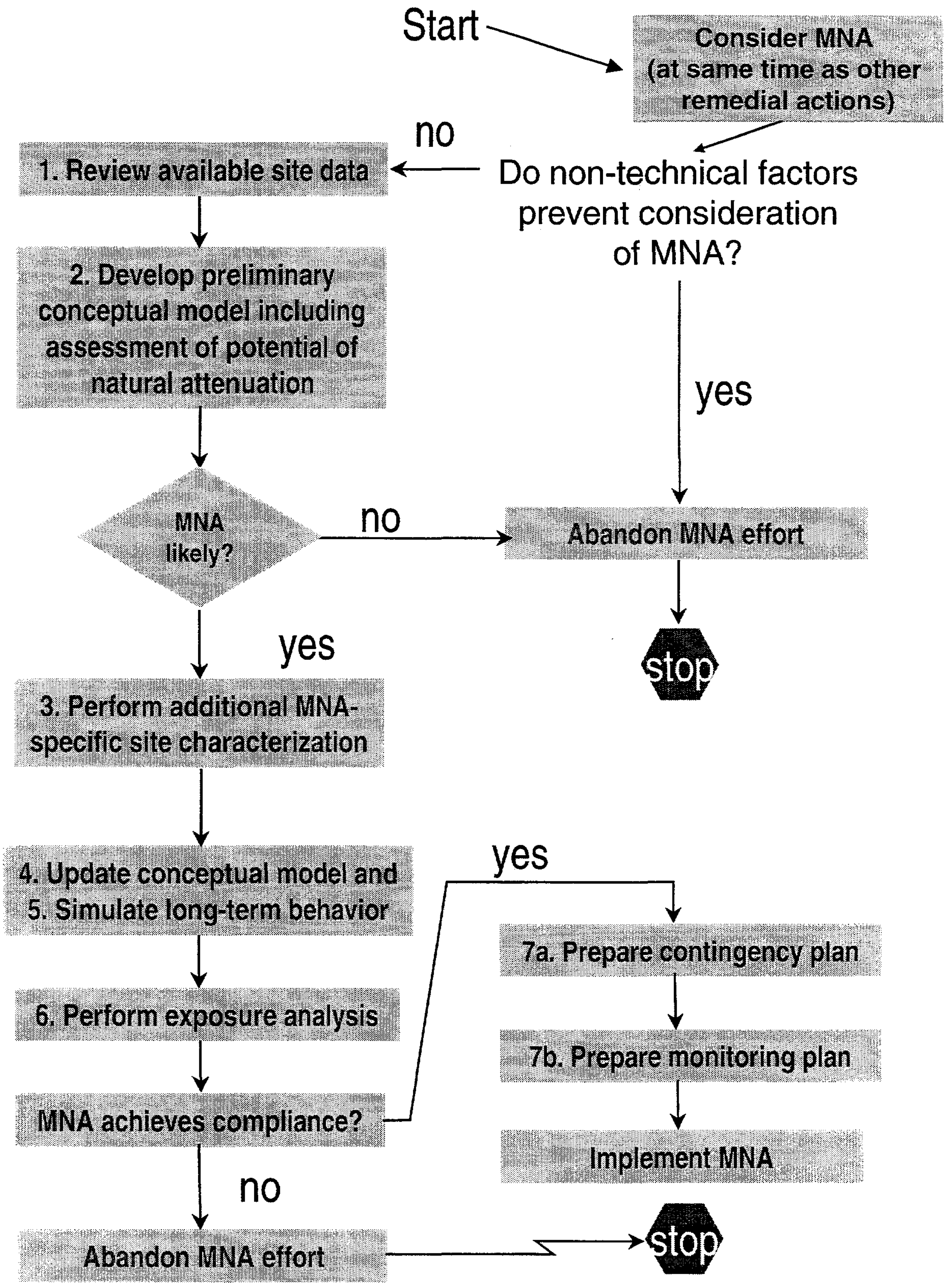


Figure 3.2 Outline of MNA approach.

Models for Natural Attenuation of Organic Contaminants

Fuel hydrocarbon and chlorinated organic solvent plumes were the first types of contaminant plumes to be targeted for MNA. Protocols have been developed for each of these types of contaminants, and the approach is relatively straightforward (Newell et al., 1996; Wiedemeier et al., 1996; Wiedemeier et al., 1995b). The *MNAtoolbox* contains links to these protocols and background information that provides the technical justification for natural attenuation of fuel hydrocarbons and chlorinated organics. The protocols that the toolbox relies on are:

- Fuel Hydrocarbons - The Air Force Center for Environmental Excellence (AFCEE) protocol (Wiedemeier et al., 1995b)
- Chlorinated Solvents - The AFCEE and RTDF protocols (Remediation Technologies Development Forum, 1996; Wiedemeier et al., 1995b).

Overviews of each are given in Appendix B, C, and D, respectively.

General features of organic breakdown by natural attenuation mechanisms will be covered here. Fuel hydrocarbons and chlorinated organics behave somewhat differently in the subsurface and are therefore best treated separately. Often the primary natural attenuation mechanism of concern for both types is biodegradation, although the specific pathways by which biodegradation occurs differ somewhat in detail.

Fuel hydrocarbons are broken down most rapidly by indigenous microorganisms under aerobic conditions (i.e., dissolved O_2 concentrations are greater than 2 mg/L) (Salanitro, 1993) when dissolved O_2 is the terminal electron acceptor (oxidant). Important components of fuel hydrocarbons include benzene, toluene, ethylbenzene, and xylenes (collectively, referred to as BTEX). Oxidation of fuel hydrocarbons, generally resulting in the formation of CO_2, in the absence of oxygen is typically slower and involves the use of NO_3^-+NO_2^-, Mn(IV), Fe(III), SO_4^{2-}, and ultimately, under reducing conditions, CO_2 as the terminal electron acceptor (e.g. Stumm and Morgan, 1996). The availability of microorganisms able to cause the breakdown under the various redox conditions does not appear to limit the process (Ludvigsen et al., 1995). In other words, indigenous microorganisms often appear to adapt on a sufficiently rapid timescale. Addition of oxygen to the subsurface may (or may not) cause biodegradation to occur more rapidly. In most cases (particularly when the source term, the separated-phase product, is removed), the availability of electron acceptors is not likely to limit breakdown. In other words, the oxidative capacity of soils and groundwaters (i.e., the sum of the potential terminal electron acceptors) typically exceeds the potential electron donor load required by fuel hydrocarbon plumes. Obviously, the total available capacity will ultimately depend on the volume of soil or aquifer encountered by a plume on the path from source to receptor. More involved analysis and calculations of electron budgets are outlined in Wiedemeier et al. (1995b), Barcelona and Holm, (1991) and Scott and Morgan (1990).

Oxidation of fuel hydrocarbons can be tracked in the subsurface in one of four ways: (1) monitoring the disappearance of reactant(s) - e.g., benzene and Fe(III), for the case of benzene oxidation by Fe(III); (2) monitoring the appearance of degradation products - e.g., CO_2 and Fe(II); (3) quantifying indirect effects of organic oxidation on soil CO_2 and/or alkalinity levels (see e.g. Siegel et al., 1992); or (4) establishing shifts in isotopic ratios of reactants or products (Aggarwal and Hinchee, 1991). Focusing on the first two, in general, fuel hydrocarbon breakdown involves the disappearance of electron acceptors and the appearance of electron donors. Often at least one of the two can be effectively measured in the subsurface. The appearance of Fe(II) at concentrations much higher than background, in combination with an observed decrease in hydrocarbon level, can be used as evidence of breakdown involving Fe(III) (typically in solid form) as the terminal electron acceptor. By the same token, higher than background concentrations of Mn(II) points to utilization of Mn(IV) hydroxides as the terminal electron acceptor. Decreases in sulfate and an inverse increase in H_2S, points to sulfate-reduction as the breakdown pathway. The various breakdown pathways, their theoretical efficiencies, and field case studies have been outlined in great detail elsewhere (see e.g. Baedecker et al., 1993; Baedecker et al., 1988; Bennett et al., 1993; Rice et al., 1995; Rifai et al., 1988; Rifai et al., 1995a; Rifai et al., 1995b; Wiedemeier et al., 1996; Wiedemeier et al., 1995a; Wiedemeier et al., 1995b; Wilson et al., 1994). It should be emphasized here that MNA of fuel hydrocarbons has become widely accepted at the state and federal level and, when combined with source removal, is probably the primary means for remediating fuel hydrocarbon contaminated soils. The *MNAtoolbox*, in the absence of measured degradation rates, uses a range of default values from the literature to screen sites for MNA effectiveness.

Figure 3.3 gives a simplified view of the breakdown pathways that affect chlorinated organics, such as PCE, TCE, DCE, TCA (trichlorethane), carbon tetrachloride (CT), PCA (tetrachloroethane), VC, and DCA (dichloroethane) in soils and groundwaters. Chlorinated organics are common contaminants in soils and groundwaters and are often the most mobile fraction that dissolves off the fringes of dense nonaqueous phase liquids (DNAPLs). Typically DNAPL components present at concentrations of 1% and above their respective water solubilities are used to infer the presence of DNAPLs. Highly chlorinated organics (e.g., CT, PCE, PCA) are already quite oxidized relative to BTEX compounds, hence their further oxidation by microorganisms provides relatively little energy to the latter. Instead, the breakdown of highly chlorinated contaminants in soils and groundwaters typically occurs through sequential reductive dechlorination, whereby hydrogens are exchanged for chloride groups to produce breakdown products that are less chlorinated and more reduced. For chlorinated alkenes, the breakdown sequence is:

$$\text{PCE} \Rightarrow \text{TCE} \Rightarrow \text{DCE} \Rightarrow \text{VC}.$$

Reductive dechlorination occurs most rapidly under reducing conditions (oxidation/reduction potential < -190 mV). At many sites, high concentrations of degrading commingled BTEX compounds can lead to a drawdown of O_2, followed by anaerobic conditions that are conducive to the reduction of chlorinated organics. Although oxidation of chlorinated organics, such as TCE, is relatively slow compared to reductive degradation, field degradation half-lives are not inconsequential and are probably 10 yrs or less.

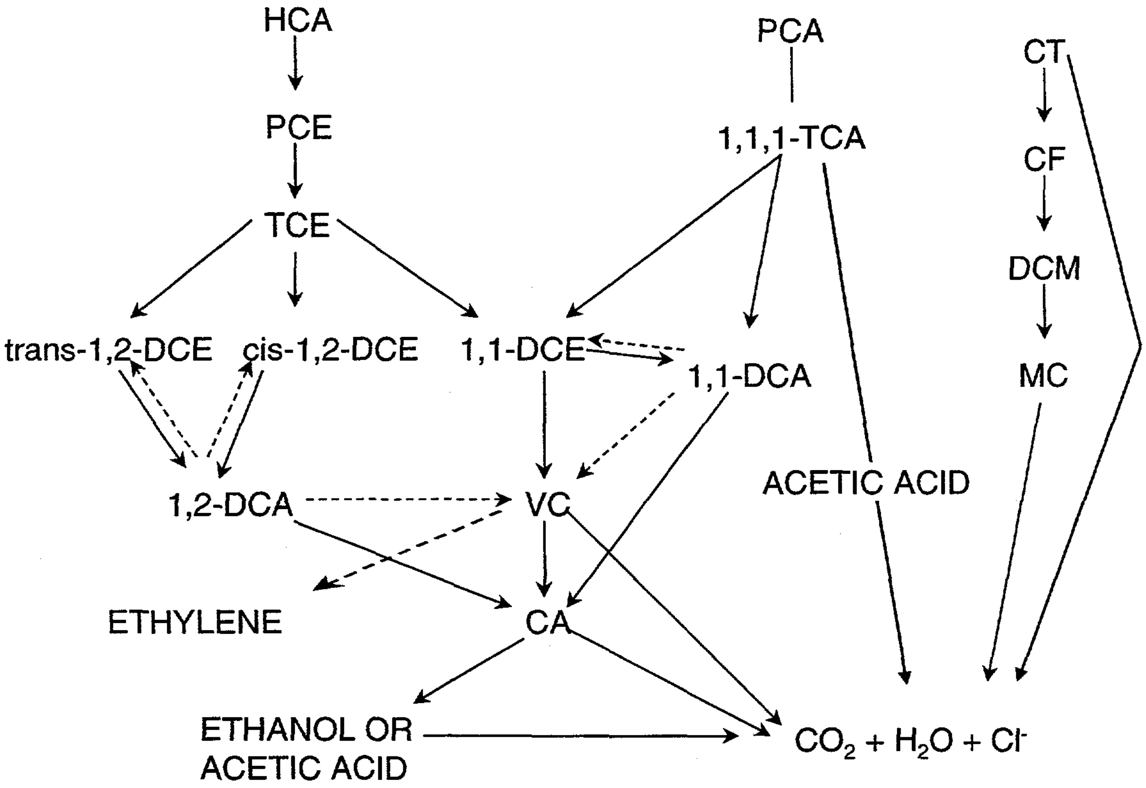


Figure 3.3 Degradation paths for chlorinated organics (after Barbee, G. C., 1994, 129-140, Fall 1994, GWMR).

Because the daughter compounds are less oxidized, they often accumulate under reducing conditions and may themselves pose a health threat. Complete breakdown to CO_2 therefore requires subsequent oxidizing conditions. Figure 3.4 shows good and bad scenarios for chlorinated organics emanating from a DNAPL. The worst-case involves reduction of highly chlorinated organics near the source and their subsequent accumulation. The best-case scenario involves reducing conditions near the source and oxidizing conditions farther out. Another worst-case would have oxidizing conditions prevailing at the source. The difference between best and worst-case scenarios is reflected in a marked uncertainty in the biodegradation rate constants to be used in assessing the transport and risk of chlorinated organic plumes (see below).

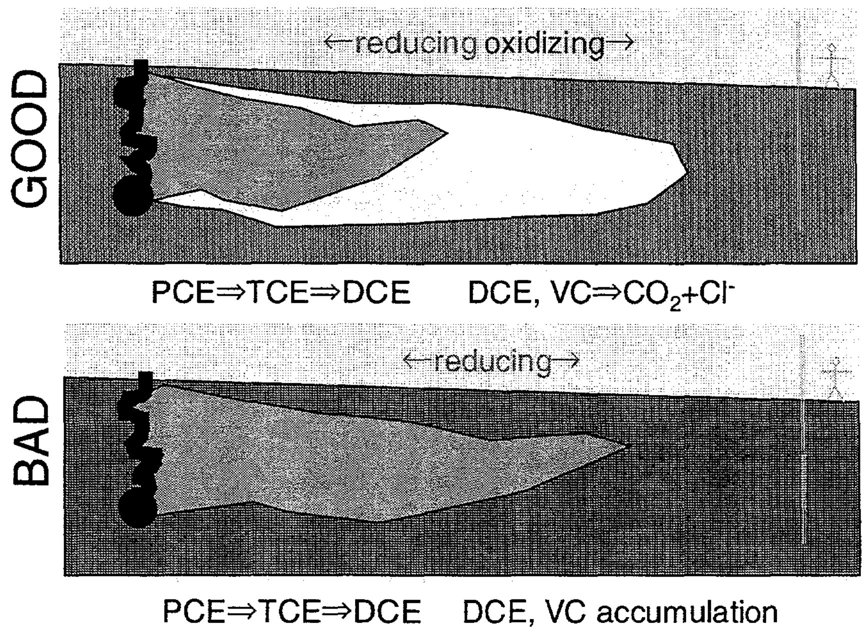


Figure 3.4 Good and bad scenarios for chlorinated organic breakdown.

Secondary measurements that might indicate biodegradation of chlorinated organics include (1) increases in chloride levels above the background, (2) a marked increase in *cis*-1,2-DCE levels, relative to the source region, and (3) a shift in the abundance of chlorine isotopes.

MNA of chlorinated organics has been estimated to be a potentially effective remedy at perhaps 30% of U. S. Air Force contaminated sites. Moreover, there are a large number of Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) records of decision (RODs) that rely on natural attenuation of chlorinated organics. The *MNAtoolbox* provides links to the specific CERCLA RODs mentioning natural attenuation at sites containing chlorinated organics and outlines the likely breakdown pathways of several of the chlorinated organics of concern. To screen sites contaminated with chlorinated organics for implementation of MNA, *MNAtoolbox* uses the AFCEE protocol (Appendix C) for assessing biodegradation. The AFCEE protocol uses input parameters describing site redox conditions and daughter product concentrations to determine the likelihood of chlorinated organic breakdown.

MNAtoolbox links the latter determinations to default values for the biodegradation rate constants. Where there is poor evidence for biodegradation, the worst-case breakdown half-life of 5 yrs is used in the site-screening process. Limited evidence links to a half-life of 3 yrs, while adequate evidence links to a half-life of 1 yr. Strong evidence of biodegradation links to a biodegradation half-life of 6 months. *MNAtoolbox* estimates the irreversibly sorbed fraction of chlorinated organics using published algorithms (Kan et al., 1998) and provides a default value. The user may replace the default values with measured degradation rates and irreversibly sorbed fractions, values which are much more preferred.

Models for Natural Attenuation of Inorganics

Although natural attenuation has been selected by EPA over the last several years as part of the final remedy at several Superfund sites containing both hazardous organic and inorganic contaminants, the technical basis for natural attenuation of the inorganics is less clear. The acceptance of natural attenuation of hazardous inorganics at mixed organic/inorganic waste sites indicates that: (1) the presence of hazardous inorganics does not prevent the selection of MNA for hazardous organics, and (2) MNA is an acceptable remedy for hazardous inorganics. However, at sites containing both hazardous organics and inorganics, MNA of just the organics may still require a costly, active remediation for the inorganics. In other words, MNA of inorganics may limit the remediation of the sites co-contaminated with more rapidly attenuated organics.

Inorganics can be removed from soil solutions and groundwaters by: (1) sorption to mineral surfaces and/or soil organic matter; (2) precipitation of sparingly soluble solids; (3) uptake by plants and organisms; and (4) occasionally through volatilization (e.g., methylation of mercury). The focus will be restricted to the formation of adsorbed species (surface complexes), sparingly soluble solids, and uptake by plants. Common to the process is the importance of metal/radionuclide speciation which depends primarily on the ambient biological and geochemical conditions of the soil or groundwater. pH, redox state (electron availability), alkalinity, and the presence of chelating (e.g., ethylenedinitrilotetraacetic acid (EDTA), natural organic acids) or solid-forming (e.g., phosphate in a number of cases) ligands are critically important (ionic strength is probably a secondary factor) to defining these conditions.

Table 3.2 outlines likely natural attenuation pathways and attenuation mitigators for inorganic contaminants of concern. More extensive summaries of the fate and transport of the respective inorganic contaminants of concern are listed in Appendix E. The specific data provided for each inorganic in *MNAtoolbox* include:

1. Likely solubility-controlling solid and dominant aqueous species (sometimes these stabilities are highlighted through the use of phase diagrams);
2. Soil background concentrations of contaminant inorganics;
3. MNA pathways;
4. MNA mitigators; and
5. Future use caveats.

The phase diagrams included in *MNAtoolbox* were generated using the Geochemist's Workbench (Bethke, 1984), a speciation computer code that relies on the thermodynamic database from EQ3/6 (Wolery, 1983). The phase diagrams are presented as either: (1) total concentration (mol/L) versus pH or (2) redox potential (E_H) for those inorganic contaminants that are greatly influenced by E_H versus pH (e.g., Cr, Tc). The default soil solution used consisted of 0.3 mmol Na^+, 0.1 mmol Cl^-, 0.1 mmol sulfate and carbon dioxide partial pressure ten times atmospheric. The likely solid and dominant aqueous species are indicated on the phase diagram as well as being listed separately. Many of the aqueous species and pathways are taken from standard reference sources (McBride, 1994; Rai and Zachara, 1984) to which the reader is directed for a deeper technical treatment.

Table 3.2 Natural Attenuation Pathways for Inorganics (after Brady et al., 1997)

Chemical	Natural Attenuation Pathways	Mitigating Conditions
Pb	Sorption to iron hydroxides, organic matter, carbonate minerals; formation of sparingly soluble carbonates, sulfides, sulfates, phosphates.	Low pH destabilizes carbonates and iron hydroxides. Commingled organic acids and chelates (e.g., EDTA) may decrease sorption. Low E_H dissolves iron hydroxides but favors sulfide formation.
Cr(VI) as CrO_4^{2-}	Reduction, sorption to Fe/Mn hydroxides; formation of $BaCrO_4$	Low pH destabilizes iron hydroxides. Low E_H dissolves iron hydroxides but favors reduction.
As(III or V)	Sorption to iron hydroxides and organic matter; formation of sulfides	Low pH destabilizes iron hydroxides. Low E_H dissolves iron hydroxides.
Zn	Sorption to iron hydroxides, carbonate minerals; formation of sulfides; ion exchange.	Low pH destabilizes carbonates and iron hydroxides. Commingled organic acids and chelates may decrease sorption. Low E_H dissolves iron hydroxides but favors formation of sulfides.
Cd	Sorption to Fe/Mn hydroxides and carbonate minerals; formation of sparingly soluble carbonates, phosphates, and sulfides.	Low pH destabilizes carbonates and iron hydroxides. Commingled organic acids and chelates may decrease sorption. Low E_H dissolves iron hydroxides, but favors formation of sulfides.
Ba	Formation of sparingly soluble sulfate minerals; ion exchange.	Low E_H may destabilize sulfates.
Ni	Sorption to Fe/Mn hydroxides; ion exchange; formation of sulfides.	Commingled organic acids and chelates may decrease sorption. Low E_H dissolves iron hydroxides but favors sulfide formation.
Hg	Formation of sparingly soluble sulfides; sorption to organic matter.	Is methylated by organisms
N(V) as NO_3^-	Reduction by biologic processes.	
U(VI)	Sorption to iron hydroxides; precipitation of sparingly soluble hydroxides and phosphates; reduction to sparingly soluble valence states.	Low pH destabilizes carbonates and iron hydroxides. Commingled organic acids and chelates may decrease sorption. High pH and/or carbonate concentrations decrease sorption. Low E_H dissolves iron hydroxides but favors reduction.
Pu(V and VI)	Sorption to iron hydroxides; formation of sparingly soluble hydroxides and carbonates.	May move as a colloid. Low E_H dissolves iron hydroxides.
Sr	Sorption to carbonate minerals and clays; formation of sparingly soluble carbonates and phosphates	Low pH destabilizes carbonates. High dissolved solids favor leaching of exchange sites.
Am(III)	Sorption to carbonate minerals; formation of carbonate minerals.	Low pH destabilizes carbonates. High pH increases solubility of Am-carbonate minerals.
Cs	Sorption to clay interlayers.	High NH_4^+ concentrations may lessen sorption. Low K^+ concentrations may increase plant uptake.
I	Sorption to sulfides and organic matter.	Sorbs to very little else in oxidized state.
Tc(VII) as TcO_4^-	Possible reductive sorption to reduced minerals (e.g., magnetite); forms sparingly soluble reduced oxides and sulfides.	Sorption to other phases extremely limited.
Th	Sorption to most minerals; formation of sparingly soluble hydroxide.	May move as a colloid.
^3H	None	
Co	Sorption to iron hydroxides, organic matter, and carbonate minerals.	Low pH destabilizes carbonates. Low E_H dissolves iron hydroxides. Stable complexes form with chelators.

Lastly, there is a critical difference between non-radioactive and radioactive contaminants. Even extremely hazardous levels of a given radioactive isotope in soils are typically greatly outnumbered by the number of non-radioactive isotopes. Consequently, the reactivity of some radioisotopes will be dominated by the concentration of the stable element. This is outlined in greater detail in Appendix E.

MNA Scorecard

A useful decision-making aid in the *MNAtoolbox* is the site screening scorecard which is associated with each contaminant. The scorecard range is designed to help the site manager rapidly determine if natural attenuation may be possible under their site-specific conditions. As such, it is intended to involve minimal additional site information. The scorecard is contaminant specific and is subdivided into hydrologic and geochemical sections. Credit is added, or subtracted, based on the presence of, respectively, favorable or unfavorable conditions. A high score approaching the maximum of 100 indicates that MNA is likely to be effective for the specified input parameters and site characteristics and should be considered as a remediation option for that contaminant. A low score does not necessarily discourage consideration of MNA at a particular site. This may simply indicate that a greater level of effort is required to collect site characterization data and conduct more detailed modeling to support MNA for a particular contaminant at a particular site.

In theory, using data from different parts of the plume to calculate a score would give an indication of the potential efficacy of natural attenuation at each individual sampling location. The degree to which this indication will guide subsequent decision-making will vary from site to site. For example, strong indications of attenuation at the front edge of a plume might, depending on the circumstances, outweigh poor indications of attenuation nearer the source where attenuation mechanisms with limited capacity have been overwhelmed.

Plume behavior at a given site will depend on the hydrogeochemical characteristics of the particular contaminant, and plumes containing multiple contaminants, or multiple plumes are likely to exist at sites. For multi-contaminant plumes (or plumes from different sources that overlap), utilization of the scorecard is best focused on the contaminant that is estimated to impact receptors most rapidly. If natural attenuation is likely to prevent any impact from the fastest migrating contaminant, it is reasonable to then assume that MNA should be explored for the less mobile contaminants. On the other hand, if MNA is clearly inappropriate for the most mobile contaminants, it is reasonable to expect active treatment of such contaminants, and the implementation of an active remedy is likely to change the subsurface character affecting the attenuation of all the contaminants. The scorecard should then be applied to the slower contaminants under the changed hydrogeochemical conditions resulting from active remediation of the fast contaminants.

The scorecard provides an estimate of the potential for natural attenuation by summing contaminant attenuation due to five factors: hydrologic dilution, sorption, irreversible uptake by the soil matrix, mineral formation (see below), and biodegradation (which includes radioactive decay). In essence, the natural attenuation factor (NAF) is the sum of a hydrologic dilution factor (HDF), a sorption factor (SF), an irreversible uptake factor (R_{irv}), and a biodegradation/chemical transformation factor (BF):

$$NAF = HDF + SF + R_{irv} + BF \tag{3.1}$$

The linkages between attenuation processes and the functions in Equation 3.1 are outlined schematically in Figure 3.5. While the functional form and mechanistic underpinning of each factor are outlined in greater detail below, the first, second, and fourth terms in Equation 3.1 roughly track the decrease in dissolved contaminant concentration along a flow path resulting from dilution, sorption (reversible + irreversible), and biodegradation/chemical transformation, respectively.

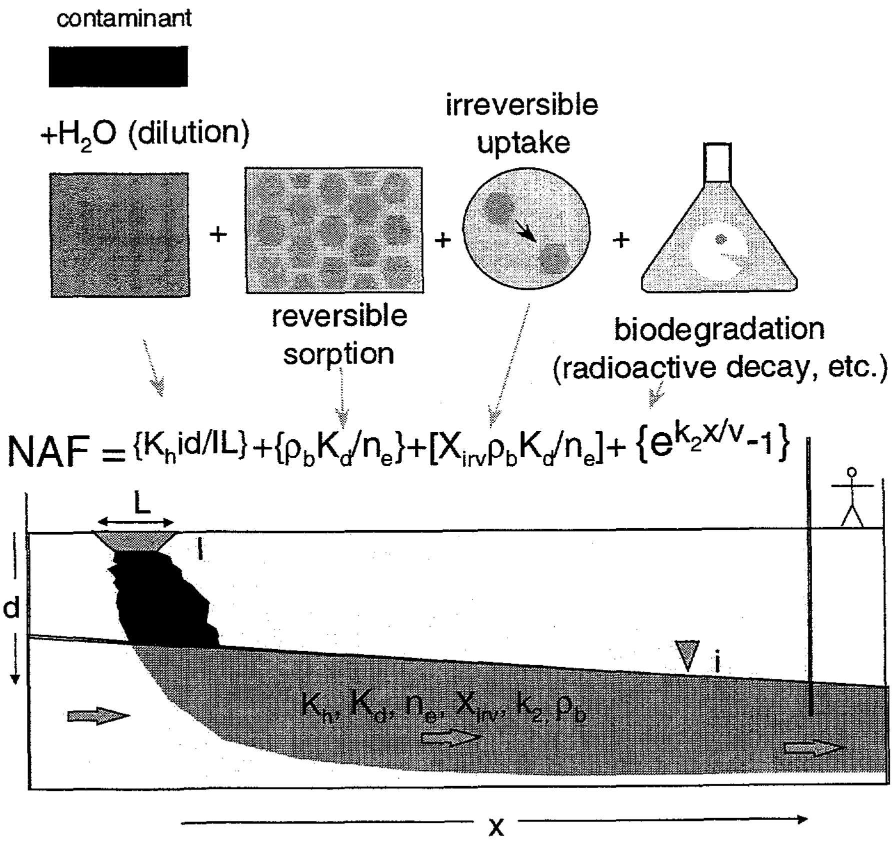


Figure 3.5 Schematic of natural processes and variables contributing to the calculation of the NAF.

Irreversible uptake of sorbed contaminants is counted a second time through the third term in Equation 3.1 (see below). SF is calculated from tabulated K_d values (sorption coefficients), the majority of which are measured by monitoring the uptake of contaminants from solution by a solid (termed adsorption K_d values). Often a significant amount of this uptake fraction cannot be subsequently released to contaminant-free recharge because it is no longer present at the soil-solution interface but is instead bound up in the solid. Therefore, desorption K_d values, partition coefficients measured by monitoring how much of a sorbed contaminant is liberated by a contaminant-free solution, are typically larger than adsorption K_d values. If sorption was truly reversible, adsorption and desorption K_d values would be identical. This irreversible removal of contaminant from the system must be accounted for.

Although Equation 3.1 is somewhat analogous to a step-wise dilution calculation, we do not imply a specific physical meaning or reactive-transport implication. Equation 3.1 has as its sole objective the interpretive summation of the various mass removal mechanisms. The degree of conservatism in the scorecard calculation depends on the degree of conservatism associated with the selection of input parameters. Where possible, conservative values have been used for the default inputs. However, the effect of conservatism depends on the process one is examining. For example, the use of minimum K_d values will lead to a conservative estimate of contaminant transport. However, the use of maximum K_d values provides a conservative estimate of the maximum amount of contaminant sorbed to a soil, which could be important to estimating rates and costs of remediating contaminated soils.

Hydrologic Dilution Factor (HDF)

The hydrologic dilution and sorption terms are both based, to the greatest extent possible, on the EPA soil screening methodology (U. S. Environmental Protection Agency, 1996). Specifically, dilution factors are calculated according to the simple water balance and dilution model outlined in the EPA soil screening guidance.

A few of the assumptions behind the EPA soil screening guidance must be reemphasized here. To begin with, the contaminant source term in the model is assumed to be infinite. Secondly, no attenuation is considered as the contaminant moves through the unsaturated zone to the water table. The aquifer is assumed to be unconfined and unconsolidated, as well as homogeneous and isotropic. Obviously, this is inappropriate for contaminant transport through fractured rock or karst aquifers. The simple dilution model does not consider non-dissolved transport processes (colloids, DNAPL's, etc.). As noted in the EPA guidance, all of these processes are likely to be site-specific. The fast pathways associated with karst aquifers probably disqualifies such sites from MNA implementation. This may not be the case for fractured aquifers. Although colloidal transport of contaminants has been observed (see e.g. McCarthy and Zachara, 1989), it is difficult to demonstrate that colloid-associated contaminants constitute widespread and significant human health risks. DNAPL's typically move at velocities much lower than the groundwaters that transport their soluble components. It is therefore probably reasonable to apply the screening approach to the dissolved phase as it often constitutes the primary potential risk to human health.

Calculation of the HDF requires the input of several site-specific hydrologic parameters including: K_h, the hydrologic conductivity (m/yr); i, the hydraulic gradient (m/m); d, the mixing zone depth (m); I, the recharge rate (m/yr); and L, the length of the source parallel to flow (m). The default option used by the EPA, and in *MNAtoolbox* as well, assumes a square-shaped 0.5 acre contaminant source.

$$HDF = K_h id/IL; \tag{3.2}$$

where

$$d = (2\alpha_v L)^{0.5} + d_a\{1-\exp\{(-LI)/(V_s n_e d_a)\}\} \tag{3.3}$$

α_v is the vertical dispersivity (m) and is calculated from the approximation of Gelhar and Axness (1981), $\alpha_v = 0.0056x$ (x is the distance (m) the contaminant travels in groundwater at velocity v (m/yr) to the nearest receptor); V_s is the horizontal seepage velocity (m/yr); n_e is the effective aquifer porosity; and d_a is the aquifer depth (m). The recharge rate, I, multiplied by the source area is the contaminant flux into the aquifer. Site managers can estimate the infiltration rate by simply using the local recorded natural value, i.e. the precipitation rate (if the site is uncapped) or by lowering this number to design specification for a site that has some hydrologic barrier on top of it. Default values in *MNAtoolbox* are: K_h = 10 m/yr; hydraulic gradient = 0.01 m/m; infiltration rate = 1 m/yr; length of source parallel to flow = 10 m; aquifer depth = 10 m; effective aquifer porosity n_e= 0.2. These can all be easily modified during the input to reflect actual site conditions.

Equation 3.2 may not adequately account for dilution if the latter varies as a function of infiltration rate. This is a particular problem at arid and semi-arid sites where recharge is intermittent and where subsequent flushing might be underestimated.

Sorption Factor (SF)

The sorption factor, SF, accounts for reversible sorption and is calculated as:

$$SF = \rho K_d/n_e \tag{3.4}$$

where ρ is the bulk density (kg/L) of the soil. Equation 3.4 is used to account for reversible sorption of a contaminant onto the rock/soil matrix. There are a number of more complex formalisms for representing sorption. The use of K_d values is the simplest, but chemically least realistic, approach. Langmuir adsorption isotherms are more realistic. Surface complexation models provide an even clearer picture of mineral surface interactions. A comprehensive review of the origins of each treatment can be found in Stumm and Morgan (1996).

Organics

For non-ionizable organic contaminants: K_d is estimated as,

$$K_d = om \times K_{om},$$

where om = soil organic matter content (kg/kg), and K_{om} (L/kg) is the soil adsorption coefficient normalized to organic matter. K_{oc} (L/kg) is the soil adsorption coefficient normalized to organic carbon content. It is related to K_{om} by the equation $K_{oc} = 1.724 \times K_{om}$ (U. S. Environmental Protection Agency, 1996). K_{oc} values can, in turn, be calculated for organic contaminants from tabulated octanol-water partition coefficients (K_{ow}) and the equation (U. S. Environmental Protection Agency, 1996):

$$\log K_{oc} = 0.0784 + (0.7919 \times \log K_{ow}) \tag{3.5}$$

Measured values of K_{ow} are tabulated in Table 3.3 for the primary organic contaminants of concern. Therefore to calculate the K_d for a non-ionizable organic contaminant, all that is required is the fraction of organic matter in the soil. The fraction of organic matter in soil is one of the input parameters used in the organic contaminant modules in *MNAtoolbox*. For ionizable organics (e.g., pentachlorophenol, benzoic acid), the equation above must be modified to account for the different reactivity of the ionized groups that vary as a function of pH (see e.g. U. S. Environmental Protection Agency, 1996).

Table 3.3 Octanol-Water Coefficients for Primary Organic Contaminants of Concern to DOE (from U. S. Environmental Protection Agency, 1996)

Contaminant	K_{ow}(L/kg)
Trichloroethylene	512
Trichloroethane	112-309
Dichloroethylene	72-135
Perchloroetheylene	468
Dichloroethane	30
Carbon tetrachloride	537
Perchloroethane	245
Chlorobenzene	725
BTEX	134-1479

Inorganics

Inorganic K_d values are typically pH-dependent because sorbing contaminants and mineral surfaces are ionizable; hence the net surface charge depends on pH. K_d values are not fundamental chemical parameters or constants, but merely convenient descriptive parameters which may result from several chemical processes and mineral-specific soil reactions. Surface complexation models (Davis and Kent, 1990; Dzombak and Morel, 1990; Stumm, 1992) provide a more defensible model of surface interactions but require far more input parameters than are typically available to the user of *MNAtoolbox*. Because K_d values are not completely transferable among sites, they are best used as a rule-of-thumb measure of the affinity of contaminants for specific soils under specific geochemical conditions. Because of the pH effect on soil-solution partitioning of contaminants, a significant amount of uncertainty in K_d values can be avoided by measuring and applying them only over similar, limited pH ranges.

Where possible, *MNAtoolbox* uses the values of the EPA soil screening guidelines for default K_d values. These K_d values were calculated originally using the MINTEQA2 geochemical code (Felmy et al., 1984) for a reference soil assumed to contain 0.31 wt% iron oxide minerals, the assumed primary sorbing agent for inorganic contaminants (along with organic matter). The calculated K_d values were found to compare roughly with earlier K_d compilations. The assumptions and limitations to this approach are as follows: equilibrium sorption is assumed; redox potential changes are ignored; sorption on clays, carbonates, sulfates, and sulfides (among others) are neglected; and metal competition or interaction at sorption sites are not considered. pH-dependent default K_d values from the Superfund soil screening guidelines are shown in Figure 3.6. Sorption coefficients for the various inorganic contaminants not considered in the EPA soil screening guidance have been taken from the literature. Specifically, we use values from Moody (1982) where $K_d = 500$ for Th and Pu; $K_d = 50$ for Am; and $K_d = 5$ ml/g for U(VI). These K_d values (with the exception of Am) are less than or equal to draft default values being developed for EPA and are therefore thought to be conservative. In lieu of Ra K_d values we have used EPA Ba K_d values as defaults. By the same token, we have used Ni K_d values for the default Co K_d values. In each case sorption by the analogue is typically seen to be greater than that of the actual metal of interest. Consequently, the substitution is conservative for transport calculations. These values will be updated with non-substituted values in the near future.

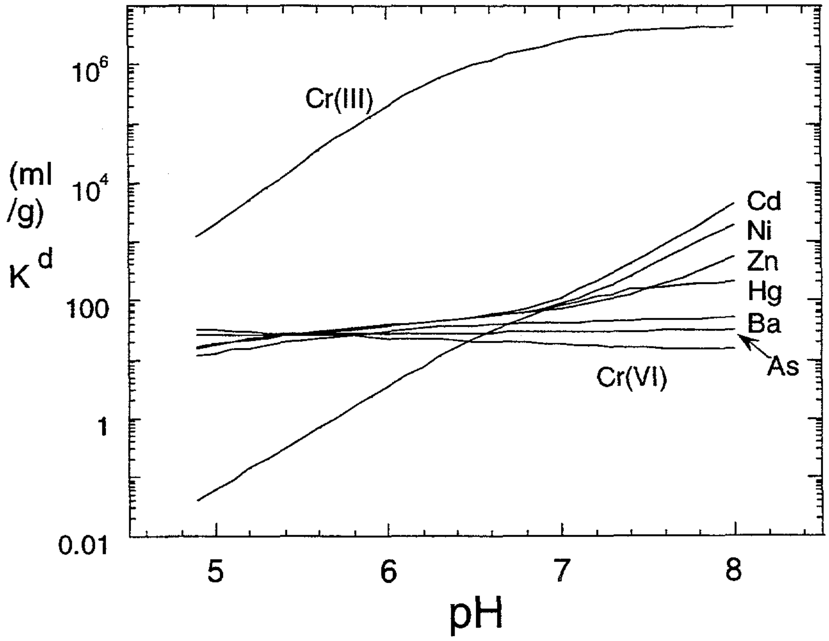


Figure 3.6 Distribution coefficient (K_ds) used in the calculation of the NAF for metal contaminants (from U. S. Environmental Protection Agency, 1996).

In part, because of the accumulated uncertainties, K_d values measured under site-specific conditions (see e.g., ASTM method #D4646-87) are preferable as input into the site scoring section of *MNAtoolbox*. The latter values can easily be substituted for the default K_d values in the calculation.

Irreversible Uptake (R_{irv})

Despite widespread evidence for various degrees of irreversible uptake of contaminants by soils and soil minerals (see e.g., Ainsworth et al., 1994; Alexander, 1995; Alexander, 1996; Bunzl et al., 1995; Comans and Middleburg, 1987; Comans et al., 1991; Comans and Hockley, 1992; Coughlin and Stone, 1995; Coughtrey et al., 1986; Coughtrey and Thorne, 1983; Davis and Upadhyaya, 1996; Davis et al., 1987; Kan et al., 1998; Kan et al., 1997; Kan et al., 1993; Kan et al., 1994; Kan et al., 1996; Schultz et al., 1987; Schulz and Riedel, 1961; Zachara et al., 1991), existing transport codes (and for that matter, the EPA soil screening guidelines) do not typically account for irreversible uptake of contaminants by the rock/soil matrix. The degree of reversibility can depend on the amount of time that the contaminant has been in contact with the mineral. Typically, ion exchange reactions are completely reversible over time spans less than minutes (Cs exchange onto some clays is often an exception – see below). Sorption onto amorphous iron hydroxides, organic matter, and metal carbonate minerals is often observed to be irreversible over time spans exceeding years.

In most transport codes, contaminants are assumed to sorb and desorb reversibly, that is, rapidly and up to the level predicted by a K_d. Irreversible sorption of inorganics is somewhat analogous to the biodegradation of organics in that, as far as groundwaters are concerned, the contaminant is permanently removed, unless the host mineral, or sorbing surface, redissolves at some point. Nevertheless, there is no universally agreed upon method for quantifying or predicting irreversible uptake (for recent reviews - see Kennedy et al. (1997) for inorganics, and Alexander (1996) or Kan et al. (1998) for organics). Measurement of the exchangeable fraction of soil contaminants and/or sequential soil extractions (described subsequently) provide first-order estimates of the fraction of contaminant(s) available to biota and the residual fraction that is naturally attenuated or unavailable.

As a first approximation, irreversible uptake is estimated in *MNAtoolbox* as:

$$R_{irv} = \rho X_{irv} K_d / n_e.$$

For each contaminant metal and/or radionuclide, X_{irv} is the average fraction of sorbed contaminant that cannot be exchanged from a contaminated laboratory or field sample. The other variables have been defined above. It should be emphasized that the processes controlling irreversible uptake are complex and not completely describable or predictable from chemical data; therefore, they lend themselves to rough approximation only. Because irreversible sorption often removes a major fraction of some organics, as well as inorganic contaminants from groundwaters, it is particularly critical that this process be included in any site screening procedure.

Inorganics

For inorganics, EPA's MNA directive states that "... Determining the existence and demonstrating the irreversibility of these mechanisms are key components of a sufficiently protective MNA remedy." Irreversibility is often examined using leach tests. The toxicity characteristic leach procedure (TCLP - see ASTM method D5233-92), uses a pH 5 acetate buffer solution (meant originally to mimic the composition of a typical landfill leachate) that tends to consume some mineral hosts (e.g., calcite) and consequently, exaggerates the bioavailability of some contaminant inorganics. The test also provides no information about the specific identity of the host mineral(s) that might sequester particular contaminants. The absence of information about the host limits consideration of the potential future use of sites. Some minerals are less affected than others by likely changes in groundwater chemistry. Consider the example of Pb contamination of limestone-containing soils versus SO_4-rich soils. Pb might be considered to be naturally attenuated if largely bound up irreversibly in either matrix. Pb, if bound up in a carbonate mineral, might be liberated by soil acidification, although the Pb in the SO_4 matrix probably would not dissolve. On the other hand, a change in land use to agriculture may involve soil liming, raising soil pH, and thus, result in an attenuation of any SO_4-bound Pb. Thus, knowing the chemical form of a contaminant is critical to addressing the effect of future land use changes on MNA.

Metal and radionuclide uptake by soils was extensively and critically reviewed in the '80s by Coughtrey et. al. (1986; 1983). In *MNAtoolbox* the default fraction of inorganics taken up irreversibly by soils is, in most cases, taken from the Coughtrey et al. (1986) review. To fill in data gaps for data not available in Coughtrey et al. (1986; 1983), other literature sources describing irreversible uptake, typically and where possible in field situations, were used for *MNAtoolbox* values. In a number of occasions, the latter results disagreed with Coughtrey et al. (1986). Specifically, the exchangeable fraction estimated in soils by Coughtrey et al. (1986) for Pb, Cu, Zn, and Ni seemed significantly lower than the majority of the field data would indicate. For these cases, *MNAtoolbox* incorporates the more recent literature values, although the difference is noted below for each case.

Table 3.4 gives default X_{irv}s for inorganic contaminants. The values given in Table 3.4 have been derived by a wide variety of methods that may not be strictly comparable (the numbers are probably no more accurate than ±30%). Consequently, a site-specific measurement of a contaminant X_{irv} is eminently preferable for use in *MNAtoolbox* (these can be input manually). Again, it should be reemphasized that Table 3.4 is useful only in the complete absence of a site-specific measurement. An excellent explanation of how best to do such tests is outlined by Amonette et al. (1994).

Table 3.4 Fraction of Contaminant Metal Taken Up Irreversibly (default values)

Contaminant	X_{irv}	Notes
Am	0.6	(Coughtrey et al., 1986)
As	0.9	(Kavanagh et al., 1997)
Ba	0.5	Assumed to be similar to Ra.
Cd	0.5	(Coughtrey et al., 1986)
Cs	0.9	See Appendix F.
Cr	0.5	(Coughtrey et al., 1986)
Co	0.9	Unavailable to soils; a large fraction appears available to plants (Coughtrey et al., 1986).
Cu	0.9	Coughtrey et al. (1986) suggest 25% availability. The references in Appendix F suggests a higher value.
I	0.9	(Coughtrey et al., 1986)
Pb	0.9	Coughtrey et al. (1986) give 50% availability. The references in Appendix F suggest a higher value.
Hg	0	Assumed.
Ni	0.9	(Coughtrey et al., 1986)
Ra	0.5	If $BaSO_4$ is present, ~99% of Ra is likely to be unavailable; otherwise, availability ranges from 6 to 84% (Landa, 1991).
Sr	0.15	From (Coughtrey et al., 1986). Values as high as 0.4 unavailable have been observed.
Tc	0.1	(Coughtrey et al., 1986)
Th	0.99	Assumed to be equal to Pu
^3H	0	Assumed.
U	0.1	See Appendix F.
Pu	0.99	(Coughtrey et al., 1986)
Zn	0.9	Coughtrey et al. (1986) estimated a lower value than the values in Appendix F suggest.

Organics

Resistance to release of organic contaminants by soils and sediments has been extensively documented (see e.g., Adey et al., 1996; Alexander, 1995; Alexander, 1996; Biswas et al., 1991; Cho et al., 1993; Doust and Huang, 1992; Hirata et al., 1992; Kan et al., 1998; Kan et al., 1996; Parker and Genuchten, 1984; Pavlostathis and Jaglal, 1991; Pavlostathis and Mathavan, 1992). Nevertheless, desorption of organic compounds is commonly treated as being reversible in fate, risk, and remediation calculations (e.g. Parker and Genuchten, 1984). This tends to ignore observations that: (1) a significant fraction of contaminants associated with soils persists in the face of tens of years of fresh recharge; and (2) there is a poor correlation between field-observed partition coefficients and predicted equilibrium partition constants, K_p, derived from conventional K_{oc}/K_{ow} relationships (Kan et al., 1998; Kan et al., 1996). A significant fraction (e.g., 48-90% of TCE (Pavlostathis and Mathavan, 1992)) of sorbed contaminants often remains in soils and sediments, even after extensive treatment, and is unavailable for uptake by microorganisms (Adey et al., 1996; Alexander, 1995; Biswas et al., 1991; Cho et al., 1993; Doust and Huang, 1992; Hirata et al., 1992).

No universally accepted theory explains the resistance of adsorbed organic compounds to desorption. At the very least, there must be a physical-chemical rearrangement in the solid phase after adsorption occurs, indicating that desorption takes place from a different molecular environment than characterized adsorption. Over short time scales, resistance of sorbed organic contaminants to desorption appears to depend on the contact time between contaminant and soil matrices, suggesting that compounds diffuse to "remote" sites where they are sequestered (Alexander, 1995; Pavlostathis and Jaglal, 1991). Adsorption hysteresis may also arise when sorption occurs on organic polymers possessing higher energies of interaction more specific to the particular contaminant (Weber and Huang, 1996). Organic matter content in soils and sediments, therefore, is probably an important indicator of the extent of irreversible sorption of organic contaminants.

Kan and co-workers used laboratory and field data to propose a semiempirical equation that described irreversible adsorption of organic compounds (Kan et al., 1998). *MNAtoolbox* uses this expression to calculate default sorption characteristics. Again, an actual measurement from the site is of much greater value. Each sediment-contaminant pair has a fixed maximum irreversible adsorption level, q^{irv}_{max}, that can be correlated with the K_{ow} of the compound and the organic carbon (OC) content of the sediment. An OC-normalized partition constant (K^{irv}_{oc}) for the irreversible component appears to be essentially constant, $10^{5.53\pm0.48}$ ml/g, for the studied compounds (0.005 < solubility < 517 mg/L) and sediments (0.27 < OC < 4.1%). The total adsorption (q) is the sum of reversible (q^{rev}) and irreversible adsorption (q^{irv}):

$$q\ (\mu g/g \text{ of sediment}) = q^{rev} + q^{irv} \tag{3.6}$$

Reversible sorption can be represented by a linear isotherm, $q^{rev} = K_{oc} \times OC \times C$. A Langmuir isotherm is used to describe irreversible sorption. Overall sorption is thus:

$$q = K_{oc} \times \mathrm{OC} \times C + \frac{K_{oc}^{irv} \times \mathrm{OC} \times q_{max}^{irv} \times f \times \mathrm{C}}{(q_{max}^{irv} \times f) + (K_{oc}^{irv} \times \mathrm{OC} \times C)} \tag{3.7}$$

where f ($0 \leq f \leq 1$) is the fraction of the irreversible compartment that is filled at the time of initial saturation. q^{irv}_{max} is related to OC and K_{ow}:

$$q^{irv}_{max} = 37765 \times OC \times (K_{ow})^{-0.23} \tag{3.8}$$

The value of f in Equation 3.7 can be assumed equal to 1 when the exposure concentration is greater than about 0.5 of the aqueous solubility of the organic contaminant, which is the case for most point source contamination. To predict sorption uptake in the absence of a measurement, the measured OC and the solution phase contaminant concentration (C) are needed. The value of K^{irv}_{oc} is constant, and q^{irv}_{max} is calculated from the K_{ow} and OC, respectively. In addition, the irreversible fraction of contaminant sorption can be estimated by Equation 3.7 if the total adsorption, q, is known. Values of irreversible uptake $\{ X_{irv} = q^{irv} / (q^{rev} + q^{irv}) \}$ in *MNAtoolbox* can be estimated from site characterization data, specifically, q, C and OC, and/or from the literature values of K_{ow} and K_{oc}. Table 3.5 lists sorption and solubility parameters for a number of important contaminant compounds.

Table 3.5 Sorption and Solubility Parameters of Selected Organic Contaminants (Schwarzenbach et al., 1993; U. S. Environmental Protection Agency, 1996).

Contaminant	log K_{ow} (ml/g)	Mol. Wt. (g/mol)	q^{irv}_{max} (µg/g)	Solubility (µg/ml)
Trichloroethene	2.71	131.4	44.95	1198.3
1,1,1-Trichloroethane	2.48	133.4	50.78	1135.4
1,1,2-Trichloroethane	2.05	133.4	63.76	3805
1,2-Dichloroethene	2.07	97	63.09	7704
1,1-Dichloroethane	1.79	99	73.17	4961.7
1,2-Dichloroethane	1.47	99	86.69	8426.2
Perchloroethene	2.67	165.8	45.92	151.2
Carbon Tetrachloride	2.73	153.8	44.48	970.4
Chlorobenzene	2.86	112.6	41.52	502.9
1,1,2,2-TCA	2.39	167.9	53.25	3055.2
Ethylbenzene	3.15	106.2	35.61	168.3
Xylene	3.13	106.2	35.99	570
Toluene	2.75	92.1	44.01	517.9
Benzene	2.13	78.1	61.12	1789.1

Figure 3.7 shows the maximum amount of irreversible adsorption (normalized to OC) of a number of compounds calculated from Equation 3.8 assuming an organic carbon content of 0.5% and f = 1. Figure 3.8 shows the ratio of irreversible to total sorption as a function of solution organic concentrations. When solution concentrations are low relative to the solubility of the compounds, sorption is dominantly irreversible. The plateau of the sorption isotherm indicates saturation or nears saturation of irreversible sorption sites. At relatively high solution concentrations, sorption is largely reversible because the irreversible sites have been completely filled.

The portion of irreversibly sorbed organic contaminant on soils or sediments can be determined by subtracting the amount of reversibly sorbed compound from the total sorbed (see Figure 3.8). The amount of reversible sorption is usually quantified by mixing the soil or sediment with water and stirred for 24 hours and then measuring the contaminant concentration in the aqueous phase. Total sorption of the contaminant is determined by extracting the contaminant from the soil with an organic solvent such as methane, hexane, acetone etc. (or a mixture of them). Frequently, destructive and/or vibration techniques (e.g., ultrasonic) are employed during extraction (see e.g. Kan et al., 1993)

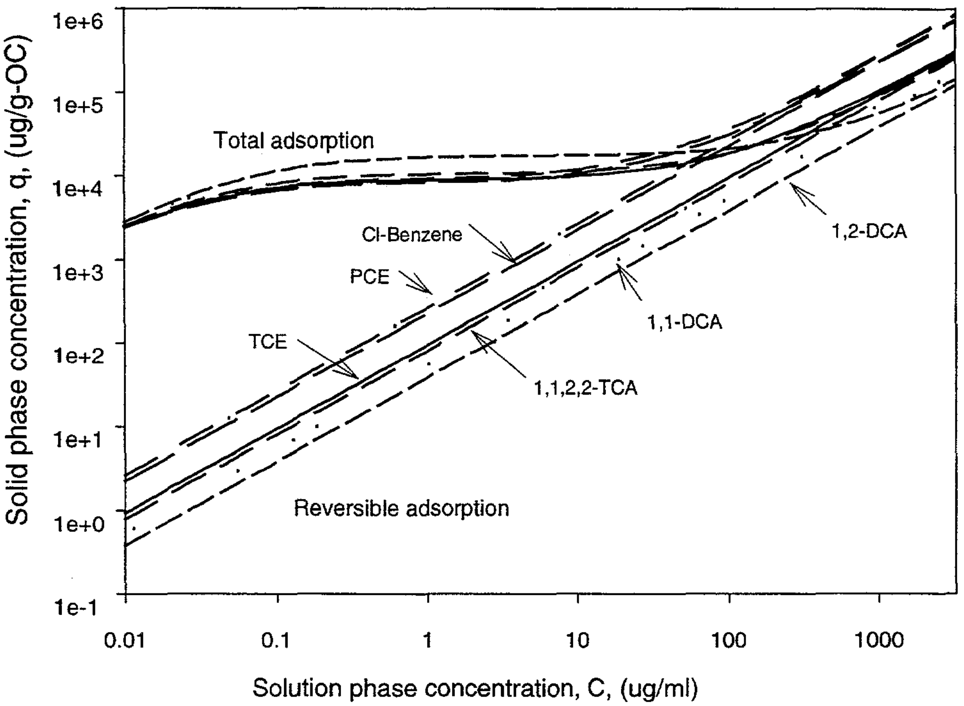


Figure 3.7 Irreversible and reversible sorption of organic contaminants normalized to organic carbon levels (OC = 0.5% and f =1).

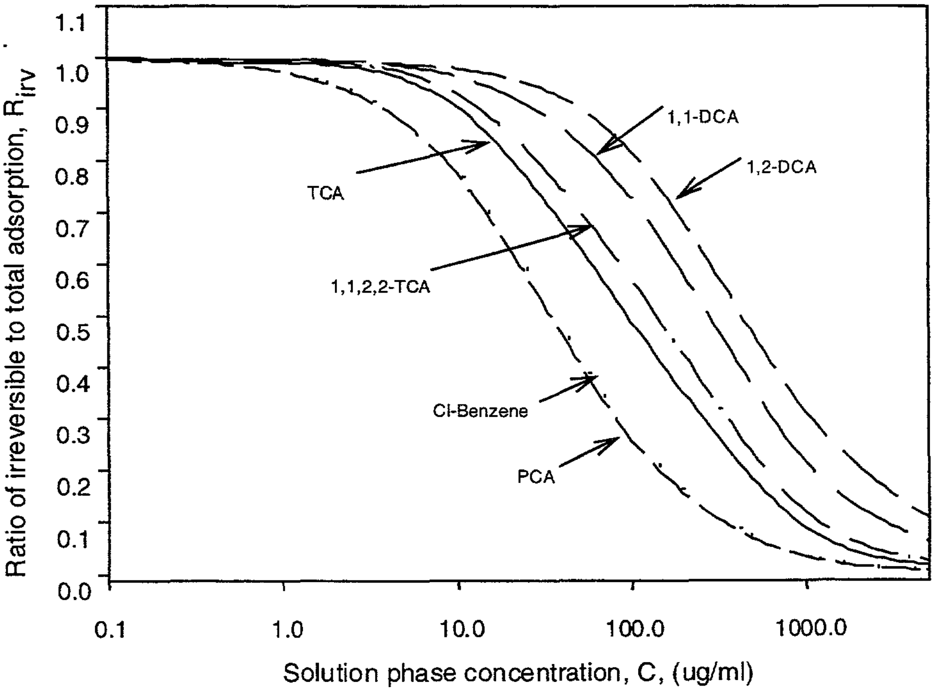


Figure 3.8 Ratio of irreversible to total sorption of organic contaminants normalized to organic carbon levels as a function of solution contaminant levels (OC = 0.5% and f =1).

Biodegradation/Chemical Transformation (BF)

Typically, biodegradation obeys a first order rate law; that is, breakdown rates are proportional to the amount of available contaminant. Degradation rate constants are site-specific and can vary by orders of magnitude depending upon redox state (nature and abundance of electron donors), nutrient supply, etc. For the breakdown of most organic contaminants, the default rate constants in *MNAtoolbox* are set, where available, to the default values used in *Bioscreen* (Newell et al., 1996), a natural attenuation screening tool for fuel hydrocarbons developed by the EPA. Default degradation rate constants for chlorinated organic contaminants, and others, have been taken from the literature. The corresponding degradation half-lives and references are listed in Table 3.6. Alternatively, the AFCEE protocol (Appendix B and C) can be used in *MNAtoolbox* to provide bounding estimates of biodegradation rates. The desirability of site-specific degradation rate constants cannot be overemphasized. The uncertainty associated with using generic default values is likely to be very large. There is an implicit assumption in the screening calculation that biodegradation will occur to all contaminants at all sites. If MNA is to actively be relied upon, this assumption of microbiologic breakdown must be verified, preferably through a field-based method.

Table 3.6 Biodegradation and Radionuclide Decay Half-Lives

Contaminant	Half-life (yrs)	Notes	Contaminant	Half-life (yrs)
Benzene	0.02-2.0	(ASTM, 1995)	$^{241}\mathrm{Am}$	433
Toluene	0.02-0.17	(ASTM, 1995)	$^{137}\mathrm{Cs}$	30.2
Ethylbenzene	0.016-0.62	(ASTM, 1995)	$^{60}\mathrm{Co}$	5.27
Xylene	0.038-1	(ASTM, 1995)	$^{129}\mathrm{I}$	1.57e7
TCE	0.27-4.5	(Howard et al., 1987)	$^{226}\mathrm{Ra}$	1,600
PCE	0.5-4.5	(Howard et al., 1987)	$^{228}\mathrm{Ra}$	5.76
TCA	0.37-2	(Howard et al., 1987)	$^{90}\mathrm{Sr}$	29.1
DCE	0.08-8	(Howard et al., 1987)	$^{99}\mathrm{Tc}$	2.13e5
DCA	0.09-1	(Howard et al., 1987)	$^{229}\mathrm{Th}$	7,300
Carbon tetrachloride	0.02-1	(Howard et al., 1987)	$^{230}\mathrm{Th}$	75,400
Vinyl chloride	1.22	(Buchanan, 1996)	$^{232}\mathrm{Th}$	1.4e10
			$^{3}\mathrm{H}$	12.3
			$^{234}\mathrm{U}$	2.46e5
			$^{235}\mathrm{U}$	7.04e8
			$^{238}\mathrm{Pu}$	87.7
			$^{239}\mathrm{Pu}$	24,100
			$^{240}\mathrm{Pu}$	6,560
			$^{241}\mathrm{Pu}$	14.4
			$^{238}\mathrm{U}$	4.51e9
			Cr(VI) reduction	2.5

Notes: Buchanan (1996) examined breakdown of chlorinated solvents at 43 sites and calculated half-lives (yrs) of: 1.2 for PCE→TCE; 1.19 for TCE→DCE;1.05 for DCE→VC; and1.22 for VC→Eth. Actual degradation rates for chlorinated organics depend critically on the redox state at the source and edge of the plume (Chapelle, 1996). The chromate reduction half-life is a field value determined by Henderson (1994).

Integration of a first-order degradation rate law for contaminant concentration as a function of time C(t) gives the expression for the biodegradation/chemical transformation factor (BF):

$$BF = C_o/C(t) - 1 = e^{kt} - 1 = e^{kx/v} - 1 \tag{3.9}$$

where C_o is the concentration of contaminant present at time t = 0 yr; and k is the degradation rate constant (yr^{-1}). The substitution of x/v for t allows time-dependent breakdown to be expressed in terms of contaminant movement (x is the distance separating the source and receptor; v is the subsurface velocity of the dissolved contaminant). Input is consequently taken either as an estimated travel time, or velocity and distance, to the nearest receptor. This approach assumes constant subsurface fluid velocities, hence constant potentiometric gradients and infiltration rates.

For radionuclides, the BF term measures radioactive decay. The rate constant, k, is equal to $0.693/t_{1/2}$, where $t_{1/2}$ is the radioactive half-life (yr).

Because the rate of chromate [Cr(VI)] reduction to Cr(III) follows a first order rate law under certain conditions, the *MNAtoolbox* module for chromate includes a BF and rate constant for conversion of hexavalent chromium to sparingly soluble trivalent chrome. A similar approach might be applied to consider reduction of Tc(VII) or U(VI).

Rate constants and their supporting documentation are linked to the respective contaminant modules in *MNAtoolbox*. The user can override the BF values in the *MNAtoolbox* with site-specific values.

Calculation of the Score

Each of the terms in the NAF expression (Equation 3.1) is equal to zero if there is no attenuation; i.e., HDF = 0 if there is no dilution; SF = 0 if K_d is zero because there is no sorption, etc. If no attenuation is predicted by any process, NAF is zero. Also, each term becomes greater than zero if attenuation is predicted to occur. If attenuation is predicted, NAF is greater than zero. The score that is initially calculated in the scorecard is:

$$\text{Score} = NAF/(1+NAF/100); \tag{3.10}$$

The objective of Equation 3.10 is to provide a score that linearly scales with the NAF at relatively low values of the latter, but asymptotically approaches 100 at very high values of NAF. The relation between the NAF and the score is shown in Figure 3.9. This score is subsequently modified for many of the inorganic contaminants to account for the formation of sparingly soluble solids that can occasionally decrease contaminant concentrations below maximum contaminant levels (MCLs). This is explained below for each contaminant, where appropriate. It should be recognized that in some cases there probably exists a gradation between irreversible sorption of contaminants and the formation of separate, contaminant-bearing phases. Sites that score above 50 and near 100 possess hydrological and/or geochemical characteristics that are predicted to favor MNA. Low scores predict the opposite.

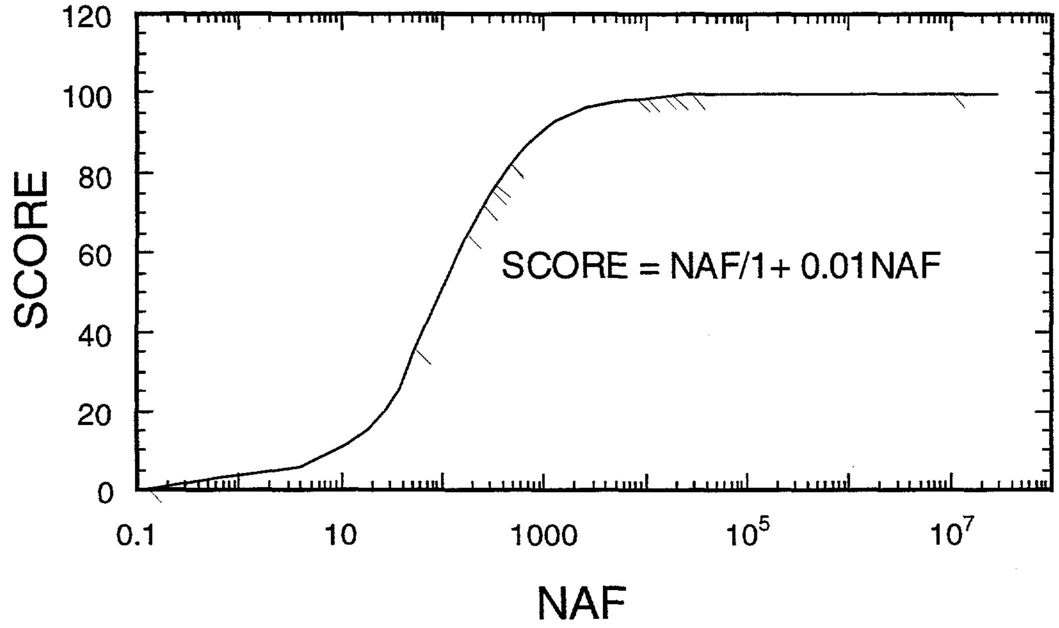


Figure 3.9 Relation between NAF and Score.

The scoring procedure serves only to indicate the likelihood of natural attenuation. It says nothing about whether or not the amount of attenuation at a site will be enough to achieve compliance with regulatory targets. By outlining the pathways, as well as obstacles, to contaminant attenuation on a contaminant-specific basis, usage of *MNAtoolbox* provides site managers a clear identification of likely data needs for MNA implementation.

The data used as input for the scorecard (e.g. K_d values, degradation rates, etc.) are also the input needed to construct full conceptual models for predicting contaminant behavior over time. The sensitivity of the score to the various input factors consequently gives a rough indication of the importance of the respective pathway, and supporting data, to a full model. Values of NAF vary between 0.13 for I, Tc, and Hg, and 10^7 for tritium using the defaults in *MNAtoolbox*. Scores vary between 0.13 and 100. The low scores of I, Tc, and Hg, occur primarily because there is negligible sorption and only minor chemical breakdown (for Tc). The high score for tritium arises due to its short half-life. Because a great deal of information is lost if only the score is considered, it is arguably more useful to consider the NAF itself or the contributions of the individual terms in Equation 3.1. In particular, doing the latter gives an approximate picture of the primary process(es) likely to affect natural attenuation at a site for a given contaminant.

Geochemical Summaries of How Specific Inorganics Are Dealt With in *MNAtoolbox*

Barium

Barium sulfate is sparingly soluble and forms rapidly. Solubility calculations suggest that ppm concentrations of sulfate will limit barium concentrations under all but the most extreme conditions (very low pH) to less than drinking water standards. Consequently, the final score calculated in *MNAtoolbox* is adjusted upwards to 100 if sulfate concentrations are greater than 1 ppm. Barium K_d values are EPA default values (U. S. Environmental Protection Agency, 1996).

Cadmium

Cadmium carbonate is sparingly soluble. Moreover, it grows quite rapidly on an environmental time scale. At pH values above 7 solubility, calculations indicate that cadmium concentrations would be reduced below drinking water limits by the formation of cadmium carbonate. This assumes that aqueous carbonate concentrations are set by equilibrium with a soil atmosphere 10 times atmospheric concentrations. This concentration was chosen to account for elevated CO_2 production associated with organic breakdown and biologic respiration (soil concentrations of CO_2 are typically 10 to 100 times those in the atmosphere). For the reasons cited above, if the pH > 7, the final score for Cd is automatically adjusted upwards to 100. Cadmium K_d values are EPA default values (U. S. Environmental Protection Agency, 1996).

The picture for Cd and a number of metals is complicated by the potential presence of organic acids and/or chelating agents such as EDTA. Although commingled chelators like EDTA are conservatively assumed to work against MNA, the longer-term effects of chelators on increased contaminant migration is probably minimal. Clearly, in the short term, the presence of chelators, which form strong complexes with various hazardous and radioactive contaminants, will likely result in increased solubility of and thus, decreased adsorption of contaminants in soils. However, many common synthetic chelators, including EDTA, diethylenediaminepentaacetic acid (DTPA), and nitrilotriacetic acid (NTA), are quite biodegradable (Bolton et al., 1993; Means et al., 1980; Thomas et al., 1998; Tiedje, 1977a; Tiedje, 1977b). Citric acid, another frequently employed chelating agent, and various of its metallic complexes also has been observed to rapidly biodegrade in soil (Boudot et al., 1980; Huang et al., 1998); though not in all cases – see Francis (1994). First-order rate constants for biodegradation of EDTA, DTPA, and NTA in sediments under environmentally realistic conditions have been determined to range between 0.011 and 0.038 day^{-1} (Bolton et al., 1993). Although the nature of the complexed metal has been observed to depress the rate of biodegradation, EDTA, when complexed with Fe, Cu, Co, Ni, and Cd, as well as the abundant Ca, Mg, and Na species, has been found to biodegrade readily (Thomas et al., 1998). Once the synthetic chelator has been biodegraded aerobically as an energy source by microbes in sediments in the time frame of months (as inferred from such rate constants), the long-term behavior of the liberated contaminant will then be dominated by the inorganic adsorption and fixation mechanisms representative of a non-commingled soil interaction scenario. Thus, once the contaminant source has been terminated by source control and/or remedial actions, the influence of any commingled chelators on site performance should be limited to about a year. Further contaminant migration modeling at a site should thus be limited to inorganic chemical reactions in soil.

Chromium

Trivalent Cr is sparingly soluble. If chromium contamination is largely trivalent in form, solubility calculations indicate that the formation of chromium hydroxide will limit Cr concentrations to below drinking water standards at pH 5 and above. Cr-Fe-OH minerals may often form as well - (Rai and Zachara, 1984). Hexavalent and trivalent Cr K_d values are EPA default values.

Copper

Formation of Cu oxides and hydroxides can limit Cu concentrations under reasonably oxidizing conditions to less than 1 ppm if pH values are greater than 6. Consequently, the score is adjusted upwards to 100 if pH > 6. In the absence of copper K_d values, the MNA toolbox module for Cu uses EPA Zn K_d values. Typically pH-dependent Cu and Zn sorption edges on metal hydroxides are nearly identical (*see* e.g., Dragun, 1988).

Lead

Lead forms sparingly soluble phosphates and hydroxyl carbonate solids if dissolved phosphate or carbonate is abundant. pH values greater than 8 cause the appearance of Pb-solids, which can limit aqueous Pb concentrations to below drinking water standards (Hem, 1989). Consequently, the score is adjusted to 100 if pH > 8. However, the presence of EDTA can mitigate against immobilization of Pb. In the absence of lead K_d values, the MNA toolbox module for Pb uses EPA K_d values for Zn. This is conservative because the Zn sorption edge occurs on metal hydroxides at a higher pH than the Pb sorption edge. The same trend was assumed to hold for sorptive soil organic matter as well.

Zinc

The formation of Zn hydroxides and Zn hydroxyl carbonates occurs at high pH, and pH values much greater than 7 will limit concentrations of dissolved Zn below 1 ppm. The presence of EDTA can also cause remobilization of Zn. If pH > 7, the Zn score is set upwards to 100.

Radionuclides

Whereas MCL values are sometimes used in the score calculation to estimate the effect of solubility, theoretical doses must be considered to do the same for radionuclides. The Safe Drinking Water Act (SDWA) defines MCLs in drinking water for certain radionuclides and classes of radionuclides (40 CFR Part 141.15-16) in terms of either concentrations or dose rates. These concentrations are outlined in Table 3.7.

Table 3.7 SDWA Limits for Radionuclides (from 40 CFR Part 141.15-16)

Radionuclide(s)	Limits
Combined radium-226 and radium-228	5 pCi/L maximum
Gross alpha particle activity (including radium-226 but excluding radon and uranium)	15 pCi/L maximum
Beta particle and photon radioactivity from man-made radionuclides	4 mrem average annual dose to total body or any internal organ
Tritium	20,000 pCi/L
Sr-90	8 pCi/L
All other man-made radionuclides	4 mrem average annual dose to total body or any internal organ

Concentration-based limits (pCi/L) can be converted to molar concentrations, M_i (mol/L), using the following equation:

$$M_i = LC \cdot \frac{T_{1/2}}{\ln(2)} \cdot \frac{1}{N_A} \tag{3.11}$$

where LC is the limiting concentration (pCi/L) from the SDWA; $T_{1/2}$ is the half-life of the radionuclide (sec), and N_A is Avogadro's number (6.022×10^{23} atoms/mol).

The dose-based limits (mrem/y) have been converted to molar concentrations (mol/L) using the following equation:

$$M_i = DL \cdot \frac{1}{WC} \cdot \frac{1}{DCF} \cdot \frac{T_{1/2}}{\ln(2)} \cdot \frac{1}{N_A} \tag{3.12}$$

where DL is the dose limit (mrem/y) from the SDWA and WC is the assumed water consumption rate (730 L/y) (U. S. Environmental Protection Agency, 1980). The dose conversion factors (DCF) were taken from Eckerman et al. (1988). The limiting value for DCF for each radionuclide was determined as the larger of the DCF from either the critical organ or effective dose to the total body. The DCF, critical organ, and resulting molar concentration limit values are listed in Table 3.8.

Table 3.8 MCL, DCF, and Limiting Molar Concentrations for Radionuclides

Nuclide	SDWA MCL	Critical Organ	DCF ([a]Sieverts/Bq)	M_i (mol/L)
H-3	20000 pCi/L	Whole body	-	6.9E-13
Co-60	4 mrem/y	Whole body	7.28E-09	3.0E-15
Sr-90	8 pCi/L	Bone marrow	-	6.5E-16
Tc-99	4 mrem/y	Whole body	3.95E-10	2.2E-09
I-129	4 mrem/y	Thyroid	2.48E-06	2.6E-11
Cs-137	4 mrem/y	Whole body	1.35E-08	9.3E-15
Ra-226	5 pCi/L	Bone surface	-	2.2E-14
Ra-228	5 pCi/L	Bone surface	-	8.1E-17
Th-229	15 pCi/L	Bone surface	-	3.1E-13
Th-230	15 pCi/L	Bone surface	-	3.2E-12
Th-232	15 pCi/L	Bone surface	-	5.9E-07
[b]U-234	4 mrem/y	Bone surface	1.13E-06	9.0E-13
U-235	4 mrem/y	Bone surface	1.05E-06	2.8E-09
U-238	4 mrem/y	Bone surface	1.01E-06	1.8E-08
Pu-238	15 pCi/L	Bone surface	-	3.7E-15
Pu-239	15 pCi/L	Bone surface	-	1.0E-12
Pu-240	15 pCi/L	Bone surface	-	2.8E-13
Pu-241	4 mrem/y	Bone surface	3.48E-07	1.7E-16
Am-241	15 pCi/L	Bone surface	-	1.8E-14

[a]1 Sievert = 100 rem. [b]The MCL for U is 20 ppb.

Radionuclide scores are calculated using Equations 3.1 and 3.10, similar to the other inorganics. Alternatively, one could roughly estimate the net effect of the combined biological and geochemical processes in decreasing radionuclide concentrations towards a regulatory target using the dose-based limits listed in Table 3.8. To do this in theory, the solubility of each radionuclide would be divided by the product of the retardation factor, the dilution factor, and the amount of radioactive decay that occurs along the way. This would be equivalent to assuming that: (1) the concentration of the particular isotope leaving the source area is controlled by the solubility of that radionuclide; and (2) concentrations downgradient decrease due to sorption, dilution, and radioactive decay. In the absence of source-term information, this model assumes a continual source and roughly estimates how much step-wise attenuation would occur between the source and a receptor. Ra, I, Tc (under oxidizing conditions), tritium, and Sr (under acid conditions) typically do not form sparingly soluble minerals, hence the calculation should not be applied to them.

Technetium and uranium represent special cases that must be discussed further. Dissolved Tc is present as pertechnetate (TcO_4^-), the most common form of technetium in oxidizing environments. Pertechnetate forms no sparingly soluble solids and, being anionic, sorbs sparingly at best. Under reducing conditions, however, dissolved technetium is present in the +4 valence state, which forms sparingly soluble solids such as $TcO_2 \cdot 2H_2O$. The scorecard in *MNAtoolbox* is set up to reflect low solubility by taking E_H and pH as input and calculating whether or not the conditions were likely to favor formation of $TcO_2 \cdot 2H_2O$ so that concentrations of dissolved Tc would be decreased below dose-based limits. Under the E_H-pH conditions where formation of $TcO_2 \cdot 2H_2O$ is predicted to limit pertechnetate below dose-based limits, the score is set to 100. This picture can be complicated though at high pH where Tc(IV)-carbonate complexes can elevate the mobility of otherwise insoluble Tc(IV).

Uranium possesses a non-radiologic recommended MCL of 20 ppb. U(VI) is relatively soluble, but U(IV) is sparingly soluble. *MNAtoolbox* uses K_d values for U(VI) that are probably much smaller than K_d values of U(IV). Reduction of mobile U(VI) to immobile U(IV) occurs under reducing conditions and would constitute a natural attenuation process. Although U(VI) reduction rates are not presently provided in *MNAtoolbox*, an independent measure of a first-order reduction rate is all that would be needed to model the effect in *MNAtoolbox*. The same observation applies to the reduction of Tc(VII).

4.0 *MNAimplement*

This section outlines the use of *MNAimplement*, a web-based tool that guides site managers through implementation of MNA after *MNAtoolbox* is used for site screening. *MNAimplement* builds on the *MNAtoolbox* results and guides site managers through: (1) collection of needed MNA-specific data; (2) refinement of the conceptual model describing natural attenuation for the specific contaminants of interest; (3) prediction of long-term contaminant behavior; (4) determination of whether MNA is likely to achieve regulatory cleanup objectives; and if so, (5) preparation of a long-term monitoring plan. Long-term monitoring component of an MNA program has the following two roles: (1) it provides more precise calibration of the conceptual model, and (2) it gives early warning of any unexpected contaminant movement with respect to a point of compliance. *MNAimplement* is used only if the preliminary assessment of the site characteristics using *MNAtoolbox* suggests that site-specific conditions favor MNA or if the user selects this option regardless of the *MNAtoolbox* scorecard results.

Collection of MNA-Specific Data

Conceptual models of natural attenuation answer the question: is natural attenuation occurring at the site, and if so, why? Typically this will involve identification of one or more attenuation pathways and *MNAtoolbox* is used to limit the likely number of pathways. For full-scale reliance on natural attenuation, a more detailed understanding of the pathway(s) will be required, particularly as some predictive capability will ultimately be needed. Before proceeding further, it should be stressed that site-specific data are required for developing a conceptual model. In the EPA MNA guidelines, there is a clear preference for site-specific data (as opposed to generic computer exercises and/or laboratory studies). Consequently, the development of a conceptual model describing natural attenuation should depend, as much as possible, on actual site data. Given detailed site specific information, numerical models and laboratory tests are often necessary to interpret this information and to evaluate potential impacts of changing geochemical conditions on the conceptual model.

For organic contaminants, a refinement of a conceptual model typically requires a close examination of soil redox conditions and plume movement. A reasonably clear understanding of the subsurface hydrology is an important starting requirement for both organic and inorganic contaminants. For many organic contaminants, there may already exist a framework for predicting long-term plume dynamics on the basis of data gathered during MNA-specific site characterization, namely through such numerical codes as Bioscreen (Newell et al., 1996) and Bioplume III (Rifai et al., 1998). Therefore, assessing the ability of MNA to achieve regulatory targets may be somewhat easier for organics than for metals. *MNAimplement* links to these tools that are needed for conceptual model development for most organics.

For inorganics, refinement of the conceptual model will typically require a plume analysis, as well as the performance of sequential soil extractions to identify where and how much contaminant is irreversibly bound up in the soil matrix. Isotopic exchangeability studies, as outlined in Appendix F, could also provide strong evidence of irreversible sorption in soils. Nevertheless, uncertainties surrounding the controls on irreversible uptake of metals may make predictions of MNA efficiencies somewhat speculative. Additional measurements of soil chemical parameters or characteristics may also be required.

The MNA pathways for the various metal contaminants depend on the metal as well as the soil and/or groundwater type (in addition to dilution, which has been treated elsewhere). Moreover, the long-term efficacy of natural attenuation of metals often will depend on the permanence and extent of the irreversible sorption mechanism.

An effective test of MNA (ignoring dilution) for metals must do the following in a scientifically defensible and reproducible fashion:

1. Quantify the amount of contaminant that is irreversibly sorbed (i.e., non-exchangeable), and

2. Identify the host(s) or soil mineral phase(s) responsible for the irreversible contaminant sorption.

Sequential extraction procedures (SEPs) (see e.g., Kennedy et al., 1997; Schultz et al., 1996; Tessier et al., 1979; Wasay et al., 1998; Yong et al., 1993) might achieve both objectives. Selective sequential extraction uses a series of chemical reagents of increasing strength to sequentially release different contaminant fractions upon the destruction of each binding soil phase. Typically, the chemical reagents are weak acids, oxidizing agents, reducing agents, and/or concentrated electrolyte solutions. SEPs are outlined in greater detail in Appendix F. SEPs give an idea of the maximum contaminant fraction available for transport in groundwater and provide information to constrain the specific chemical form of the natural attenuation mechanism.

Refinement of Conceptual Models

For natural attenuation of contaminants, the following conditions must be demonstrated:

1. **Attenuating agents are present along the flow path and in sufficient quantities to decrease contaminant concentrations to acceptable values by the time a receptor is reached.** The exposure of contaminants to attenuating agents and the full extent to which attenuation will occur (see Step 2) will depend strongly on hydrologic paths and travel times. For attenuation of most metals, minerals that sorb or sequester contaminants must be present along the travel path. Chromate can be reduced to concentrations below the MCL by reduction to Cr(III), followed by its precipitation and/or sorption, if sufficient suitable electron donors are available along the path. For long-lived radionuclides, the combined effects of sorption and dilution must be able to reduce dissolved concentrations below allowable dose-based limits. The travel time of relatively short-lived radionuclides must be sufficiently long that 10 half-lives have elapsed before the nearest receptor is reached. (In general, this much decay allows acceptable concentrations to be reached.)

For organics, the question is somewhat similar to the redox-sensitive behavior of chromate. Namely, are electron acceptors (such as oxygen for fuel hydrocarbons) or electron donors (for the case of PCE and TCE) available in sufficient quantities along the travel path to assure breakdown of the contaminants of concern before they can reach the point of compliance?

2. **Attenuation will occur rapidly enough to decrease contaminant concentrations to regulatory targets.** This will depend on at least a semi-quantitative assessment of attenuation rates. For organics, the rate of breakdown to non-toxic phases is critical. For metals, the rate of irreversible uptake may be most critical. For radionuclides, irreversible uptake and hydrologic travel time must be taken into account. For chromate, U(VI), and pertechnetate, rates of reduction must be considered. Longer travel times require less rapid attenuation and vice versa.

3. **Changes in geochemical conditions will not occur that negate the first two factors.** For inorganics, an SEP of the contaminated soil/aquifer material may provide a rough answer to the first condition above. The second condition above requires a clear assessment of chemical transformation rates that are not always well understood. The largest fraction of irreversible uptake of metals appears to occur quite rapidly on environmental time scales of years. For example, Krouglov et al. (1998) showed that irreversible uptake of Cs and Sr went to apparent

completion, or steady-state, in three years or less at Chernobyl. Supporting evidence for rapid sequestration is the observation that contaminant uptake measured in the laboratory over days to weeks approaches or overlaps values measured in the field over much longer time spans.

Quantification of the attenuation capacity of a flowpath is relatively straightforward. For example, if irreversible sequestration of metals by iron hydroxides is identified as a primary uptake process, the available mass of the iron hydroxides likely to be encountered by the contaminant in transit from the source to the nearest receptor must be estimated and then compared to total mass of contaminant. This comparison, by design, is site-specific. The sequestering capacity can be roughly estimated by:

$$\text{Sequestering Capacity (mol)} = \text{Vol}_{\text{rock}} \times C_{\text{max}} \times X_{\text{irv}} \qquad (4.1)$$

where Vol_{rock} (liters) is the volume of soil estimated to be encountered by a plume, and C_{max} is the maximum contaminant concentration measured in the soil (mol/L). The calculation of Vol_{rock} will be most difficult for cases of fracture flow. C_{max} and X_{irv} are most reasonably measured near the contaminant source. In many cases, contaminants will be present in trace amounts, and the sequestering capacity will greatly exceed the contaminant source term. The sequestering capacity must be compared against the contaminant mass in the subsurface; the latter is calculated by:

$$\text{Contaminant mass} = \text{Vol}_{\text{rock}} \times \{\{i^{aq}\}n_e + 1000\rho_b\{i^{tot}\}\} \qquad (4.2)$$

where $\{i^{aq}\}$ is the dissolved concentration of contaminant i (mol/L); ρ_b is the bulk rock density (g/mL); and $\{i^{tot}\}$ is the total amount of contaminant in the rock or soil (mol/g). The comparison is obviously going to involve some uncertainty, and order-of-magnitude estimates may be the only level that is achievable. Estimating the reactive volume that the plume will actually encounter may involve addressing the uncertainty associated with "fast paths", or effective porosity versus total porosity, that may control fluid flow. Estimating the attenuation capacity for inorganics is somewhat analogous to calculating the oxidative (or reductive) capacity of soils for assessment of organic attenuation (see e.g. Scott and Morgan, 1990).

Forward-Modeling of MNA

The ability to forward-model natural attenuation to estimate horizons for achievement of regulatory targets poses the greatest challenge to the implementation of MNA. In addition to the uncertainties associated with existing hydrogeologic forecasting, two other uncertainties arise: (1) transformation rates of organic compounds are site-specific; and (2) irreversible uptake of metals and long-lived radionuclides are not adequately accounted for in existing reactive-transport codes used to estimate contaminant concentrations at distance from the source. For organic contaminants prone to biodegradation, site-specific rate constants can be derived using Bioscreen (Newell et al., 1996) or Bioplume III (Rifai et al., 1998) to iteratively fit plume characteristics. The model is then "run forward" to predict contaminant concentrations at the point of compliance over time. Published examples of the approach can be found in the supporting documentation of the respective codes.

Forward-modeling predictions are not so clear-cut for metals and long-lived radionuclides. A simplistic way of doing this is through the use of the "tipping bucket" model (McBride, 1994) that assumes a contaminant front progresses through a soil profile at the rate that sorption capacity (in essence, the attenuation capacity) is exhausted. Sorption capacities are calculated as a maximum adsorbed concentration, C_s, from a Langmuir adsorption isotherm equation:

$$[>\text{-}i] = k_l[i^{aq}]C_s/1+k_l[i^{aq}] \qquad (4.3)$$

where $[>\text{-}i]$ is the sorbed concentration of contaminant i; $[i^{aq}]$ is the dissolved concentration of i; and k_l is a constant proportional to the strength of binding (in essence, a K_d). Predicting contaminant movement becomes simply a matter of measuring C_s, the contaminant sorption capacity, quantifying the dissolved contaminant as a function of $[>\text{-}i]$, and dividing one by the other.

Equation 4.3 does not address what happens after contaminant loading ceases in real systems (in essence after the source term at the surface has been removed) because it predicts complete release of contaminants by mineral surfaces as dissolved concentrations drop. Often no such complete re-equilibration is observed. A more realistic approach for numerically describing the process is through the use of two Langmuir adsorption isotherms: one for the reversible fraction, and another to describe the sequestered fraction of contaminant:

$$[>X\text{-}i] = k_x[i^{aq}]C_{sx}/1+k_x[i^{aq}] \qquad (4.4)$$

$$[>Y\text{-}i] = k_y[ii^{aq}]C_{sy}/1+k_y[i^{aq}] \qquad (4.5)$$

where X represents the reversible, weak sites, and Y represents the strong, or irreversible sites. The process is schematically illustrated in Figure 4.1. The site density term for the weak sites, C_{sx}, is fixed to the maximum observed exchangeable fraction of the soil. The strong site density term is the remainder. The strong binding constant, k_y, is then set to very high value. The net effect is that changes in dissolved contaminant concentrations in soil will affect contaminant populations two very different ways. Contaminants sorbed to weak sites will desorb in response to decreases in dissolved contaminant concentrations. Contaminants sorbed to strong sites will remain unaffected.

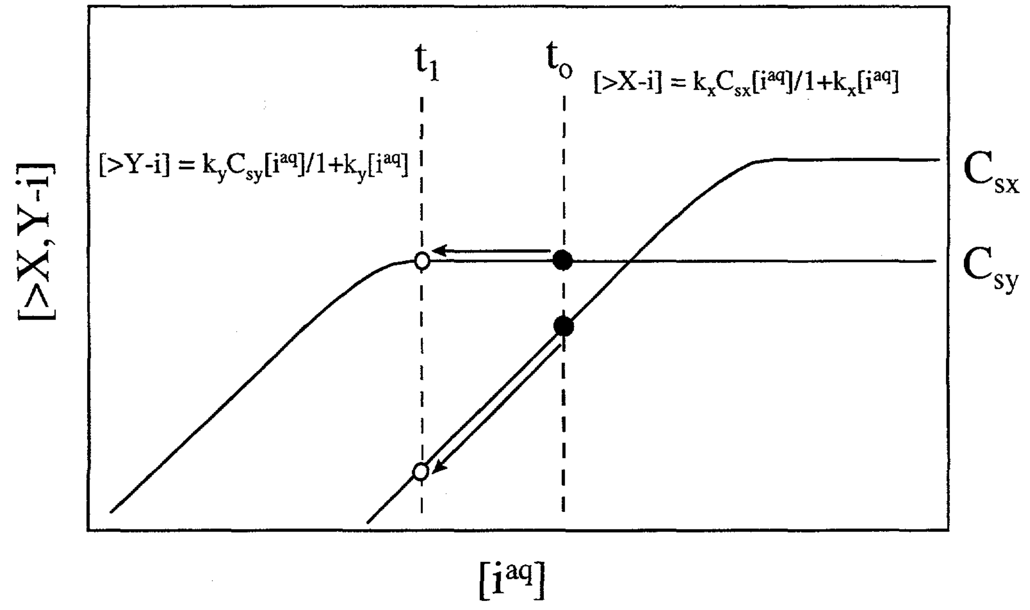


Figure 4.1 Two-site Langmuir model for calculating irreversible uptake.

Brian Spalding and co-workers from have developed a computer program, *langmuir.exe,* that allows site managers to assess the effect of irreversible uptake on long-term transport of organic and inorganic contaminants. *Langmuir.exe* uses as input isotherm parameters (k_x, k_y, C_{sx}, and C_{sy}) measured through laboratory adsorption studies or obtained from published results. A contaminant mass balance equation (4.6) and the above definitions are employed to combine both isotherms and thus, to solve for $[i^{aq}]$ from a given and known total amount of contaminant (X_t):

$$X_t = ([i^{aq}] \times VOL) + (X_x \times WT) + (X_y \times WT) \tag{4.6}$$

where VOL = volume of water or leachate in equilibrium and WT = weight of soil or rock in equilibrium. X_t is a known or measurable total amount of contaminant which can be independently and sequentially adjusted for soluble inputs and outputs from a soil cell or layer with a given or measured starting quantity of contaminant, X_x. The combined equation, resulting from substituting Equation 4.4 and Equation 4.5 into Equation 4.6, cannot be explicitly solved for $[i^{aq}]$, and thus, is solved iteratively, trying values of $[i^{aq}]$ that converge to the known value of X_t. Application of *langmuir.exe* allows estimates to be made of: (1) the net long-term flux of contaminant and (2) the amount of time required for contaminant levels to decrease below regulatory targets. The programs are in the process of being tested and validated but once tested (late 1998), will be linked with *MNAimplement.* The programs can be downloaded from `http:\\www.ornl.gov\LANGMUIR\bpsintro.htm`.

Long-Term Monitoring for MNA

Long-term monitoring performs the following two functions in the MNA approach.

1. Demonstrates the predicted trend in the respective attenuation mechanism and/or provides data for further calibration and optimization of the conceptual model (Process Monitoring); and
2. Provides early warning of the failure of the attenuation mechanism; hence, it acts as a trigger for implementation of contingency measures (compliance monitoring).

The first function has as its objective the scaling back of near-source monitoring. If attenuation trends continue as predicted by the conceptual model, the coherence between prediction and measurement should be used as an 'off-ramp' to no further action, or at least decreased monitoring. Agreement between model predictions and data indicates a low degree of uncertainty.

On the other hand, significant deviations from the predicted baseline, even if less than agreed upon trigger concentrations, indicate unacceptable levels of uncertainty and should be used as a basis on which to update the conceptual model. This may require further site characterization to identify poorly understood biological and geochemical behavior. It also may require further measurement to better calibrate the conceptual model.

Compliance monitoring should be done sufficiently far from the point of compliance that contingency measures, if required, can be effectively implemented to prevent harmful exposures at and beyond the point of compliance. Compliance monitoring can be done in one of two ways: directly, by focusing on changes in contaminant availability levels; or indirectly, by focusing on changes in the biological and geochemical characteristics that are indicators of the conceptual model of attenuation. An example of the first case would be observed substantial increases in the availability of a contaminant, above and beyond that predicted by the conceptual model. Using attenuation of TCE by reductive dechlorination as the baseline attenuation mechanism, compliance monitoring might detect a ceasing of breakdown (i.e., time-invariant TCE concentrations) caused by a shift to more oxidizing conditions. Indirect compliance monitoring would note the shift in oxidation state and relate this back to the fact that an MNA approach relying on reductive dechlorination also requires reducing conditions.

If data that confirms the conceptual model accumulates, there should be a shift in emphasis from process towards compliance monitoring, reflecting the decreased uncertainty. Although the implementation of compliance monitoring is ultimately dictated by the extent to which observations can be translated into effective enaction of contingency measures before a point of compliance is reached, process monitoring that confirms the original conceptual model might be used to argue for a decrease in compliance monitoring frequency. Monitoring that neither reduces uncertainty by refining the conceptual model, nor acts as a trigger, should be avoided. DOE is presently developing detailed monitoring guidelines for MNA.

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Appendix A. The OSWER MNA Directive

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
Directive 9200.4-17

November, 1997

NOTICE: This document provides guidance to EPA 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 for the remediation of contaminated soil and groundwater at sites regulated under Office of Solid Waste and Emergency Response (OSWER) programs. These include programs administered under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund), the Resource Conservation and Recovery Act (RCRA), the Office of Underground Storage Tanks (OUST), and the Federal Facilities Restoration and Reuse Office (FFRRO).

EPA remains fully committed to its goals of protecting human health and the environment, remediating contaminated soils and groundwater, and protecting uncontaminated groundwaters and other environmental resources[1] at all sites being remediated under OSWER programs. EPA does not consider monitored natural attenuation to be a "presumptive" or "default" remedy—it is merely one option that should be evaluated with other applicable remedies. EPA advocates using the most appropriate technology for a given site. EPA does not view monitored natural attenuation to be a "no action" or "walk-away" approach, but rather considers it to be an alternative means of achieving remediation objectives that may be appropriate for a limited set of site circumstances where its use meets the applicable statutory and regulatory requirements. As there is often a variety of methods available for achieving a given site's remediation objectives[2], monitored natural attenuation 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, monitored natural attenuation should be selected only where it meets all relevant remedy selection criteria, where it will be fully protective of human health and the environment, and where it will meet site remediation objectives, within a time frame that is reasonable compared to that offered by other methods. In the majority of cases where monitored natural attenuation 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. Monitored natural attenuation should be used very cautiously as the sole remedy at contaminated sites. Furthermore, the availability of monitored natural attenuation 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.

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

[2] 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, minimizing further migration of contaminants from source areas, minimizing 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.

Use of monitored natural attenuation does not signify a change in OSWER's remediation objectives, including the control of source materials and restoration of contaminated groundwaters, where appropriate (see Section 1, under "Implementation"). Thus, EPA expects that source control measures will be evaluated for all sites under consideration for any proposed remedy. As with other remediation methods, selection of monitored natural attenuation 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 monitored natural attenuation toward a site's remediation objectives should be carefully monitored and compared with expectations. Where monitored natural attenuation'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 rapidly. 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 monitored natural attenuation may 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 monitored natural attenuation to meet remedial objectives that are protective of human health and the environment, **source control and performance monitoring are fundamental components of any monitored natural attenuation remedy**.

This Directive is not intended to provide detailed technical guidance on evaluating monitored natural attenuation remedies. At present, there is a relative lack of EPA guidance concerning appropriate implementation of monitored natural attenuation remedies. With the exception of Chapter IX in OUST's guidance manual (USEPA, 1995a), EPA has not yet completed and published specific technical guidance to support the evaluation of monitored natural attenuation for OSWER sites. However, technical resource documents for evaluating monitored natural attenuation in groundwater, soils, and sediments are currently being developed by EPA's Office of Research and Development (ORD). In addition, technical information regarding the evaluation of monitored natural attenuation as a remediation alternative is available from a variety of 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 information can be obtained. Although non-EPA documents may provide regional and state site managers, as well as the regulated community, with useful technical information, these non-EPA guidances are not officially endorsed by EPA, 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 remedial 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; 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 contaminants, and for this reason, EPA expects that monitored natural attenuation will be most appropriate at sites that have a low potential for plume generation and migration (see Section 3 under “Implementation”). 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) The contaminant may be converted to a less toxic form through destructive processes such as biodegradation or abiotic transformations;

(2) Potential exposure levels may be reduced by lowering of concentration levels (through destructive processes, or by dilution or dispersion); and

(3) Contaminant mobility and bioavailability may be reduced by sorption to 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 (see Section 3 under “Implementation” for a discussion of favorable site conditions). 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, monitored natural attenuation will be used in conjunction with active remediation measures. For example, monitored natural attenuation could be employed in lower concentration areas of the dissolved plume and as a follow-up to active remediation in areas of higher concentration. EPA also encourages the consideration of innovative approaches which may offer greater confidence and reduced remediation time frames at a modest additional cost.

While monitored natural attenuation is often dubbed "passive" remediation because it occurs 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 monitored natural attenuation 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.

Transformation Products

It also should be noted that some natural attenuation processes may result in the creation of transformation products[3] that are more toxic 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 monitored natural attenuation remedy is appropriate and protective in the long term. Additionally, some natural attenuation processes may 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). Such cross-media transfer is not desirable, and generally not acceptable except under certain site-specific circumstances, and would likely require an evaluation of the potential risk posed by the contaminant(s) once transferred to that medium.

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, ethyl benzene, 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 may

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[3] The term "transformation products" in the Directive includes biotically and abiotically formed products described above (*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 and sediment.

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, monitored natural attenuation alone is generally not sufficient to remediate even a petroleum release site. Implementation of source control measures in conjunction with monitored natural attenuation is almost always necessary. Other controls (*e.g.*, institutional controls[4]), in accordance with applicable state and federal requirements, may also be necessary to ensure protection of human health and the environment. Furthermore, while BTEX contaminants tend to biodegrade with relative ease, other chemicals (*e.g.*, methyl tertiary-butyl ether [MTBE]) that are more resistant to biological or other degradation processes may also be present in petroleum fuels. In general, monitored natural attenuation is not appropriate as a sole remediation option at sites where non-degradable and nonattenuated contaminants are present at levels that pose an unacceptable risk to human health or the environment. Where non-degradable contaminants are present, all processes (listed on page 4) which contribute to natural attenuation should be evaluated to ensure protection of human health and the environment.

Chlorinated Solvents

Chlorinated solvents, such as trichloroethylene, represent another class of common contaminants that may also biodegrade under certain environmental conditions. 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 may not often occur. Because of the nature and the distribution of these compounds, natural attenuation may not be effective as a remedial option. If they are not adquately addressed through removal or containment measures, source materials can continue to contaminate groundwater for decades or even centuries. Cleanup of solvent spills is also complicated by the fact that a typical spill includes multiple contaminants, including some that are essentially non-degradable.[5] 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.

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[4] 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.

[5] 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 are other solvents under the same environmental conditions.

Inorganics

Monitored natural attenuation 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[6] 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 because some mechanisms are more desirable than others. 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 are key components of a sufficiently protective monitored natural attenuation remedy.

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. It is critical that the near surface or surface soil pathways be carefully evaluated and eliminated as potential sources of radiation exposure.

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 are less mobile, not bioavailable, and/or non-toxic. Therefore, natural

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[6] When a contaminant is associated with a solid phase, it is usually not known if the contaminant is precipitated as a three-dimensional molecular 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.

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

Monitored natural attenuation has several potential advantages and disadvantages, and its use should be carefully considered during site characterization and evaluation of remediation alternatives. **Potential advantages** of monitored natural attenuation 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 contaminated media;
- Less intrusion as few surface structures are required;
- Potential for application to all or part of a given site, depending on site conditions and cleanup objectives;
- Use in conjunction with, or as a follow-up to, other (active) remedial measures; and
- Lower overall remediation costs than those associated with active remediation.

The **potential disadvantages** of monitored natural attenuation include:

- Longer time frames may be required to achieve remediation objectives, compared to active remediation;
- Site characterization may be more complex and costly;
- Toxicity of transformation products may exceed that of the parent compound;
- Long term monitoring will generally be necessary;
- 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 are likely to change over time and could result in

renewed mobility of previously stabilized contaminants, adversely impacting remedial effectiveness; and

- More extensive education and outreach efforts may be required in order to gain public acceptance of monitored natural attenuation.

IMPLEMENTATION

The use of monitored natural attenuation is not new in OSWER programs. For example, in the Superfund program, selection of natural attenuation as an element in a site's groundwater remedy goes as far back as 1985. Use of monitored natural attenuation in OSWER programs has continued since that time, slowly increasing 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 soil and groundwater cleanup objectives. However, complete reliance on monitored natural attenuation is appropriate only in a limited set of circumstances at contaminated sites. The sections which follow seek to clarify OSWER program policies regarding the use of monitored natural attenuation. Topics addressed include site characterization; the types of sites where monitored natural attenuation may be appropriate; reasonable remediation time frames; the importance of source control; performance monitoring; and contingency remedies where monitored natural attenuation 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 monitored natural attenuation 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 monitored natural attenuation, can be a complex process. Therefore, monitored natural attenuation should be carefully evaluated along with other viable remedial approaches or technologies (including innovative technologies) within the applicable remedy selection framework. **Monitored natural attenuation 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[7]. Although there are differences among these programs, they share several key principles that should generally be considered during selection of remedial measures, including:

- Source control actions 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.[8]
- Contaminated groundwaters should be returned to "their beneficial uses[9] wherever practicable, within a time frame 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" (which may be appropriate).[10]
- Contaminated soil should be remediated to achieve an acceptable level of risk to human and environmental receptors,

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[7] Existing program guidance and policy regarding monitored natural attenuation 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).

[8] Principal threat wastes are those source materials (*e.g.*, non-aqueous phase liquids [NAPL], saturated soils) that are highly toxic or highly mobile that generally cannot be reliably contained (USEPA, 1991). Low level threat wastes are source materials that can be reliably contained or that would pose only a low risk in the event of exposure. Contaminated groundwater is neither a principal nor a low-level threat waste.

[9] Beneficial uses of groundwater could include uses for which water quality standards have been promulgated, such as a drinking water supply, or as a source of recharge to surface water, 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 1997b, or contact your state implementing agency.

[10] This is a general expectation for remedy selection in the Superfund program, as stated in the National Contingency Plan (USEPA, 1990a, §300.430 (a)(1)(iii)(F)). 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."

> 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.

Consideration or selection of monitored natural attenuation as a remedy or remedy component does not in any way change or displace these (or other) remedy selection principles. Nor does use of monitored natural attenuation diminish EPA's or the regulated party's responsibility to achieve protectiveness or to satisfy long-term site cleanup objectives. **Monitored natural attenuation is 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 time frame that is reasonable compared to other alternatives.** The effectiveness of monitored natural attenuation in both near-term and long-term time frames should be demonstrated to EPA (or other regulatory authority) through: 1) sound technical analysis which provides confidence in natural attenuation's ability to achieve remediation objectives; 2) performance monitoring; and 3) backup or contingency remedies where appropriate. **In summary, use of monitored natural attenuation does not imply that EPA or the responsible parties are "walking away" from the cleanup or financial responsibility obligations at a site.**

It also should be emphasized that the selection of monitored natural attenuation as a remedy does not imply that active remediation measures are infeasible, or are "technically impracticable." Technical impracticability (TI) determinations, which EPA makes based on the inability to achieve required cleanup levels using available remedial technologies and approaches, are used to justify a change in the remediation objectives at Superfund and RCRA sites (USEPA, 1993a). A TI determination does not imply that there will be no active remediation at the site, nor that monitored natural attenuation will be used at the site. Rather, a TI determination simply indicates that the cleanup levels and objectives which would otherwise be required cannot practicably be attained within a reasonable time frame 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 containment for an area contaminated with dense non-aqueous phase liquids (DNAPL), in addition to approaches intended to restore to beneficial uses the portion of the plume with dissolved contaminants. Several remedial approaches could be appropriate to address the dissolved plume, one of which could be monitored natural attenuation under suitable conditions. However, the evaluation of natural attenuation processes and the decision to rely upon monitored natural attenuation for the dissolved plume should be distinct from the recognition that restoration of a portion of the plume is technically impracticable (*i.e.*, monitored natural attenuation 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 monitored natural attenuation 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 natural attenuation 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; 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 natural attenuation can be appropriately applied at a site. Demonstrating the efficacy of this remediation approach likely will require analytical or numerical simulation of complex attenuation processes. Such analyses, which are critical to demonstrate natural attenuation's ability to meet remedial action objectives, generally require a detailed conceptual site model as a foundation[11].

Site characterization should include collecting data to define (in three spatial dimensions over time) the nature and distribution of contamination sources as well as the extent of the groundwater plume and its potential impacts on receptors. However, where monitored natural attenuation will be considered as a remedial approach, certain aspects of site characterization may require more detail or additional elements. For 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 required. 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.

Monitored natural attenuation may not be appropriate as a remedial option at many sites for technological or economic reasons. For example, in some complex geologic

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[11] A conceptual site model 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.

systems, technological limitations may preclude adequate monitoring of a natural attenuation remedy to ensure with a high degree of certainty 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 channels (*e.g.*, solution channels, foliations, fractures, joints). 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 channels that carry contaminated groundwater through the subsurface. Monitored natural attenuation will not generally be appropriate where site complexities preclude adequate monitoring. Although in some situations 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 monitored natural attenuation is high compared to the cost of other remedial alternatives. Under such circumstances, natural attenuation would not necessarily be the low-cost alternative.

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. Therefore, the impacts of any ongoing or proposed remedial actions should be factored into the analysis of natural attenuation's effectiveness. When considering source containment/treatment together with natural attenuation of chlorinated solvents, the potential for cutting off sources of organic carbon (which are critical to biodegradation of the solvents) should be carefully evaluated.

Once the site characterization data have been collected and a conceptual model developed, the next step is to evaluate the efficacy of monitored natural attenuation as a remedial approach. Three types of site-specific information or "evidence" should be used in such an evaluation:

(1) Historical groundwater and/or soil chemistry data that demonstrate a clear and meaningful trend[12] 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

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[12] For guidance on the statistical analysis of environmental data, please see USEPA, 1989 and 1992b, listed in the "References Cited" section at the end of this Directive.

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 implementing state agency determines that historical data (Number 1 above) are of sufficient quality and duration to support a decision to use monitored natural attenuation, EPA expects that 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 monitored natural attenuation at those sites with contaminants which do not readily degrade through biological processes (*e.g.*, most non-petroleum compounds, inorganics), at sites with contaminants that transform into more toxic and/or mobile forms than the parent contaminant, or at sites 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 physical characteristics of the environmental setting (*e.g.*, hydrogeology, ground cover, or 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 monitored natural attenuation are collected and evaluated by capable technical specialists with expertise in the relevant sciences. Further, EPA expects that the results will be provided in a timely manner to EPA or to the state implementing agency for evaluation and approval.

Sites Where Monitored Natural Attenuation May Be Appropriate

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

In determining whether monitored natural attenuation is an appropriate remedy for soil or groundwater at 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 the resulting transformation products present a greater risk than do the parent contaminants;
- The nature and distribution of sources of contamination and whether these sources have been or can be adequately controlled;
- Whether the plume is relatively stable or is still migrating and the potential for environmental conditions to change over time;
- The impact of existing and proposed active remediation measures upon the monitored natural attenuation component of the remedy;
- Whether drinking water supplies, other groundwaters, surface waters, ecosystems, sediments, air, or other environmental resources could be adversely impacted as a consequence of selecting monitored natural attenuation as the remediation option;
- Whether the estimated time frame of remediation is reasonable (see below) compared to time frames required for other more active methods (including the anticipated effectiveness of various remedial approaches on different portions of the contaminated soil and/or groundwater);
- Current and projected demand for the affected aquifer over the time period that the remedy will remain in effect (including the availability of other water supplies and the loss of availability of other groundwater resources due to contamination from other sources); and
- Whether reliable site-specific vehicles for implementing institutional controls (*i.e.*, zoning ordinances) are available, and if an institution responsible for their monitoring and enforcement can be identified.

For example, evaluation of a given site may determine that, once the source area and higher concentration portions of the plume are effectively contained or remediated, lower concentration portions of the plume could achieve cleanup standards within a few decades through monitored natural attenuation, if this time frame is comparable to those of the more aggressive methods evaluated for this site. Also, monitored natural attenuation would more likely be appropriate if the plume is not expanding, nor threatening downgradient wells or surface water bodies, and where ample potable water supplies are available. The remedy for this site could include source control, a pump-and-treat system to mitigate only the highly-contaminated plume areas, and monitored natural attenuation in the lower concentration portions of the plume. In combination, these methods would maximize groundwater restored to beneficial use in a time frame consistent with future demand on the aquifer, while utilizing natural attenuation processes to reduce the reliance on active remediation methods (and reduce cost).

Of the above factors, the most important considerations regarding the suitability of monitored natural attenuation as a remedy include whether the groundwater contaminant plume is growing, stable, or shrinking, and any risks posed to human and environmental receptors by the contamination. **Monitored natural attenuation should not be used where such an approach would result in significant contaminant migration or unacceptable impacts to receptors.** Therefore, sites where the contaminant plumes are no longer increasing in size, or are shrinking in size, would be the most appropriate candidates for monitored natural attenuation remedies.

Reasonableness of Remediation Time Frame

The longer remediation time frames typically associated with monitored natural attenuation should be compatible with site-specific land and groundwater use scenarios. Remediation time frames generally should be estimated for **all** remedy alternatives undergoing detailed analysis, including monitored natural attenuation[13]. Decisions regarding the "reasonableness" of the remediation time frame for any given remedy alternative should then be evaluated on a site-specific basis. While it is expected that monitored natural attenuation may require somewhat longer to achieve remediation objectives than would active remediation, the overall remediation time frame for a remedy which relies in whole or in part on monitored natural attenuation should not be excessive compared to the other remedies considered. Furthermore, subsurface conditions and plume stability can change over the extended timeframes that are necessary for monitored natural attenuation.

Defining a **reasonable time frame** is a complex and site-specific decision. Factors that should be considered when evaluating the length of time appropriate for remediation include:

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[13] EPA recognizes that predictions of remediation time frames may involve significant uncertainty; however, such predictions are very useful when comparing two or more remedy alternatives.

- Classification of the affected resource (*e.g.*, drinking water source, agricultural water source) and value of the resource[14];

- Relative time frame in which the affected portions of the aquifer might be needed for future water supply (including the availability of alternate supplies);

- **Uncertainties** regarding the mass of contaminants in the subsurface and predictive analyses (*e.g.*, remediation time frame, 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 extended time for remediation; and

- Provisions by the responsible party for adequate funding of monitoring and performance evaluation over the period required for remediation.

Finally, individual states may provide information and guidance relevant to many of the factors discussed above as part of a Comprehensive State Groundwater Protection Program (CSGWPP). (See USEPA, 1992a) Where a CSGWPP has been developed, it should be consulted for groundwater resource classification and other information relevant to determining required cleanup levels and the urgency of the need for the groundwater. Also, EPA remediation programs generally should defer to state determinations of current and future groundwater uses, when based on an EPA-endorsed CSGWPP that has provisions for site-specific decisions (USEPA, 1997b).

Thus, EPA or other regulatory authorities should consider a number of factors when evaluating reasonable time frames for monitored natural attenuation at a given site. These factors, on the whole, should allow the regulatory agency 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 returned to beneficial uses within a reasonable time frame. When these conditions cannot be met using monitored natural attenuation, a remedial alternative that does meet these expectations should be selected instead.

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[14] In determining whether an extended remediation time frame 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.

Remediation of Contaminated Sources and Highly Contaminated Areas

The need for control measures for contamination sources and other highly contaminated areas should be evaluated as part of the remedy decision process at all sites, particularly where monitored natural attenuation is under consideration as the remedy or as a remedy component. Source control measures include removal, treatment, or containment measures (*e.g.*, physical or hydraulic control of areas of the plume in which NAPLs are present in the subsurface). EPA
prefers remedial options which remove or treat contaminant sources when such options are technically feasible.

Contaminant sources which are not adequately addressed complicate the long-term cleanup effort. For example, following free product recovery, residual contamination from a petroleum fuel spill may continue to leach significant quantities of contaminants into the groundwater. Such a lingering source can unacceptably extend the time necessary to reach remedial 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 and threaten 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.

Performance Monitoring

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 monitored natural attenuation than for other types of remedies due to the longer remediation time frames, potential for ongoing contaminant migration, and other uncertainties associated with using monitored natural attenuation. 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 remedy performance as well as define the anticipated performance objectives of the remedy. In addition, all monitoring programs should be designed to accomplish the following:

- Demonstrate that natural attenuation is occurring according to expectations;
- Identify any potentially toxic transformation products resulting from biodegradation;

- Determine if a plume is expanding (either downgradient, laterally or vertically);
- Ensure no 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;
- 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[15]; and
- Verify attainment of cleanup objectives.

Performance monitoring should continue as long as contamination remains above required cleanup levels. Typically, monitoring is continued for a specified period (*e.g.*, one to three years) after cleanup levels 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 State implementing agency as part of any proposed monitored natural attenuation 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

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[15] 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 monitored natural attenuation because of the lack of engineering controls to control contaminant migration.

call for modification and enhancement 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 employed 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.

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 measures. Such criteria might include the following:

- Contaminant concentrations in soil or groundwater at specified locations exhibit an increasing trend;
- Near-source wells exhibit large concentration increases indicative of a new or renewed release;
- Contaminants are identified in sentry/sentinel wells located outside of the original plume boundary, indicating renewed contaminant migration;
- 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 monitored natural attenuation remedy.

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

EPA recommends that remedies employing monitored natural attenuation be evaluated to determine the need for including one or more contingency measures that would be capable of achieving remediation objectives. EPA believes that a contingency measure may be particularly appropriate for a monitored natural attenuation remedy which has been selected based primarily on predictive analysis (second and third lines of evidence discussed previously) as compared to natural attenuation remedies based on historical trends of actual monitoring data (first line of evidence).

SUMMARY

The use of monitored natural attenuation does **not** signify a change in OSWER's remediation objectives; monitored natural attenuation should be selected only where it will be fully protective of human health and the environment. EPA does not view monitored natural attenuation 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. Monitored natural attenuation 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 monitored natural attenuation should include a comprehensive site characterization, risk assessment where appropriate, and measures to control sources. Also, monitored natural attenuation should not be used where such an approach would result in significant contaminant migration or unacceptable impacts to receptors and other environmental resources. 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 time frame that is reasonable compared to time frames associated with other methods. Where monitored natural attenuation'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 monitored natural attenuation will be, at many sites, a reasonable and protective component of a broader remedial strategy. However, EPA believes that there will be many other sites where uncertainties too great or a need for a more rapid remediation will preclude the use of monitored natural attenuation as a stand-alone remedy. This Directive should help promote consistency in how monitored natural attenuation remedies are proposed, evaluated, and approved.

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http://www.epa.gov/ada/kerrlab.html
Office of Research and Development, R.S. Kerr Environmental Research Laboratory

http://www.epa.gov/OUST/cat/natatt.htm
Office of Underground Storage Tanks, information on natural attenuation

http://www.epa.gov/swerffrr/chlorine.htm
Federal Facilities Restoration and Reuse Office, fact sheet on natural attenuation of chlorinated solvents

http://www.epa.gov/swerffrr/petrol.htm
Federal Facilities Restoration and Reuse Office, Fact sheet on natural attenuation of petroleum contaminated sites

http://www.epa.gov/hazwaste/ca/subparts.htm
Office of Solid Waste, information on RCRA Subpart S

http://www.epa.gov/swerosps/bf/
Office of Outreach Programs, Special Projects, and Initiatives, information on Brownfields

Other Internet Web Sites

http://clu-in.com
Technology Innovation Office, information on hazardous site cleanups

Appendix B. The AFCEE Protocol for MNA of Fuel Hydrocarbons

Much of the following is abstracted from the review of Brady et al. (1997). The most comprehensive cleanup protocol that includes consideration of natural attenuation is that of Wiedemeier et al. (1995b) for the cleanup of fuel hydrocarbons at Department of Defense (DOD) facilities. Natural attenuation is considered as a potential remedy at the very first step of the process, and many of the most critical decision points rely on a conceptual understanding of contaminant degradation in the subsurface.

Wiedemeier et al. (1995b) condense the protocol into an eight step approach:

1. Review available site data;
2. Develop a preliminary conceptual model and assess the potential for intrinsic remediation;
3. If intrinsic remediation is selected as potentially appropriate, perform site characterization in support of intrinsic remediation;
4. Refine the conceptual model based on site characterization data, complete pre-modeling calculations, and document indicators of intrinsic remediation;
5. Simulate intrinsic remediation using analytical or numerical solute fate and transport codes that allow incorporation of a biodegradation term, as necessary;
6. Conduct an exposure pathways analysis;
7. If intrinsic remediation alone is acceptable, prepare long-term monitoring (LTM) plan; and
8. Present findings to regulatory agencies and obtain approval for the intrinsic remediation with the LTM option.

Step 1, the review of all available site data, should consider the possibility of using natural attenuation as the remedial option. This focus could lead to a preliminary conceptual model (Step 2) which might, in turn, guide subsequent site characterization to fill in data gaps. Obvious data which should be considered in Step 1 include the nature and extent of the contamination, the timing of the release, and the nature of the contaminant (Wiedemeier et al., 1995b). The nature of the contaminant is particularly important, and a preliminary assessment of natural attenuation pathways based on the history of similar sites should be made early in the process. Standard hydrologic data (potentiometric surface, flow direction, hydraulic conductivity, flow rates, and lithology) should also be assessed in Step 1. An initial determination of pathway and distance to the most likely receptor should also be made.

The preliminary conceptual model is not a computer model, but a 'ballpark' understanding of the site. The development of the preliminary conceptual model (Step 2) requires the integration of the contaminant history, the assessment of biological and geochemical attenuation, the site hydrology data, and the exposure determination.

Step 3 involves filling in the data gaps identified in Steps 1 and 2. In other words, construction of more than a preliminary conceptual model will more than likely be impossible because critical data (e.g., hydraulic conductivities, plume location and geometry) do not exist. Step 3 entails the collection of these data, particularly those that track natural attenuation in the subsurface. Obvious examples of the latter include electron acceptor (and/or methane) concentrations (e.g., O_2, NO_3^-, Fe(III)) pointing to the oxidation of fuel hydrocarbons.

Step 4 is the refining of the conceptual model by filling in the data gaps. To document natural attenuation, Wiedemeier et al. (1995b) highlight the usefulness of contaminant contour maps, electron acceptor, metabolic byproduct, and alkalinity maps. For subsequent refinement of the conceptual model, sorption must be estimated.

In Step 5, to make predictions using models requires rate constants for the relevant breakdown reactions. In other words, it is not sufficient to make the case that biodegradation is occurring at depth. Actual rates are needed to estimate the ultimate lifetime of a plume. Table B.1 compiles a large number of fuel hydrocarbon biodegradation rate constants measured in the lab and the field.

The measurement of degradation rates in the laboratory involves monitoring the breakdown of the contaminant of interest over time in a microcosm and is fairly straightforward. Estimating a degradation rate in the field can be done by a number of different techniques. One can assume that a plume source (NAPL) bleeds off soluble components to remain at equilibrium with groundwater flowing past. In this case a steady-state flux of contaminant can be calculated as the product of the flow rate (liters/m^2day), the cross-sectional area of the zone of contamination (m^2), and the solubility of the contaminant (mol/L), to give a degradation rate in mol/day. If the plume is at steady-state (neither advancing or retreating), the calculated degradation rate is equivalent to the actual degradation rate. If the plume is receding, the calculated degradation rate is less than the actual degradation rate. If the plume is still expanding, the calculated degradation rate is greater than the real degradation rate.

Table B.1 Fuel Hydrocarbon Degradation Rates (from Rifai et al., 1995b)

Site	Contaminant	V (m/d)	Field Results	Lab Results
Borden, Ontario (Barker et al., 1987)	BTX stock solution injected into uncontaminated aquifer	0.09	benz. = 30 mg/d tol. = 37 mg/d *m*-xyl = 47 mg/d *p*-xyl = 55 mg/d *o*-xyl = 33 mg/d	benz. = 58 mg/d tol. = 61 mg/d *m*-xyl = 50 mg/d *p*-xyl = 65 mg/d *o*-xyl = 54 mg/d
Rocky Point, North Carolina (Borden et al., 1994)	residual gasoline from UST	0.08	benz. = 0.0002 /d tol. = 0.0021 /d e-benz. = 0.0015 /d *m,p*-xyl. = 0.0013 /d *o*-xyl. = 0.0021 /d	benz. = 0.0002 /d tol. = 0.0021 /d e-benz. = 0.0015 /d *m,p*-xyl. = 0.0013 /d *o*-xyl. = 0.0021 /d
Kalkaska, Michigan (Chiang et al., 1989)	natural gas condensate-BTEX	0.2	benz. = 0.007 /d *p*-xyl = 0.0107 /d napthalene = 0.0064 /d *o*-DCB = 0.0046 /d	BTX = 0.01 to 0.1 /d
Columbus, MS (MacIntyre et al., 1993)	stock solution of benzene, *p*-xylene, napthalene, *o*-dichlorobenzene			
Sleeping Bear, Michigan (Wilson et al., 1994)	residual gasoline from UST release BTEX	0.2	benz. = not significant tol. = 0.02 - 0.07 /d e-benz. = 0.03 - 0.011 /d *m*-xyl = 0.004 - 0.014 /d *p*-xyl = 0.002 - 0.010 /d *o*-xyl = 0.004 - 0.011 /d	benz. = not significant tol. = 0.007 - 0.04 /d e-benz. = not significant *m,p*-xyl = not significant *o*-xyl = not significant
Indian River, Florida (Kemblowski et al., 1987)	gasoline from UST-BTEX	0-0.4	benz. = 0.0085 /d	benz. = 0.02 to 0.2 /d
Morgan Hill, California (Kemblowski et al., 1987)	gasoline-BTEX	0.05	benz. = 0.0035 /d	
(Wilson et al., 1994)	JP-4 jet fuel	1.3	benz. = below detection tol. = 0.05 to 0.013 /d e-benz. = 0.03 - 0.05 /d *m*-xyl = 0.02 to 0.1 /d *p*-xyl = 0.02 - 0.08 /d *o*-xyl = 0.21 /d	
Hill AFB, Utah (Wiedemeier et al., 1995a)	JP-4 jet fuel	0.5	benz. = 0.03 to 0.09 /d e-benz. = 0.01 to 0.08 /d *m*-xyl = 0 to 0.03 /d *p*-xyl = 0.01 to 0.03 /d *o*-xyl = 0 to 0.02 /d	
Patrick AFB, Florida (Wiedemeier et al., 1995a)	unleaded gasoline from UST	0.13	benz. = 0 to 0.004 /d tol. = 0.0006 - 0.004 /d e-benz. = 0.0001 - 0.004 /d *m*-xyl = 0.0001 - 0.004 /d *p*-xyl = 0.001 - 0.003 /d *o*-xyl = 0.004 - 0.02 /d	

Site	Contaminant	V (m/d)	Field Results	Lab Results
Fairfax, Virginia (Bushcheck et al., 1993)		0.015	benzene = 0.00055 /d tol. = 0.00045 /d e-benz. = 0.00045 /d *m,p,o*-xyl = 0.004 /d	
San Francisco, California (Bushcheck et al., 1993)		0.03	benzene = 0.0028 /d tol. = 0.0022 /d e-benz. = 0.0033 /d *m,p,o*-xyl = 0.0023 /d	
Alameda County, California (Bushcheck et al., 1993)	gasoline-BTEX	0.01	benz. = 0.002 /d tol. = 0.0017 /d e-benz. = 0.002 /d *m,p,o*-xyl = 0.0023 /d	
Elko County, Nevada (Bushcheck et al., 1993)	gasoline-BTEX	0.04	benzene = 0.001 /d	
Traverse City (Wilson et al., 1990)	aviation gasoline from UST-BTEX	1.5	benzene = 0.001 /d tol. = 0.2 /d *m,p,o*-xyl = 0.004 /d	Toluene and ethylbenzene rapidly degraded in denitrifying microcosms after 56 day lag period
Broward Co., Florida (Caldwell et al., 1992)	gasoline from UST-BTEX and MTBE	0.1	BTEX = 0.00012 /d	
Bemidji, Minnesota (Baedecker et al., 1993)	crude oil-BTEX	0.25	toluene and o-xylene depleted over 20 meters (200 day travel time); benzene and e-benzene depleted over 100 meters. Downgradient migration was limited by mixing with uncontaminated water.	98% benzene loss in 125 days and 99% toluene loss in 45 days in anaerobic microcosms
Perth, Australia (Thierrin et al., 1993)	UST-BTEX	0.4	benzene = not significant tol. = 0.006 /d e-benz. = 0.003 /d *m,p*-xyl = 0.004 /d *o*-xyl - 0.006 /d napthalene - 0.004 /d	anaerobic columns with 14 ppm sulfate benz. = not significant tol. = 2.3 /d e-benz. = not significant *o*-xyl = not significant
Manufacturing Plant (Davis et al., 1994)	benzene	0.16	benzene > 0.01 /d	over 90% benzene loss after 77 days under methanogenic and sulfate-reducing conditions

A more precise approach, applicable to plumes of dissolved contaminants which shrink over time, assumes that all contaminant mass loss is due to biodegradation and that contaminant concentrations do not vary vertically. In this model (Bushcheck and Alcantar, 1995);

$$C_{(t)} = C_{(t=0)}\exp[-kt] \qquad (A.1)$$

where C is contaminant concentration (mol/L) at a given time, t (days); and k is the first order rate constant for degradation. Plotting the natural logarithm of $C_{(t)}$, measured at a given location against time, should trace a straight line (if biodegradation is first order, and if the other assumptions are appropriate as well) having a slope of -k, the degradation rate constant.

If the plume is stable, the approach of Kemblowski et al. (1987) may be followed, where x/v (= distance/velocity) is substituted in the equation above for time to give:

$$C_{(x)} = C_{(x=0)}\exp[-kx/v] \tag{A.2}$$

where $C_{(x)}$ is the contaminant concentration at a given distance along the plume axis relative measured from the source, which is at x = 0. $C_{(x=0)}$ is the contaminant concentration at the source. A series of analyses done along the plume axis at a given time, when plotted as $\ln C_{(x)}$ against x, should define a line having a slope of -k/v. Multiplication of the latter term by the groundwater velocity, v, gives the rate constant. Both of the approaches above lump all contaminant loss pathways (sorption, dispersion, and biodegradation) into a degradation rate constant. If biodegradation is the dominant contaminant breakdown process, the k's calculated above correspond to true biodegradation rate constants. On the other hand, if sorption and/or dispersion are significant, the calculated k's will overestimate biodegradation. An alternative approach is to use an exact analytical solution to specifically determine a biodegradation rate from observations of plume morphology. Analytical solutions for one-dimensional transport that permit the estimation of advection, dispersion, sorption and biodegradation are presented by Bushcheck and Alcantar (1995) and Domenico (1987). Perhaps the simplest method for extracting rate constants from field measurements may be to use a computer program, such as BIOSCREEN, to iteratively fit contaminant concentrations measured along the plume axis (for stable or receding plumes). BIOSCREEN will be discussed in greater detail below.

Step 5 of the AFCEE (Wiedemeier et al., 1995b) protocol requires that plume behavior be predicted in space and time. Computationally this involves solving a number of differential equations describing fluid transport and chemical reaction. Numerous sources outline the mathematical underpinnings of reaction transport modeling - see for example (Huyakorn and Pinder, 1983) or (Oelkers et al., 1996). The object of the modeling is to reproduce effectively the chemical and physical behavior of the site from a sufficiently fundamental understanding of the particular processes so that the long-term behavior of the plume might be confidently predicted. A host of site-specific factors, such as hydrologic and biological and geochemical heterogeneities, guarantee that Step 5 will, at best, only roughly approximate reality. If field data have been collected over sufficiently long periods of time, no model is needed to predict the future. Rarely is this the case though, and in the absence of data, a well-calibrated model is the next best substitute.

A model is only as good as its input. Required input includes (Wiedemeier et al., 1995b):

1. Hydraulic conductivity,
2. Initial hydraulic head distribution,
3. Flow direction and gradient,
4. Effective porosity,
5. Coefficient of hydrodynamic dispersion,
6. Coefficient of retardation,
7. Initial solute concentrations,
8. Contaminant source concentration configuration, and rate of source decay/removal,
9. Distribution and continuity of aquifer and aquitards,
10. Groundwater recharge and discharge,
11. Definition of physical and chemical boundary conditions, and
12. Rates of chemical reactions.

The more site-specific the input values are, the more realistic the model output will be. Some of those above will be very difficult to approximate given the general quantity of knowledge at most sites.

A variety of codes have been advanced to perform these calculations. Bioplume II (Rifai et al., 1988) has been used to argue successfully the natural attenuation option for fuel hydrocarbons at a number of sites. One of the more recent computer programs for this purpose is BIOSCREEN (Newell et al., 1996), which, in all likelihood, will be used with increasing frequency in the future to support remediation of organic contaminants by natural attenuation. It therefore deserves some further explanation. BIOSCREEN was generated through collaboration between AFCEE and the R. S. Kerr Environmental Research Center and was intended to be used as a screening tool to specifically determine whether or not a full-scale evaluation of natural attenuation at a large site was warranted or, in the case of smaller sites, as the primary evidence for natural attenuation (Newell et al., 1996). BIOSCREEN can be downloaded from the EPA web site at Ada, Oklahoma - http://www.epa.gov/ada/kerrlab.html. The following summary follows the downloadable documentation. BIOSCREEN, when given inputs of a number of hydrological and geochemical factors (see below), performs a series of calculations to specifically answer:

1. How far will a dissolved contaminant plume extend if no engineered remediation or source reduction is carried out? and
2. How long will the plume persist before natural attenuation processes cause it to dissipate?

The equation BIOSCREEN solves is Domenico's (1987) analytical expression for multi-dimensional transport of a decaying contaminant species. The primary assumptions of the latter are that the aquifer and flow field are homogeneous and isotropic; molecular diffusion is minor and can be neglected; and adsorption can be treated with a linear isotherm (in essence, with a K_d). The spreadsheet calculation requires as input the following hydrologic and geochemical data:

1. Seepage velocity (interstitial groundwater velocity);
2. Hydraulic conductivity;
3. Hydraulic gradient;
4. Effective porosity;
5. Longitudinal, transverse, and vertical dispersivity (BIOSCREEN uses published relationships to calculate these values, given a user estimate of plume length);
6. Retardation factor (If this is unknown, BIOSCREEN calculates it given input values of bulk density, f_{OC}, and, K_{OC});
7. First order decay coefficient (Alternatively, given a half-life $t_{1/2}$, the decay coefficient = $0.693/t_{1/2}$);
8. The respective differences in O_2, NO_3^-, Fe^{++}, SO_4^{2-}, and CH_4 between background and the source area;
9. The model area length and width;
10. Simulation time;
11. Source zone width, thickness, concentration, and soluble mass; and if available,
12. Contaminant measurements from the field to calibrate the model.

Step 6 in the protocol of Wiedemeier et al. (1995b) simply requires that the most likely pathways for exposure be determined under current and reasonable future use scenarios. If natural attenuation is demonstrably effective at minimizing exposure, a long-term monitoring plan should be formulated.

The objective of Step 7 is partly to provide a check on the possibility that uncertainties in the model and characterization have led to an overestimation of the efficacy of natural attenuation. Wiedemeier et al. (1995b) suggest two types of monitoring wells: (1) long-term monitoring wells to determine if the behavior of the plume is changing; and (2) point of compliance (POC) wells to detect contaminant movement outside the negotiated perimeter of containment. The latter might be used to trigger more active remediation, such as pump and treat, to contain the plume. The LTM wells, by their function, should include analyses for contaminant concentrations, and if the latter are organic, likely electron acceptors (and/or methane) as well. POC wells, in the same situation, should sample for contaminant concentrations as well as dissolved oxygen (Wiedemeier et al., 1995b). Sampling frequency will depend on the trend seen in prior sampling. If predicted trends hold, there is less impetus for high frequency sampling.

For fuel hydrocarbons, the argument for natural attenuation relies primarily on three observations (Rifai et al., 1995b):

1. Compound disappearance. Obviously, the best evidence of all is if the contaminant of concern can be shown to be rapidly decreasing in concentration. Generally this requires the comparison of contaminant concentrations to the same for some non-reactive component (e.g., MTBE in a LUFT). Additionally, the differences in the rates tracer and contaminant plume's move can provide evidence of compound disappearance.

2. Loss of electron donors. Depressed electron donor (e.g., O_2, NO_3^-, SO_4^{2-}, etc.) concentrations, relative to a measured background, is good evidence that organic matter is being degraded.

3. Degradation products. Fe^{++}, H_2S, CO_2, and methane are produced during the degradation of fuel hydrocarbons. Elevated concentrations relative to the background also point to degradation.

Appendix C. The AFCEE Protocol for MNA of Chlorinated Organics

Much of the following is abstracted from the review of Brady et al. (1997). The AFCEE protocol for MNA of chlorinated organics emphasizes iterative development of a conceptual model of natural attenuation and stresses assembling multiple lines of evidence for natural attenuation. The three lines of evidence used in the AFCEE protocol for natural attenuation of chlorinated aliphatic hydrocarbons are:

1. Observed reduction in contaminant concentrations along the flow path downgradient from the contaminant source;
2. Documented loss of contaminant mass using geochemical data (e.g., loss of parent compound, appearance of daughter compounds, depletion of electron donors and acceptors, accumulation of metabolic byproducts), or loss measured against the transport of a non-reactive tracer; and
3. Microbiological laboratory data attesting to biodegradation.

According to Wiedemeier et al. (1996), at a minimum, the first and second, or first and third lines of evidence must be obtained. The second and third are used primarily for calculating biodegradation constants. A reduction in contaminant concentrations downgradient might reflect any of a number of processes (adsorption, volatilization, dispersion, biodegradation); hence, the appearance of daughter products, such as vinyl chloride, is a more definite evidence of biodegradation. By the same token, decreasing contaminant concentrations might indicate biodegradation if confirmatory evidence of biodegradation from microcosm studies are observed as well.

Wiedemeier et al. (1996), on the basis of the primary substrate (electron donor), identify four types of chlorinated solvent plumes - Types 1, 2, 3, and mixed. For Type 1 behavior, the primary substrate is anthropogenic carbon, such as BTEX compounds or landfill leachate. Under Type 2 behavior, conditions are generally reducing, and there is rapid breakdown of highly chlorinated solvents. For Type 2, the primary substrate is native organic carbon, and breakdown of the more chlorine-rich organics is somewhat slower. In Type 3 plumes, there is little native or anthropogenic carbon, and the plume is relatively aerobic. In Type 3 plumes, breakdown of the highly chlorinated organics is minimal. Degradation of less chlorinated organics, which are more reduced, is more rapid, assuming they are present in the first place. Single plumes can have areas which fall under each type. This is referred to as mixed behavior. Mixed behavior is important because often the juxtaposition of one type behavior against another hastens the sequential breakdown of oxidized, highly chlorinated compounds (PCE & TCE) to chlorine-poor, relatively reduced daughters (DCE and VC) to CO_2.

The AFCEE protocol is a 9-step approach that is similar to the AFCEE fuel hydrocarbon protocol:

1. Review available site data, and develop a preliminary conceptual model;
2. Screen the site and assess the potential for intrinsic remediation;
3. Collect additional site characterization data to support natural attenuation, as required;
4. Refine the conceptual model, complete pre-modeling calculations, and document indicators of natural attenuation;
5. Simulate intrinsic remediation using analytical or numerical solute fate and transport codes that allow incorporation of a biodegradation term, as necessary;
6. Identify potential receptors, and conduct an exposure pathways analysis;
7. Evaluate the practicability and potential efficiency of supplemental source removal options;
8. If natural attenuation alone is acceptable, prepare long-term monitoring (LTM) plan; and
9. Present findings to regulatory agencies and obtain approval for remediation by natural attenuation.

Step 7, the evaluation of the practicability and potential efficiency of supplemental source removal, is the only step which does not have a corresponding number in the AFCEE fuel hydrocarbon protocol (Appendix B). Because of the correspondence between the two, there will be less emphasis on what each step entails and more on the areas which are specifically different.

Site screening is focused on determining if biodegradation is occurring. If it is, the remaining 5 steps are used to determine: (1) how great a distance separates the contaminant from the nearest receptor; and (2) how rapidly the contaminant is being degraded along the way. The six steps of the screening procedure will be dealt with in turn.

Step 1 determines whether biodegradation is occurring. This involves sampling at least six wells that are representative of the plume (The analytical protocol of Wiedemeier et al. (1996) is listed in Table C.1).

Table C.1 Soil and Groundwater Analytical Protocol (from Wiedemeier et al., 1996)

Matrix	Analysis	Method/ Reference	Comments, Data Use	Frequency	Sample Volume-Container-Preservation	Location
Soil	VOCS	SW8260A	Handbook method modified for field extraction of soil using methanol	Each soil sampling round	Collect 100 g of soil in a glass container with Teflon-lined cap; cool to 4°C	Fixed-base
	TOC	SW9060, modified for soil samples	Procedure must be accurate over the range of 0.5 to 15% TOC	At initial sampling	Collect 100 g of soil in a glass container with Teflon-lined cap; cool to 4°C	Fixed
	O_2, CO_2	Field soil gas analyzer		At initial sampling and respiration testing	Reusable 3-L Tedlar bags	Field
	Fuel and Chlorinated VOCs	EPA Method TO-14		At initial sampling	1 l Summa cannister	Fixed-base
Water	VOCs	SW8260A	Handbook method; analysis may be extended to higher molecular-weight alkylbenzenes	Each sampling round	Collect water samples in a 40 ml VOC analysis vial; cool to 4°C; add hydrochloric acid to pH 2	Fixed-base
	PAHs (optional)	Gas chromatography/ Mass Spectroscopy method SW8310; High performance liquid chromatography method SW8310	Analysis only needed for regulatory compliance	As required by regulations	Collect 1 l of water in a glass container; cool to 4°C	Fixed-base
	Oxygen	DO meter	Refer to method A4500 for a comparable laboratory procedure	Each sampling round	Measure DO on site using a flow-through cell	Field
	Nitrate	Ion chromatography Method E300; anion method	Method E300 is a handbook method; also provides chloride data	Each sampling round	Collect up to 40 ml of water in a glass or plastic container; add H_2SO_4 to pH less than 2; cool to 4°C	Fixed-base
	Iron(II)	Colorimetric HACH Method 8146	Filter if turbid	Each sampling round	Collect 100 ml of water in a glass container	Field
	Sulfate	Ion Chromatography Method E300 or HACH Method 8051	Method E300 is a handbook method. HACH Method 8051 is a colorimetric method; use one or the other	Each sampling round	Collect up to 40 ml of water in a glass or plastic container; cool to 4°C	E300 = Fixed-base HACH Method 8051 = Field
	Methane, ethane, or ethene	(Kampbell et al., 1989)	Method used by EPA researchers	Each sampling round	Collect water samples in 50 ml glass serum bottles with butyl gray/Teflon-lined caps; add H_2SO_4 to pH less than 2; cool to 4°C.	Fixed-base
	Alkalinity	HACH alkalinity test kit model AL AP MG-L		Each sampling round	Collect 100 ml of water in a glass container	Field
	E_H	A2580B		Each sampling round	Collect 100 to 250 ml of water in a glass container	Field
	pH	Field probe with direct reading meter	Field	Each sampling round	Collect 100 to 250 ml of water in a glass or plastic container; analyze immediately	Field

Matrix	Analysis	Method/ Reference	Comments, Data Use	Frequency	Sample Volume-Container-Preservation	Location
	Temperature	Field probe with direct reading meter	Field only	Each sampling round	Collect 100 to 250 ml of water in a plastic container	Field
	Conductivity	E120.1/SW9050, direct reading meter	Protocols/Handbook methods	Each sampling round	Collect 250 ml of water in a glass container	Field
	Chloride	Mercuric nitrate titration A4500 Cl- C	Ion chromatography Method E300; Method SW9050 may also be used	Each sampling round	Collect 250 ml of water in a glass container	Fixed-base
	Chloride (optional; see data use)	HACH chloride test kit MODEL 8-P	Silver nitrate titration	Each sampling round	Collect 100 ml of water in a glass container	Field
	Total organic carbon	SW9060	Laboratory	Each sampling round	Collect 100 ml of water in a glass container	Laboratory

Analyses other than those listed may be required for regulatory compliance.
"SW" refers to the Test Methods for Evaluating Solid Waste, Physical, and Chemical Method (U.S. Environmental Protection Agency, 1986).
"E" refers to Methods for Chemical Analysis of Water and Wastes (U.S. Environmental Protection Agency, 1983).
"HACH" refers to the HACH company catalog.
"A" refers to Standard Methods for the Examination of Water and Wastewater (American Public Health Association, 1992).
"Handbook" refers to the AFCEE handbook to Support the Installation Restoration Program (IRP) Remedial Investigations and Feasibility Studies (RI/FS)(AFCEE, 1993)
"Protocols" refers to the AFCEE Environmental Chemistry Function Installation Restoration Program Analytical Protocols (AFCEE, 1992).

Samples should be taken from the source; downgradient from the source but still in the plume; downgradient from the plume; and upgradient and laterally removed from the plume. Sampling at the source defines the primary electron donor (e.g., BTEX or indigenous soil organics). Sampling along the plume axis from upgradient to downgradient should quantify electron donor/acceptor concentrations, determine any attenuation in contaminant concentrations, define the plume limits, and provide a picture of the background water chemistry. The right hand column of Table C.2 provides a scoring system to make it easier to determine whether biodegradation is occurring.

Table C.2 Analytical Parameters and Weighting for Preliminary Screening

Analyte	Concentration in Most Contaminated Zone	Interpretation	Points Awarded
Oxygen[a]	<0.5 mg/l	Tolerated; suppresses reductive dechlorination at higher concentrations	3
Oxygen[a]	>1 mg/l	Vinyl chloride may be oxidized aerobically - but reductive dechlorination will not occur	-3
Nitrate[a]	< 1 mg/l	May compete with reductive pathway at higher concentrations	2
Iron(II)[a]	> 1 mg/l	Reductive pathway possible	3
Sulfate[a]	< 20 mg/l	May compete with reductive pathway at higher concentrations	2
Sulfide[a]	> 1 mg/l	Reductive pathway possible	3

Analyte	Concentration in Most Contaminated Zone	Interpretation	Points Awarded
Methane[a]	> 0.1 mg/l	Ultimate reductive daughter product	2
	> 1	Vinyl chloride accumulates	3
	< 1	Vinyl chloride oxidizes	
E_H[a]	< 50 mv against Ag/AgCl	Reductive pathway possible	< 50 mv = 1 < -100 mV = 2
pH[a]	5 < pH < 9	Tolerated range for reductive pathway	
DOC	> 20 mg/l	Carbon and energy source; drives dechlorination; can be natural or anthropogenic	2
Temperature[a]	> 20°C	At > 20°C biochemical process is accelerated	1
CO_2	> 2x background	Ultimate oxidative daughter product	1
Alkalinity	> 2x background	Results from interaction of carbon dioxide with aquifer minerals	1
Chloride[a]	> 2x background	Daughter product of organic chlorine	2
H_2	> 1 nm	Reductive pathway possible; vinyl chloride may accumulate	3
	< 1 nm	Vinyl chloride oxidized	
Volatile fatty acids	> 0.1 mg/l	Intermediates resulting from biodegradation of aromatic compounds: carbon and energy source	2
BTEX[a]	> 0.1 mg/l	Carbon and energy source; drives dechlorination	2
PCE[a]		Material released	
TCE[a]		Material released or daughter product of PCE	2[b]
DCE[a]		Material released or daughter product of TCE; if amount of *cis*-1,2-dichloroethene is greater than 80% of total dichloroethene, it is likely a daughter product of TCE	2[b]
Vinyl chloride[a]		Material released or daughter product of dichloroethenes	2[b]
Ethene/Ethane[a]	< 0.1 mg/l	Daughter product of vinyl chloride/ethene	> 0.01 mg/l = 2 > 0.1 = 3
Chloroethane		Daughter product of vinyl chloride under reducing condition	2
1,1,1-Trichloroethane[a]		Material released	
1,1-dichloroethene		Daughter product of TCE or chemical reaction of 1,1,1-trichloroethane	

[a] Required analysis.

[b] Points awarded only if it can be shown that the compound is a daughter product (i.e. not a constituent of the source NAPL).

Table C.3 interprets the points awarded in Table C.2 and indicates if natural attenuation is likely to occur. If the score exceeds 15 in the protocol of Wiedemeier et al. (1996), the next step (Step 2) is moved to (If the score <15, another remedy besides MNA must be considered).

Table C.3 Interpretation of Points Awarded During Screening

Points	Interpretation
0 to 5	Inadequate evidence for biodegradation of chlorinated organics
6 to 14	Limited evidence for biodegradation of chlorinated organics
15 to 20	Adequate evidence for biodegradation of chlorinated organics
> 20	Strong evidence for biodegradation of chlorinated organics

Steps 2 through 5 involve refining the conceptual model to predict attenuation. In Step 2 a number of standard fluid flow and transport parameters (gradient, hydraulic conductivity, porosity, dispersivity, contaminant K_d) are collected for further assessment of contaminant movement. Some of these can be estimated, although it is better to have site-specific values. Step 3 requires identification of nearest receptors. Step 4 involves the estimation of the biodegradation rate constant. Degradation of chlorinated solvents is generally assumed to be described by a first-order rate law. Consequently, rate constants can be calculated by the approaches outlined in Appendix B. Alternatively, BIOSCREEN can be used to estimate a rate constant by trial-and-error fitting of measured values. Step 5 involves using a reaction-transport code to forward model plume migration towards receptors (For this, Wiedemeier et al. (1996) suggest using BIOSCREEN) and to perform a sensitivity analysis of the calculation. If contaminant concentrations are calculated to attenuate to concentrations desired by regulators, the screening procedure is continued to Step 6. If natural attenuation will not reach these concentrations, and there are no data gaps, other remediation methodologies must be considered. If a lack of relevant data prevents a clear assessment, more data must be acquired and Steps 1 through 5 must be repeated.

Step 6 requires that the satisfactory achievement of the screening criteria be scrutinized. Specifically, the consistency between predicted and observed plume movement must be assessed. The likelihood of the contaminant degrading before affecting receptors must be ascertained as well.

The remaining steps (Steps 7 through 9 of the AFCEE protocol) are straightforward and are quite similar to the analogous steps outlined in the AFCEE protocol for natural attenuation of fuel hydrocarbons.

Appendix D. The RTDF Guidance Handbook for MNA of Chlorinated Organics

Much of the following is abstracted from the review of Brady et al. (1997). The RTDF guideline states that natural attenuation should be considered when one or more of the following conditions is present at a site:

1. Natural attenuation processes are observed, or are strongly expected, to be occurring;
2. There are no receptors that are (or will be) adversely impacted or potential receptors in the vicinity of the plume are, or can be, protected;
3. A continuing source that cannot be easily and cost-effectively removed will require a long-term remedial effort;
4. Alternative remedial technologies are not cost-effective or are technically impracticable;
5. Alternative remedial technologies pose added risk by transferring contaminants to other environmental media, spreading contamination, or disrupting adjacent ecosystems; and
6. Minimal disruption of facility operations and infrastructure is desired.

The draft protocol also states that natural attenuation should not be considered when it won't protect human and environmental health and when alternative technologies can more reliably and cost-effectively treat the contaminants to minimize risk.

Of the triggers listed above for the consideration of natural remediation, the first is the most important. Documentation of natural attenuation should rely on one of three lines of evidence (Remediation Technologies Development Forum, 1996):

1. Documented loss of contaminants at the field scale;
2. Presence and distribution of geochemical and biochemical indicators of natural attenuation; and
3. Direct microbiological evidence.

The first generally requires long-term monitoring of contaminant concentrations at a site, whereas the second might rely on the identification of other geochemical indicators such as breakdown products or electron donor/acceptor variation at a site. Chloride, the ultimate product of the breakdown of chlorinated organics, might be used to track degradation in cases where background concentrations are low. As noted in the fuel hydrocarbon breakdown section, alkalinity can be used to track biodegradation. Concentrations of dissolved oxygen and the other common electron acceptors can also be analyzed to point to the redox state of the aquifer. Hydrogen concentrations are probably most useful for unraveling anaerobic conditions. Methane, ethene, and ethane are all breakdown products of chlorinated solvents. Although the first two are not all that common in uncontaminated groundwaters, methane can come from a number of sources (e.g., bacterial fermentation). Consequently, it must be determined by some other test such as stable isotope analysis of the methane carbon.

Microbiological evidence can come in two forms: demonstration that chlorinated solvent degrading microorganisms are present at the site, or that the indigenous bacteria are capable of breaking down chlorinated solvents in a microcosm. Comparison of microbial population densities from the site, and from a non-contaminated control, can also be done to support an active role of microorganisms in degradation. In general, soil microcosms are used to demonstrate that in situ biodegradation of organic contaminants (chlorinated and non-chlorinated) is taking place. In the absence of field results, the degradation rates measured in the lab are occasionally used as input in reaction-transport models to model plume behavior over long periods of time. Again, the emphasis is on the measurement of gross biological and geochemical behavior, not the identification of individual biodegrading microorganisms or the various metabolic pathways (see e.g. Chapelle, 1993). Table D.1 from the RTDF draft protocol outlines four hypothetical contaminant patterns, and then relates them to three specific levels of data collection. The latter data needs are listed in Table D.2.

Table D.1 Common Patterns of Chlorinated Solvent Presence and Distribution and Suggested Data Collection Tier to Support Natural Attenuation (from Remediation Technologies Development Forum, 1996)

Pattern	VOC Presence	VOC Distribution	Attenuation Mechanism(s)	Site Scenario	Data Collection Tier
1	Parent VOCs only, no detectable degradation products	Observed distribution equals expected distribution (based on groundwater transport calculations and modeling)	Physical processes only (dispersion, dilution, sorption, stabilization, volatilization).	Parent chlorinated solvents were released into an aquifer having low organic content.	I
2	Parent VOCs only, no detectable degradation products	Observed distribution does **not** correspond with expected distribution (based on groundwater transport calculations and modeling).	Physical processes, possibly biological or chemical degradation processes that do not produce detectable VOC intermediates (e.g., direct mineralization, aerobic cometabolism, abiotic transformation).	1) Parent chlorinated solvents that can be directly mineralized (e.g., DCM) were released. 2) Parent chlorinated Solvents were released in association with a known co-metabolite (e.g., toluene).	II
3	Parent VOCs and degradation products. Ratio of parent VOC to degradation products is high (e.g., > 10:1)	Observed distribution does **not** correspond with expected distribution (based on groundwater transport calculations and modeling).	Physical, biological, and chemical processes.	Chlorinated solvents were released into an aquifer having high natural organic content or released in association with low levels of co-metabolites.	II
4	Parent VOCs and degradation products. Ratio of parent VOC to degradation products is low (e.g., < 10:1)	Observed distribution does **not** correspond with expected distribution (based on groundwater transport calculations and modeling).	Physical, biological, and chemical processes.	Chlorinated solvents were released as part of a mixed waste containing sewage, simple solvents such as methanol, and/or petroleum	III

VOC - volatile organic compound

Table D.2 Data Collection Tiers for Evaluation and Implementation of Natural Attenuation (from Remediation Technologies Development Forum, 1996)

Parameter	Data Type	Ideal Use, Value Status, and Comments	Method	Data Collection Tier
Area Geology	Topography, soil type, surface water, climate	Provides inferences about natural groundwater flow systems, identify recharge/discharge areas, infiltration rates, evaluation of types of geological deposits in the area which may act as aquifers or aquitards.	Consult published geologic/soil/topographic maps, air photo interpretation, field geological mapping.	I, II, III
Subsurface Geology	Lithology/ Stratigraphy/ Structure	Identify water-bearing units, thicknesses, confined/unconfined aquifers, effect on groundwater flow and direction (anisotropy).	Use published hydrogeologic surveys/maps; Review soil boring/well installation logs; Conduct surface or subsurface geophysics.	I, II, III I, II, III III
Hydrology	Hydraulic conductivity/ permeability	Measure of saturated hydraulic conductivity of the geological matrix. If site is very layered or complex, measure the vertical/horizontal K_h.	Estimate range based on geology. Conduct Pump, slug, or tracer tests. Estimate with grain size analysis. Permeameter test. Downhole flowmeter/dilution test.	I, II, III II, III III III *
	Gradient	Measure of the potential of the fluid to move.	Water table and piezometric surface measurements.	I, II, III
	Porosity	Measure of pore space.	Estimate range based on geology. Measure bulk and particle mass density.	I, II, III *
	Flow field	Estimate direction of groundwater flow.	Water and piezometric contour maps. Downhole flow meter.	I, II, III *
Dispersion/ Sorption	f_{oc}	Fraction of organic carbon; used to estimate the retardation of chemical migration relative to the average linear groundwater velocity.	Estimate or measure f_{oc} in soil samples, estimate from published values, or compare migration of reactive and non-reactive (tracer) chemicals in the groundwater.	I, II, III
	Dispersion	Longitudinal and horizontal dispersion spreads out the chemicals along the flow path.	Estimate based on distribution of chemicals or use tracers	I, II, III
Chemistry	VOCs	Identify parent solvents and degradation products; assess their distribution.	US EPA Method 8240.	I, II, III
	semi VOCs	Selected VOCs (e.g., phenols, cresols, alcohols) may support biodegradation of cVOCs.	US EPA Method 8270, 8015M.	III
	Volatile fatty acids	Can provide information about type of microbial activity, also can act as electron donor.	Standard analytical methods or published modified methods using ion chromatography.	III
	Methane, ethene, ethane, propane, propene	Provides evidence of complete dechlorination. Methane also might form from methanogenic bacteria. Isotope analysis might tell which. Methane, propane, and propene also serve as co-metabolites for aerobic degradation of cVOCs.	Modified analytical methods, GC-FID.	II, III
	TOC/BOD/COD/TPH	Potential availability of general growth substrates.	US EPA Methods 415.1, 405.1, 410.1, 8015M.	II, III
	Alkalinity	Increased levels indicative of carbon dioxide production (mineralization of organic compounds).	US EPA Method 310.1.	

Parameter	Data Type	Ideal Use, Value Status, and Comments	Method	Data Collection Tier
Inorganic/ Physical	Ammonia	Nutrient, evidence of dissimilatory nitrate reduction, and serves as an aerobic co-metabolite.	US EPA Method 350.2.	II, III
	Chloride	Provides evidence of dechlorination, possible use in mass balancing, may serve as conservative tracer. Road salt may interfere with chloride data interpretation.	US EPA Method 300.0.	I, II, III
	Calcium/Potassium	Used with other inorganic parameters to assess the charge balance error and accuracy of the chemical analysis.	US EPA Method 6100.	III
	Conductivity	Used to help assess the representativeness of water samples, and assess well development after installation (sand pack development).	Electrode measurement in the field. Standard electrode.	I, II, III
	Dissolved oxygen	Indicator of aerobic environments, electron acceptor.	Use flow through apparatus to collect representative DO measurements by electrode.	
	Hydrogen	Concentrations in anaerobic environments can be correlated with types of anaerobic activity. Hydrogen may be the limiting factor for complete dechlorination of cVOCs.	Field measurement. Flow through cell equipped with bubble chamber. As groundwater flows past chamber, hydrogen gas will partition into headspace. Headspace sampled with gas-tight syringe and analyzed in the field using GC. Equipment for analysis is not yet widely available. Relationship to dechlorination activity is still unclear and subject to further R & D.	*
	Iron	Nutrient, Fe^{++} indicates activity of iron-reducing bacteria. Fe^{3+} is used as an electron acceptor.	US EPA Method 6010A.	II, III
	Manganese	Nutrient, indicator of iron and manganese-reducing conditions.	US EPA Method 6010.	III
	Nitrate	Used as an electron acceptor by denitrifying bacteria, or is converted to ammonia for assimilation.	US EPA Method 300.0.	II, III
	Nitrite	Produced from nitrate under anaerobic conditions.	US EPA Method 300.0.	II, III
	pH	Measurement of suitability of environment to support wide range of microbial species. Activity tends to be reduced outside of pH range of 5 to 9, and anaerobic microorganisms are typically more sensitive to pH extremes. pH is also used to help assess the representativeness of the water sample taken during the purging of wells.	pH measurements can change rapidly in carbonate systems and during degassing of groundwater. Therefore, pH measurements must be made immediately after sample collection or continuously with a flow through cell.	I, II, III
	Phosphorous	Limiting nutrient.	US EPA Method 300.0	III

Parameter	Data Type	Ideal Use, Value Status, and Comments	Method	Data Collection Tier
	E_H	Measure of oxidation-reduction potential of the environment from +500 mV for aerobic environments to -500 mV for anaerobic environments.	Use flow through apparatus in the field to collect representative redox measurements by electrode. Standard. Redox measurements can be affected by geochemical speciation of organic/inorganic chemical species. The measured redox (using probes) can be confirmed by examining chemical speciation of redox couples.	I, II, III
	Sodium	Check on chloride detected is associated with road salt.	US EPA Method 6010.	III
	Sulfate	Used as an electron acceptor. Changes in its concentration may provide evidence of activities of sulfate-reducing bacteria.	US EPA Method 300.0.	II, III
	Sulphide	May provide evidence of sulfate reduction. May not be detected even if sulfate-reducing bacteria are active because it can react with various oxygenated chemical species and metals.	US EPA Method 376.1.	II, III
	Temperature	Used to help assess the representativeness of water samples and to correct temperature sensitive parameters/measuring devices. Microorganisms are active over a wide temperature range.	Field measurement, standard thermometer.	I, II, III
	Toxic metals	Some (e.g., Pb, Cu, As) can reduce microbial activity. Microorganisms are generally resistant.	US EPA Method 6010.	*
Microbiology	Microorganisms per unit soil or groundwater	Microbial population density between impacted and non-impacted/treated areas can be compared to assess whether microbial populations are responsible for observed degradation. The value of biomass measurements is still being explored for cVOCs.	There are three general techniques available: culturing (plate counts, biolog, MPN enumerations); direct counts (microscopy); and indirect measurement of cellular components (ATP, phospholipid fatty acids).	*
	Biodegradation rate and extent	Demonstrate that indigenous microorganisms are capable of performing the predicted transformations. Determine nutrient requirements and limitations. Measure degradation rates and extent.	Varied. Shake flasks, batch, column, bioreactors designs.	*
	Species/ general/ functional group	The presence of certain microbial species or functional groups (e.g., methanogenic bacteria) that have been correlated to cVOC biodegradation can be assessed.	There are three general techniques available: culturing and direct counts; indirect measurement of cellular components; and molecular techniques (16s RNA, DNA probes, RFLP).	*

* means the parameter is optional depending on site complexity.

The 9-step approach to integrating natural attenuation into the remediation strategy can be downloaded from the world wide web (http://www.icubed.com/rtdf/html/), and will be briefly outlined here.

Step 1 involves a review of the available site data, e.g., results from the RI (remedial investigation), risk assessment, and feasibility study. Further site characterization may be needed, particularly to document natural attenuation at depth. (Protocols for the various steps - e.g., drilling, sample collection, storage, quality assurance, etc. are listed in an appendix which should be downloaded for more specific details.)

Step 2 requires the formulation of a conceptual model for the site from the available data. This is, in effect, a broad-brush understanding of the likely hydrological and geochemical behavior of a site and is used to:

1. Present and explain chemical distributions relative to groundwater flow;
2. Help identify contaminant sources, release mechanisms, transport pathways, and potential receptors; and
3. Identify data gaps.

Step 3 involves an initial screening of data for evidence of natural attenuation and the development of an initial hypothesis to account for natural attenuation. This screening and hypothesis development is done on the basis of documented contaminant mass loss (have parent compound concentrations decreased?), degradation product changes (how prevalent are known degradation products, e.g., DCE and VC? Has the ratio of daughter compound to parent compounds increased over time?), and variation in secondary indicators (do variations in the latter - e.g., chloride, electron acceptor/donor concentrations - favor degradation?). If the answers are positive to any of these questions, natural attenuation is probably occurring, and degradation should be more closely examined (Steps 4 through 9).

In Steps 4 through 9 more data are gathered to refine and then buttress a model to explain natural attenuation in the subsurface. For cases where there is little initial evidence for natural attenuation, there is a subsequent reevaluation in Step 8, the exposure pathways analysis.

In Step 4, the identification of additional data requirements, the conceptual model should be compared against the four hypothetical contamination patterns in Table D.1. The best fit between the conceptual model and Table D.1 will point to the level of data collection required (Table D.2). Sites for data collection should subsequently be selected to test/support the conceptual model. At the same time, microcosm studies should be considered to provide supporting evidence for natural attenuation under the redox conditions similar to those which prevail at the site.

Steps 5 and 6 are refining processes. Step 5 involves further data collection to assure quality and integrity of the data. Step 6 entails a refinement of the conceptual model using the new data gained in Steps 4 and 5. The revised conceptual model should lend itself to the estimation of mass balances for parent and daughter products, as well as intermediates; fluxes of parent and daughter products (and, if possible, electron donors+acceptors and co-metabolites); sorption and retardation of contaminants (from literature or laboratory); biodegradation half-lives or rate constants; and the long-term capacity of the aquifer to sustain natural attenuation. The conceptual model should also lend itself to performing groundwater fate and transport modeling and doing a sensitivity analysis.

Step 7 involves a check to see if the new data fit the original hypothesis developed in Step 3. If they don't, the hypothesis should be refined and retested. If they do, an exposure pathways assessment should be done (Step 8).

In Step 8 the conceptual model is applied to determine if the rates of natural attenuation are sufficiently rapid to decrease human and ecological health risk to acceptable levels. If the answer is yes, then natural attenuation should be considered as a final remedy. If the answer is no, the ability of other engineering controls or technologies to control or further reduce the risk in a cost-effective manner must be examined. If other remedies do reduce the risk sufficiently, they should be implemented. If engineering controls are technically impracticable (e.g., DNAPLs), natural attenuation may be the default risk-reduction mechanism and should be incorporated into any long-term site management strategy (Step 9).

The long-term performance of natural attenuation will depend on adequate numbers of electron donors and electron acceptors existing in the right places. The conceptual model should allow an estimate to be made regarding whether or not the appropriate configuration will exist for the lifetime of the plume. If natural attenuation is predicted to do so, the long-term management strategy should focus on monitoring and process validation to assure that regulatory targets are achieved. If, on the other hand, natural attenuation is predicted to fall short, a cost-benefit analysis should be done between natural attenuation and other potential remedies. Indirect costs might include reduced land values and legal costs.

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Appendix E. Inorganic Reactivity

In this section, the basic chemical characteristics of inorganic contaminants are summarized. Also discussed are their general environmental behavior and their probable responses to changes in soil/aquifer properties. The chemical forms of the probable irreversibly sorbed contaminant phases are discussed with references to the scientific literature, particularly to support examination of irreversible sorption of radionuclides of unique concern to DOE. More detailed examinations of the origins of inorganic reactivity can be found in: Stumm and Morgan (1996) and Rai and Zachara (1984).

Arsenic

Arsenic is common in soils and is found predominately in a sparingly soluble, adsorbed form. Elevated concentrations may appear in natural mineral deposits or from anthropogenic sources - arsenic is used to process glass and was formerly a component of pesticides. Low concentrations of arsenic are found in most fossil fuels (oil, coal, gasoline, and wood); therefore, burning of these materials results in low concentrations of inorganic arsenic emissions into the air. Soil background concentrations are 2.2 to 25 ppm (world) and 3.6 to 8.8 ppm (US) (Kabatas-Pendias and Pendias, 1984).

Arsenic exists in most soils and groundwaters in the +3 (arsenite) and/or the +5 (arsenate) state. Arsenate exists under aerobic conditions. Arsenite exists under anaerobic conditions, and a number of soil microorganisms (and Mn hydroxides) are able to oxidize any available arsenite to arsenate under aerobic conditions. Arsenite typically forms the following aqueous species: $As(OH)_3^o$, $As(OH)_4^-$, $AsO_2(OH)^{2-}$, and AsO_3^{3-}. Arsenate in solution forms AsO_4^{3-} (and its protonated derivatives) and behaves chemically in a fashion similar to phosphate. At $6.9 < pH < 11.5$, $HAsO_4^{2-}$ is the primary species. At $2.2 < pH < 6.9$, $H_2AsO_4^-$ is the primary arsenate species. Sorption of arsenate is greatest at low pH but also depends on the availability of sorbing minerals. High sodium concentrations decrease sorption due to the formation of aqueous Na-arsenate complexes. Arsenite exists as $As(OH)_4^-$ at $pH > 9.3$ and typically sorbs less readily relative to arsenate, yet arsenite is, in general, less soluble.

Clays with high anion exchange capacities are particularly effective at taking up arsenate. Association with organic material, iron, and/or calcium are also important processes that fix arsenic in sparingly soluble forms. Arsenic in water and soil may be reduced and methylated by fungi, yeasts, algae, and bacteria.

Bioconcentration of arsenic occurs in aquatic organisms, primarily in algae and lower invertebrates. Biomagnification in aquatic food chains does not appear to be significant , although some fish and invertebrates contain high concentrations of relatively inert arsenic compounds. Plants may accumulate arsenic via root uptake from soil solution and certain species may accumulate substantial concentrations.

A rise in pH in high iron soil, a drop in pH in lime soil, or a change in redox potential may lead to resolubilization of fixed arsenic. Leaching of arsenic is usually important only in surficial soil. Leaching carries arsenic deeper in sandy soils than in clay or loam soils. Arsenate, initially sorbed to iron (hydr)oxides under aerobic conditions, might be released and transported in groundwaters if a shift to anaerobic conditions were to cause the dissolution of the host phase. However, over time and under anaerobic conditions, the arsenate might convert to less soluble arsenite. The net result would be only a temporary increase in the mobility of the arsenic, followed by a net decrease in availability. Under strongly reducing conditions, microorganisms tend to methylate arsenic to a mobile form.

Barium

Barium occurs naturally in small but widely distributed amounts in the earth's crust. Soil background concentrations are 84-838 ppm (world) and 264-835 ppm (US) (Kabatas-Pendias and Pendias, 1984). The primary source for naturally-occurring barium in water is leaching and eroding of sedimentary rocks. Under natural conditions, barium is stable in the +2 valence state. In aquatic media, barium is likely to precipitate out of solution as a sparingly soluble sulfate, $BaSO_4$ (barite), whenever sulfate is present. From alkaline solutions, $BaCO_3$ (witherite) may also form. Waterborne barium may also adsorb to suspended particulate matter. Barium is somewhat immobile in soils due to ion exchange onto clays and sorption. Relative to the amount of barium found in soils, little is bioconcentrated by plants. To the extent that soil reduction can remove sulfate from soil solution, the former is a concern for the long-term attenuation of Ba.

Cadmium

Chemically, cadmium behaves much like zinc. Although natural sources of cadmium are relatively minor, cadmium is widely distributed in the earth's crust and is commonly found at detectable concentrations in soil, surface water, and groundwater. Soil background concentrations are: 0.06 to 1.1 ppm (world) (Kabatas-Pendias and Pendias, 1984). Cadmium enters the environment to a limited extent from the natural weathering of minerals but to a much greater degree from pollutant inputs. Cadmium is used in plating operations and to make batteries as well as polyvinyl chloride pipe. Cadmium is divalent in soils and forms soluble aqueous complexes with chloride and organic chelates, such as EDTA. Cadmium sorbs strongly to most soils, particularly at high pH. Sorption by iron oxides, clays, and humic substances; precipitation as cadmium sulfide in the presence of sulfide; and precipitation as cadmium carbonate at relatively high alkalinities, all can potentially limit cadmium transport. High soil acidity favors the release of Cd^{++} and its uptake by plants.

Cadmium is not reduced or methylated by microorganisms; however, it is strongly accumulated by all organisms both through food and water. Bioconcentration in the aquatic environment is greater for invertebrates like mollusks and crustaceans, followed by fish and aquatic plants. Cadmium initially sorbed to iron (hydr)oxides under aerobic conditions might be released and transported in groundwaters if a shift to anaerobic conditions were to cause the dissolution of the host phase. As noted earlier, soil acidification would mitigate against immobilization on/in calcium carbonate minerals.

Chromium

Chromium is found in the environment in three valence states: chromium(0), chromium(III), and chromium(VI). The first and the last are produced by industrial processes, particularly coal and oil combustion, in metal plating and through use as a cleaning and antimicrobial agent. Background concentrations in soil are 7-221 ppm (world) and 20-85 ppm (US) (Kabatas-Pendias and Pendias, 1984).

Most of the Cr(III) in surface water is eventually expected to precipitate in sediments. Cr(III) sorbs strongly to soils and forms a sparingly soluble hydroxide that usually limits dissolved Cr concentrations to below drinking water *concentrations. Small amounts of Cr(III) may remain in solution as soluble* complexes. Cr(VI), though, is often quite soluble but tends to be reduced to sparingly soluble Cr(III) by organic matter, as well as by other reducing agents such as iron and sulfur, in soils. Cr(VI) sorbs to soils, although not as strongly as Cr(III) and also forms sparingly soluble Ba compounds. In the pH range of 6 to 9, oxidation of Cr(III) to Cr(VI) is usually slow.

Chromate initially sorbed to iron (hydr)oxides under aerobic conditions might be released and transported in groundwaters if a shift to anaerobic conditions were to cause the dissolution of the host phase. Any shift to a lower E_h would also tend to favor reduction to immobile Cr(III).

Copper

Copper occurs naturally in rock, soil, water, sediment, and air. It also occurs naturally in plants and animals, and it is an essential element for all organisms. Background concentrations are 7 to 221 ppm (world) and 20-85 ppm (US) (Kabatas-Pendias and Pendias, 1984). Copper emissions to the atmosphere occur naturally as wind blown dust resulting from the weathering of rocks and minerals. Additional natural sources of atmospheric copper include volcanic discharge, vegetative decay, forest fires, and sea spray. Anthropogenic sources are mining and manufacturing.

In water, copper exists predominantly as cupric (+2) or cuprous (+1) valence forms and often form hydroxy or carbonate complexes. The primary stable cuprous (+1) forms are the sparingly soluble cuprous sulfide, cuprous cyanide, and mixed-valence copper sulfides. Cupric copper forms sparingly soluble oxides and hydroxides at pH 5 and above. Cupric ion sorption to iron hydroxides and organic matter is also pH-dependent and increases with pH. Copper is most mobile in sandy soils with low pH. In many soils, binding to immobile organic matter limits mobility.

Bioconcentration of copper in terrestrial and aquatic organisms is relatively low. The future use caveats that apply to zinc apply similarly to copper.

Lead

Enrichment of lead in near-surface soils has occurred through airborne deposition from many anthropogenic sources including gasoline and coal combustion. Background concentrations are: 10-84 ppm (world) and 17-26 ppm (US) (Kabatas-Pendias and Pendias, 1984). Lead is also released to land and to surface and subsurface water from ferrous and non-ferrous metal smelting and processing, secondary metal producing, lead battery manufacturing, and pigment and chemical manufacturing.

Lead is generally divalent in soil solutions but forms aqueous complexes with chloride and hydroxyls. Lead hydroxycarbonate solids at greater than neutral pH are thought to limit the solubility of lead. High sulfate concentrations may lead to the formation of lead sulfate minerals under at least mildly oxidizing conditions. Under reducing conditions, and in the presence of high sulfide concentrations, lead sulfide can form and limit aqueous lead concentrations. Lead also forms sparingly soluble phosphate minerals.

A significant fraction of lead carried by surface water is expected to be in an undissolved form, which can consist of colloidal particles or lead compounds incorporated in or on other components of particulate matter from surface runoff. The ratio of lead in suspended solids to lead in dissolved form ranges from 4:1 to 27:1. Most lead in soil is retained there, and typically very little is transported into surface water or groundwater.

Lead does not appear to significantly bioaccumulate in most fish. However, bioaccumulation of tetraethyl lead can occur in aquatic organisms. Plants commonly take up lead from soil and therefore, may cycle it upon their senescence and subsequent decomposition.

Lead initially sorbed to iron (hydr)oxides under aerobic conditions might be released and transported in groundwaters if a shift to anaerobic conditions were to cause the dissolution of the host phase. Anoxic conditions might result from, for example, prolonged waterlogging of the soil. Soil acidification would tend to remobilize any lead carbonate.

Mercury

Mercury occurs naturally as a metallic mineral (quicksilver) or as cinnabar (HgS), which is found in sulfide ores. Mercury is commonly associated with the by-products of complex ore processing that contain sulfide, oxide, and chloride minerals. Soil background concentrations are 20-410 ppb (world) and 40-280 ppb (US) (Kabatas-Pendias and Pendias, 1984). The major use for mercury at present is in mercury-cell chloralkali plants where mercury is relied on to liberate chlorine gas from brines. Mercury has also been used in batteries, lamps, switches, dental amalgrams, measuring devices, control instruments, and laboratory processes and shows up in electrolytic refining waste.

The specific state and form in which the mercury is found in an environmental medium is dependent upon a number of factors, including the redox potential and pH of the medium. The most reduced form of mercury is metallic mercury, which is a liquid at ambient temperatures but readily vaporizes. In soils and surface waters, mercury can exist as mercuric (Hg^{+2}) and mercurous (Hg^{+}) ions. Mercury(II) forms relatively strong complexes with Cl^{-}, OH^{-}, and CO_3^{2-}. In aerobic freshwater the HgOHCl species often predominates (Stumm and Morgan, 1981). Additionally, other Cl^{-} species present under aerobic conditions include $HgCl^{+}$, $HgCl_2$, $HgCl_3^{-}$, and $HgCl_4^{2-}$. Mercury also forms complexes with F^{-}, Br^{-}, I^{-}, SO_4^{2-}, S^{-}, and PO_4^{3-}. Mercury(II) forms strong complexes with sulfhydryl groups, amino acids, humic acids, and fulvic acids.

The solubility of mercury is very high under oxidized aquatic conditions due to its strong complexation with inorganic and organic ligands. Additionally, the solubilities of some mercury solid phases (HgS, HgO, and $HgCl_2$) increase in the presence of humic acids.

Mercury is likewise strongly sorbed to humic materials. Inorganic mercury sorbed to particulate material is not readily desorbed. Thus, freshwater sediments are important repositories for inorganic forms of the compound, and leaching is a relatively insignificant transport process in soils. However, surface runoff is an important mechanism for moving mercury from soil to water, particularly for soils with high humic content.

The most common organic form of mercury, methylmercury, is soluble and mobile and quickly enters aquatic food chains. Methylmercury in surface water is rapidly accumulated by aquatic organisms; concentrations in carnivorous fish at the top of freshwater food chains (e.g., pike) are biomagnified on the order of 10,000 to 100,000 times the concentration found in ambient waters. The biological half-life of methylmercury in mussels is estimated to be 1,000 days. Aquatic macrophytes also have been found to bioconcentrate methylmercury.

Nickel

Nickel is a first-row transition metal, normally present at trace levels in the near-surface terrestrial environment; background concentrations are 4-55 ppm (world) and 13-30 ppm (US) (Kabatas-Pendias and Pendias, 1984). The primary sources of nickel (Ni) contamination are from mining and smelting operations, electroplating, production of alloys and alkaline batteries, and combustion of fossil fuels.

Nickel in the environment exists as +2 valence state. The availability of Ni in soil increases with soil water logging, indicating the importance of iron and manganese hydroxides as contaminant hosts. Thermodynamic calculation indicates that the solubility of Ni in natural waters is controlled by $NiFe_2O_4$ (Hem, 1977). This is supported by the results from Ni over the hydrous iron oxides and goethite surfaces in aqueous suspensions. Ni^{2+} concentrations were controlled by the $NiFe_2O_4$, suggesting the formation of solid $NiFe_2O_4$ in the systems containing iron oxide (Sadiq and Zaidi, 1981). Generally, NiS is the stable nickel solid controlling the solubility of Ni in deep groundwater if sulfur is present. The release of Ni, which was associated with manganese oxides, into groundwater was found due to the excessive Fe^{2+} produced from pyrite reduction when water logging occurs (Larsen and Postma, 1997). In alkaline soils, Ni was irreversibly immobilized and this was attributed to formation of nickel hydroxides in soil (Bowman et al., 1981; Bowman et al., 1982). However, the slower dissolution rate and lower solubility of the precipitates formed on the clay surfaces, as compared to that of crystalline nickel hydroxides, were attributed to the formation of Ni-Al-hydroxides (Scheidegger et al., 1996b).

Ni (as Ni^{2+}) is commonly weakly adsorbed at low pH where competition with protons for adsorption sites and unfavorable electrostatic interactions are stronger than its specific interaction. However, it shows a sharp and strong adsorption edge with increasing pH as the surface becomes negatively charged and protons are less abundant (Ward, 1995). At clay surfaces, e.g., pyrophyllite, following adsorption, Ni forms multinuclear surface complexes though hydrolysis promoted by the clays surface. Formation of the multinuclear surface complexes decreases the aqueous Ni concentration (Scheidegger et al., 1996a; Scheidegger et al., 1996b).

Zinc

Zinc is present in certain minerals, most rocks, and some carbonate sediments. Background concentrations are 17-125 ppm (world) and 34-84 ppm (US) (Kabatas-Pendias and Pendias, 1984). Anthropogenic sources of zinc are mining activities and galvanizing processes. Zinc occurs in soils mainly in the +2 oxidation state. Sorption is the dominant zinc immobilization reaction, and sorption onto hydrous iron and manganese oxides, clay minerals, and organic material leads to the enrichment of zinc in suspended and bed sediments. The stability of zinc surface complexes is pH-dependent, being greatest at high pH. The mobility of zinc under anaerobic conditions is low, possibly due to the formation of sulfide minerals.

Zinc is an essential nutrient that is present in all organisms. Microbial decomposition of biota in water can produce ligands (e.g., humic acids) that can mobilize zinc. Zinc can accumulate in freshwater organisms from 51 to 1130 times the concentration present in the ambient water. Plant species do not generally concentrate zinc above the concentrations present in the soil. Although zinc is actively bioaccumulated in aquatic systems, the biota appear to represent a relatively minor uptake factor compared to the sediments.

Zinc initially sorbed to iron (hydr)oxides under aerobic conditions might be released and transported in groundwaters if a shift to anaerobic conditions were to cause the dissolution of the host phase. Typically, zinc is less mobile under anaerobic conditions.

Radionuclides

Radioactive isotopes of an element have similar environmental and toxicological behavior to the non-radioactive isotopes - the number of protons determines virtually all chemical and physical properties. If introduced into the body by inhalation or ingestion, the chemical properties of the element will determine its ultimate destination in the body. For example, strontium and radium are chemically similar to calcium and tend to deposit on bone surfaces and bone marrow with that element; tritium (hydrogen-3) becomes bound to water molecules and is distributed throughout the body.

The main difference between radioactive and non-radioactive isotopes is that the radioactive isotopes (radionuclides), as they decay to more stable forms, emit *one or more types of ionizing radiation: alpha particles (a helium nucleus comprised* of two protons and two neutrons), beta particles (electrons), and gamma rays. The type and energy level of the emitted radiation is nuclide-specific. The frequency of radiation emission for a given amount of nuclide is defined by half-life: the time required for the initial amount of activity to be reduced by one-half. Half-life is also nuclide-specific.

Longer-lived radionuclides decay slowly and are more persistent in the environment. However, their specific activity, the amount of activity per unit mass, is relatively low. Shorter-lived radionuclides decay more quickly to stable forms, and their specific activity is generally much higher than for those of longer-lived radionuclides. Many radionuclides decay to other radionuclides, which can also provide significant doses, on their way to stable forms. For example, ^{90}Sr decays to ^{90}Y which in turn decays to stable ^{90}Zr. The dose contribution from ^{90}Y is approximately 8% that of ^{90}Sr based on drinking water contaminated with ^{90}Sr.

Compared to metal and stable element contaminants, radioactive contaminants have one inherent and rather significant difference that dominates their behavior in all natural attenuation mechanisms. Even when radioisotopic contaminants are present in soil or groundwater at radiologically extremely hazardous radioactivities (e.g., 10^6 disintegrations per minute (dpm) per mL or cm^3), they have no significant effect on the combined mass concentration of that radioisotope and the natural background of stable isotopes of that element. For example, either of the dominant hazardous fission products, ^{90}Sr and ^{137}Cs, if present in groundwater at 10^6 dpm/mL, would only amount to a mass concentration of about 10^{-9} g/mL. A typical groundwater would exhibit a background of 10^{-5} and 10^{-6} g/mL for the concentrations of, respectively, natural stable isotopic forms of these elements. Strontium-90, at its MCL of 8 pCi/L (0.018 dpm/mL), represents a mass concentration of less than 10^{-16} g/mL. Thus, the chemically reactive behavior of most radioisotopes of an element will be dominated by the concentration of the stable isotopic forms of the element which is usually present at many orders-of-magnitude greater levels. Only in the case of a long-lived radioisotope (e.g., ^{239}Pu, $t_{1/2}$ = 24,000 yr) would an environmentally significant activity, such as the MCL, create any potentially significant impact with its mass concentration of less than 10^{-9} g/mL. In the case of Pu, most other transuranic elements, and Tc, there are no natural background concentrations of these elements because there have no stable isotopes. Their reactive chemistry in soil is analogous to that of similar elements (e.g. the rare earth elements) present in much greater abundance than the radioisotopes.

Although the dissolved chemical behavior of radioactive contaminants will often be determined by the much greater mass concentrations of the corresponding stable isotopes, it should not be expected, indeed it will rarely be the case, that either the dissolved concentration of a radioactive contaminant or its stable isotope will be in equilibrium with many of the solid phases containing that element. For example, stable isotopes of Sr and Cs constitute trace constituents of many mineral phases in soil that have evolved over thousands to millions of years during the soil's formation and weathering. Thus, many elements in structural positions within soil minerals are not in contact and/or equilibrium with the dissolved components in the surrounding groundwater. For any stable element, the ratio of dissolved to total element concentration in soil would be expected to be considerably lower than the corresponding ratio of dissolved to adsorbed radioisotope that could only have entered into the soil weathering process within, at most, the past fifty years. Thus, fractional radioisotopic adsorption in soil should be expected to differ substantially from the fractional stable element adsorption because of the orders-of-magnitude difference in equilibration (reaction) times.

In the following sections an overview of the sources, uses, and potential for natural attenuation is provided for several radionuclides important to DOE environmental remediation. The sections on ^{137}Cs and ^{90}Sr are particularly extensive due to the large contribution of these two contaminants to the DOE environmental remediation task.

Americium-241 (^{241}Am)

Americium-241 is not a naturally occurring radionuclide; no stable isotopes of americium exist. The primary source of ^{241}Am in the environment is associated with the manufacturing of atomic weapons. A commercial use of ^{241}Am is in sealed sources (e.g., smoke detectors). Americium-241 enters the environment from reactor operations and decommissioning, atomic weapons production and when sealed sources containing ^{241}Am are manufactured, used and disposed.

Americium-241 has a half-life of 432.2 yrs. It decays to ^{237}Np ($T_{1/2}$ = 2.14 million yrs) with the emission of an alpha particle and associated gamma and x-rays. Americium exists primarily in the trivalent state. For most soil types (except those with low calcium or sodium concentrations), ^{241}Am is not mobile, and only small quantities can be expected to migrate within the soil to the biosphere. Sorption to carbonate minerals is a known attenuation mechanism (see e.g. Higgo and Rees, 1986; Shanbhag and Morse, 1982). Lower pH values tend to destabilize the carbonate minerals and increase americium mobility.

The main route of uptake for plants is through the roots. The area of concentration of americium in plants may vary with each species, although most seem to collect americium in the root with only a small amount translocating into the shoot. Chelating agents increase transport of americium through the plant. Because ^{241}Am is primarily an alpha emitter, it is most dangerous in humans when it is taken into the body via inhalation or ingestion where it can interact with living tissue. The critical organs of concern in internal exposures are the bone, liver and lung. Biological half-lives are 70,000 days for the bone and total body and 30,000 days for the liver and kidneys.

Cesium-137 (^{137}Cs)

Cesium-137 is not a naturally occurring radionuclide. The primary source of ^{137}Cs in the environment has been radioactive fallout from nuclear weapons testing and accidental releases (e.g., the Windscale accident in 1957 and the Chernobyl accident in 1986).

Cesium-137 has a half-life of 30.2 yrs. Ninety-four percent of the time it decays to metastable ^{137m}Ba ($T_{1/2}$ = 153 s) with the emission of a 514 keV maximum energy beta particle and with no accompanying gamma-ray. The remaining 6% decays directly to stable ^{137}Ba with the emission of a 1176 keV maximum energy beta particle. The ^{137m}Ba nucleus usually (~90%) decays to stable ^{137}Ba with the emission of a 662 keV gamma-ray; the remaining 10% of decays are by low energy electrons. It is the 662 keV gamma-ray emitted by the ^{137m}Ba nucleus that is of most concern from a health perspective.

Cesium belongs to the alkali metals group and therefore, behaves somewhat like lithium, sodium, potassium, or rubidium. In groundwater, dissolved cesium tends to be present in the Cs^+ form. Cesium adsorption to soil and soil minerals is a research topic which has generated many seemingly contradictory conclusions about its general behavior in soil. Much of the apparent conflict results from interpretation of cesium adsorption results under two extreme chemical situations. First, many studies have been carried out within a range of stable elemental Cs concentrations where Cs composes a significant fraction of a soil's or clay mineral's cation exchange sites. Confounding the interpretation of results, many of these studies employ radioactive cesium, often ^{137}Cs, as a tracer for the much larger concentrations of elemental Cs often ranging between 10^{-7} up to 10^{-3} *M* (i.e., about 10 up to 10,000 ppm). At such dissolved concentrations, a soil's or clay's cation exchange sites can be saturated from near 1% up to more than 90% with Cs cations. At such total fractional loadings of the exchange complex, Cs exhibits weak adsorption and is easily exchanged by other common cations (K, Na, Ca, Mg, ammonium (NH_4), Al, and H) in groundwater (Grutter et al., 1986; Khan et al., 1994; Sikalidis et al., 1988). When distribution coefficients for Cs are calculated at such loadings, rather low values are frequently obtained (i.e., <100 mL/g). Thus, the scientific literature is full of such low-K_d values for Cs adsorption to soils, and this literature is frequently cited for examples of the potentially significant environmental mobility of ^{137}Cs. Additionally, the cation exchangeable nature of Cs at such loadings often causes concern for its potential to desorb from soil if chemical inputs to the soil are increased (e.g., fertilizers), particularly those containing chemically similar cations like NH_4 or K.

However, Cs behaves quite differently in soil under a second and more environmentally realistic set of conditions when present at only trace or background concentrations or as a radioactive contaminant (i.e., ^{137}Cs). As discussed previously, when ^{137}Cs is present in soil even at radiologically extremely hazardous levels (e.g., 10^6 dpm/mL), its mass concentration amounts to approximately 10^{-9} g/mL or less than 10^{-8} *M*. Thus, the impact of ^{137}Cs on total Cs loading of the soil's cation exchange sites is insignificant and its adsorptive behavior is much different than that of stable Cs under environmentally perturbed conditions as discussed in the previous paragraph. When Cs adsorption is studied systematically over a wide range (typically six orders of magnitude), the adsorption of Cs at the trace or at pure radioisotope concentrations is found to be much stronger and specific than what is observed at significant soil loadings (Grutter et al., 1986; Khan et al., 1994; Sikalidis et al., 1988). As pointed out by Sikalidis et al. (1988), when ^{137}Cs contaminates soil, the ratio of the radioisotope to the sum of all competing cations in the soil can approach $1{:}10^9$; at such concentrations, they found that vermiculite, a common and ubiquitous soil clay mineral, showed a high affinity for removing ^{137}Cs from solution in the presence of environmentally elevated concentrations of H, NH_4, K, Na, Mg, and/or Ca. Sikalidis et al. (1988) also observed weak and reversible Cs adsorption via typical cation exchange mechanisms at higher fractional loading of these exchange sites. Grutter et al. (1986) found Cs strongly adsorbed at low or trace loadings and strongly fixed against desorption but weakly adsorbed at higher fractional loadings of the cation exchange sites. Khan et al. (1994) observed strong Cs adsorption and high K_d on bentonite as total Cs concentration approached 10^{-7} *M* with about 95% of the Cs irreversibly adsorbed at this low loading. Thus, high K_d values for ^{137}Cs in soil (typically > 1000 mL/g) have been generalized as representative for United State soils (Baes and Sharp, 1983). High K_d values are generally correlated with and are often indicative of strong fixation. Thus, ^{137}Cs as a soil contaminant, when under evaluation for MNA, should be generically assumed to exhibit a high soil K_d and a large irreversibly adsorbed fraction, i.e., > 0.9. Qualification of *MNAToolbox* scores for desorption potential by added fertilizer constituents, particularly K and NH_4, does not seem technically appropriate.

Cesium is taken up by plants and tend to concentrate in the roots, lower part of the foliage, and the veins of the leaves of plants. Uptake by fodder crops is one of the fundamental transfer processes in the animal and human food chain. In the human body, cesium is absorbed almost completely from the gastro-intestinal tract and concentrates, although not strongly retained, mainly in soft tissues and muscles. The biological half-life of ^{137}Cs (the rate that it is removed from the body) is approximately 100 days in adults. Therefore, external exposure to ^{137}Cs from the surface of contaminated soil is typically the pathway providing the greatest dose.

Cobalt-60 (^{60}Co)

The primary source of ^{60}Co in the environment has been low-level radioactive waste material generated as a result of neutron activation of stable ^{59}Co that is present in structural components of nuclear reactor vessels. This isotope is also produced for industrial and medical uses, such as for radiation sources for cancer treatment and nondestructive testing of metals and welds. Cobalt-60 may enter the environment as a result of nuclear reactor operations and decommissioning and when industrial and medical sources are being manufactured, used, or disposed.

Cobalt-60 has a half-life of approximately 5.3 yrs. It decays to stable ^{60}Ni with the emission of a 1480 keV maximum energy beta particle. The high energy gamma rays also emitted during decay (1170 and 1330 keV) means that the radiation from this radionuclide is often the limiting radiation for personnel exposure during reactor maintenance activities. Cobalt is a member of the first transition series of the periodic table, which includes iron, nickel, scandium, titanium, vanadium, chromium, manganese, copper, and zinc. Of these, cobalt behaves most like nickel in the environment. Cobalt exists in two primary oxidation states, +2 and +3, with +2 being the most common. In the +2 oxidation state, cobalt forms hydroxides and sulfide solid phases. Cobalt(II) forms numerous complexes with ammonia and chelate amines as well as EDTA.

In soils cobalt sorbs primarily to iron and manganese oxides. Cobalt in soils is only loosely associated with organic matter; it is easily exchangeable. The association of cobalt with iron oxides is supported by the fact that Co availability to plants goes up in waterlogged soils. To an extent, uptake by iron hydroxides is irreversible. Schultz et al. (1987) observed irreversible laboratory uptake of roughly 35%. Field measurements tend to indicate appreciably greater uptake. In the White Oak Creek watershed in Oak Ridge, Cerling and Spalding (1982) found about 60% of the ^{60}Co strongly bound to the hydrous ferromanganous oxide phase of the streambed sediments.

Research on uptake of ^{60}Co by plants indicates that roots tend to accumulate the greatest fraction of the nuclide. Uptake by plants decreases with increasing pH.

The high gamma radiation strength of ^{60}Co results in relatively large doses due to external exposure to this nuclide. For internal irradiation, the assumed fractional absorption from the gastrointestinal tract of 0.2 is conservatively high and may overestimate the actual value by as much as a factor of 10 in some cases. The inhalation classification is Y (year) for (hydr)oxides, halides and nitrates and W (week) for all others. Cobalt distributes itself relatively uniformly throughout the body except for the liver, which can have higher concentrations. The biological half-life of ^{60}Co in the body is 9.5 days.

Iodine-129 (^{129}I)

Iodine-129 is not a naturally occurring radionuclide. It is generated in nuclear power plants as a fission product. In nuclear reactors, ^{129}I is found in wastes from a wide range of processes, including ion-exchange resins, filter sludges, evaporator bottoms, off-gas cartridge filters, trash, and decommissioning wastes.

Iodine-129 has a half-life of 16 million yrs. It decays to stable ^{129}Xe with the emission of a 150 keV maximum energy beta particle. Twenty-three isotopes of iodine exist; the only stable species is ^{127}I. Because of the latter, there is typically a significant isotopic dilution of radioiodine in many natural systems.

Iodine exists in oxidation states ranging from +7 to -1. The three most common oxidation states are 0 (elemental iodine, I_2), -1 (iodide, I^-) and +5 (iodate, IO_3^-).

In soils, iodine is present mainly as iodide. However, if soils turn more arid and alkaline, the concentration of iodate will increase and then predominate. Organic fixation of iodide and iodate in soil appears to retard the migration of ^{129}I. Soils containing clays have some small ability to sorb iodide and iodate because of aluminum and iron coating on the particles. Iodide adheres strongly to metal sulfides, such as HgS and CuS (Balsley et al., 1996; Zhuang et al., 1995).

The iodine concentration in plants and soils are directly correlated in the early stages of plant development. Later, the concentration is higher in the aerial regions of the plant because of folar uptake. Starchy food products are lower in iodine concentration than leafy shoots, showing that mobility of iodine in phloem is restricted. Radiation doses resulting from external exposure of ^{129}I is negligible because the emitted beta particle is weak. Inhalation of volatile forms is a health concern. Iodide moves relatively quickly to the thyroid gland. The health consequences of ingested ^{129}I depends on the solubility of the form ingested. The most important ingestion pathway for humans is the air-vegetable-cow-milk pathway, especially for children and infants. Accumulation in the thyroid occurs largely within the first twelve hours. The biological half-life of ^{129}I is approximately 100 days for the thyroid, 14 days for the bone, and 7 days for the kidney, spleen and reproductive organs.

Plutonium

Except for trace quantities of plutonium in pitchblende and small amounts produced in natural reactors (e.g., the Oklo natural reactor in Gabon), plutonium does not exist as a naturally occurring element. Significant quantities of plutonium have been released into the environment, primarily as radioactive fallout from nuclear weapons testing and accidental releases (e.g., again, the Windscale accident in 1957 and the Chernobyl accident in 1986). Fifteen isotopes of plutonium are known to exist; the three most common ones are ^{239}Pu (~94%), ^{240}Pu (~6%), ^{241}Pu (0.4%).

Plutonium-239 has a half-life of 24,000 yrs. It decays to ^{235}U ($T_{1/2}$ = 700 million yrs) with the emission of an alpha particle. Due to the long half-life of ^{235}U, remaining isotopes in the decay chain are not significant to dose. Plutonium-240 has a half-life of 6560 yrs. It decays to ^{236}U ($T_{1/2}$ = 20 million yrs) with the emission of an alpha particle. Due to the long half-life of ^{236}U, remaining isotopes in the decay chain are not significant to dose. Plutonium-241 has a half-life of 14.4 yrs. It decays to ^{241}Am ($T_{1/2}$ = 433 yrs) with the emission of a beta particle. Americium-241 subsequently decays to ^{237}Np ($T_{1/2}$ = 2.14 million yrs) with the emission of an alpha particle. Due to the long half-life of ^{237}Np, remaining isotopes in the decay chain are typically not significant to dose. Because ^{241}Pu is difficult to measure and ^{239}Pu and ^{240}Pu cannot be radiometrically differentiated, only total plutonium (^{239}Pu + ^{240}Pu) is usually reported.

Plutonium has four possible oxidation states (i.e., +3, +4, +5, and +6) and can exist in any of these in aqueous solutions. The +4 state is the most stable one in soils, and plutonium in this form sorbs to iron hydroxides and forms sparingly soluble hydroxides as well. Plutonium mobility in soils appears to depend on pH, clay content, the presence of calcium carbonate, and organic matter. Microbial activity may also enhance the movement of plutonium.

Most research on plant uptake concludes that the majority of plutonium found in native plants and agricultural crops comes from surface contamination rather than soil-plant uptake via the roots. Root absorption does occur; however, translocation to the aboveground portion of the plant is limited to less than 0.01% of the total plutonium concentrations in the soil.

In the human body, most ingested plutonium is eventually deposited in the skeleton and the liver, where it tends to be immobile (biological half-lives of 84 yrs and 73 yrs, respectively). Because the alpha particles emitted by plutonium can cause significant damage to the lung tissue, inhalation of airborne particles can be a significant pathway for human exposure to plutonium. Plutonium is extremely toxic because of the relatively short half-life and the fact that all the energy from the alpha particles produced by decay is absorbed in a very short distance..

Radium

Radium exists as ^{226}Ra and ^{228}Ra. The half-life of ^{226}Ra, a daughter product of ^{238}U, is 1600 years. Radium is often found in waters draining uranium-bearing rocks. The MCL for total radium (^{226}Ra + ^{228}Ra) is 5 pCi/L. Radium exists in natural waters typically as a large, divalent cation. Ra behaves similarly to barium or calcium and may form aqueous complexes with sulfate ions or, to a lesser extent, carbonate ions. Ra does not sorb strongly to mineral surfaces but does tend to go onto exchange sites on clays.

Strontium-90 (^{90}Sr)

Strontium-90 is not a naturally occurring radionuclide. It is created as a fission product in nuclear reactors, is contained in spent fuel, and exists in wastes from reprocessing fuel and other activities employing fission products. The primary source of ^{90}Sr in the environment has been radioactive fallout from nuclear weapons testing and accidental releases (e.g., the Windscale accident in 1957 and the Chernobyl accident in 1986). However, radioactive releases from nuclear power plants, propulsion reactors (submarines), and intentional radioactive waste disposal in the oceans all contribute to the background inventory of man-made radioactive isotopes, including ^{90}Sr.

Strontium-90 has a half-life of approximately 29 yrs. It decays to Yttrium-90 (^{90}Y) ($T_{1/2}$ = 64 h) with the emission of a 546 keV maximum energy beta particle and with no accompanying gamma-ray. The ^{90}Y nucleus usually (~99.98%) decays to stable ^{90}Zr with the emission of a 2284 keV maximum energy beta particle. Infrequently (~0.02%), the ^{90}Y nucleus emits a 523 keV maximum energy beta particle and produces a 1750 keV gamma-ray.

When in the soluble form, strontium can be taken up by plants through their roots, which is the principal pathway into the food chain. Being a chemical isomorph for calcium in biogenic material like bone, strontium tends to accumulate in the bone and bone marrow. Because ^{90}Sr is an abundant and ubiquitous radioactive contaminant in nuclear waste, because it is one of the radiologically most toxic contaminants, and because it is one of the more mobile radionuclides in soil and groundwater, the following detailed review of research findings on its potential for adsorption and fixation in soil is warranted. Given a normal mixture of radionuclides in low-level nuclear waste, ^{90}Sr is likely to dominate calculated environmental and human health risks at many sites and, thus, to exert the most constraint on the selection of remedial actions. A median value for soil K_d for Sr, as representative of United States soils, equal to only 27 mL/g has been proposed (Baes and Sharp, 1983).

Much of the early research on speciation and behavior of radiostrontium in soil was reviewed rather thoroughly by Francis (1978) and is summarized here. Most of this review considered research motivated by the potential consequences of atmospheric fallout from above-ground nuclear weapons testing and disposal of liquid radioactive wastes to ground up to the late 1960's. Early investigations by Klechkovskii et al. (1958) and by Schulz, Overstreet, and Babcock (1958) indicated that radiostrontium added to the soil in a water-soluble form became associated with the soil-exchange complex. Since the radionuclide could be readily displaced from the soil by other cations, it was considered to be essentially completely available to plants growing in the soil. In twenty-six strontium-contaminated California soils having a wide range of physical and chemical characteristics (Schulz et al., 1958), no evidence of strontium fixation was observed after drying at 50 or 110°C and extracting with 1 *N* $CaC1_2$ or 1 *N* ammonium acetate {NH_4OAc}. These two extracting solutions were equally effective in removing radiostrontium, except for the case of the noncalcareous soils, where the calcium chloride removed slightly more radiostrontium than did the ammonium acetate. Although the removal by both extractants was not complete, using one part of soil to five parts of extracting solution removed an amount the authors calculated was predicted by the Vanselow cation exchange equation. Other experiments conducted to ascertain the degree of fixation in soils and extractability from soils of various fission products (^{90}Sr, ^{106}Ru, ^{91}Y, ^{137}Cs, and ^{144}Ce) revealed that nonexchangeable radiostrontium was present in the soil as a smaller fraction than those of any of the other radionuclides (Nishita et al., 1956). When nonextractable forms of radiostrontium were added, they were slowly converted to exchangeable forms, which manifested a significant water soluble fraction.

Libby (1958) suggested that, with the passage of time, radiostrontium deposited on soils would become fixed in a nonexchangeable form. Libby further postulated that these nonexchangeable soil reaction products would result in the radiostrontium being less available to plants than water-soluble or exchangeable soil radiostrontium. It was a widely accepted hypothesis that radiostrontium was adsorbed onto and/or coprecipitated by various soil carbonates, mostly calcium and sodium, in neutral, alkaline, and saline soils (Flocker and Fuller, 1956; Kulikov et al., 1970; Menzel et al., 1968; Mokady and Gal, 1964; Schulz and Riedel, 1961; Varga and Jacobs, 1970). Other hypotheses concerning nonexchangeable radiostrontium soil mechanisms were advocated including:

1. The formation of sparingly soluble strontium phosphates, silicates, and sulfates (Ames et al., 1958; Andersen, 1965; Dev, 1965; Evans and Dekker, 1965; Frere, 1962; Gregors-Hansen, 1964; Gulyakin, 1963; Kvaratskhelia and Arnautov, 1967; Mel'nikova and Kudelya, 1966; Skadchenko, 1964; Skadchenko, 1968).

2. The irreversible adsorption of radiostrontium onto iron and aluminum sesquioxides (Frere and Champion, 1967; Tamura, 1964; Tamura and Stuxness, 1963).

3. The substitution of radiostrontium for calcium in calcium-bearing minerals including carbonates and phosphates (Gulyakin et al., 1966; Heald, 1960; Nishita and Haug, 1971; Nishita et al., 1968).

4. The occlusion of radiostrontium by soil organic matter (Taylor, 1968).

5. The diffusion of radiostrontium into interlayered clay minerals (Roberts and Menzel, 1961).

Evidence for Nonexchangeable Radiostrontium

The influence of aging on the fixation of soil radiostrontium into nonexchangeable forms was evaluated by Schulz and Riedel (1961). Three soils, a Hanford very fine sandy loam (a slightly alkaline soil containing traces of calcium carbonate) and a Columbia very fine sandy loam and a Yorkville loam (two acid soils), were contaminated with carrier-free ^{90}Sr. Extractions of the three soils were made 2.5 and 3.5 yrs after contamination and were compared with extractions made one week after contamination. The extraction procedure used was rather vigorous: a 25-g soil sample was mixed with 100 mL of one of the extracting reagents (1*N* solutions of $CaCl_2$, $SrCl_2$, and NH_4OAc adjusted to pH 7), and the resulting suspension was heated for 2 hr on a steam bath before filtering. In the soil that contained traces of calcium carbonate, the first extraction by each of the three extractants removed about 5% less radiostrontium from the aged samples than from the freshly contaminated samples. Since this was not observed in the extractions from the acidic soils, the possible retention of radiostrontium either on (occluded) or in (coprecipitated) calcium carbonate crystals was hypothesized. For all three soils, a small degree of radiostrontium fixation was observed (less than 10% of the total applied), which, according to the investigators, was caused by adsorption of radiostrontium onto solid-phase carbonates or phosphates.

Mokady and Gal (1964) further demonstrated the strontium removal by calcium carbonate in soils: X-ray-diffraction patterns of calcareous soil samples showed the disappearance of calcium carbonate and the appearance of strontium carbonate after the addition of 0.01*N* $SrCl_2$ solutions. Other work has shown that, after 4 yrs under field conditions, only 90% of the ^{90}Sr added to the soil could be displaced by repeated acidic ammonium acetate (pH 4.6) extractions (Wiklander, 1964). Because higher radiostrontium fixation occurred in limed than in unlimed soils, this fixation was postulated to result from either the isomorphic substitution of strontium for calcium or the adsorption of strontium onto calcium-bearing minerals.

It has also been observed that slightly less radiostrontium could be extracted with 0.01*N* $CaC1_2$ from five soils, aged 3.5 yrs after contamination, than from soils freshly contaminated with ^{90}Sr (Squire, 1960). Furthermore, this trend was continued after repeated extractions with boiling 8*M* nitric acid. The reaction mechanism responsible was not established, however, because the quantity of radiostrontium retained was small (less than 10%). Thus, it was concluded that such a mechanism would have little effect on either the movement of radiostrontium in soil or its uptake by plants.

Radiostrontium was completely removed from four calcareous Arizona soils by continued extraction (Arizona Agricultural Experiment Station, 1964). The first extraction with 1*N* $CaCl_2$ removed 96 to 98% of the added radiostrontium, and the second and third extractions removed the residual radiostrontium. When the soils were extracted with 1*N* NH_4OAc buffered at pH 8.3, 80 to 90% of the radionuclide was removed, regardless of the length of time of contaminant contact. These experiments demonstrated that the radiostrontium reaction products in these calcareous soils were rapidly destroyed by highly ionic extraction solutions. In most calcareous soils the fraction of total radiostrontium not exchangeable was considerably less than 10%.

Investigations revealed that as much as 50% of the ^{90}Sr in some acidic Atlantic Coastal Plain soils of the southeastern United States was not present in readily exchangeable forms (Roberts and Menzel, 1961; Taylor, 1968). Soil samples equilibrated for 40 days with solutions of carrier-free ^{85}Sr did not immediately release their radiostrontium when extracted with 1 *N* $SrCl_2$, but, after the samples were suspended in 1 *N* $SrCl_2$ for 4 weeks, essentially complete isotopic equilibrium was reached. After the readily exchangeable radioactive strontium was removed, the residual radiostrontium could be removed only with time, not with agitation or replacement of the extracting cation. Therefore the term "occluded strontium" appears to be a better description of the soil strontium reaction product than the term "fixed strontium." When ^{85}Sr-contaminated soils were extracted with sodium, calcium, or strontium nitrate solutions, Taylor (1968) found that the sodium salt solution extracted much greater amounts of strontium than did the other salt solutions. Because sodium is a much less efficient exchanging ion than either calcium or strontium, the desorption would not seem to be controlled by conventional cation exchange equilibria; the enhanced desorption probably resulted from the increased particle dispersion characteristic of sodium-saturated suspensions.

Additional experiments (Taylor, 1968) indicated that the release of the occluded strontium resulted from the slow diffusion of radiostrontium through a matrix of soil organic matter. Supporting evidence for this hypothesis that organic matter played an important role in the retention of radiostrontium was the fact that the amount of occluded radiostrontium was reduced to a very small fraction after the removal of the organic matter by hydrogen peroxide. The assumption that the removal of the occluded radiostrontium resulted from the removal of the soil organic matter is not unambiguous, however, because the destruction of the soil organic matter by hydrogen peroxide was carried out in a slightly acidic medium under elevated temperatures. Weakly acidic solutions are also known to extract considerable quantities of slowly exchangeable aluminum from soils similar to the acidic soils used by Taylor (1968), which contained predominantly kaolinite and vermiculite clay minerals. The vermiculite-chlorite intergrade minerals in these soils have significant amounts of slowly exchangeable aluminum within their interlayer regions. Conceivably, the occluded radiostrontium reported by Taylor (1968) resulted from the strontium that had diffused into the interlayers of the vermiculite clay mineral. The removal of the occluded strontium depends on the diffusion rates around the aluminum containing "gibbsite islands" (Jackson, 1964), which have become an inherent part of these chloritized vermiculites.

Frere and Champion (1967) anticipated a similar reaction and tried to simulate the fixation of strontium by sesquioxide gel-kaolinite clay systems prepared under laboratory conditions. The strontium-fixation capacity of these suspensions was very low, particularly under acid conditions and with aging. Roberts and Menzel (1961) concluded that such fixation was not likely to be the dominant process involved in the strontium fixation observed in some of the acidic soils of the southeastern United States coastal plain. However, the unsuccessful confirmation of a strontium-fixation product in a sesquioxide gel-kaolinite system is not inconsistent with the existence of the previously mentioned process of radiostrontium diffusion into the interlayer regions of vermiculite-chlorite intergrade minerals.

At the Oak Ridge site, a variety of research on the speciation and extractability of radiostrontium from soils and sediments has been carried out over the years. In a sampling of streambed sediments in the White Oak Creek watershed (which receives many point and diffuse discharges for ORNL's reactors, waste disposal sites, and radiochemical processing facilities), selective extraction was employed by Cerling and Spalding (1982) to determine the form of the three major radionuclides, ^{90}Sr, ^{137}Cs, and ^{60}Co. Warm 1*N* NaCl or NH4OAC were found to remove 80-90% of the ^{90}Sr from these sediments, whereas hot 8*N* nitric acid was required for its quantitative extraction. Thus, Cerling and Spalding (1982) concluded that the majority of the ^{90}Sr was present in the sediments as a weakly adsorbed exchangeable cation, although a minor but significant fraction was fixed in the sediment. Examination of 16 soils contaminated with ^{90}Sr and surrounding waste burial trenches at ORNL revealed that an average of 10% of the ^{90}Sr was fixed: it required three extractions with hot 8*N* nitric acid following previous extractions with 1*M* KCl and 0.1*N* HCl for its removal (Spalding, 1985). Of particular note in this investigation was the strong fixation of ^{90}Sr as a coprecipitant with $CaCO_3$ when groundwater conditions were, or were adjusted to, a supersaturated condition with respect to calcite. In subsequent investigations to attempt to increase the fixation of ^{90}Sr in solid phases of ORNL soils, supplemental additions of carbonate, phosphate, and fluoride were observed to significantly decrease the leachability of ^{85}Sr from soil columns (Spalding, 1981a). In acid (pH<5) soils, additional supplements of Ca were required to form a sufficient calcium mineral phase to immobilize more than 10-20% of the contaminating ^{85}Sr (Browman and Spalding, 1984). The almost identical behavior of radiostrontium and calcium in ORNL soils and in precipitated calcium phases in soil had been previously established observing the identical behavior of ^{45}Ca and ^{85}Sr tracers (Spalding, 1981b). Thus, fixation of a significant fraction (10-20%) of ^{90}Sr appears to arise naturally in contaminated ORNL soil and sediments, and under calcite precipitating conditions even greater fractions of ^{90}Sr contamination can be expected to be irreversibly adsorbed/precipitated in these soils.

Technetium-99 (^{99}Tc)

Technetium-99 is not a naturally occurring radionuclide; there are no stable isotopes of technetium nor are there common elements with a similar enough chemistry that ^{99}Tc can follow as a trace constituent. It is generated in nuclear power plants as a fission product and in medical laboratories and academic institutions. In nuclear reactors, ^{99}Tc is found in wastes from a wide range of processes, including ion-exchange resins, filter sludges, evaporator bottoms, cartridge filters, trash, and decommissioning wastes.

Technetium-99 has a half-life of 213,000 yrs. It decays to stable ^{99}Ru with the emission of a 293 keV maximum energy beta particle. The majority of technetium is generated as ^{99m}Tc from decay of the ^{99}Mo fission product. This metastable form ($T_{1/2} = 6$ h) decays to ^{99}Tc with the emission of a 140 keV gamma-ray.

Oxidation-reduction reactions dominate the chemistry of ^{99}Tc. It exists in eight oxidation states ranging in charges from +7 to -1. The two most common oxidation states are +7 and +4. The pertechnetate ion (TcO_4^-) is the dominant chemical form of dissolved Tc(VII) and total technetium in the environment. The anionic pertechnetate does not form complexes with chelating agents nor does it co-precipitate with particles unless it is first reduced to a lower valence state such as Tc(IV), which precipitates solids such as TcO_2 or $TcO_2 \cdot 2H_2O$. As the redox potential decreases, TcO_2 becomes the dominant solubility control for dissolved technetium. TcO_2 is typically sparingly soluble in water (the formation of Tc(VI)-CO_3 complexes may have some role in solubility and transport). Under reducing conditions, TcS_2 may form as well.

Under oxidizing soil conditions, the pertechnetate ion is very mobile (up to 90% of groundwater velocity). If sufficient reducing conditions exist, the pertechnetate ion will be reduced to a sparingly soluble oxidation state. Reduced species are readily adsorbed by soil constituents or form complexes with organic matter and become fixed to the soil. Reduced forms of technetium may not be likely to reoxidize under normal conditions.

As noted elsewhere, pertechnetate sorbs sparingly. The majority of ^{99}Tc found in plant tissue is in the form of the pertechnetate ion. The greatest concentration of the pertechnetate ion occurs in the older tissues of the plant.

Radiation doses resulting from external exposure of ^{99}Tc are negligible because the emitted beta particle is quite weak. Ingested ^{99}Tc localizes in the thyroid gland and the gastrointestinal tract. Within 10 hours, it redistributes to the stomach and organs with excretory functions. Its biological half-life in the body is approximately 60 hours.

Because there are very few natural attenuation mechanisms for technetium, future land use changes are less important than they are for other contaminants. Nevertheless, if technetium is retarded due to reduction processes, as in a wetland environment, a subsequent return to oxidizing conditions in the soil should be avoided.

Thorium

Thorium occurs in thorite and in thorianite. Thorium is about three times as abundant as uranium and about as abundant as lead or molybdenum. Thorium is recovered commercially from the mineral monazite, which contains from 3 to 9% ThO_2, along with rare-earth minerals.

Twenty-five isotopes of thorium are known with atomic masses ranging from 212 to 236. All are unstable. ^{232}Th occurs naturally and has a half-life of 1.4×10^{10} yrs. It is an alpha emitter. ^{232}Th goes through six alpha and four beta decay steps before becoming the stable isotope ^{208}Pb. ^{232}Th is sufficiently radioactive to expose a photographic plate in a few hours. Thorium disintegrates with the production of "thoron" (^{220}Rn), which is an alpha emitter and presents a radiation hazard.

Solubility of hydrous thorium (IV) oxides, the dominant forms of thorium (IV) in aqueous environment, decreases with increasing pH. At low pH, pH < 3, numerous mononuclear and polynuclear hydrolysis species are reported, including $ThOH^{3+}$, $Th(OH)_2^{2+}$, $Th_2(OH)_2^{6+}$, $Th_4(OH)_8^{8+}$, $Th_4(OH)_{12}^{4+}$, and $Th_6(OH)_{15}^{9+}$, but the mononuclear species in particular are usually relatively minor species in the solution. At higher pH values, the hydrous oxides precipitate, and dissolved Th concentrations decrease rapidly. In this higher-pH region, the dissolved Th concentrations are very low, and only the unhydrolyzed Th^{4+} ion and/or mononuclear hydrolysis species ($ThOH^{3+}$, $Th(OH)_2^{2+}$) are expected to be important (Felmy et al., 1984; Fuger, 1992).

Thorium is assumed immobile in the aqueous environment due to the low solubility of thorianite and the high particle reactivity of thorium. Th concentrations may become elevated due to formation of Th-carbonate complexes (see e.g., LaFlamme and Murray, 1987).

Tritium (^{3}H)

Tritium is naturally produced in very small quantities by the interaction of cosmic rays with atoms and molecules of the upper atmosphere. Although it is constantly created throughout the atmosphere, its relatively short half-life (12.3 yrs) results only in very low natural terrestrial concentrations. The primary source of tritium in the environment has been radioactive fallout from testing of thermonuclear weapons (i.e., hydrogen bombs) and discharges from nuclear power plants. Tritium is also used in industrial thickness gauges, luminous paints, non-powered (self-luminous) light sources, fusion research, as a radioactive tracer in chemistry and biological experiments, and in production of nuclear weapons.

Tritium decays to stable ^{3}He by emission of a weak beta particle and no gamma ray. The energy of the beta particle (18.6 keV maximum) is the lowest known. Chemically, tritium behaves like ordinary hydrogen. However, due to its higher mass, many of its reactions take place at a slower rate. Besides being found in water, along with water containing normal hydrogen and deuterium, tritium may exist in minerals such as mica that contain water of hydration.

In soil and groundwater, tritium ultimately exists as a tritiated water molecule. Theoretically, tritium ions are capable of exchanging with ordinary hydrogen ions and other ions in the soil. However, tritium is usually in an aqueous solution before contacting soils, so the most common mechanism of tritium incorporation is isotopic exchange with water molecules. Most field studies indicate that tritium K_d values are very low - tritium migration velocities are close to those of the accompanying groundwater. Tritium breakthrough curves lag only slightly behind that for chloride ion breakthrough curves in soils containing clays and silts.

Under most circumstances tritium uptake by plants would be expected to make a negligible contribution to the dose to man. Due to its low beta energy level, and thus high MCL (20,000 pCi/L), external radiation from tritium is a negligible hazard to man. The biological half-life of tritium in the human body is ~12 days. Ingested tritiated water is assumed to be completely absorbed from the gastrointestinal tract, mixing rapidly with body water.

Uranium

Uranium is a naturally occurring element consisting of three isotopes, ^{234}U (0.0057%), ^{235}U (0.71%), and ^{238}U (99.3%). The primary isotope of interest for nuclear reactors and nuclear weapons is the fissile ^{235}U; therefore, the uranium remaining after separation of this isotope, primarily ^{238}U, is frequently called depleted uranium (DU). Anthropogenic sources of uranium include mine and mill tailings, DU from the enrichment processes, and spent fuel from nuclear reactor. Because uranium in recovered fuel is reprocessed, the resulting radioactive waste contains little uranium.

Uranium-234 has a half-life of 250,000 yrs. It decays through a series of radionuclides to stable ^{206}Pb, emitting alpha and beta particles and gamma rays. ^{222}Rn ($T_{1/2} = 3.8$ days) is one of the radionuclides of concern in the decay chain because it is a gas that can easily enter the lungs. Uranium-235 has a half-life of 700 million yrs. It decays through a series of radionuclides to stable ^{207}Pb, emitting alpha and beta particles and gamma rays. Uranium-238 has a half-life of 4.5 billion yrs. Like ^{234}U, it decays through a series of radionuclides to stable ^{206}Pb, emitting alpha and beta particles and gamma rays. Note again that the MCL for U is 20 ppb.

Uranium speciation is complex because uranium can exist in the IV, V, and VI valence state. U(IV) and U(VI) are the most likely valence states and are present in reducing and oxidizing conditions, respectively. Primary dissolved U(IV) species include: U^{++++}, UOH^{+++}, and $U(OH)_4^{o}$. In carbonate-free solutions, primary dissolved U(VI) species include UO_2^{++} (uranyl ion), UO_2H^{+}, $(UO_2)_3(OH)_5^{+}$, and $(UO_2)_3(OH)_7^{-}$. Typically, carbonate levels of natural solutions cause conversion of hydroxyl U(VI) species to dissolved U(VI)-carbonate species - $UO_2CO_3^{o}$, $UO_2(CO_3)_2^{--}$, and $UO_2(CO_3)_3^{----}$. The latter anionic species dominate at above neutral pH and tend to cause the desorption of U(VI) from mineral surfaces and the solubilization of U(VI) solids. In addition to carbonate, U(VI) forms soluble aqueous complexes with sulfate, flouride, and phosphate.

Uranium in soil is easily incorporated into plants, leading to direct and indirect exposures of humans. When ingested, uranium tends to concentrate in the bones and bone marrow. Because of its long half-life, inhaled uranium can also provide a significant dose to the lungs. Uranium is removed from the body by biological means, and its biological half-life is 300 days for the bones and 100 days for general contamination of the body. Chemical toxicity of uranium is generally more significant than its radiotoxicity. Soil reduction would tend to favor the mobilization of that fraction of uranium initially associated with iron hydroxides. Nevertheless, uranium is typically found to be less mobile under reducing conditions and irreversibility tends to become more pronounced (e.g., Barney, 1984).

Appendix F. Measurement of Irreversible Uptake of Inorganic Contaminants

This appendix outlines how irreversible uptake of inorganic contaminants is measured and reviews a number of case studies to set some limits on the amount of irreversible uptake that is typically observed. Two approaches for measuring the nature and extent of irreversible uptake of inorganic contaminants are considered: sequential extraction procedures (SEPs) and isotopic pulsing.

Sequential Extraction Procedures

The SEP approach outlined below is a form of the method for extraction being calibrated by the U. S. National Institute of Standards and Technology (NIST) (Schultz et al., 1996). The reagent/sample ratios and extraction times were chosen somewhat arbitrarily from the NIST matrix pending their final selection of an optimal SEP.

SEP procedures generally target six soil fractions sequentially extracted in the following order:

1. **Ion exchangeable phase** - This phase includes metals that are reversibly sorbed (non-specifically) to soil minerals, amorphous solids, and/or organic material. The electrostatic forces that control their binding are overcome by using a concentrated electrolyte (e.g., 1*M* $MgCl_2$, $CaCl_2$, ammonium acetate, or $NaNO_3$) leachant that displaces the contaminant ions from the solid surfaces. Although the concentrated electrolyte will displace contaminant ions, it will not dissolve any of the mineral phases. The pH of these reagents is near neutral, and there is no potential for electron transfer reactions. Analysis of the effluent consequently is thought to measure only the fraction of contaminant in the ion exchangeable phase.

2. **Organic phase** - Any metal associated with soil organic matter (e.g., humic acids) will either be in the ion exchangeable phase or be irreversibly bound in the organic phase by chemical bonds stronger than the electrostatic bonding of exchangeable ions. The exchangeable fraction is previously removed using the above electrolyte leach. Oxidation of soil organic matter (using 5% NaOCl, pH 8.5) that remains after the exchangeable contaminants have been removed will bring into solution contaminants that are irreversibly bound to organic groups. The leach solution is sufficiently selective that it appears to avoid liberating any remaining contaminant fraction that is not associated with organics (Schultz et al., 1996).

3. **Carbonate phase** - Contaminant metals that are irreversibly sorbed, or otherwise bound up in metal carbonate minerals (primarily calcite and/or dolomite), can be removed through mild acid dissolution. A 1*M* NaOAc solution in 25% HOAc adjusted to pH 5 will dissolve all soil carbonate minerals while leaving behind iron hydroxides and clays. Analysis of the leachate characterizes the contaminants in the carbonate-associated fraction.

4. **Metal (hydr)oxide phase** - Contaminant metals bound to hydroxides of iron, manganese, and/or aluminum are extracted using an acidic reducing agent (e.g., 0.1 M hydroxylamine hydrochloride) in pH 2 nitric acid. The reducing agent is used to prevent subsequent re-precipitation of Fe or Mn.

5. **Acid/sulfide fraction** - Any contaminant metal associated with sulfide minerals might be removed by leaching with 4M HNO_3 at 95°C due to the dissolution of crystalline and amorphous sulfide host.

6. **Residual fraction** - The remaining contaminants will be distributed between silicates, phosphates, and refractory oxides (e.g., titanium dioxide) and can be determined by NaOH fusion analysis. However, this harsh reagent also dissolves hydrous ferromanganous minerals and some aluminosilicates.

There is considerable evidence that SEPs done with synthetic contaminants are plagued with uncertainties arising from the tendency for contaminants to readsorb once their original host is digested (Gruebel et al., 1988; Nirel and Morel, 1990). It has subsequently been argued that the same difficulties are less overwhelming when SEPs are applied to natural samples (see e.g., Tessier and Campbell, 1991; Wasay et al., 1998). Consequently, there is considerable reliance on SEP procedures to semi-quantitatively assess the binding and transport of contaminant metals in soils and groundwaters (see e.g., Lopez-Sanchez and Rauret, 1993; Schultz et al., 1996).

Figure F.1 outlines schematically how to conduct the selective soil extraction procedure outlined above to identify the natural attenuation processes for inorganics. All extractions may be carried out using 50 ml PTFE tubes. Five grams of sample are brought into contact with 25 ml of 1.0 $MgCl_2$ and shaken for 1 hour at 25°C. Leachate is then separated by high-speed centrifugation (>10,000 cpm), followed by passage through a 0.1 μm filter for subsequent analysis. The residue is then weighed and brought into contact with 25 ml of 5% NaOCl (pH 8.5) and shaken for 1 hour at 25°C. Leachate is then separated by centrifugation for subsequent analysis. The residue is then weighed and combined with 25 ml of HOAc-NaOAc and shaken for 2 hours at 25°C. The leachate is separated by high-speed centrifugation and passage through a 0.1 μm filter. The residue is then weighed and combined with 25 ml of 0.1M hydroxylamine hydrochloride in pH 2 nitric acid and digested for 1 hour. Leachate is then separated by high speed-centrifugation and filtration for subsequent analysis. The residue is weighed and combined in a 1:5 mix with 4M HNO_3 and digested for 1 hour at 95°C. Leachate is then separated by high speed-centrifugation and filtration for subsequent analysis. Analysis of the residual is done by fusion of a 1:5 sample to NaOH mix at 500°C for 3 hours and subsequent analysis.

Obviously, further analyses (e.g., X-ray diffraction) of the solids are needed to estimate the proportion of uranium minerals in the soils. This in turn helps in estimating the respective amounts of contaminant that is irreversibly sorbed versus existing as a separate mineral phase. Any metals naturally present in the soil will show up in the leach procedure as well, emphasizing the importance of knowing the ambient background concentrations ahead of time.

At the very least, the SEP estimates the available fraction of a contaminant released over the several hours needed to complete these extractions. Longer extraction times would presumably release more contaminant, leading to slightly smaller estimates of the irreversibly adsorbed fraction. Site-specific information on any time dependence of contaminant release in the SEP would buttress the validity of this assumption about the size of the irreversibly adsorbed fraction.

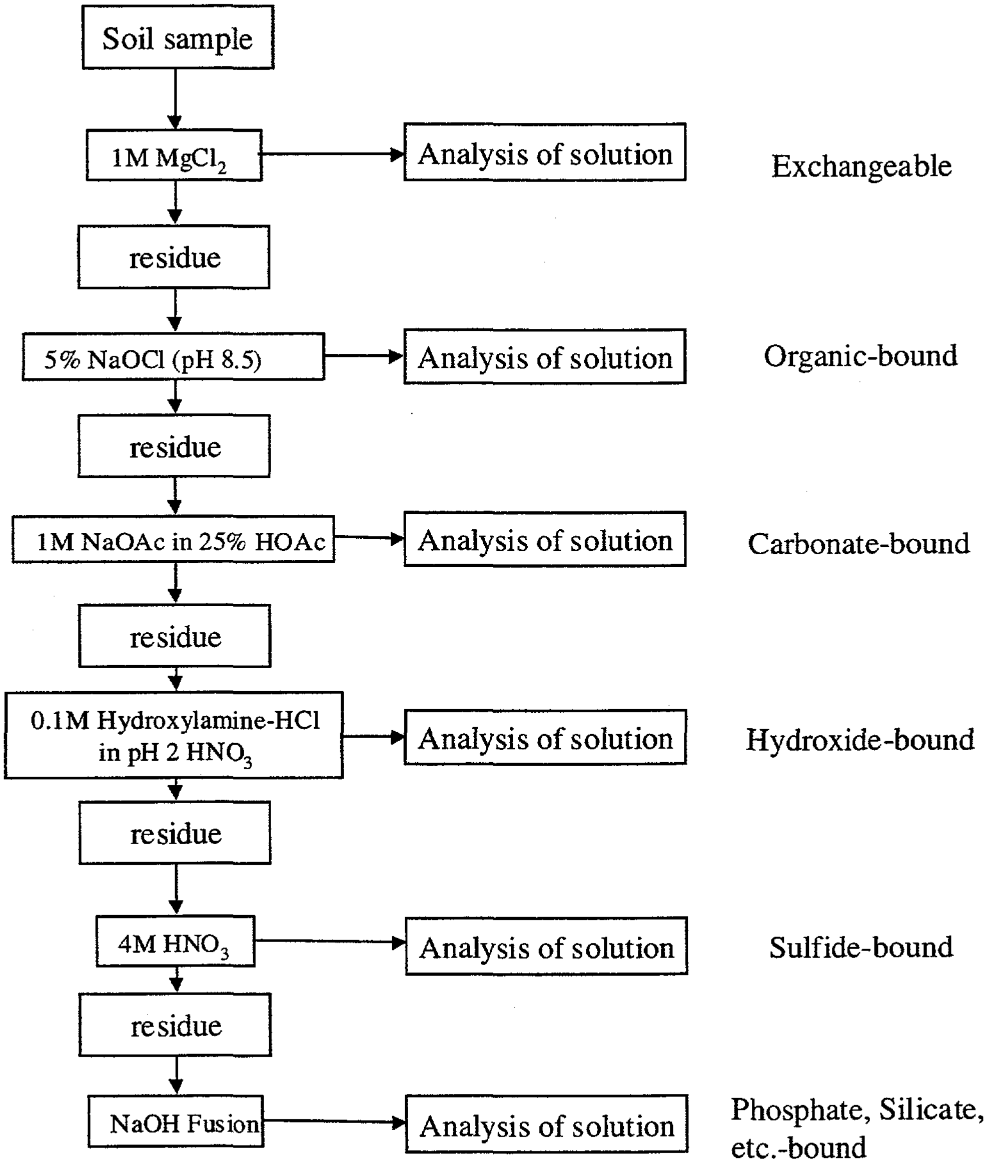

Figure F.1 Sequential soil extraction procedure to determine phases active in the irreversible sorption of contaminants.

Isotopic Pulsing

The distribution of a radioisotope between dissolved and adsorbed soil phases can be used to measure the amount of the adsorbed stable element. The dissolved stable element concentration is in equilibrium with any constituent radioactive isotopes of the element because the dissolved stable element and the radioisotope are well mixed in the aqueous phase. This equilibrium offers a powerful tool to assess the degree of reversibly, or isotopically-exchangeably, adsorbed element and, by difference from the total, the amount of fixed or attenuated element in a soil. By adding a radioisotope (e.g., ^{85}Sr) spike to a ^{90}Sr-contaminated soil-groundwater mixture in the laboratory and measuring its resulting distribution between dissolved ($^{85}\mathrm{Sr}_{\mathrm{aqueous}}$) and adsorbed ($^{85}\mathrm{Sr}_{\mathrm{adsorbed}}$) phases and the analytically determined dissolved stable Sr ($\mathrm{Sr}_{\mathrm{aqueous}}$) concentration, the isotopically-exchangeable ($\mathrm{Sr}_{\mathrm{adsorbed}}$) phase can be determined from the relationship:

$$^{85}\mathrm{Sr}_{\mathrm{aq}} / ^{85}\mathrm{Sr}_{\mathrm{adsorbed}} = \mathrm{Sr}_{\mathrm{aq}} / \mathrm{Sr}_{\mathrm{adsorbed}} \qquad \text{(F.1)}$$

The irreversibly-bound or fixed ($\mathrm{Sr}_{\mathrm{fixed}}$) can then be calculated from the measured total ($\mathrm{Sr}_{\mathrm{total}}$) soil element:

$$\mathrm{Sr}_{\mathrm{fixed}} = \mathrm{Sr}_{\mathrm{total}} - \mathrm{Sr}_{\mathrm{adsorbed}} \qquad \text{(F.2)}$$

Although stable Sr is not a hazardous contaminant and thus, measuring its fixed and adsorbed phases would not be of interest in natural attenuation, this radioisotopic equilibration technique can be readily used to determine the amount of fixed hazardous radioisotope (e.g., ^{90}Sr) in a soil by adding a second radioisotope spike of the same element. For example, the amount of fixed ^{90}Sr in a soil can be determined by adding to the soil a convenient shorter-lived radioisotope, e.g., ^{85}Sr ($t_{1/2}$ = 64 days) and calculating from the above equations. This pulsing technique with a second radioisotope can be carried out after various soil aging intervals of contact with the primary radioisotope to determine the effect of time on the degree of fixation. Equally important, such techniques can also be employed to measure the amount of fixed stable contaminant, such as Cd, by pulsing soil-water suspensions with a convenient Cd radioisotope, e.g., ^{109}Cd. Many hazardous elements have readily available radioisotopes which can be employed to determine the amounts of fixed stable hazardous element in soils by such methods. Radioisotopic equilibration times can be varied up to any length of time of interest or, more likely, until little or no change in the degree of adsorption of the isotope can be observed. This technique offers an alternative to selective extraction to determine the amount of fixed or attenuated contaminant in a soil. It has the additional advantage of avoiding some of the ambiguities of selective extraction regarding a contaminant's phase of origin and potential contaminant redistribution inherent in selective extraction procedure. Such radioisotopic dilution techniques have been widely used and established (Olsen and Sommers, 1982) to measure labile or readily exchangeable pools on nutrient elements in soils. The use of such radioisotopic dilution techniques in determining stable Cs adsorption and fixation is well established (Grutter et al., 1986; Sikalidis et al., 1988). Thus, isotopic pulsing determinations should be a valuable tool for the measurement of contaminant fixation during natural attenuation in soils.

The SEP studies in the next two sections were based on field samples or represent experiments wherein contaminant-soil contact times were greater than a year. This does not represent an exhaustive compilation. It should indicate the broader ranges of uptake that can be expected.

Field Measurements - Inorganic Contaminants

Several studies attest to the limited extractability of Cr: generally around 95% is irreversibly bound (Coughtrey and Thorne, 1983). Nevertheless, because Cr exists as both sparingly soluble trivalent Cr and reasonably mobile hexavalent Cr in soils, it is difficult to put a single number on the uptake of chromate alone by soil matrices. Coughtrey and Thorne (1983) state that Cr availability to plants may exceed 5% in anaerobic acid soils, or highly alkaline soils, but even then the available fraction is unlikely to exceed 10% of the total. Asikainen and Nikolaidis (1994) found that, using 0.1M KH_2PO_4/K_2HPO_4 (pH 7.2), on average 65% of Cr was extractable from soils contaminated by a plating facility in Connecticut. Irreversible uptake of chromate has been observed on iron hydroxides (Schultz et al., 1987).

Barona and Romero (1996) used 1M NH_4OAc in a 1:10 ratio to measure exchangeable lead in soils from a rural location in northern Spain at 5 to 40% of the total. Howard and Shu (1996) used a 1M $MgCl_2$ solution (and nitrilotriacetic acid (NTA) to prevent resorption of metals) to measure exchangeable Pb, Ni, and Zn from three contaminated sediments and one soil. For each metal, the water-soluble and exchangeable fractions varied with NTA concentration, reaching maximum values of, respectively, 4.6 and 6.0% (lead), 35.2 and 23.1% (nickel), 44.7 and 15.7% (zinc). Gibson and Farmer (1986) examined 90 contaminated soils near Glasgow, Scotland (using 1M NH_4OAc as the extractant) and found that exchangeable lead was 4% or less. Exchangeable zinc was 5% or less. Exchangeable copper was 2% or less. Exchangeable cadmium varied between 21 and 60%. Borovec (1996) examined contaminated surface stream sediments (silt-clay fraction) from the Elbe river basin and used 1M NH_4OAc as the extractant. Exchangeable fractions were: ~6% - Ni; ~5% - Co; ~0% Cr; ~3% As; ~20% Cu; ~35% Cd; and ~0% Pb.

Kavanagh et al. (1997) examined As contamination in mine wastes and adjacent agricultural soils and determined that water-extractable As in the adjacent agricultural soils was 0.05-0.3%; water-extractable As in the mine wastes was 0.02 to 1.2%.

Field Measurements - Radionuclides

In general, Pu binds very strongly to soils, and very little is available. Coughtrey et al. (1986) estimate the latter to be less than one percent. Litaor and Ibrahim (1996) used 0.01M $CaCl_2$ as an extractant and measured Pu in Rocky Flats soil to be 0.04 to 0.08% exchangeable. Available Am was estimated by Coughtrey et al. (1986) to vary in soils between 32 and 57%. Bunzl et al. (1995) measured exchangeable $^{239+240}$Pu (0.5-1%) and ^{241}Am (1.5-15%) from fallout-contaminated soils in Germany using 1M NH_4OAc as the extractant.

Landa (1991) measured exchangeable radium from mill tailings components with a 1 M NH_4Cl solution and found that only 0.03% was exchangeable when barite was present; but 16 to 94% was exchangeable from the other components.

Typically around 15% of soil Cs is available for plant uptake (Coughtrey et al., 1986). The remainder is generally attributed to uptake by clays, which goes to completion over the time of days to several months. The uptake of strontium by plants appears to correlate directly with available strontium, the amount that can be extracted with ammonium acetate. In general, between 10 and 20% of strontium in soils cannot be extracted. The magnitude of the non-exchangeable fraction appears to depend upon soil pH and soil organic matter content (Coughtrey and Thorne, 1983). Fawaris and Johanson (1995) examined ^{137}Cs uptake in soils exposed to Chernobyl fallout and, using 1M NH_4OAc, measured the exchangeable fraction to be 13% (the water extractable fraction was 8%). Riise et al. (1990) measured ^{137}Cs and ^{90}Sr exchangeability in Norwegian soils contaminated by the Chernobyl accident using IM NH4Ac. Less than 10% of the ^{137}Cs was easily leachable. Between 40 and 60% of the ^{90}Sr was exchangeable. Krouglov et al. (1998) used 1 M NH_4OAc to measure exchangeable ^{90}Sr, ^{106}Ru, ^{137}Cs, and ^{144}Ce in Chernobyl soils. Exchangeable ^{137}Cs was on the order of 10%; exchangeable ^{90}Sr was on the order of 60%. Oughton et al. (1992) examined ^{137}Cs and ^{90}Sr movement in Chernobyl-contaminated soils from Norway, Byelorussia, and the Chernobyl region and found that >80% of the ^{137}Cs was non-exchangeable, whereas up to 70% of the ^{90}Sr was exchangeable (1M NH_4OAc was the extractant). Spalding (1981b) showed that 80 to 95% of ^{90}Sr was exchangeable from contaminated Oak Ridge soils using NH_4OAc or KCl. Schulz and Reidel (1961) measured exchangeability of ^{90}Sr from spiked soils aged for up to 3.5 yrs. Values measured using 1 N NH_4Ac varied between 80 and 92.8%.

Interaction with residual organic matter (and possibly clays) apparently limits the available fraction of iodide. Schmitz and Aumann (1995) measured uptake of natural and radioiodine in soils downwind from the Karlsruhe Nuclear Fuel Reprocessing Plant. 2.5 to 4% of the natural iodine was water-soluble, compared to 38 to 49% of the recently added radioiodine. The exchangeable fraction of the natural iodine was 7.8%; that of the radioiodide was 9.4%.

Typically soil technetium under oxidizing conditions is completely available. At most, 10% may be fixed by clay matrices and/or organic matter. Anaerobic conditions at depth may cause this number to increase slightly.

Measurements on Artificially Contaminated Minerals

The following measurements were done on soils or model minerals artificially contaminated over short periods of time. Reed et al. (1995) measured exchangeable lead from a sandy loam artifically contaminated with Pb^{++}, $PbSO_4$,

$PbCO_3$, or Pb-napthalene. The amount of lead removed by 1M $CaCl_2$ in batch tests was 47% Pb^{++}; 85% $PbSO_4$; 15% $PbCO_3$; and 64% Pb-napthalene. In column tests 1M $CaCl_2$ removed respectively, 78% - Pb^{++}, 96% - $PbSO_4$, and 14% - $PbCO_3$. Cline and Reed (1995) measured removal efficiencies of artificial lead ($Pb(NO_3)_2$) contamination from soils using 1M $CaCl_2$ and found an average removal efficiency of 47.2% (the value decreased somewhat with decreasing contaminant loading). Vidal and Rauret (1994) examined two Mediterranean soils contaminated with ^{85}Sr and ^{134}Cs three months before analysis. They used 1M $MgCl_2$ as the extractant and measured the exchangeable fractions of 1.3% for ^{134}Cs and 69.1% for ^{85}Sr.

Irreversible uptake of metals by ferrihydrite and/or goethite has been measured by a number of authors. The more salient results are outlined in Table F.1. (In a number of these cases the irreversibly bound fraction was determined from the trend of desorption curves.) Table F.1 also includes the irreversible uptake of metals onto calcite measured by Zachara et al. (1991). (These values were plotted incorrectly in Brady et al. (1997) and (Brady and Borns, 1997). The correct values are listed in the table below).

Table F.1 Irreversible Uptake of Metals by Model Minerals in Laboratory Experiments

Element	Substrate	Equilibration time	% uptake	Reference
Cd	goethite	overnight	3-97	(Davis and Upadhyaya, 1996)
Cr	ferrihydrite	1-3 hrs	94	(Schultz et al., 1987)
Pb	ferrihydrite	1-3 hrs	41-48	(Schultz et al., 1987)
Ni	ferrihydrite	1-3 hrs	0-37	(Schultz et al., 1987)
Cu	ferrihydrite	1-3 hrs	0-13	(Schultz et al., 1987)
Zn	ferrihydrite	1-3 hrs	4-11	(Schultz et al., 1987)
Cd	ferrihydrite	1-3 hrs	0-9	(Schultz et al., 1987)
Co	goethite	18 hr	~12	(Coughlin and Stone, 1995)
Ni	goethite	18 hr	~18	(Coughlin and Stone, 1995)
Cu	goethite	18 hr	~25	(Coughlin and Stone, 1995)
Pb	goethite	18 hr	~17	(Coughlin and Stone, 1995)
Cu	goethite	18 hr	8.7-26	(Coughlin and Stone, 1995)
Cd	ferrihydrite	11 wk	~20	(Ainsworth et al., 1994)
Cd	ferrihydrite	16 wk	~20	(Ainsworth et al., 1994)
Co	ferrihydrite	2 wk	~15	(Ainsworth et al., 1994)
Co	ferrihydrite	9 wk	~30	(Ainsworth et al., 1994)
Co	ferrihydrite	15 wk	~50	(Ainsworth et al., 1994)
Cd	ferrihydrite	11 wk	18	(Ainsworth et al., 1994)
Co	ferrihydrite	9 wk	30	(Ainsworth et al., 1994)
Cd	ferrihydrite	86 wk	59	(Ainsworth et al., 1994)
Co	ferrihydrite	86 wk	82	(Ainsworth et al., 1994)
U	goethite	10, 20, 35, 56 days	15-25	Bryan and Siegel (unpublished)
Cd	calcite	10 hr	80	(Zachara et al., 1991)
Mn	calcite	10 hr	72	(Zachara et al., 1991)
Zn	calcite	10 hr	25	(Zachara et al., 1991)
Co	calcite	10 hr	20	(Zachara et al., 1991)
Ni	calcite	10 hr	15	(Zachara et al., 1991)

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