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Pacific Northwest
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Subsurface Contaminant Focus Area: Monitored Natural Attenuation (MNA) – Programmatic, Technical, and Regulatory Issues

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Prepared for the U.S. Department of Energy
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[a] This report represents a joint effort by staff from several U.S. Department of Energy national laboratories. The names of these contributors and their laboratory affiliations are in the Foreword.

Foreword

This report and literature review was prepared for the lead laboratory team as an emerging issue and represents a joint effort by staff representing several U.S. Department of Energy national laboratories. The principal contributors(a) from these organizations include the following:

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Executive Summary

Natural attenuation processes are commonly used for remediation of contaminated sites. A variety of natural processes occur without human intervention at all sites at varying rates and degrees of effectiveness to attenuate (i.e., decrease) the mass, toxicity, mobility, volume, or concentrations of organic and inorganic contaminants in soil, groundwater, and surface water systems. As defined in the U.S. Environmental Protection Agency (EPA) policy for monitored natural attenuation as a remediation alternative, these in situ, natural attenuation processes include biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants. The major driver for using this approach for site remediation is the perception that monitored natural attenuation will be simpler and less costly to implement as compared to using active remediation technologies. However, this cost argument is not valid when considering all requirements described in EPA's regulatory and technical guidance for monitored natural attenuation.

The objective of this review was to identify potential technical investments to be incorporated in the Subsurface Contaminant Focus Area (SCFA) Strategic Plan for monitored natural attenuation (MNA). When implemented, the technical investments will help site managers and their supporting contractors more effectively evaluate and implement monitored natural attenuation as a remediation option at U.S. Department of Energy (DOE) sites. This review included a literature search that identified a number of important resources, including the EPA's OSWER Directive 9200.4-17, *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites*; EPA's *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater*; DOE's published guidance documents and screening tools (e.g., MNAtoolbox) for monitored natural attenuation; recently published reviews by the National Research Council on monitored natural attenuation for groundwater remediation and on the DOE Environmental Management Science Program (EMSP); EPA's Science Advisory Board (SAB) review of EPA's Research Program for monitored natural attenuation of contaminants in groundwater, soils, and sediments; and other published and Internet sources on monitored natural attenuation. Our evaluation of a bibliography generated from a search of computerized reference databases indicates that the majority of the published research pertain to natural attenuation of organic contaminants. As noted by the National Research Council, DOE's guidance and protocol for monitored natural attenuation is unique in that it is the only technical protocol to specifically address inorganic as well as organic contaminants.

The outcome of this review is a set of conclusions and general recommendations on research needs, programmatic guidance, and stakeholder issues pertaining to monitored natural attenuation for the DOE complex. These conclusions and recommendations, which are discussed in

Section 2 of this report, are based on the authors' judgment as well as several of the cited documents. These recommendations include the following:

- Determine whether other contaminants should be added to DOE lists of contaminants of environmental concern.

- Conduct a peer review of the technical aspects of MNAtoolbox and DOE guidance on monitored natural attenuation.

- Complete a literature review to identify studies and data for the irreversible sorption of contaminants of DOE interest; geochemical factors, including future land use scenarios, that affect such processes and values; and issues associated with the measurement of such values.

- Review Record of Decision (ROD) and related regulatory remediation decision documents to identify at which DOE sites and for what specific contaminants natural attenuation processes are being used or considered for remediation of contaminated soils, sediments, groundwaters, or surface waters.

- Review the DOE research portfolio to identify which basic research projects support identification of the "footprints" [a concentration change of one or more reactants (in addition to the contaminants) and products of the process that is transforming or immobilizing the contaminants (NRC 2000b)], performance monitoring parameters, and sampling and analysis methods needed to assess natural attenuation processes for each contaminant of DOE interest and what additional research may be needed.

- Determine whether components of DOE Preferred Alternatives Matrices (PAMs) can be used with modification in DOE guidance and screening tools to evaluate the effectiveness of monitored natural attenuation.

- Improve consistency among DOE and its national laboratories and contractors in the use of the terms "monitored natural attenuation" and "natural attenuation" as defined by EPA's Directive 9200.4-17.

- Develop linkages and consistency in DOE's remediation guidance documents and software tools with DOE decision-making framework guide and long-term monitoring document for monitored natural attenuation.

- Develop a dialogue with EPA to leverage the two research programs with respect to natural attenuation processes, site characterization, and performance-monitoring methodologies.

- Identify communication strategies and lessons learned from other DOE programs that could be integrated into DOE monitored natural attenuation guidance.

- Identify, summarize, and prioritize technical issues that are not adequately addressed in the technical literature, DOE guidance documents and screening tools with respect to monitored natural attenuation.

Based on the material reviewed in this study, several additional issues do not appear to be addressed in DOE guidance for monitored natural attenuation. Given the nature of contamination at DOE sites and DOE's responsibilities for closeout of such sites, the following issues are also potentially important when evaluating and implementing monitored natural attenuation at DOE sites:

- Role of monitored natural attenuation in remediation of contaminated vadose-zone and surface-water systems

- Evaluation of monitored natural attenuation for remediation of single-versus multi-contaminant plumes

- Detrimental effects from active remediation activities on monitored natural attenuation of contaminants away from the source term

- Guidance for setting trigger levels for contaminant concentrations at which active remediation technologies at a site change to passive, monitored natural attenuation

- Role of future land use scenarios relative to the long-term effectiveness of monitored natural attenuation at a site

- Role of ecological risk relative to evaluating the suitability of monitored natural attenuation at a site

- Relationship of performance monitoring elements associated with monitored natural attenuation to long-term stewardship issues.

A review should be conducted to identify, summarize, and prioritize such issues.

Acknowledgments

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Acronyms and Abbreviations

AFCEE	U.S. Air Force Center for Environmental Excellence
BNL	Brookhaven National Laboratory
BTEX	benzene, toluene, ethylbenzene, and xylene
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CY	calendar year
DCA	dichloroethane
DCE	dichloroethylene
DDT	dichlorodiphenyltrichloroethane
DLL	FORTRAN dynamic link library
DNAPL	dense nonaqueous phase liquid
DOD	U.S. Department of Defense
DOE	U.S. Department of Energy
DTPA	diethylenetriamine pentaacetic acid
EDTA	ethylenediamine tetraacetic acid
EMSP	DOE's Environmental Management Science Program
EPA	U.S. Environmental Protection Agency
FY	fiscal year
HFBR	High Flux Beam Reactor
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetraazozine
ITRD	DOE Innovative Treatment Remediation Demonstration Program
LANL	Los Alamos National Laboratory
LLNL	Lawrence Livermore National Laboratory
LLW	low level radioactive waste
MGP	manufactured gas plant
MNA	monitored natural attenuation
MtBE	methyl-tertiary-butyl ether

NABIR	DOE Natural and Accelerated Bioremediation Research program
NAF	natural attenuation factor
NAS	National Academy of Science
NETO	DOE National Environmental Training Office
NRC	National Research Council
NTA	nitriloacetic acid
ORD	EPA Office of Research and Development
OSWER	EPA Office of Solid Waste and Emergency Response
OU	operable unit
OUST	EPA Office of Underground Storage Tanks
PAH	polycyclic aromatic hydrocarbon
PAMs	DOE Preferred Alternatives Matrices
PCB	polychlorinated biphenyl
RCRA	Resource Conservation and recovery Act
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine
RFETS	Rocky Flats Environmental Technology Site
ROD	Record of Decision
RTDF	Remediation Technologies Development Forum
SAB	EPA Science Advisory Board
SCFA	DOE Subsurface Contaminant Focus Area
SNL	Sandia National Laboratories
TCA	trichloroethane
TCE	trichloroethylene
TIE	DOE Technical Information Exchange Program
TNT	trinitrotoluene
TRU	transuranic (waste)
USGS	U.S. Geological Survey
UST	underground storage tank(s)
VC	vinyl chloride
VISITT	EPA Vendor Information System for Innovative Treatment Technologies

Contents

Tables

1.0 Introduction

Natural processes occur in soil,[(a)] groundwater, and surface water systems at all sites at varying rates and degrees of effectiveness to attenuate (i.e., decrease) the concentrations of organic and inorganic contaminants. Following current regulatory guidance OSWER Directive 9200.4-17, *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites* (discussed in Section 3) from the U.S. Environmental Protection Agency (EPA), natural attenuation processes 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 concentrations of contaminants in soil or groundwater. These in-situ processes include biodegradation; dispersion; dilution; sorption;[(b)] volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants* (our emphasis).

The term "natural attenuation," as defined by this statement, will be used to refer to this group of processes throughout the remainder of this paper.

The EPA uses the term "monitored natural attenuation" when referring 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*" (our emphasis).

(a) The terms "sediment" and "soil" have particular meanings depending on the technical discipline. "Sediment" is often reserved for naturally transported and deposited particles derived from soil, rocks, or biological material. "Soil" is sometimes limited to the top layer of the earth's surface that is suitable for plant life. In this report, "soil" refers to all unconsolidated geologic materials.

(b) The term "sorption" is used in this report, as in the above EPA definition, as a generic term devoid of mechanism for describing the partitioning of a dissolved contaminant to a solid phase. It is commonly not known whether a contaminant is adsorbed onto the surface of the solid, absorbed into the crystalline structure of the solid, precipitated as a three-dimensional molecular coating on the surface of the solid, or absorbed into organic matter.

1.1 Background

Site monitoring is one of four key elements in EPA's regulatory guidance (see Section 3). To be consistent with EPA's Directive and U.S. Department of Energy (DOE) guidance documents on monitored natural attenuation (see Section 4), the term "monitored natural attenuation" is used to refer to the reliance on natural attenuation processes as a remediation option. Several terms are used in the literature to refer to or in association with natural attenuation, especially within the context of site remediation. These terms include "intrinsic remediation," "intrinsic bioremediation," "passive bioremediation," "natural recovery," "natural assimilation," and "natural flushing."

Legal and technical issues associated with reliance on natural attenuation processes as a remediation alternative are reviewed in NRC (2000b) and Brady et al. (1997). The major driver for using this approach for site remediation is the perception that it will be simpler and less costly to implement than active remediation technologies. However, this cost argument is not valid when considering all requirements described in EPA's regulatory and technical guidance for monitored natural attenuation. The OSWER Directive 9200.4-17 lists several potential advantages and disadvantages for monitored natural attenuation as a remediation option for a contaminated site. These include the following:

Potential advantages:

- Generation of lesser volume of remediation wastes
- Reduced potential for cross-media transfer of contaminants associated with ex situ treatment
- Reduced risk of human exposure to contaminants, contaminated media, and other hazards
- Reduced disturbances to ecological receptors
- Possible in situ destruction of certain types of contaminants
- Less intrusion from fewer surface structures
- Potential application to all or part of a given site
- Possible use in conjunction with, or as a follow-up to, active remedial measures
- Potentially lower overall remediation costs than those associated with active remediation.

Potential disadvantages:

- More complex and costly site characterization
- More extensive (including time frame) long-term performance monitoring
- Possible longer time frames to achieve remediation objectives compared with active remediation options
- Toxicity and/or mobility of transformation products that may exceed that of the parent compound
- Necessity of institutional controls to ensure long-term protectiveness
- Potential of continued contamination migration, and/or cross-media transfer of contaminants
- Potential over time for change in hydrologic and geochemical conditions which could remobilize previously stabilized contaminants (or naturally occurring metals) and thus adversely impact remediation effectiveness
- Need for more extensive education and outreach efforts to gain public acceptance of monitored natural attenuation.

To achieve cleanup objectives such as minimizing further migration of contaminants from source materials, as required by CERCLA and RCRA Corrective Action programs, monitored natural attenuation will not likely be used as a stand-alone, “passive” remediation method but will be used in conjunction with “active” remedial methods. Although the data are probably outdated, the EPA’s *A Citizens Guide to Natural Attenuation* (EPA 1996), for example, states that 73 groundwater contaminated sites in the Superfund program have chosen natural attenuation (this guide predates EPA’s Directive 9200.4-17 on “monitored natural attenuation”) as one of the remediation cleanup methods, but it was the singular remediation treatment at only six of these sites. The application of monitored natural attenuation in conjunction with other remediation options is especially true during the later stages of site cleanup, when the efficiency of active remediation technologies will generally decrease due to the lower concentrations of contaminant(s) in the soil and groundwater. The concentration limit for when a site “switches” from the active to the passive remediation phases for a particular contaminant differ from site to site.

B. H. Kjartanson[a] and coworkers, for example, are using a natural attenuation approach, which they call "Monitored Enhanced Natural Attenuation" (MENA), to deal with the low biodegradation potential of the larger polycyclic aromatic hydrocarbon (PAH) compounds released from coal tar residuals and the dense nonaqueous-phase liquid (DNAPL) coal tar residuals themselves. The MENA approach (e.g., Golchin et al. 1998) emphasizes the use of engineered remedial technologies as an implicit part of the process to remove and treat, destroy or immobilize contaminants and/or to enhance the natural attenuation processes. Examples of engineered enhancements in use at manufactured gas plant (MGP) sites are removal and treatment of contaminated soils, recovery of DNAPLs and use of air sparging/soil vapor extraction to rapidly reduce the overall mass of contamination and accelerate natural attenuation processes that are occurring at the site.[b] B. H. Kjartanson suggests that the inclusion of "Enhancement" in the title for "Monitored Natural Attenuation" would boost stakeholder confidence in the approach in the same way as expected with the inclusion of the term "Monitored."

The specific types of natural attenuation processes and numerous case studies are discussed in detail by NRC (2000b) and Brady et al. (1997). The physical, chemical, and biological processes and the rate and extent to which these natural attenuation processes occur will be different for each contaminant and site hydrologic and geochemical conditions. These processes are typically categorized as either nondestructive or destructive. Non-destructive processes reduce the potential risk from a particular contaminant by decreasing its concentration and thus bioavailability in groundwater or surface water by dispersion and dilution processes and/or decreasing its mobility and solution concentration by binding to soil minerals and organic matter via several sorption processes. Destructive processes reduce the potential risk from a contaminant by converting the contaminant to a less toxic form via biodegradation or abiotic transformations.

Some organic contaminants, like petroleum hydrocarbons [e.g., benzene, toluene, ethylbenzene, and xylenes (BTEX)] and chlorinated solvents [e.g., trichloroethylene (TCE)], can be biodegraded by microorganisms that occur naturally in the subsurface environment to less toxic or nontoxic compounds. Organic contaminants vary widely in their tendency to biodegrade by this process. For example, BTEX compounds are easily biodegraded to carbon dioxide by microorganisms under aerobic conditions. Biodegradation of chlorinated solvents, however, is less predictable and varies from site to site. For some organic compounds, the biodegradation process is not complete, and the intermediate degradation products are as toxic as (or worse than) the original compounds.

Inorganic contaminants may be transformed by abiotic and biotic, nondestructive reaction processes to forms that have low mobility, toxicity, or bioavailability. It is important to note that

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(a) Iowa State University, Ames.

(b) B. H. Kjartanson – personal communication.

inorganic contaminants, including most radionuclides, persist in the surface and subsurface environments because they are not attenuated, except for radioactive decay,(a) by destructive processes. The nondestructive reactions (collectively referred to as "sorption") that attenuate inorganic contaminants include precipitation, adsorption on the surfaces of soil minerals, absorption into the matrix of soil minerals, or partitioning into organic matter. At those sites where an inorganic contaminant has been immobilized by sorption, the contaminant may be remobilized at a future date due to changes in the hydrologic and/or geochemical conditions, such as changes in pH, oxidation/reduction (redox) conditions, and concentrations of complexing ligands. Natural in situ microbial processes can affect these immobilization reactions for inorganic compounds as a consequence of enzymes produced by the microbes or indirectly by microbiological modification of the geochemical environment [e.g., change in oxidation-reduction conditions]. Changes in redox state can change the valence states of some inorganic contaminants to less soluble forms [e.g., Tc(VII) (pertechnetate) to Tc(IV)] or less toxic forms [e.g., Cr(VI) (chromate) to Cr(III)]. For example, when reductants (e.g., dissolved ferrous iron [Fe(II)], Fe(II)-containing minerals, reduced sulfur, and/or soil organic matter) are present, dissolved chromium is transformed from the more toxic, more mobile hexavalent form of chromium, Cr(VI), to the less toxic trivalent form, Cr(III). Palmer and Puls (1994) discuss in detail the natural attenuation of chromate in groundwater and soil. Under alkaline to slightly acidic conditions, Cr(III) precipitates as a fairly insoluble hydroxide, which decreases the concentration of dissolved chromium via the formation of a precipitate that is immobile and may not readily redissolve even under oxidizing conditions.

The nondestructive sorption reactions that are important to the natural attenuation of inorganic contaminants in the sediments, soils, groundwaters, and/or surface waters at a site will be different for each contaminant and the associated geochemical conditions. These reactions (i.e., attenuation "pathways") are summarized for important inorganic contaminants by Brady et al. (1997, 1999), and listed in Table 1.

A wide range of organic and inorganic (metals and radionuclides) contaminants exist at DOE sites, although not all of these contaminants automatically translate into cleanup requirements. Riley et al. (1992) completed a detailed review of individual contaminants and contaminant mixtures that have been reported at 18 DOE facilities within the weapons complex. The different classes of individual contaminants identified in their review are summarized in Table 2.

(a) Radioactive decay as a natural attenuation mechanism is pertinent to radionuclides such as ^{3}H, ^{137}Cs, and ^{90}Sr, which have relatively short half-lives of 12.3, 30.1, and 28.8 years, respectively. Other radionuclides of environmental importance have longer half-lives and may form radioactive or nonradioactive daughter products that are more mobile or toxic than their parents (e.g., ^{241}Am and ^{237}Np from ^{241}Pu).

Table 1. Potential, Nondestructive Natural Attenuation Processes for Specific Inorganic Contaminants (from Brady et al. 1997)

Inorganic Contaminant	Potential Natural Attenuation Pathways
Am(III)	Sorption to carbonate minerals; formation of carbonate minerals
As(III and V)	Sorption to iron hydroxide minerals and organic matter; formation of sulfide minerals
Ba	Formation of sparingly soluble sulfate minerals; ion exchange
Cd	Sorption to Fe/Mn hydroxide and carbonate minerals; formation of sparingly soluble carbonate, phosphate, and sulfide minerals
Co	Sorption to iron hydroxides, organic matter, and carbonate minerals
Cr(VI) as CrO_4^{2-}	Reduction, sorption to Fe/Mn hydroxide minerals; formation of $BaCrO_4$ solid
Hg	Formation of sparingly soluble sulfide minerals; sorption to organic matter
I	Sorption to sulfide minerals and organic matter
N(V) as NO_3^-	Reduction by biologic processes
Ni	Sorption to Fe/Mn hydroxide minerals; ion exchange; formation of sulfide minerals
Pb	Adsorption to iron hydroxide minerals, organic matter, carbonate minerals; formation of sparingly soluble carbonate, sulfide, sulfate, and phosphate minerals
Pu(V and VI)	Sorption to iron hydroxide minerals; formation of sparingly soluble hydroxide and carbonate solids
Sr	Sorption to carbonate and clay minerals; formation of sparingly soluble carbonate and sulfate minerals
Tc(VII) as TcO_4^-	Possible reductive sorption to reduced minerals (e.g., magnetite); forms sparingly soluble reduced oxide and sulfide minerals
Th	Sorption to most minerals; formation of sparingly soluble hydroxide solid
U(VI)	Sorption to iron hydroxide minerals; precipitation of sparingly soluble hydroxide and phosphate minerals; reduction to sparingly soluble valence states [e.g., U(IV)]
Zn	Sorption to iron hydroxide and carbonate minerals; formation of sulfide minerals; ion exchange

The catch phase “natural attenuation” is a relatively new term in the literature and has been used extensively in reference to studies of the natural attenuation (i.e., biodegradation) of organic compounds. Although studies labeled as “natural attenuation” of inorganics and radionuclides in the literature are less common than those involving organic contaminants, there is a large body of literature in the disciplines of soil chemistry, geochemistry, and agricultural science that pertains to the fate and transport of trace metals, radionuclides, and/or anions in sediment, soil, groundwater, and surface water. Published studies identified with keywords like “labile,” “readily

Table 2. Contaminants Reported at 18 DOE Facilities in the Weapons Complex (Riley et al. 1992) (these compounds are found at some DOE sites but are not necessarily the most important compound in that class at a particular site or across the DOE complex)

Organic Contaminants		Inorganic Contaminants[(a)]	
Classes of Contaminants	Representative Constituents	Classes of Contaminants	Representative Constituents
Chlorinated hydrocarbons	trichloroethylene	Metals	chromium, lead, mercury
Fuel hydrocarbons	benzene, toluene, xylene	Anions	cyanide, fluoride, nitrate
Plasticizers (phthalates)	bis-2-ethylhexylphthalate	Radionuclides (metals and anions)	cesium-137, cobalt-60, iodine-129, plutonium isotopes, strontium-90, technetium-99, thorium, tritium, uranium isotopes
PCBs	arochlor 1248, arochlor 1260		
Explosives	HMX, RDX, trinitrotoluene		
Ketones	acetone, methyl ethyl ketone		
Pesticides	chlordane, lindane, 4,4'-DDT		
Alkyl phosphates	tributyl phosphate		
Complexation agents	EDTA, DTPA, NTA		
Organic acids	oxalic acid, citric acid		

(a) Several of the inorganic contaminants can be grouped into more than one class depending on the environmental conditions.

available," or "isotopically exchangeable" include research on why micronutrients, when added to agricultural soils, rapidly became unavailable to aid in plant nutrition. Although such studies are not classified by the phrase "natural attenuation," the results from such studies will generally have some applicability to understanding and predicting the mechanisms affecting the rate and extent of natural attenuation of inorganics in the natural environment.

1.2 Scope

The objective of this review is to identify potential technical investments to be incorporated in the Subsurface Contaminant Focus Area (SCFA) Strategy Plan for monitored natural attenuation (MNA). When implemented, the technical investments will help site managers and their supporting contractors evaluate and implement monitored natural attenuation more effectively as a remediation option at DOE sites.

To support this objective, a literature review was conducted of publicly available resources available from libraries and the Internet pertaining to natural attenuation and its potential use as a remediation option. These publications included the current EPA regulatory guidelines, DOE guidance documents and software tools, and published reviews, books, journal articles, and reports from the government laboratory and academic communities.

Several key conclusions were made as a result of the natural attenuation information found and not found during our review. These conclusions were primarily based on the sources listed in the references (Section 8) and are the basis for our recommendations regarding potential technical investments for SCFA with respect to monitored natural attenuation (Section 2).

Section 3 includes a review of EPA OSWER Directive 9200.4-17, *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites.* This Directive provides national regulatory policy as opposed to technical guidance regarding proposing, evaluating, and approving monitored natural attenuation for the remediation of organic and inorganic (metals and radionuclides) contaminants. Technical guidance documents cited in the Directive include Chapter IX for evaluation of natural attenuation in EPA's alternative cleanup technologies manual for leaking underground storage tank (UST) sites, which is currently under revision,(a) and the EPA's technical protocol for monitored natural attenuation at chlorinated solvent sites (Wiedemeier et al. 1998; EPA 1998b), which is briefly summarized in Section 3.

Section 4 discusses DOE's guidance documents and screening tools for monitored natural attenuation. During the course of this review, we also identified other DOE programmatic elements, such as basic and applied research programs, remediation technology screening tools, and environmental training, that have activities relevant to monitored natural attenuation. These are briefly noted in Section 4.3.

Section 5 summarizes two recently published reviews by the National Research Council. These include reviews on monitored natural attenuation for groundwater remediation and on DOE's Environmental Management Science Program (EMSP) with respect to addressing subsurface contamination problems at DOE sites. The National Research Council's review and specific findings focused on the following four areas of natural attenuation: community

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(a) The UST cleanup technology manual (EPA 1995) is at http://www.epa.gov/swerust1/pubs/tums.htm, but Chapter IX (Natural Attenuation) is under revision and has an indefinite date for completion.

concerns about natural attenuation, scientific basis for natural attenuation, approaches for evaluating natural attenuation, and protocols for natural attenuation. Their review included a discussion of EPA OSWER Directive 9200.4-17 as well as assessments of monitored natural attenuation guidance and protocols from DOE and various branches of the Department of Defense. The National Research Council review of DOE's Environmental Management Science Program addressed the issues of program vision, research emphases, and implementation. Many of the National Research Council's recommendations in the latter two categories crosscut technical needs that are also important to monitored natural attenuation. The pertinent recommendations from National Research Council in the technical areas of subsurface characterization, conceptual model development, and site monitoring are listed in Section 5.

Section 6 summarizes the principal findings and recommendations from a recent review by EPA's Science Advisory Board (SAB) of EPA's research program for monitored natural attenuation of contaminants in groundwater, soils, and sediments. The SAB's review focused on research pertaining to the monitored natural attenuation of 1) chlorinated solvents, 2) underground storage tank sites contaminated by MBTE and other oxygenates, 3) inorganic contaminants, and 4) aquatic sediments contaminated with persistent organic and/or inorganic compounds. Section 7 summarizes other published and Internet sources of information pertinent to monitored natural attenuation.

2.0 Conclusions and Recommendations

The following conclusions and recommendations can be made regarding research needs, programmatic guidance, and stakeholder issues pertaining to the evaluation and application of monitored natural attenuation as a remediation option at contaminated sites in the DOE complex. The recommendations are potential technical investments to be incorporated into the Subsurface Contaminant Focus Area (SCFA) Strategy Plan for monitored natural attenuation and, when implemented, will help site managers and their supporting contractors assess the use monitored natural attenuation more effectively.

These conclusions and recommendations are based on the authors' judgment as an outcome of the materials reviewed in this study and are taken from several of the sources discussed in Sections 3 through 7 of this report as well. The principal sources on which these conclusions and recommendations are based include the U.S. Environmental Protection Agency's (EPA) OSWER Directive 9200.4-17, *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites,* DOE's published guidance documents and screening tools (e.g., MNAtoolbox™) for monitored natural attenuation, the recently published review by the National Research Council on monitored natural attenuation for groundwater remediation, and EPA's SAB review of EPA's Research Program for monitored natural attenuation of contaminants in groundwater, soils, and sediments. The majority of the published research identified during this review pertains to natural attenuation of organic contaminants. The DOE protocol for monitored natural attenuation is unique in that it is the only protocol to specifically address inorganic as well as organic contaminants.

The conclusions and recommendations are grouped into four categories: research issues, programmatic issues, stakeholder issues, and other related issues. Most conclusions and recommendations, however, crosscut others in other categories.

2.1 Research Issues

- DOE contaminants of interest
  - Conclusion
    - The list of contaminants at DOE sites is extensive (e.g., see Table 2 in Section 2). The screening tool MNAtoolbox and the National Research Council assessment of the efficacy of natural attenuation (see Tables 4a and 4b in Section 5) do not include all of the contaminants identified at DOE sites. For example, Tables 4a and 4b, which are taken from the National Research Council natural attenuation assessment, do not include plasticizers, pesticides, alkyl phosphates, organic complexation

agents, organic acids, cyanide, fluoride, and thorium like the list of organic and inorganic contaminants in Riley et al. (1992, Table 2). MNAtoolbox includes only contaminants from two of the classes of organic contaminants listed in that table and does not include the explosives TNT and RDX.

- Recommendations
  - A review should be conducted to determine if any additional contaminants should be added to those identified by Riley et al. (1992) based on a review of 18 facilities within the weapons complex and from any similar reviews conducted since that time.
  - Based on this revised list of contaminants of DOE interest, the following activities should be conducted in the order listed.

    - Following the approach of the National Research Council's assessment of the efficacy of natural attenuation processes (see Tables 4a and 4b), a review should be completed to assess the "current level of understanding" and "likelihood of success given current level of understanding" for a revised list of contaminants more inclusive of those of DOE interest. This assessment, in combination with that reported by the National Research Council, could be used to prioritize basic research studies specific to natural attenuation.
    - Because MNAtoolbox is part of DOE's guidance on monitored natural attenuation, a review should be conducted to identify which individual organic and inorganic contaminants (and in what priority) should be added to MNAtoolbox along with the written documentation. These additions should include appropriate phase diagrams, potential natural attenuation pathways and mitigating conditions, future use caveats, relevant aqueous species, solid compounds, potential chelators that affect the contaminant's mobility, soil background levels, and any CERCLA precedents for each contaminant.
    - A review should be conducted to identify what contaminants (and in what priority) should be added to other important DOE remediation guidance documents and software tools such as DOE Preferred Alternatives Matrices (PAMs). The physical, chemical, and biological processes and the degree to which these processes affect natural attenuation are different for each contaminant. Therefore, the review should also evaluate whether the contaminant groupings (e.g., organic versus fuel hydrocarbons versus benzene) used in these documents and tools are sufficiently specific for the user to assess the efficacy of monitored natural attenuation and associated technical issues for a particular contaminant at a DOE site.

- MNAtoolbox and DOE's protocol

  - Conclusion
    - The National Research Council was critical of DOE's protocol and the scoring system calculations in MNAtoolbox. Sandia National Laboratories (SNL), who developed MNAtoolbox for DOE, responded to these criticisms noting that MNAtoolbox was developed as a screening tool for evaluating potential applications of monitored natural attenuation.

  - Recommendation
    - A peer review should be conducted, as recommended by National Research Council, of the technical aspects of MNAtoolbox. The evaluation should include dual reviews by the academic community and nonacademic end users (possibly including regulators). Although several researchers from other DOE national laboratories reviewed MNAtoolbox and contributed to the documentation (Brady et al. 1999), this broader, more independent review would provide more credibility for DOE's approach, guidance, and user tools for monitored natural attenuation.

- Irreversible sorption of inorganic contaminants

  - Conclusions
    - Most basic and applied research studies related to sorption of contaminants in soil and groundwater systems typically focus on the uptake of contaminants. However, considerably less information exists on the rate(s) of the reversibility of these processes and the geochemical conditions that enhance or reduce these rates. These conditions are important to long-term monitoring and future land use considerations at a site where monitored natural attenuation is proposed as a remediation option.
    - The fraction of irreversibly sorbed inorganic contaminants (Xirv) is a key parameter in MNAtoolbox and its screening scorecard calculations (see Appendix A). MNAtoolbox includes default Xirv values for 20 inorganic contaminants based on the sources and assumptions described in Brady et al. (1999). Ten of the 20 default values listed for Xirv equal 0.9 or greater.

  - Recommendation
    - Given the importance of sorption as a natural attenuation process, especially for the sequestration of inorganic contaminants in groundwater and surface-water systems, a detailed literature review should be conducted to identify studies and data for the irreversible sorption of contaminants of DOE interest; geochemical factors, including future land use scenarios, that affect such processes and data; and issues associated with the measurement of such values. The results of this review would

    identify basic research needs and could be used to supplement the default values currently in MNAtoolbox for the parameter Xirv.

- Application of monitored natural attenuation at DOE sites

  - Conclusion
    - Natural attenuation processes are likely being relied on for remediation of a variety of organic and/or inorganic contaminants at numerous DOE sites. However, the extent to which this remediation strategy is being applied and for which specific contaminants and types of environmental media do not appear to be documented for the DOE complex.

  - Recommendation
    - A review should be conducted of Record of Decision (ROD) and related regulatory remediation decision documents for DOE sites to identify at which sites and for what specific contaminants natural attenuation processes are being used or considered for remediation of contaminated soils, sediments, groundwaters, and/or surface waters. Because monitored natural attenuation will likely be used, especially early in the remediation cycle, in conjunction with active remediation methods, the review should also identify any concentrations limits that have been approved for DOE to switch from active to passive (i.e., monitored natural attenuation) strategies. The results of such a review could be used to identify monitored natural attenuation success stories, important specific organic and inorganic contaminants and contaminated media (i.e., soils, sediments, groundwaters, and/or surface waters), and key geochemical and physical contaminant-specific attenuation processes being considered within the context of monitored natural attenuation across the DOE complex.

- DOE’s research portfolio

  - Conclusions
    - DOE conducts several applied and basic research programs in bioremediation, environmental sciences, and geosciences. Some of these programs include the Subsurface Contaminants Focus Area (SCFA), the Natural and Accelerated Bioremediation Research (NABIR) program, Environmental Management Science Program (EMSP), and Geosciences Research Program in the DOE Office of Science’s Office of Basic Energy Sciences. Based on the objectives of these programs, the results from these studies should help to extend our mechanistic understanding of natural attenuation processes, identify under what conditions and to what extent these processes are reversible, and develop analytical methods to characterize and monitor such processes and their degradation products.

    - Validation of sampling and analysis methods for natural attenuation parameters, including nonintrusive characterization technologies, is important relative to site characterization and monitoring in monitored natural attenuation protocols. These would include methods such as bubble strip sampling techniques for sampling hydrogen in groundwater; development of direct reading instruments to measure time-sensitive natural attenuation parameters such as hydrogen, ethane, methane and ethene; and sample preservation techniques for time-sensitive parameters.
    - The National Research Council recently published the results of a review of DOE's Environmental Management Science Program (EMSP) with respect to addressing subsurface contamination problems at DOE sites. As one of the recommendations in the area of program integration, the National Research Council suggested that DOE "Integrate existing data and ideas from both DOE sites and basic research programs outside DOE..."

  - Recommendation
    - A review should be conducted of DOE's research portfolio to identify areas where past and currently-funded basic research projects support identification of, borrowing a term used by National Research Council, the "footprints,"[a] performance monitoring parameters, and sampling and analysis methods needed to assess and monitor natural attenuation processes for each contaminant of DOE interest. The results of such a review will identify and prioritize what additional research studies may be needed.

- DOE's Preferred Alternatives Matrices (PAMs)

  - Conclusion
    - DOE has developed PAMs as a tool for DOE site managers and supporting contractors to help select the most appropriate remediation options for individual sites and types of contaminants. A PAM is a list of proven, available technologies that are matched against a hierarchy of environmental conditions or problem sets. Contaminant types include radioactive, mixed LLW, mixed TRU, organic, inorganic, energetics, and sanitary. However, the lowest level of subclassifications (i.e., pH for organic/energetic contaminants and soluble versus nonsoluble for inorganic/radioactive contaminants) are not adequate indicators for the potential of important

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(a) The NRC (2000b) defines "footprint" as a concentration change of one or more reactants (in addition to the contaminants) or products of the process that is transforming or immobilizing the contaminants. We believe the NRC may have been the first to use the term "footprint" within the context of natural attenuation.

natural abiotic and/or biotic processes that affect the extent and rate of natural attenuation processes in soil, groundwater, and surface water systems at a site.

- Recommendation
  - A review should be completed to evaluate whether components of PAMs can be used with modification in DOE guidance and screening tools to assist the user with evaluation of monitored natural attenuation as a remediation option. PAMs may provide an effective graphical hierarchy to demonstrate the characterization, monitoring, and other technical issues associated with using monitored natural attenuation at a site. Modifications are, however, likely required, because the PAMs hierarchy does not appear to be sufficiently specific for individual contaminants or hydrologic and geochemical conditions important to mobility and attenuation of individual organic and inorganic contaminants.

2.2 Programmatic Issues

- Use of the term "monitored natural attenuation"

  - Conclusions
    - EPA uses the term "monitored natural attenuation" (MNA) when referring to the reliance on natural attenuation processes in a carefully controlled and monitored site remediation approach to achieve cleanup objectives. This definition indicates the importance of site monitoring and communicates to stakeholders, especially when presented in the context of the other elements in EPA Directive, that this remediation option is not a "walk-away" scenario.
    - DOE's decision-making framework guide, long-term monitoring guidance document, and software tool MNAtoolbox are consistent with EPA's Directive regarding DOE's use of the terms "monitored natural attenuation" and "natural attenuation."

  - Recommendation
    - DOE Headquarters, Field Offices, national laboratories, and supporting contractors should be consistent with EPA's Directive regarding the use of terms "monitored natural attenuation" and "natural attenuation" in presentations, documents (e.g., RODs), and decision tools (e.g., PAMs). "Monitored natural attenuation" should be used when referring to a remediation alternative, whereas "natural attenuation" refers to the natural processes that will be relied on for monitored natural attenuation.

- Linkage of other DOE activities with DOE and EPA guidance on monitored natural attenuation

  - Conclusion
    - DOE has prepared a decision-making framework guide, a long-term monitoring technical guidance document, and a software screening tool (MNAtoolbox) to help site managers and supporting contractors evaluate "monitored natural attenuation" as a remediation option at their site. The DOE has other guidance documents and user tools such as PAMs that identify "natural attenuation" as a possible remediation technology option.

  - Recommendation
    - All of DOE's remediation technologies guidance documents and user tools that include natural attenuation as a remediation option for contaminated sites should be linked and consistent with EPA's OSWER Directive 9200.4-17 and DOE's decision-making framework guide and long-term monitoring document for "monitored natural attenuation."

- EPA research activities

  - Conclusion
    - The EPA is currently considering the recommendations of the National Research Council in developing a plan for EPA's natural attenuation research.

  - Recommendation
    - If a dialogue does not already exist, DOE should develop a dialogue with EPA, one of DOE's major stakeholders, to identify opportunities to leverage the two research programs in natural attenuation and its "footprints," site characterization, and performance-monitoring methodologies.

2.3 Stakeholder Issues

  - Conclusions
    - As noted in the National Research Council review, there are important communication issues associated with proposing "natural attenuation" as a remediation option at a site, especially to nontechnical audiences.
    - The NABIR program has supported the development of *Guidelines—A Primer for Communicating Effectively with NABIR Stakeholders* (Bilyard et al. 2000). The purpose of this report was to provide a tool to help scientists effectively communicate technical information to expert and nonexpert stakeholder groups.
    - DOE's Office of Environmental Management funds DOE's Innovative Treatment Remediation Demonstration (ITRD) Program. The program was initiated to help accelerate the use of innovative remediation technologies. The ITRD Program is

based on a public-private technology demonstration concept that improves communications and teamwork among key participants.

- Recommendation
  - DOE should review the communication guidelines document by Bilyard et al. (2000) and DOE's ITRD Program to identify communication strategies and lessons learned that could be integrated, with modification, into its monitored natural attenuation guidance as a model for effective communication of technical information.

2.4 Other Natural Attenuation Issues of Potential Interest to DOE

- Conclusions
  - The main focus of the majority of natural attenuation studies and reviews has been on groundwater systems, especially on microbial, physical, and chemical attenuation processes for individual contaminants in such systems. Given the nature of contamination at DOE sites and DOE's responsibilities for closeout of such sites, there are a number of other issues that are potentially important to the use of monitored natural attenuation at DOE sites but do not, however, appear to be addressed in DOE programmatic and technical guidance for monitored natural attenuation. These issues include the following:

    - Role of monitored natural attenuation in remediation of contaminated vadose-zone and surface-water systems
    - Guidance provided for the assessment of monitored natural attenuation of single- versus multi-contaminant plumes
    - Detrimental effects from active remediation of the source terms on monitored natural attenuation of other contaminants' down-flow at that site (as noted in the National Research Council review of natural attenuation)
    - Guidance regarding setting trigger levels for contaminant concentrations at which active remediation technologies at a site change to passive, monitored natural attenuation
    - Role of future land use scenarios relative to the long-term effectiveness of monitored natural attenuation at a site
    - Role of ecological risk relative to evaluating the suitability of monitored natural attenuation, especially with respect to surface water and soil contamination, at a site
    - Relationship of performance monitoring elements associated with monitored natural attenuation to long-term stewardship issues at DOE sites.

- Recommendation

    - A review should be conducted to identify, summarize, and prioritize such issues that are not adequately addressed in the technical literature, DOE guidance documents, and screening tools, and possibly in EPA's OSWER Directive 9200.4-17.

3.0 Environmental Protection Agency Regulatory Guidance

3.1 OSWER Directive 9200.4-17

Until recently, there has been no regulatory guidance from EPA relative to proposing, evaluating, and approving monitored natural attenuation (MNA) for the remediation of organic and inorganic (metals and radionuclides) contaminants. On April 21, 1999, EPA's Office of Solid Waste and Emergency Response (OSWER) issued its final Directive, *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites* (OSWER Directive 9200.4-17).[a] This Directive clarifies EPA's policy regarding the use of monitored natural attenuation for the remediation of contaminated soil and groundwater at sites regulated under OSWER. It provides guidance to EPA staff, the public, and the regulated community on how EPA intends to exercise its discretion in implementing national policy on the use of monitored natural attenuation for organic and inorganic contaminants. The EPA cautions the user to be aware of the federal and state[b] statutory and regulatory requirements that apply to a site for which monitored natural attenuation is being evaluated as a remediation option.

The OSWER Directive 9200.4-17 defines natural attenuation processes to include the following:

> *...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 concentrations of contaminants in soil or groundwater. These in-situ processes include* ***biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation or destruction of contaminants*** (emphasis added).

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[a] The EPA issued the "draft interim final" version of this Directive in November 1997. The OSWER Directive 9200.4-17 is available at http://www.epa.gov/swerust1/oswermna/mna_epas.htm.

[b] Brady et al. (1997) note that state policies on natural attenuation were almost all being changed. Brady et al. (1997, Appendix 1) summarizes the results of a review completed by Ritz (1996) regarding acceptance of natural attenuation at the state level. When Ritz wrote his report (late 1996), 38 states were reviewing their positions on natural attenuation and expecting to modify their policies.

To employ monitored natural attenuation at a given site, OSWER Directive 9200.4-17 requires the following key elements:

- **Source Control**. Control of contamination sources and other highly contaminated areas should be evaluated as part of the remediation decision process. Source control measures include removal, treatment, or containment measures.

- **Detailed Site Characterization and Analysis**. The decision to use monitored natural attenuation requires that the decisions be thoroughly and adequately supported by site-specific characterization and analysis. The OSWER Directive states, "...the level of site characterization necessary to support a comprehensive evaluation of natural attenuation is more detailed than that needed to support active remediation." Three types of "evidence" should be used in such an evaluation:

    - *Historical groundwater and/or soil chemistry data that demonstrate a clear and meaningful trend of decreasing contaminant mass and/or concentrations over time at appropriate monitoring or sampling points.*
    - *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."*
    - *Data from field or microcosm studies....which directly demonstrate the occurrence of a particular natural attenuation process at the site and its ability to degrade the contaminant of concern...*

- **Time Frame**. The longer time frames typically associated with using monitored natural attenuation should be compatible with site-specific land and groundwater use scenarios.

- **Performance Monitoring**. The EPA views performance monitoring as more important for monitored natural attenuation than other types of remediation options due to the longer time frames, potential ongoing contaminant migration, and other uncertainties associated with natural attenuation. For this reason, the EPA links "monitoring" with "natural attenuation" when discussing remediation options. The monitoring programs should be designed to (OSWER Directive 9200.4-17):

    - demonstrate that natural attenuation is occurring as expected
    - detect changes in environmental conditions (e.g., geochemical, hydrogeologic, microbiological) that may affect the effectiveness of natural attenuation processes
    - identify any potentially toxic and/or mobile transformation products
    - confirm the contaminant plume is not expanding
    - ensure no unacceptable impact to downgradient receptors

  - detect new releases of contaminants that could affect the effectiveness of the natural attenuation processes
  - demonstrate the effectiveness of institutional controls
  - detect changes in environmental conditions (e.g., geochemical hydrogeologic, or microbiological, or others) that could affect effectiveness of the natural attenuation processes
  - confirm achievement of cleanup objectives.

- **Contingency Remedy**. The EPA requires that a contingency remedy should also be specified in the site remedy decision document. The contingency remedy is a remediation approach that can be used as backup if the selected remediation option (e.g., monitored natural attenuation) does not function as expected. The EPA recommends that criteria be established to indicate unacceptable performance of the natural attenuation processes and when to implement contingency remedies. Examples include increasing trends in contaminant concentrations in wells, detection of contaminants in wells outside the original plume boundary, and changes in land and/or water use.

OSWER Directive 9200.4-17 cautions the reader that:

- *Monitored natural attenuation should not be considered a default or presumptive remedy at any contaminated site.*

- *...use of monitored natural attenuation does not imply that EPA or the responsible parties are walking away from the cleanup or financial obligations at a site.*

3.2 Technical Guidance

Because OSWER Directive 9200.4-17 is a policy document, the Directive was not intended to include technical guidance on the evaluation of monitored natural attenuation remedies. Although the EPA's Office of Research and Development (ORD) is developing technical resource documents for evaluating monitored natural attenuation, the EPA notes that few EPA guidance documents currently exist on this subject. Technical guidance documents cited in the Directive include Chapter IX for evaluation of natural attenuation in EPA's alternative cleanup technologies manual for leaking underground storage tank (UST) sites (EPA 1995)[a] and the EPA's technical protocol for monitored natural attenuation at chlorinated solvent sites

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(a) The UST cleanup technology manual is available at http://www.epa.gov/swerust1/pubs/tums.htm, but the site notes that Chapter IX (Natural Attenuation) is under revision and has an indefinite date for completion.

(Wiedemeier et al. 1998; EPA 1998b).[a] Although technical information regarding monitored natural attenuation is available from a variety of other sources, such as those listed at the end of OSWER Directive 9200.4-17, the EPA notes that it does not officially endorse these non-EPA guidances nor necessarily agrees with all their conclusions.

The EPA's *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater* (Wiedemeier et al. 1998; EPA 1998b) is particularly noteworthy. This document (more than 240 pages) focuses on the technical issues associated with data collection and analysis to evaluate monitored natural attenuation through biological processes for remediating groundwater contaminated with mixtures of fuels and chlorinated aliphatic hydrocarbons. This protocol provides technical guidance with respect to initial site screening; collection of additional site characterization data in support of natural attenuation; refining the conceptual model, pre-model calculations and document indicators of natural attenuation; simulating natural attenuation using solute fate and transport models; conducting receptor exposure pathway analyses; evaluating supplemental source removal options; preparing a long-term monitoring plan; and presenting findings. The document also contains three extensive appendixes. Appendix A in Wiedemeier et al. (1998) discusses field investigation methodologies, including the collection of groundwater samples and completion of field analyses to evaluate the demonstration of remediation by monitored natural attenuation; Appendix B reviews the important nondestructive and destructive (biotic and abiotic) attenuation mechanisms affecting the fate and transport of chlorinated solvents and fuel hydrocarbons in groundwater; Appendix C deals with data interpretation; natural attenuation calculations such as hydraulic parameter calculations, contaminant source term calculations, and confirming and quantifying biodegradation; and the design, implementation, and interpretation of microcosm studies.

Wiedemeier et al. (1998) summarize the steps necessary to demonstrate natural attenuation and the important regulatory decision points for implementing natural attenuation at sites contaminated with chlorinated solvents. The protocol includes the following nine steps:

1. Review available site data, develop a preliminary conceptual model, and determine whether receptor pathways have already been completed.

2. If sufficient existing data of appropriate quality exist, screen the site and assess the potential for natural attenuation.

(a) Wiedemeier et al. (1998) and EPA (1998) are used interchangeably in the literature as the reference citation for EPA's protocol for monitored natural attenuation at chlorinated solvent sites. Both citations refer to the same EPA document number. This protocol can be viewed on the Internet by selecting its title from the list of EPA reports at http://www.epa.gov/clariton/clhtml/pubtitle.old.html.

3. If preliminary site data suggest natural attenuation is potentially appropriate, collect additional site characterization to further evaluate natural attenuation.

4. Refine conceptual model based on site characterization data, complete pre-modeling calculations, and document indicators of natural attenuation.

5. Simulate natural attenuation using solute fate and transport models that allow incorporation of a biodegradation term.

6. Identify potential receptors and exposure points and conduct an exposure pathway analysis

7. Evaluate whether supplemental source control measures are needed to allow monitored natural attenuation to be a viable remedial option.

8. Prepare a long-term monitoring and verification plan for the selected alternative, which may include monitored natural attenuation alone or in concert with supplemental remediation systems.

9. Present findings of natural attenuation studies in an appropriate regulatory remedy selection document.

The EPA's technical protocol for monitored natural attenuation at chlorinated solvent site identifies specific research needs based on the lines of evidence required to evaluate the feasibility of monitored natural attenuation at a site. The protocol provides a useful "map" to indicate and possibly prioritize where research and certain types of site characterization data, site-screening calculations, and specialized computer modeling calculations are needed for evaluating the feasibility of monitored natural attenuation at a site.

4.0 U.S. Department of Energy

4.1 Guidance and Screening Tools

The DOE's decision-making framework (contact: Steve Golian, DOE Office of Technical Program Integration, EM-22) for evaluating the effectiveness of monitored natural attenuation as a remediation option is described in the DOE document, *Decision-Making Framework Guide for the Evaluation and Selection of Monitored Natural Attenuation Remedies at Department of Energy Sites* (DOE 1999a).[a] The DOE used the principles described in EPA's OSWER Directive 9200.4-17 for monitored natural attenuation as a foundation to develop this guide. The document was prepared for remedial project managers who must evaluate various remediation action alternatives at waste sites. The guide is intended to be used in conjunction with other DOE guidance that includes the document *Technical Guidance for the Long-Term Monitoring of Natural Attenuation Remedies at Department of Energy Sites* [DOE 1999b; contact: Steve Golian, EM-22)][b] and the software screening tool MNAtoolbox (contact: Patrick Brady, Sandia National Laboratories).[c] The decision-making framework and long-term monitoring documents were designed to help direct the appraisal and implementation of monitored natural attenuation as a remediation option and were not meant to be prescriptive.

4.1.1 Decision-Making Framework

The DOE recommends a tiered approach to evaluate whether monitored natural attenuation is a feasible remediation option at a site (DOE 1999a). This three-tier framework relies on a set of favorable conditions based on guidelines contained in the EPA OSWER Directive 9200.4-17 to steer the evaluation process. The first tier is a scoping phase to determine whether existing site information sufficiently suggests that favorable conditions are or will likely be met for monitored natural attenuation to be a viable remediation option. If monitoring data are insufficient for this initial appraisal, DOE recommends that secondary lines of information (e.g., rates of dilution and dispersion and/or processes such as degradation, radioactive decay, sorption, precipitation, and/or volatilization) be considered to ascertain if monitored natural attenuation is feasible at a site.

(a) This document is available at http://www2.em.doe.gov/framework/, which can be found searching on "natural attenuation" at DOE's home page.

(b) This document is available at http://www2.em.doe.gov/techguide/, which can be located by searching on "natural attenuation" at DOE's home page.

(c) MNAtoolbox is described in detail in Brady et al. (1999). The software package and User's Guide are available on-line at http://www.sandia.gov/eesector/gs/gc/na/mnahome.html.

The second and third tiers are alternative evaluation and selection phases. Evaluations need to be completed regarding the following issues:

- What additional site-specific characterization and modeling activities are necessary to determine the probable time frame needed for monitored natural attenuation to attain site-specific remediation objectives?

- Does the hydrogeologic setting provide sufficient capacity to attenuate the contaminant load?

- What is the likely range of groundwater compositions and their potential effects on contaminant transport and thus natural attenuation processes?

- What is the extent of reversibility where sorption and/or redox reactions are considered the primary natural attenuation mechanisms?

- What are potential toxicity of transformation products resulting from the degradation of organic compounds or daughter products from the decay of radionuclides?

- Is the anticipated time frame for reaching remediation objectives via monitored natural attenuation compatible with anticipated future land and groundwater use?

4.1.2 Long-Term Monitoring

In addition to outlining the approach for determining the feasibility of monitored natural attenuation, the decision-making framework includes the design of a monitoring network as part of the evaluation process. The long-term monitoring associated with monitored natural attenuation has the following three components:

- **Ambient monitoring** upgradient of the contaminant plume to provide hydrogeologic and geochemical information about pre-contamination conditions

- **Performance monitoring** within and immediately adjacent to the plume to determine 1) contaminant concentrations within and in the vicinity of the plume; and 2) other indirect parameters (e.g., redox potential, degradation products) that indicate if attenuation mechanisms are, or likely will be, functioning as predicted

- **Detection monitoring** at the boundary of the monitored natural attenuation management zone to provide data to establish if attenuation processes are not performing adequately and previously agreed upon contingency measures should be implemented

A more detailed discussion of the role of monitoring and the key considerations in designing a monitoring network are given in DOE's 21-page *Technical Guidance for the Long-Term Monitoring of Natural Attenuation Remedies at Department of Energy Sites* (DOE 1999b). This document discusses the role of site monitoring with respect to monitored natural attenuation, uncertainties in conceptual site models, design considerations for site monitoring networks, and statistical approaches for interpreting monitoring data.

4.1.3 MNAtoolbox

To assist with these evaluation/decision processes, Sandia National Laboratories recently developed the MNAtoolbox software tool(a) (Brady et al. 1999) for DOE. MNAtoolbox is a screening tool designed to help site managers with the following monitored natural attenuation issues:

- Identify the most likely attenuation pathways for a particular contaminant at a given site
- Identify processes that might decrease natural attenuation of a particular contaminant at a given site
- Identify data needs for demonstrating natural attenuation for a particular contaminant at a given site
- Provide examples of regulatory acceptance of monitored natural attenuation for specific contaminants.

The specific contaminants included in MNAtoolbox are listed in Table 3. To begin the screening process, the user selects a particular contaminant from the table on the introductory screen. The user is then provided with several menu options that show a phase diagram, potential natural attenuation pathways (see Table 1) and mitigating conditions, future use caveats, relevant aqueous species, solid compounds, and potential chelators that affect the contaminant's mobility, soil background levels, CERCLA precedents (i.e., RODs), and linkages to other related Internet sites for the selected contaminant. For example, the MNAtoolbox lists "mineral formation" and "sorption onto iron/manganese (hydr)oxides, carbonate and phosphate minerals" as potential natural attenuation pathways for the uranium isotopes. Potential mitigating conditions for the natural attenuation of uranium isotopes include low pH conditions which stabilizes carbonates and iron hydroxides; the presence of organic acids and chelates, which may decrease

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(a) The tool and User Guide are available at http://www.sandia.gov/eesector/gs/gc/na/mnahome.html sorption; high pH and/or dissolved carbonate concentrations, which may decrease sorption; and low redox, which will dissolve iron hydroxides but cause reduction of U(VI) to U(IV), which is less soluble.

To help the user assess whether natural attenuation may be feasible for a selected contaminant at a specific site, MNAtoolbox includes a "Site Screening Scorecard." The scorecard provides a qualitative estimate of the potential for natural attenuation based on a sum of the following attenuation factors: 1) hydrologic dilution, 2) sorption, 3) irreversible uptake by the soil matrix, 4) precipitation as a mineral phase, 5) biodegradation, and 6) radioactive decay. The equations on which this screening calculation is based and site-specific data required for the calculation are briefly described in Appendix A and discussed in detail in Brady et al. (1999). If the scorecard produces a score approaching the maximum of 100, monitored natural attenuation may be effective and as a remediation option. A low score may indicate that natural attenuation is not feasible or that additional characterization data and modeling studies are needed to refine the scorecard calculation for a particular contaminant at a specific site (Brady et al. 1999).

Sandia has conducted a limited set of calibration studies using MNAtoolbox to estimate the nature and extent of natural attenuation for individual contaminant types. Recent efforts at Sandia have focused on making the scoring calculation in MNAtoolbox more "plume-specific" as opposed to its present state of being largely "contaminant-specific." Preliminary efforts to calibrate MNAtoolbox have included development of plume modules with which the scorecard could be compared and the scoring procedure subsequently optimized. The objective of the latter would be to make the calculated score more closely reflect actual plume data. There are submodules (historical case analyses) for fuel hydrocarbons,(a) chlorinated solvents, and uranium (Jove-Colon et al. 2001) at present. Some work has also been done to develop modules for ^{90}Sr and ^{137}Cs.

The nature and extent of natural attenuation has been assessed in at least a preliminary fashion for most of the plumes in these submodules, but these studies have not been finished nor the results published. Optimization of the scoring approach would be done by running the "Site Screening Scorecard" on all plume data sets in each of the plume submodules. Comparison of the scorecard results to independent evidence of natural attenuation (or its absence) at each site would allow identification of chemical and physical features critical to plume attenuation or migration and, ultimately, updating of the scoring calculation. Upon calibration, a user would be able to compare the scorecard calculations for their plume with a statistically significant number

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(a) The plume data sets for fuel hydrocarbons and chlorinated solvents were developed by D. Rice and coworkers at Lawrence Livermore National Laboratory. The historical case analyses for uranium were compiled by Jove-Colon et al. (2001).

Table 3. Contaminants Listed in MNAtoolbox

Organic Contaminants		
BTEX	Dichloroethylene (DCE)	Trichloroethylene (TCE)
Carbon tetrachloride	Tetrachloroethane	Vinyl chloride
Chlorobenzene	Tetrachloroethylene	
Dichloroethane (DCA)	Trichloroethane (TCA)	
Inorganic Contaminants		
Americium-241	Copper	Strontium-90
Arsenic	Iodine	Technetium-99
Barium	Lead	Thorium
Cadmium	Mercury	Tritium
Cesium-137	Nickel	Uranium isotopes
Chromium	Plutonium isotopes	Zinc
Cobalt-60	Radium	

of similar plumes in the plume portfolio. This would provide more credence to screening calculations used to examine (or ignore) monitored natural attenuation as a potential remedial option.

The MNAtoolbox and its “Site Screening Scorecard” were designed for DOE as a site-screening tool to help site managers assess the potential for natural attenuation of particular dissolved contaminants at site-specific conditions, and develop conceptual site model hypotheses.(a) The MNAtoolbox is not applicable to sites with active source terms or screening of natural attenuation of contaminants present as separated phases. Given the complexity of mercury contaminants in soil and groundwater systems, the user is also cautioned about applying this software to screening sites for natural attenuation of mercury. Caveats regarding the use of MNAtoolbox are listed at the end of the User’s Guide, which is provided on-line with the software tool.

(a) The National Research Council (NRC 2000) recently published a review of natural attenuation as a remediation option for groundwater contaminants (Section 5). The NRC was critical of the simplicity of DOE’s protocol and MNAtoolbox, given the complexity of natural attenuation processes and the nature of subsurface contaminations at DOE sites. Their concerns (see Section 5.3) and Sandia’s responses to these criticisms are available on-line at the Internet home page for the MNAtoolbox site-screening tool.

4.2 DOE Research Portfolios

The DOE conducts several applied and basic research programs in the areas of bioremediation, environmental sciences, and geosciences. These programs include the following:

- Subsurface Contaminants Focus Area (SCFA) in the DOE Office of Environmental Management's Office of Science and Technology (James Wright, Lead office manager, SRS)
- Natural and Accelerated Bioremediation Research (NABIR) program in the DOE Office of Science's Office of Biological and Environmental Research (John Houghton and Anna Palmisano, Program Managers, SC-74)
- Environmental Management Science Program (EMSP) in DOE's Office of Environmental Management and Office of Science (Mark Gilbertson, Director, EM-52)
- Geosciences Research Program in the DOE Office of Science's Office of Basic Energy Sciences (Nicholas Woodward, Program Director, SC-14).

Based on the objectives of these programs, results from many of the past and current studies supported by these programs should help to 1) extend our mechanistic understanding of natural processes that may attenuate certain contaminants in soils and groundwater systems via oxidation/reduction, adsorption, and precipitation; 2) identify under what conditions and to what extent these processes are reversible; and 3) develop analytical methods to characterize and monitor such processes and their degradation products. Such results address key issues of EPA's OSWER Directive 9200.4-17 (see Section 3), such as site characterization and analysis and performance monitoring as they relate to identifying and quantifying natural attenuation processes and their rates for different contaminants at a site. This research also addresses observations and recommendations identified in NRC (2000b) (discussed in Section 5.1 and Appendix C) review of reliance on natural attenuation processes as a groundwater remediation option. The results of some DOE studies, for example, may address the National Research Council's recommendation of using "footprints" to document which attenuation processes are responsible for observed decreases in contaminant concentrations at a site. The NRC (2000b) defines "footprint" as a concentration change of one or more reactants (in addition to the contaminants) or products of the process that is transforming or immobilizing the contaminants. A review of the extensive number of project descriptions and publications as described on the Internet sites for these DOE research programs is beyond the scope of our current effort. Such a review of DOE research in bioremediation, environmental sciences, and geosciences would be an opportunity to map the results expected from these studies relative to the different natural attenuation processes affecting each of the organic and inorganic contaminants of DOE interest (see Table 2). This recommendation is similar to one made recently by the NRC (2000a). At the request of DOE, the NRC (2000a) completed a review of DOE's Environment Management Science Program (EMSP) with respect to addressing subsurface contamination problems at DOE sites (see Section 4.2). One of National Research Council's (2000a) recommendations in the area of program integration was for DOE to "Integrate existing data and ideas from both DOE sites and basic research programs outside DOE.…"

In addition to fundamental research being supported by these DOE programs, there are other activities in these DOE programs that may apply to important elements in EPA's OSWER Directive 9200.4-17 and the National Research Council's review of natural attenuation. For example, the National Research Council presented several recommendations (Appendix C) with respect to addressing community concerns about natural attenuation and communicating the results of site studies and natural attenuation protocols to non-technical audiences. The NABIR program has supported the development of *Guidelines—A Primer for Communicating Effectively with NABIR Stakeholders* (Bilyard et al. 2000). The purpose of this report was to provide a tool to help scientists communicate technical information to expert and nonexpert stakeholder groups. Some of the issues associated with dynamics of basic science and risk communication between scientists and nonexperts were also discussed in a dialogue-based study reported by Word et al. (1999). These efforts could serve as a model and, with some modification, as guidelines for site management and technical staff to effectively communicate the technical information supporting their proposed use of monitored natural attenuation for remediation at a DOE contaminated site.

Similarly, communication strategies learned in DOE's Innovative Treatment Remediation Demonstration(a) (ITRD) Program may also be useful with respect to effective communication of natural attenuation site studies and protocols to non-technical audiences. The ITRD Program is funded by DOE's SCFA and is based on a public-private technology demonstration concept that improves communications and teamwork among key participants. Obstacles to using new technologies are decreased by involving government, industry, regulatory agencies, and public stakeholders in technology assessment, implementation, and validation. The ITRD Program includes projects at several DOE sites including Hanford, Mound, Oak Ridge, Paducah, Pantex, and Los Alamos. Sandia, as technical coordinator of ITRD program, establishes technical advisory groups that are responsible for recommending the best remediation options for each site considering cost, performance, and regulatory issues. The advisory groups are composed of technical representatives from DOE and the national laboratories, EPA and its laboratories, user industries with similar problems, and state and federal regulatory agencies.

(a) The DOE's Innovative Treatment Remediation Demonstration (ITRD) Program is described on the Internet at http://www.em.doe.gov/itrd/.

4.3 Other DOE Sources of Information

A query of Internet home pages for DOE and DOE-EM identified numerous references to activities, documents, and training pertaining to "natural attenuation" and "monitored natural attenuation." It was not possible to review all of these DOE sources, but a few of the pertinent sources that are not discussed elsewhere in this paper are summarized in Appendix B. These sources include DOE's Technical Information Exchange (TIE) Program, reports by Brady et al. (1999, 1997), DOE's PAMs, and DOE environmental management training on monitored natural attenuation.

The TIE program (contact: Mary McCune, DOE Office of Technical Program Integration, EM-22) provides a means of sharing information on the use of environmental management technologies within the DOE complex. The 11th annual TIE workshop, held in October 1999, included Session VII, which focused on monitored natural attenuation. The topics included in the panel sessions are listed in Appendix B.

Reports by Brady et al. (1999, 1997) (Appendix B) are of particular note. The 1999 report, *Site Screening and Technical Guidance for Monitored Natural Attenuation at DOE Sites,* was intended to support DOE's guidance document, *Decision-Making Framework Guide for the Evaluation and Selection of Monitored Natural Attenuation Remedies at Department of Energy Sites*. The 1997 report, *Natural Attenuation of Metals and Radionuclides: Report from a Workshop Held by Sandia National Laboratories,* summarizes presentations and panel discussions from a workshop held specifically on the natural attenuation of only inorganic contaminants.

DOE's Office of Environmental Restoration (EM-40) (contact: Mary McCune, EM-22) has developed a set of PAMs that identify commercially available environmental restoration technologies and rank them on the basis of performance, risk of technology failure, and cost. Natural attenuation (Appendix B) is one of the in situ treatment technologies included in PAMs.

The DOE National Environmental Training Office (NETO) (contact: Nick Delaplane, Savannah River Operations Office) provides training to DOE employees and its contractors on a variety of environmental management topics, including monitored natural attenuation. NETO is managed out of DOE's Savannah River Operations Office (under Tom Heenan, Assistant Manager for Environmental, Science, and Technology). Training Course NETO0428, "Monitored Natural Attenuation," was most recently presented on September 20, 2000 in Richland, Washington (Appendix B).

5.0 National Research Council Reviews

5.1 National Research Council Review on Natural Attenuation

5.1.1 Scope

In 1997, the National Research Council formed the 14-member Committee on Intrinsic Remediation. The tasks of this committee were the following (NRC 2000b):

- *Assess current knowledge about the natural subsurface processes that play critical roles in intrinsic remediation*
- *Outline what intrinsic remediation can and cannot achieve*
- *Assess risks associated with leaving contaminants in place*
- *Identify the measurements, observations, and monitoring needed when intrinsic remediation is chosen instead of engineered remediation*
- *Evaluate the adequacy of existing protocols for determining whether intrinsic remediation is an appropriate strategy for contaminant management.*

The committee's assessment was based on the expertise of the committee members, review of published documents and protocols pertaining to natural attenuation, interviews with other experts and community leaders, and four public information gathering meetings. The findings represent the unanimous consensus of the committee.

The committee limited their assessment to a definition of natural attenuation that is narrower than that given in EPA OSWER Directive 9200.4-17. The committee focused their review only on natural transformation and immobilization processes. They could not agree on the suitability of dilution and dispersion as remediation strategies. The committee believed that transformation and immobilization processes are 1) more difficult to understand and 2) had a more limited information base compared with dilution and dispersion. They also thought that this narrower definition of natural attenuation processes could lessen the concerns community members often have about natural attenuation.

5.1.2 Findings and Recommendations

The findings from this review were recently published by the National Research Council in the book, *Natural Attenuation for Groundwater Remediation*, and summarized in the CY-2000 papers, "Evaluating Natural Attenuation for Groundwater Cleanup" (MacDonald 2000) in *Environmental Science and Technology* and "National Research Council Guidance on Natural Attenuation" (Rittmann and MacDonald 2000) in the book, *Natural Attenuation Considerations and Case Studies*. The committee's review and specific findings (NRC 2000b) are presented in chapters on community concerns about natural attenuation, scientific basis for natural attenuation, approaches for evaluating natural attenuation, and protocols for natural attenuation. The committee's principal findings are the following (verbatim from NRC 2000b, pp.2-3):

- *Natural attenuation is an established remedy for only a few types of contaminants*
- *Rigorous protocols are needed to ensure that natural attenuation potential is analyzed properly*
- *Natural attenuation should be accepted as a formal remedy for contamination only when the processes are documented to be working and are sustainable*
- *Community members must be provided with documentation of these processes and an opportunity to participate in decision making.*

The National Research Council's specific conclusions and recommendations, taken verbatim from the NRC (2000b), are listed in Appendix C. Although all of the findings in Appendix C are important, the following specific conclusions and recommendations are particularly important to the objective of this paper:

- *Natural attenuation of some compounds can form hazardous byproducts that in some cases can persist in the environment.*
- *Natural attenuation processes cannot destroy metals but in some cases can immobilize them.*
- *In some cases, removing contaminant sources can speed natural attenuation, but in other cases it can interfere with natural attenuation.*
- *Responsible parties should use "footprints" of natural attenuation processes to document which mechanisms are responsible for observed decreases in contaminant concentration in the groundwater.*

- *Responsible parties should gather field data in order to evaluate the validity of the conceptual model and quantify the natural attenuation processes.*

- *The national consensus guidelines and all future natural attenuation protocols should be peer reviewed.*

As part of their assessment of the scientific basis for natural attenuation, the committee evaluated the potential of natural attenuation as a viable remediation option for different types of contaminants. They based their ratings on the current level of understanding of the dominant attenuation processes and the probability of favorable site-specific conditions. The committee's ratings are listed in Tables 4a and 4b.

5.1.3 Criticism of DOE's Protocol on Monitored Natural Attenuation

As noted earlier, the National Research Council review was critical of DOE's protocol and the MNAtoolbox scoring system and calculations (NRC 2000b, pp. 13, 18, 223-225). Their concerns and Sandia's responses are listed on the home page for the MNAtoolbox site-screening tool. Sandia responded that the committee's assessment was apparently based on their review of *Site Screening and Technical Guidance for Monitored Natural Attenuation at DOE Sites* (Brady et al. 1999) and MNAtoolbox and did not include the other DOE documents such as *Decision-Making Framework Guide for the Evaluation and Selection of Monitored Natural Attenuation Remedies at Department of Energy Sites* (DOE 1999a) and *Technical Guidance for the Long-Term Monitoring of Natural Attenuation Remedies at Department of Energy Sites* (DOE 1999b).

The National Research Council committee noted that DOE's protocol was the only document identified in their review that addressed inorganic as well as organic contaminants and represents "...a needed initial attempt to address a complicated subject...." However, they criticized DOE's protocol and MNAtoolbox scoring system and calculations as being an oversimplification, given the known complexity of natural attenuation processes and the nature of subsurface contamination at DOE sites. Sandia responded that the MNAtoolbox was "...specifically designed to simplify processes to the greatest extent possible" in order to provide a tool for screening the efficacy of natural attenuation at a site, and not for "...transport calculations, risk assessments, or final site decisions...." Although the committee found MNAtoolbox simple to use, they thought that the natural attenuation factor calculations were difficult to understand and an oversimplifcation of various processes. Sandia agreed that natural attenuation processes and conditions at contaminated sites were complex but responded that the scorecard calculations were designed to guide further site characterization and monitoring activities, not final site decisions.

Table 4a. Summary of National Research Council's Assessment of Efficacy of Natural Attenuation Processes for Remediation of Certain Organic Contaminants (NRC 2000b)

Chemical Class	Current Level of Understanding	Likelihood of Success Given Current Level of Understanding[(a)]
Hydrocarbons		
BTEX	High	High
Gasoline, fuel oil	Moderate	Moderate
Nonvolatile aliphatic compounds	Moderate	Low
Polycyclic aromatic hydrocarbons (PAHs)	Moderate	Low
Creosote	Moderate	Low
Oxygenated Hydrocarbons		
Low-molecular-weight alcohols, ketones, esters	High	High
MtBE	Moderate	Low
Halogenated Aliphatics		
Tetrachloroethene, trichloroethene (TCE), carbon tetrachloride	Moderate	Low
Trichloroethane (TCA)	Moderate	Low
Methylene chloride	High	High
Vinyl chloride (VC)	Moderate	Low
Dichloroethene	Moderate	Low
Halogenated Aromatics		
Highly Chlorinated		
PCBs, tetrachlorodibenzofuran, pentachlorophenol, multichlorinated benzenes	Moderate	Low
Less Chlorinated		
PCBs, dioxins	Moderate	Low
Monochlorobenzene	Moderate	Moderate
Nitroaromatics		
TNT, RDX	Moderate	Low

(a) The NRC (2000b, p. 139) defines "Likelihood of success" as the probability that at any given site, natural attenuation of a given contaminant is likely to protect human health and the environment. The National Research Council defines the qualifiers as the following:
High – scientific knowledge and field evidence are sufficient to expect that natural attenuation will protect human health and the environment at more than 75% of the contaminated sites
Moderate – natural attenuation can be expected to meet regulatory standards at about half of the sites
Low – natural attenuation is expected to be protective at less than 25% of contaminated and/or result from a poor level of scientific understanding.

Table 4b. Summary of National Research Council's Assessment of Efficacy of Natural Attenuation Processes for Remediation of Certain Inorganic Contaminants (NRC 2000b)

Chemical Class	Current Level of Understanding	Likelihood of Success Given Current Level of Understanding[(a)]
Metals		
Nickel	Moderate	Moderate
Copper, zinc	Moderate	Moderate
Cadmium	Moderate	Low
Lead	Moderate	Moderate
Chromium	Moderate	Low to moderate
Mercury	Moderate	Low
Nonmetals		
Arsenic	Moderate	Low
Selenium	Moderate	Low
Oxyanions		
Nitrate	High	Low
Perchlorate	Moderate	Low
Radionuclides		
Cobalt-60	Moderate	Moderate
Cesium-137	Moderate	Moderate
Tritium	High	Moderate
Strontium-90	High	Moderate
Technetium-99	Low	Low
Plutonium-238, -239, -240	Moderate	Low
Uranium-235, -238	Moderate	Low

(a) The definitions given by NRC (2000b) for "Likelihood of Success" and listed qualifiers are given in the footnote at the bottom of Table 4a.

The National Research Council committee was also concerned that DOE's protocol would be misused as a decision-making tool and produce misleading results because the protocol includes inorganic contaminants, addresses the concept of irreversible sorption for both inorganic and organic contaminants, and is readily accessible over the Internet. It was recommended, therefore, that DOE's protocol be peer reviewed and revised.

5.1.4 Future Impact of National Research Council Review

In addition to specific recommendations, MacDonald (2000) anticipates that the National Research Council review will also encourage more research and examination of current natural attenuation policies. MacDonald (2000) indicates that EPA's Science Advisory Board (SAB) will use the National Research Council report as a major source of input in writing a plan for the EPA's natural attenuation research (see Section 6). According to MacDonald (2000), EPA might also revise its natural attenuation policy based on National Research Council's conclusions and recommendations.

5.2 National Research Council Review of DOE's Environmental Management Science Program (EMSP)

The NRC (2000a) recently published the results of a review of DOE's Environmental Management Science Program (EMSP). The National Research Council committee was asked by DOE to provide recommendations for a long-term science program for subsurface contamination problems at DOE sites. The National Research Council based their review on the EMSP's research projects for fiscal years 1996 and 1997 and research programs conducted by other DOE offices and other federal agencies.

The NRC's (2000a) recommendations for a basic research subsurface science program addressed the issues of program vision, research emphases, and implementation. Many of the National Research Council's recommendations in the latter two issues crosscut with technical needs that are also important to the evaluation and implementation of monitored natural attenuation at contaminated sites. The National Research Council (2000a) found that projects on remediation of subsurface contamination, especially treatment and destruction of organic contaminants through physical, chemical, and biological processes, were a major area of strength in the EM Science Program. The National Research Council however recommended that the EMSP encourage more research on metals and radionuclides, especially given the importance of these contaminants at DOE sites. On the issue of program integration, the NRC (2000a) suggested that DOE integrate existing data and ideas from DOE sites and basic research programs outside DOE. The National Research Council committee established that little effort was being made to coordinate these research projects and transfer their results into the DOE remediation program.

The National Research Council's pertinent recommendations (verbatim from NRC 2000a) in the technical areas[a] of subsurface characterization, conceptual model development, and site monitoring are listed below. The National Research Council committee recommended that additional basic research was needed to support the following:

- Location and characterization of subsurface contaminants and characterization of the subsurface
    - *Improved capabilities for characterizing the physical, chemical, and biological properties of the subsurface*
    - *Improved capabilities for characterizing physical, chemical, and biological heterogeneity, especially at the scales that control contaminant fate and transport behavior*
    - *Improved capabilities for measuring contaminant migration and system properties that control contaminant movement*
    - *Methods to integrate data collected at different spatial and temporal scales to better estimate contaminant and subsurface properties and processes"*
    - *Methods to integrate such data into conceptual models.*
- Conceptual modeling
    - *New observational and experimental approaches and tools for developing conceptual models that apply to complex subsurface environments*
    - *New approaches for incorporating geological, hydrological, chemical, and biological subsurface heterogeneity into conceptual model formulations at scales that dominate flow and transport behavior*
    - *Development of coupled-process models through experimental studies at variable scales and complexities that account for the interacting physical, chemical, and biological processes that govern contaminant fate and transport behavior*
    - *Methods to integrate process knowledge from small-scale tests and observations into model formulations"*
    - *Methods to measure and predict the scale dependency of parameter values*
    - *Approaches for establishing bounds on the accuracy of parameters and conceptual model estimates from field and experimental data.*

(a) The NRC (2000a) also made recommendations regarding the technical area of waste containment and stabilization. Although these recommendations are important with respect to site remediation, they are not as directly applicable to monitored natural attenuation and therefore are not listed above.

- Monitoring and validation
    - *Development of methods for designing monitoring systems to detect both current conditions and changes in system behavior*
    - *Development of validation processes*
    - *Determining the key measurements that are required to validate models and system behaviors, the spatial and temporal resolutions at which such measurements must be obtained, and the extent to which surrogate data can be used in validation efforts*
    - *Research to support the development of methods to monitor fluid and gaseous fluxes through the unsaturated zone, and for differentiating diurnal and seasonal changes from longer-term secular changes.*

6.0 EPA's Science Advisory Board Review of EPA's Monitored Natural Attenuation Research Program

6.1 Scope of Review

The EPA Science Advisory Board (SAB) recently completed a review of EPA's research program for monitored natural attenuation of contaminants in groundwater, soils, and sediments.(a) The review was requested by EPA's Office of Research and Development (ORD). The ORD asked the SAB to focus their review on evaluating the effectiveness and quality of EPA's current and proposed research with respect to the following issues:

- EPA's *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water* (Wiedemeier et al. 1998; EPA 1998b)
- Use of monitored natural attenuation at underground storage tank (UST) sites, especially with respect to contamination by MBTE and other oxygenates
- Application of monitored natural attenuation for inorganic contaminants (e.g., arsenic and other metals) in soils and groundwater
- Use of monitored natural attenuation for contaminated aquatic sediments, especially within the context of persistent organic (e.g., PCBs, DDT, PAHs, and others) and inorganic contaminants (e.g., arsenic, mercury, and others).

6.2 Findings and Recommendations

A draft report summarizing the SAB's review, findings, and recommendations was released February 1, 2000 on the Internet for general information.(b) In its review, the SAB relied extensively on the NRC (2000b) review on natural attenuation for groundwater remediation. The principal findings and recommendations made by the SAB with respect to the above issues are the following (taken verbatim from the draft EPA-SAB report):

- Natural attenuation of chlorinated solvents

(a) A brief reference to this review was made on p. 37 of the December 11, 2000 issue of "*Chemical & Engineering News*."

(b) A draft copy of the EPA-SAB report is available at http://www.epa.gov/science1/eec00abc.pdf.

- Findings
  - *The Technical Protocol has summarized the current understanding of attenuation mechanisms for chlorinated solvents. However, results from field sites are not always consistent with results extrapolated from lab-scale research. Paramount among these inconsistencies are observed reductive dechlorination rates and accumulative products. Categorization of chlorinated solvent sites (i.e., Types I, II, III as defined in the protocol) is often inappropriate.*
  - *Much of the uncertainty results from the difficulty in obtaining accurate field information to account for all the relevant processes and quantify the reaction rates.*
  - *Other factors that contribute to uncertainties in MNA for chlorinated solvents include*
    - *Impacts of high-concentration source areas on natural attenuation, including: changes in effective solubility and partitioning over time, and effects of high concentrations on biodegradation rates near the source*
    - *Synergistic/antagonistic interactions among chlorinated solvents and other chemicals; and*
    - *Degradation by mechanisms other than reductive dechlorination.*

- General recommendations
  - *Develop and conduct laboratory and field research that will elucidate when and why site conditions allow completed degradation of chlorinated solvents.*
  - *Focus research programs on how fluxes of electronic donors and acceptors from source areas interact to control dechlorination rates at MNA sites. This work may involve establishing a database of field sites for which sites have been comprehensively characterized to document dechlorination reactions.*
  - *Promote model development to incorporate spatially heterogeneous processes (for example, spatial variations of reaction types and rates in plumes) and temporally heterogeneous processes (for example, temporal changes in source composition due to retardation in source zones).*
  - *De-emphasize simple categorization of chlorinated solvent sites (i.e., Type I, II, or III) and eliminate scoring systems.*

- Monitored natural attenuation at underground storage tank sites

  - Findings
    - *The use of MNA for the remediation for groundwater plumes has been driven historically by concerns of BTEX contamination resulting from UST fuel releases. The use of MNA for the remediation of UST sites at which BTEX compounds are the sole contaminants of concern is maturing scientifically and has been accepted at certain sites as an adequate approach to address subsurface remediation concerns.*

    - *The presence of fuel oxygenates in UST source zones, and subsequently in a down gradient plume, introduces uncertainty in the effectiveness of MNA to provide an acceptable level of protection at UST sites – compared to BTEX only sites. This uncertainty is a result of the high solubility, high mobility, and apparent persistence of MtBE (and other oxygenates) in groundwater.*
    - *Protocols, or guidelines leading to protocols, for the use of MNA should consider the complicating factors that oxygenates pose to successful remediation of plumes originating from UST.*
    - *Because fuels contain hydrocarbons other than BTEX, these hydrocarbons may be relevant for the assessment of MNA remedies. ...Because trimethylbenzene is less soluble and less volatile than benzene, it may dominate the toxicity of weathered gasoline.*

  - General recommendations
    - *Determine the biodegradability of MtBE and other oxygenates under various field conditions (for example, various electron acceptor conditions and mixtures of hydrocarbon substrates).*
    - *Improve the predictability of dissolution rates of MtBE and other fuel components and their fluxes exiting source areas.*
    - *Monitor multiple "representative" and highly characterized sites to provide an information database on indirect measures of MtBE natural attenuation (as has been done with BTEX) to support previous and ongoing site assessments.*
    - *Determine whether hydrocarbons in gasoline not on the Target Compound List should be considered for remedial risk analyses.*

- Monitored natural attenuation for inorganic contaminants

  - Findings
    - *Immobilization, the primary attenuation process operative for arsenic and metals, is not fully understood.*
    - *No footprinting or monitoring guidance is currently available for employing MNA for metals and arsenic.*
    - *Currently, it is difficult to reconcile laboratory and field data for arsenic and metal reactions in soil.*
    - *Although a framework that addresses the natural attenuation of inorganics is urgently needed, the processes that affect speciation, fate, and transport of arsenic and other metals are not sufficiently understood.*

  - General recommendations
    - *...further elucidate attenuation mechanisms governing the immobilization of arsenic and other metals*
    - *...evaluate changes in geochemical conditions responsible for the remobilization of once immobilized contaminants*
    - *...perform studies to understand the fate and behavior of arsenic and metals in co-mingled organic/inorganic plumes*
    - *Develop guidelines for obtaining field and analytical data needed for MNA (e.g., footprinting); demonstrating permanence of the immobilization process; using models to reconcile laboratory and field data; and incorporating uncertainty analysis.*

- Monitored natural attenuation for aquatic sediments

  - Findings
    - *The application of MNA to contaminated sediments has received much less attenuation than MNA for contaminated soil and groundwater. Of the relevant work completed to date, most has focused on freshwater sediments.*
    - *Sediment dynamics involve important phenomena not relevant to groundwater or most soil scenarios. The most important of these phenomena are site specific variability in sediment dynamics, the transport of the sediments themselves, and the trophic transfer of contaminants. These phenomena create unique challenges for monitoring and addressing the issue of permanence. Both can affect biodegradation and other attenuation processes acting within the sediment bed.*
    - *Technical protocols developed and tested for contaminated soil and groundwater are not sufficient for use with contaminated sediments in rivers, lakes, and marine systems, because they do not consider monitoring methodologies or contaminant transport processes unique to contaminated aquatic sediments.*
    - *The Contaminated Sediment Management Strategy (EPA 1998a) does not explicitly address the role of MNA in contaminated sediment management.*
    - *Management of contaminated sediments involves many levels of government and is, therefore, administratively complex and challenging.*

  - General recommendations
    - *Develop a scientific basis for understanding cause and effect attenuation mechanisms in sediments that can be validated using footprint analyses. The approach should consider permanence of the remedy as paramount.*

- *Develop monitoring methods to quantity attenuation mechanisms, contaminated sediment transport processes, and bioaccumulation to support footprint documentation and analysis of permanence.*
- *Redefine the research projects associated with Contaminated Sediment Management Strategy (EPA 1998a) to include MNA and develop additional research specific to MNA in fresh water, coastal and marine sediment environments.*
- *Improve collaboration with DOD and DOE for managing contaminated sediments and with affected industries for developing comprehensive research programs.*

7.0 Other Sources of Information on Natural Attenuation

Internet sites and library computerized reference/abstract databases were also searched to identify additional sources of information relating to “natural attenuation” and “monitored natural attenuation.” The purpose of these searches was to determine the extent and types of information publicly available on natural attenuation and its use as a remediation option. The Internet review focused on sites for federal government agencies and did not include those for state regulatory agencies or private companies. The queries of Internet and library databases were conducted using the terms “natural attenuation” and “monitored natural attenuation” and did not include queries based on synonyms such as “intrinsic remediation” or “natural flushing.”

An extensive body of relevant information exists on federal government Internet sites. Some of the primary sources are discussed in Appendix D, including sites for the EPA OSWER Monitored Natural Attenuation Workgroup and its various subpages of information and linked sites, EPA’s Groundwater Issues papers, Federal Remediation Technologies Roundtable (FRTR), and numerous sites for the branches of the U.S. Department of Defense (DOD). The DOD has developed several protocols for natural attenuation, and many of its facilities rely on monitored natural attenuation for remediation of organic contaminants, especially hydrocarbons. The DOD natural attenuation protocols are discussed in detail in NRC (2000b) and Brady et al. (1997, 1999).

The Internet and library abstract database searches also identified several software tools designed for screening and evaluation of natural attenuation. In addition to MNAtoolbox described in Section 4.1.3, the software tools BIOCHLOR, BIOPLUME III, BIOSCREEN, Fate 5 and RT3D are briefly described in Appendix E.

The literature searches of the computerized reference/abstract databases identified approximately 470 journal articles, technical reports, books, and site regulatory documents in which the term “natural attenuation” was listed in the title, key words, and/or abstract. These publications are listed in the extensive bibliography included in Appendix E. Approximately 120 of these documents were Records of Decision (RODs), treatability study reports, and related regulatory decision documents for sites where natural attenuation (or monitored natural attenuation) was a consideration. The titles of these regulatory documents are listed in the last section of Appendix E. Based solely on the content of the titles of the remaining 350 publications, ~50% of these publications pertained to studies of organic contaminants, ~10% to inorganic contaminants, and ~40% to a variety of subjects, including studies of unspecified contaminants, policy reviews, conference books, code documentation, etc.

It was not within the scope of this effort to review the environmental regulatory decision documents. A few of these documents are discussed in sources identified herein, such as MNAtoolbox, Brady et al. (1997), NRC (2000b), and the EPA Internet sites discussed in Appendix D. Moreover, the titles of only four of the 120 site regulatory documents discovered in our literature search identified the subject site as a DOE site. Given that the term "monitored natural attenuation" is a rather recent term within the regulatory framework, there are undoubtedly many more regulatory documents for sites where natural attenuation was a remediation consideration but was referred to possibly as intrinsic remediation, intrinsic bioremediation, passive bioremediation, natural recovery, natural assimilation, natural flushing, or simply reliance on natural processes and long-term monitoring.

As noted previously, our searches were not comprehensive but were meant to indicate the types of information publicly available on the subject of natural attenuation. The results of this review suggest that the majority of the published information and software tools is about natural attenuation of organic compounds. However, the catch phrase "natural attenuation" is a relatively new term in the literature. There is a large body of literature in the disciplines of soil chemistry, geochemistry, and agricultural science that pertains to the fate and transport of trace constituents in sediment, soil, groundwater, and surface water. Although such studies may not be identified by "natural attenuation" in the title or as a key word, the results from many such studies will generally have some applicability to understanding and predicting the mechanisms affecting the rate and extent of natural attenuation of certain contaminants.

8.0 References

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Appendix A

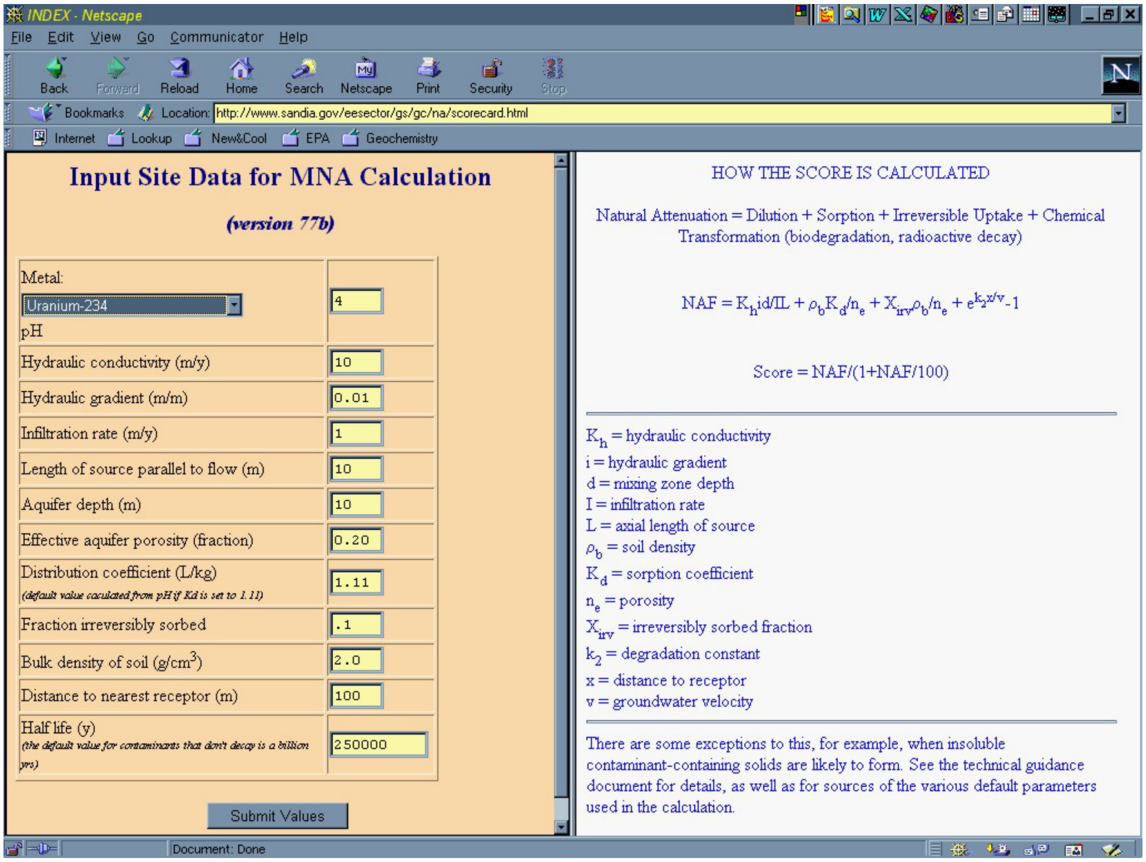
MNAtoolbox^{TM} Scorecard

Appendix A

MNAtoolbox^{TM} Scorecard

To help the user assess whether natural attenuation might be feasible for a selected contaminant at specific site, MNAtoolbox (Brady et al. 1999) includes a "*Site Screening Scorecard*." The scorecard sums the potential of contaminant attenuation that could result from factors such as the following: 1) hydrologic dilution, 2) sorption, 3) irreversible uptake by the soil matrix, 4) precipitation as a mineral phase, 5) biodegradation, and 6) radioactive decay.

The scorecard calculation is briefly described below. The scorecard calculation, the equations that represent the different attenuation processes, and specific data requirements are described in Brady et al. (1999). Figure A.1 shows the screen for entry of site-specific data required for the scorecard calculation in MNAtoolbox.



Input Site Data for MNA Calculation

(version 77b)

Metal: Uranium-234 pH	4
Hydraulic conductivity (m/y)	10
Hydraulic gradient (m/m)	0.01
Infiltration rate (m/y)	1
Length of source parallel to flow (m)	10
Aquifer depth (m)	10
Effective aquifer porosity (fraction)	0.20
Distribution coefficient (L/kg) *(default value caculated from pH if Kd is set to 1.11)*	1.11
Fraction irreversibly sorbed	.1
Bulk density of soil (g/cm^3)	2.0
Distance to nearest receptor (m)	100
Half life (y) *(the default value for contaminants that don't decay is a billion yrs)*	250000

HOW THE SCORE IS CALCULATED

Natural Attenuation = Dilution + Sorption + Irreversible Uptake + Chemical Transformation (biodegradation, radioactive decay)

$$NAF = K_h id/IL + \rho_b K_d/n_e + X_{irv}\rho_b/n_e + e^{k_2 x/v}-1$$

$$Score = NAF/(1+NAF/100)$$

K_h = hydraulic conductivity
i = hydraulic gradient
d = mixing zone depth
I = infiltration rate
L = axial length of source
ρ_b = soil density
K_d = sorption coefficient
n_e = porosity
X_{irv} = irreversibly sorbed fraction
k_2 = degradation constant
x = distance to receptor
v = groundwater velocity

There are some exceptions to this, for example, when insoluble contaminant-containing solids are likely to form. See the technical guidance document for details, as well as for sources of the various default parameters used in the calculation.

Figure A.1. Data Entry Screen for the "Site Screening Scorecard" Calculation in MNAtoolbox

The scorecard calculation is based the following equation:

$$\text{Score} = \frac{\text{NAF}}{1 + \frac{\text{NAF}}{100}}$$

where NAF is the natural attenuation factor. NAF equals 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):

$$\text{NAF} = \text{HDF} + \text{SF} + \text{R}_{\text{irv}} + \text{BF}$$

Each of these attenuation factors can be expanded into the representative equations, respectively, as the following:

$$\text{NAF} = \frac{K_h id}{IL} + \frac{\rho K_d}{n_e} + \frac{\rho X_{irv} K_d}{n_e} + (e^{\frac{kx}{v}} - 1)$$

where K_h is the hydrologic conductivity (m/yr), i is the hydraulic gradient (m/M), d is the mixing zone depth (m), I is the recharge rate (m/yr), L the length of the source (i.e., halo of residual contamination) parallel to flow (m), ρ is the bulk soil density (kg/L), K_d is the partition coefficient, n_e is the effective aquifer porosity, X_{irv} is the average fraction of sorbed contaminant that cannot be exchanged from a contaminated laboratory or field soil sample, k is the degradation or decay rate in (yr^{-1}), x is the distance separating the source and receptor, and v is the subsurface velocity of the dissolved contaminant. Each of these parameters is explained in detail in Brady et al. (1999).

Reference

Brady, P. V., B. P. Spalding, K. M. Krupka, R. D. Waters, P. Zhang, D. J. Borns, and W. D. Brady. 1999. *Site Screening and Technical Guidance for Monitored Natural Attenuation at DOE Sites*. SAND99-0464, Sandia National Laboratories, Albuquerque, New Mexico.

Appendix B

Other DOE Sources of Information on Natural Attenuation

Appendix B

Other DOE Sources of Information on Natural Attenuation

EM Technical Information Exchange (TIE)

TIE Quarterly, Winter 2000, Volume 8(3) (http://www.em.doe.gov:80/tie/laslist.html)

The eleventh annual DOE TIE Workshop was held in October 1999 in Las Vegas, Nevada. Session VII focused on monitored natural attenuation. The panel session included the following:(a)

- Steve Golian [DOE Office of Technical Program Integration (EM-22)] – Discussion of the status of DOE's recently released guidance on monitored natural attenuation MNA. The three guides included the *Decision-Making Framework Guide for the Evaluation and Selection of MNA Remedies at DOE Sites*, the MNAtoolbox, and the *Technical Guidance for the Long-Term Monitoring of Natural Attenuation Remedies at DOE Sites*.

- Patrick Brady (Sandia National Laboratories) – Discussion of the software tool MNAtoolbox which may used for screening sites for the potential of natural attenuation of particular dissolved contaminants.

- Warren Brady (IT Corporation) – Discussion of the commercial approach for application of monitored natural attenuation of metals in soils and sediments.

- Tom Anderson [Rocky Flats Environmental Technology Site (RFETS)] – Discussion of the implementation of monitored natural attenuation processes for remediation of volatile organic compounds (VOCs) at the Rocky Flats Environmental Technology Site.

- Leslie Ferry (Lawrence Livermore National laboratory (LLNL) – Discussion of LLNL proposal to use monitored natural attenuation for tritiated-contaminated groundwater cleanup at LLNL Site 300 and the use of enhanced remedial strategies to control and cleanup other contaminants at the Pit 7 Complex Operable Unit (OU).

(a) The summary of Session VII, Monitored Natural Attenuation, is available on-line at http://www.em.doe.gov:80/tie/sessvii.html.

- Donald Hickmott [Los Alamos National Laboratory (LANL)] – Discussion of LANL pursuing monitored natural attenuation for remediation of barium contamination in the Canon de Valle that resulted from contaminated soil, surface water, and groundwater at LANL's Technical Area 16. The natural attenuation mechanism proposed for barium is the precipitation of the sparingly soluble mineral barite ($BaSO_4$).

- Michael Hauptmann [Brookhaven National Laboratory (BNL)] – Discussion of BNL's proposing monitored natural attenuation, used in conjunction with other active remedial approaches, as a remediation option for three groundwater plumes: 1) the High Flux Beam Reactor (HFBR) tritium plume, 2) the agricultural fields ethylene dibromide plume, and 3) the Operable Unit III volatile organic plume.

- Bob VanPelt (Bechtel Savannah River Inc.) – Discussion of Savannah River Site's work with the State of South Carolina and its Mixing Zone policy to implement the monitored natural attenuation process in its environmental restoration projects.

- Michael Thompson (DOE Richland Operations Office) – Discussion of two major categories of groundwater contamination at the Hanford Site that require remediation that is commensurate with their proposed land uses. These include areas that 1) have restricted use or access to groundwater and have a buffer zone surrounding it, and 2) unrestricted use or access to groundwater. Remediation of the former type of sites will initially include containment and mass reduction followed by monitored natural attenuation for contaminated groundwater plumes. The unrestricted use areas will require a more rigorous remediation strategy.

Reports

- Brady, P. V., B. P. Spalding, K. M. Krupka, R. D. Waters, P. Zhang, D. J. Borns, and W. D. Brady. 1999. *Site Screening and Technical Guidance for Monitored Natural Attenuation at DOE Sites*. SAND99-0464, Sandia National Laboratories, Albuquerque, New Mexico.

  This report is intended to support DOE's *Decision-Making Framework Guide for the Evaluation and Selection of Monitored Natural Attenuation Remedies at Department of Energy Sites* (DOE; May 13, 1999). It includes sections on the EPA OSWER Directive 9200.4-17; site screening, characterization, and monitoring; future use considerations; technical approaches; MNAtoolbox; and models for natural attenuation of organic and inorganic contaminants. The report discusses in detail MNAtoolbox, the technical information that supports the information screen options in MNAtoolbox, and the equations that are the basis of the scorecard screening calculations. The appendices also include copies of the EPA OSWER Directive 9200.4-17 on monitored natural attenuation, the U.S. Air Force Center for Environmental Excellence (AFCEE) protocols for monitored natural attenuation of fuel hydrocarbons and chlorinated organics, and the Remediation Technologies Development Forum (RTDF) guidance handbook for monitored natural attenuation of chlorinated organics. Reviews of inorganic reactivity and measurement of irreversible uptake of inorganic contaminants are also included in the appendices.

- Brady, P. V., and D. J. Borns. 1997. *Natural Attenuation of Metals and Radionuclides: Report from the a Workshop Held by Sandia National Laboratories*. SAND97-2727, Sandia National Laboratories, Albuquerque, New Mexico.

  This report contains summaries and slides of the presentations from a workshop held by Sandia National Laboratories in Albuquerque, New Mexico on June 18-20, 1997. The focus of the workshop was the natural attenuation of metals and radionuclides in contaminated soils and groundwaters.

Screening Tools

- DOE (U.S. Department of Energy). June 30, 1997. *Preferred Alternatives Matrices Remediation/Waste Processing. Rev. 4*. U.S. Department of Energy, Office of Environmental Restoration, Washington, D.C. (http://www2.em.doe.gov/define/index.html).

  DOE's Office of Environmental Restoration (EM-40) (contact: Mary McCune, EM-22) has developed a set of Preferred Alternatives Matrices (PAMs) that identify commercially available environmental restoration technologies and rank them on the basis of performance, risk of technology failure, and cost. The PAMs were developed as a tool for site managers and supporting contractors to help select the most appropriate remediation options for individual sites and types of contaminants. The technologies were compiled from the Federal Remediation Technology Roundtable's *Remediation Technologies Screening Matrix and Reference Guide* and DOE technology summaries with input from the EPA's Vendor Information System for Innovative Treatment Technologies (VISITT) and general knowledge of DOE waste disposal options.

  PAMs exist for the following three areas of environmental restoration: remediation/waste processing, characterization/monitoring, and decommissioning. Remediation options for these include containment, in situ treatment, or ex situ treatment. A PAM is a list of proven, available technologies that are matched against the environmental conditions or problem sets. Natural attenuation is included as one of the in situ treatment technologies (Section 3.6). These problem sets consist of 1) the type of contaminated material or medium (e.g., groundwater, soil/sediment, etc.), combined with 2) data that define the type of contamination (e.g., radioactive, organic, etc.). Medium types include groundwater, soil/sediment/ash, sludge/residues, waste water/liquids, surface water, and solids/debris. Contaminant types include radioactive, mixed LLW, mixed TRU, organic, inorganic, energetics, and sanitary. Examples of problem sets would include inorganic or radioactive contamination in groundwater or organic contamination in sediment.

To extract a list of preferred alternatives, the PAM user must answer several questions to arrive at the correct matrix. Based on the answers to questions, the PAM user would follow the corresponding path to find a reference to a lower level of hierarchy diagram. Figure B.1 shows the hierarchy of information required to identify PAMs for a site where in situ remediation of groundwater is required.

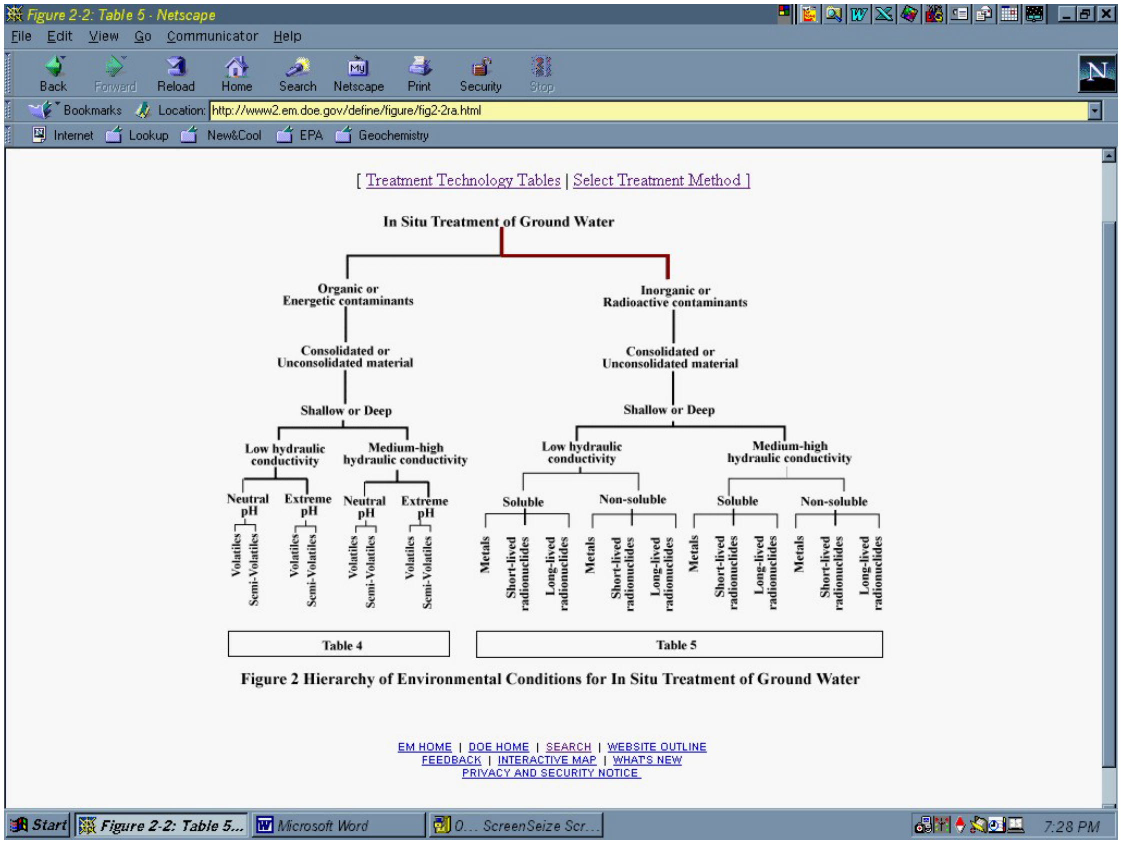


Figure B.1. Screen Capture from DOE Internet Site for PAMs Showing Hierarchy of Information Required to Identify PAMs In Situ Remediation of Groundwater

Figures B.2 and B.3 show the matrices as the lowest level of the hierarchy for in situ remediation options for groundwater with organic/energetic contaminants and inorganic/radioactive contaminants, respectively. For in situ treatment, the vertical and horizontal axes of these matrices list the remediation technologies and environmental conditions, respectively, that affect the applicability of the remediation technologies. For each set of environmental conditions, the technologies are ranked according to being a preferred alternative, probable alternative, potential alternative, possible alternative, unlikely, not applicable, and not relevant for the respective environmental conditions and type of contaminant.

PAMs include numerous matrix tables for in situ treatment, which includes natural attenuation as a remediation option, of organic/energetic and inorganic/radionuclide contaminants in surface water (two matrices), groundwater (two matrices), soil/sediment/ash (ten tables), sludge/residue (two tables), and solids/debris (two tables). The lowest level of subclassifications [pH for organic/energetic contaminants (Figure B.2) and soluble versus nonsoluble for inorganic/radioactive contaminants (Figure B.3)] are not adequate selection criteria to reflect the potential

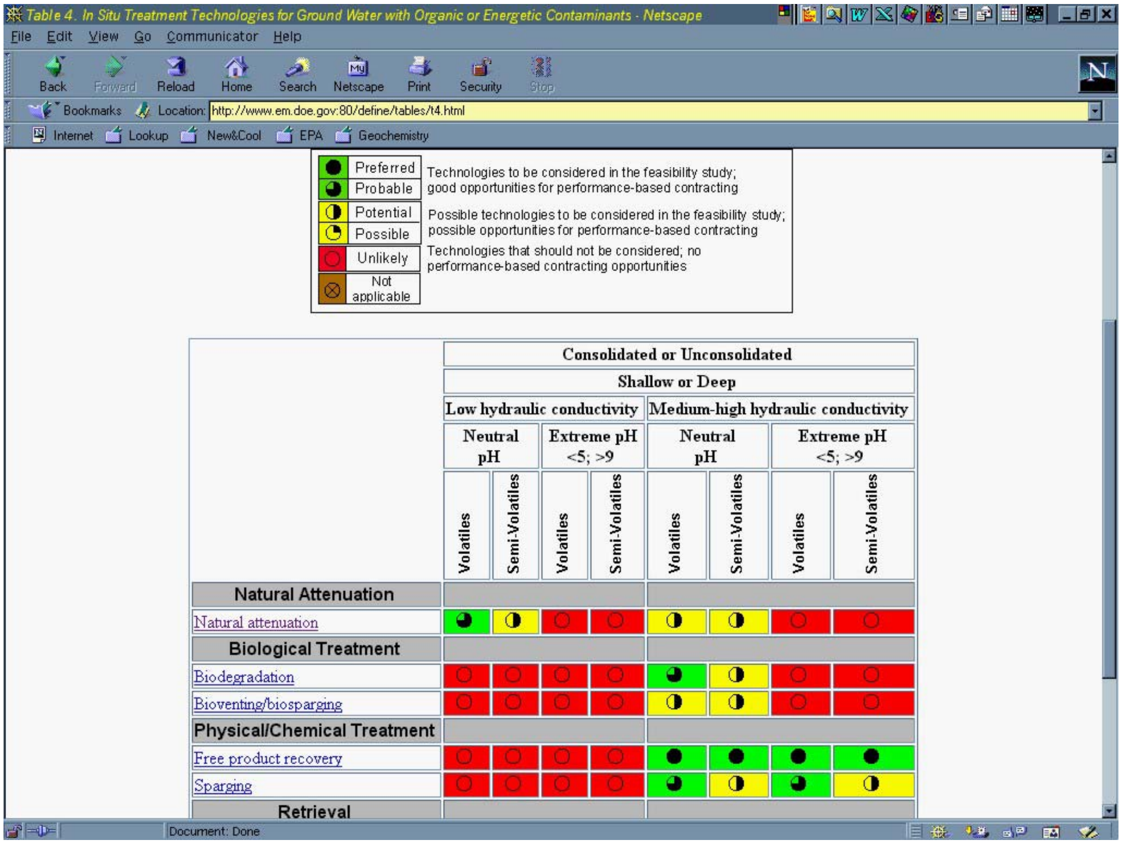


Table 4. In Situ Treatment Technologies for Ground Water with Organic or Energetic Contaminants - Netscape

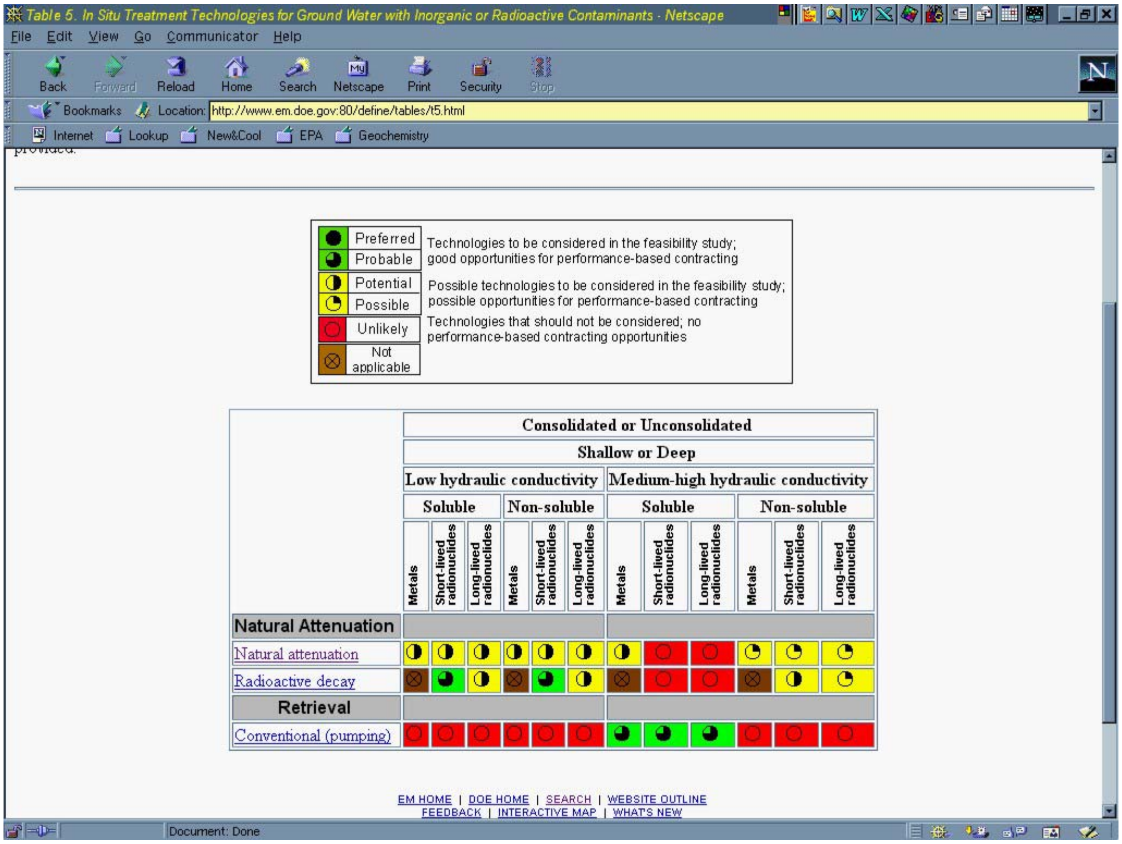
Location: http://www.em.doe.gov:80/define/tables/t4.html

●	Preferred	Technologies to be considered in the feasibility study; good opportunities for performance-based contracting
◕	Probable	
◑	Potential	Possible technologies to be considered in the feasibility study; possible opportunities for performance-based contracting
◔	Possible	
○	Unlikely	Technologies that should not be considered; no performance-based contracting opportunities
⊗	Not applicable	

	Consolidated or Unconsolidated							
	Shallow or Deep							
	Low hydraulic conductivity				Medium-high hydraulic conductivity			
	Neutral pH		Extreme pH <5; >9		Neutral pH		Extreme pH <5; >9	
	Volatiles	Semi-Volatiles	Volatiles	Semi-Volatiles	Volatiles	Semi-Volatiles	Volatiles	Semi-Volatiles
Natural Attenuation								
Natural attenuation	◕	◑	○	○	◑	◑	○	○
Biological Treatment								
Biodegradation	○	○	○	○	◕	◑	○	○
Bioventing/biosparging	○	○	○	○	◑	◑	○	○
Physical/Chemical Treatment								
Free product recovery	○	○	○	○	●	●	●	●
Sparging	○	○	○	○	◕	◑	◕	◑
Retrieval								

Document: Done

Figure B.2. Screen Capture from DOE Internet Site for PAMs Showing Part of the In Situ Treatment Technologies Matrix for Groundwater with Organic or Energetic Contaminants



●	Preferred	Technologies to be considered in the feasibility study; good opportunities for performance-based contracting
◕	Probable	
◑	Potential	Possible technologies to be considered in the feasibility study; possible opportunities for performance-based contracting
◔	Possible	
○	Unlikely	Technologies that should not be considered; no performance-based contracting opportunities
⊗	Not applicable	

	Consolidated or Unconsolidated											
	Shallow or Deep											
	Low hydraulic conductivity						Medium-high hydraulic conductivity					
	Soluble			Non-soluble			Soluble			Non-soluble		
	Metals	Short-lived radionuclides	Long-lived radionuclides	Metals	Short-lived radionuclides	Long-lived radionuclides	Metals	Short-lived radionuclides	Long-lived radionuclides	Metals	Short-lived radionuclides	Long-lived radionuclides
Natural Attenuation												
Natural attenuation	◑	◑	◑	◑	◑	◑	◑	○	○	◔	◔	◔
Radioactive decay	⊗	◕	◑	⊗	◕	◑	⊗	○	○	⊗	◑	◔
Retrieval												
Conventional (pumping)	○	○	○	○	○	○	◕	◕	◕	○	○	○

Figure B.3. Screen Capture from DOE Internet Site for PAMs Showing Part of the In Situ Treatment Technologies Matrix for Groundwater with Inorganic or Radioactive Contaminants

of important natural abiotic and/or biotic processes that control the fate and mobility of these contaminants in soils and surface and groundwater systems and thus of natural attenuation occurring at a sufficient rate at a site. The subclassifications needed to evaluate the efficacy of monitored natural attenuation should include key parameters for the microcosm environment, water composition, and reactive mineral phases that are better indicators of the potential for natural biotic and abiotic of degradation of organic contaminants or of immobilization (i.e., sorption and/or precipitation) of inorganic contaminants.

Training

The DOE National Environmental Training Office (NETO) offers training course NETO0428, "Monitored Natural Attenuation." The one-day course was recently presented on September 20, 2000 in Richland, Washington by Gaynor Dawson (Project Performance Corporation, Tri-Cities, Washington). Gaynor Dawson has supported DOE on several integration efforts pertaining to groundwater environmental issues, including the development of DOE's documents, *Decision-Making Framework Guide for the Evaluation and Selection of Monitored Natural Attenuation Remedies at Department of Energy Sites* and *Technical Guidance for the Long-Term Monitoring of Natural Attenuation Remedies at Department of Energy Sites*.

Course NETO0428 is designed for managers and professionals who are involved in the design, implementation, and monitoring of remediation efforts for contaminated soil and groundwater. It presents DOE's perspective regarding the evaluation and implementation of monitored natural attenuation as remediation option at DOE sites per the requirements of EPA OSWER Directive 9200.4-17. Course modules included the following:

- Introduction to and key issues associated with monitored natural attenuation, including EPA OSWER Directive 9200.4-17

- Evaluation and implementation of monitored natural attenuation at DOE sites, as discussed in DOE's documents, *Decision-Making Framework Guide for the Evaluation and Selection of Monitored Natural Attenuation Remedies at Department of Energy Sites* and *Technical Guidance for the Long-Term Monitoring of Natural Attenuation Remedies at Department of Energy Sites*

- Natural attenuation mechanisms

- MNAtoolbox

- Packaging of monitored natural attenuation as a remediation option

- Case studies of monitored natural attenuation.

Appendix C

National Research Council Review on Natural Attenuation Issues

Appendix C

National Research Council Review on Natural Attenuation Issues

The National Research Council (NRC) Committee on Intrinsic Remediation recently completed a review of natural attenuation and published their findings in *Natural Attenuation for Groundwater Remediation* (NRC 2000). The committee reported their findings on the following four aspects of natural attenuation: community concerns about natural attenuation, scientific basis for natural attenuation, approaches for evaluating natural attenuation, and protocols for natural attenuation. Their specific conclusions and recommendation, taken verbatim from the NRC (2000), are the following:

- Community concerns about natural attenuation
    - *At sites where natural attenuation is proposed as a formal remedy for groundwater contamination and where the contamination affects a local community, environmental agencies and responsible parties should provide the community with clear evidence indicating which natural attenuation processes are responsible for the loss of contaminants.*
    - *Federal and state environmental regulations and guidelines for cleaning up contaminated sites affecting communities should be changed to allow community involvement as soon as the presence of contamination about health-based standards is confirmed.*
    - *Environmental regulatory agencies and responsible parties should encourage affected community members to become involved in the decision making and oversight at contaminated sites.*
    - *EPA, state environmental agencies, and responsible parties should ensure that interested community groups can obtain independent technical advice about natural attenuation and other potential remedies.*
    - *Environmental regulatory agencies and responsible parties should ensure that interested community members can obtain access to all data concerning the contamination, health effects, and potential remedies at sites where communities are affected by groundwater contamination.*

- Scientific basis for natural attenuation
    - *Natural attenuation is well established as a remediation approach for only a few types of contaminants, primarily BTEX.*
    - *Natural attenuation should never be considered a default or presumptive remedy.*
    - *At sites where natural attenuation is shown to be effective, long-term monitoring will be necessary to ensure that key attenuation processes continue to control contamination.*
    - *Natural attenuation of some compounds can form hazardous byproducts that in some cases can persist in the environment.*
    - *Natural attenuation processes cannot destroy metals but in some cases can immobilize them.*
    - *In some cases, removing contaminant sources can speed natural attenuation, but in other cases it can interfere with natural attenuation.*

- Approaches to evaluating natural attenuation
    - *At every regulated natural attenuation site, the responsible company or agency proposing the remedy should document the probable processes responsible for natural attenuation.*
    - *Responsible parties should use "footprints" of natural attenuation processes to document which mechanisms are responsible for observed decreases in contaminant concentration in the groundwater.*
    - *Responsible parties should have a conceptual model of the site's hydrogeology and reactions to show where groundwater and contaminants are moving.*
    - *Responsible parties should gather field data in order to evaluate the validity of the conceptual model and quantify the natural attenuation processes.*
    - *Responsible parties should analyze the field data at a level commensurate with the complexity of the site and the contaminant type.*
    - *Responsible parties should repeatedly improve the conceptual model and data analysis for their site.*
    - *Responsible parties should provide a higher level of effort to document natural attenuation for sites at which the uncertainty is greater due to site contaminant characteristics.*
    - *When modeling studies are presented as part of a site assessment, the responsible party should present adequate documentation so that the regulator can assess the quality of the model simulations.*
    - *A long-term monitoring plan should be specified for every site where natural attenuation is approved as a formal remedy for contamination.*

- Protocols for documenting natural attenuation
  - *The EPA should lead an effort to develop national consensus guidelines for protocols on natural attenuation.*
  - *The national consensus guidelines and all future natural attenuation protocols should be peer reviewed.*
  - *The national consensus guidelines and future protocols should eliminate the use of "scoring systems" for making decisions on natural attenuation.*
  - *Developers of natural attenuation protocols should write easy-to-understand documents to explain the protocol to nontechnical audiences.*
  - *The EPA, other federal and state agencies, and organizations responsible for contaminated sites should provide additional training on natural attenuation concepts for interested regulators, site owners, remediation consultants, and community and environmental groups.*

Reference

NRC (National Research Council). 2000. *Natural Attenuation for Groundwater Remediation*. National Academy Press, Washington, D.C.

Appendix D

Other EPA and Federal Agency Sources of Information on Natural Attenuation

Appendix D

Other EPA and Federal Agency Sources of Information on Natural Attenuation

D.1 EPA OSWER Monitored Natural Attenuation (MNA) Workgroup

(http://www.epa.gov/swerust1/oswermna/index.htm)

The workgroup was formed in March 1996 to develop a policy document on the use of natural attenuation. The workgroup plans to serve as an EPA resource for ongoing and future monitored natural attenuation projects. The home page for the workgroup includes subpages for the following topics pertaining to natural attenuation: purpose of the workgroup, frequently asked questions, and descriptions of and/or links to EPA policy and technical guidance documents, non-EPA documents and articles, laboratory and field research projects, software tools, training, workshops, seminars, conferences, other related Internet sites, news items, and list of EPA contacts. The information listings at this Internet site are extensive. For example, the EPA monitored natural attenuation document subpage lists the following documents (most of which are available on-line):

- OSWER Directive 9200.4-17P (April 21, 1999)
- A Citizen's Guide to Natural Attenuation
- Annual Status Report - Ninth Edition (Chapter 4 - Groundwater Technologies)
- Commonly Asked Questions Regarding the Use of Natural Attenuation for Chlorinated Solvent Spills At Federal Facilities
- Commonly Asked Questions Regarding the Use of Natural Attenuation for Petroleum - Contaminated Sites At Federal Facilities
- Environmental News Release - EPA Selects Final Cleanup Plan for Woodstock Municipal Landfill
- Groundwater Currents
    - Natural Attenuation of Chlorinated VOCs in Wetlands
    - Natural Attenuation Research at Dover
    - Natural Attenuation of Hexavalent Chromium
- Guidance Handbook on Natural Attenuation of Chlorinated Solvents
- Monitored Natural Attenuation of Chlorinated Solvents
- Monitored Natural Attenuation of Petroleum Hydrocarbons

- Monitoring and Assessment of In-Situ Biocontainment of Petroleum Contaminated Groundwater Plumes
- Natural Attenuation of Chlorinated Solvents in Groundwater: Principles and Practices
- Natural Attenuation Study in Wisconsin and Illinois
- Proceedings of the Symposium on Natural Attenuation of Chlorinated Organics in Groundwater
- Seminars: Monitored Natural Attenuation for Groundwater
- Seminar Series (eight chapters) on Monitored Natural Attenuation for Groundwater
- Symposium on Natural Attenuation of Groundwater
- State and Federal Issues Impacting Natural Attenuation: Meeting Overview
- Monitored Natural Attenuation (MNA) Region 6 Fact Sheet
- Farmer's Mutual Cooperative Company Hospers, Iowa September 1998 Region 7 Fact Sheet
- Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater
- Region 3 Hazardous Site Remediation Division
  - Woodlawn County Landfill, Woodlawn, Maryland
- Region 4 Waste Management Division NPL Sites
  - Davis Park Road TCE Site, Gastonia, Gaston County, North Carolina
  - Hipps Road Landfill Jacksonville Heights, Duval County, Florida
  - Chevron Chemical Company, Orlando, Orange County, Florida
  - Cedartown Municipal Landfill, Cedartown, Polk County, Georgia
- Record Of Decision (ROD) Abstracts
  - Travis Air Force Base, Travis, California
  - B&B Chemical Co., Inc., Hialeah, Florida
  - East Mount Zion, Springettsbury, Pennsylvania
  - Bendix Corp./Allied Automotive, St. Joseph, Michigan
  - Galen Myers Dump/Drum Salvage, Osceola, Indiana
  - Oak Grove Sanitary Landfill, Oak Grove Township, Minnesota
  - New Castle Spill Site, New Castle, Delaware.

D.2 EPA Groundwater Issue Papers

(available at http://www.epa.gov/ada/pubs/issue.html)

- Azadpour-Keeley, A., H. H. Russell, and G. W. Sewell. 1999. *Microbial Processes Affecting Monitored Natural Attenuation of Contaminants in the Subsurface*. EPA/540/S-99/001 (EPA Groundwater Issue Paper), 18 p., U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma

- Palmer, C. D., and R. W. Puls. 1994. *Natural Attenuation of Hexavalent Chromium in Groundwater and Soils*. EPA/540/5-94/505 (EPA Groundwater Issue Paper), 12 p., U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma.

D.3 Federal Remediation Technologies Roundtable (FRTR) *Remediation Technologies Screening Matrix and Reference Guide, Version 3.0*

(available at http://www.frtr.gov/matrix/top_page.html)

The Federal Remediation Technology Roundtable (FRTR) was established in 1991 as an interagency committee to exchange information and to provide a forum for joint action regarding the development and demonstration of innovative technologies for hazardous waste remediation. The committee includes membership from the DOE Environmental Management, EPA Technology Innovation Office, EPA National Risk Management Research Laboratory, U.S. Army Environmental Center, U.S. Army Corps of Engineers Hazardous Toxic and Radioactive Waste Center of Expertise, U.S. Air Force Center for Environmental Excellence, U.S. Navy Facilities Engineering Service Center, and U.S. Geological Survey. The *Remediation Technologies Screening Matrix and Reference Guide. Version 3.0* provides a “yellow pages” of remediation technologies. The document was designed to be used by remediation project managers to screen and evaluate remediation technology options for contaminated sites.

The guide was prepared by reviewing and compiling remediation technology information from several U.S. Government agencies into one compendium document. The U.S. Government reports that have been incorporated into this compilation are tabulated in the Background Chapter of this guide. The guide includes the following eight contaminant groups: nonhalogenated and halogenated volatile organic compounds (VOCs), nonhalogenated and halogenated semivolatile organic compounds (SVOCs), fuels, inorganics, radionuclides, and explosives.

Sections 4.4 and 4.35 in Version 3.0 of the guide profile natural attenuation as in situ remediation technology for soil and groundwater, respectively. For each remediation technology profile, the document includes a technology description, a list of synonyms, a discussion of applicability, a list of limitations, general data requirements, a brief statement of extent of use (e.g., “used at 45 sites”), discussion of cost, supporting references, links to information on sites that have used the particular remediation technology, points of contact, linkages to government and non-government Internet sites that contain information about the technology, vendor information and a discussion of health and safety issues.

D.4 DOD Information

Much of the information available from the U.S. Department of Defense (DOD) on natural attenuation pertains to remediation of organic contaminants, especially fuel components. DOD guidance documents, such as the U.S. Air Force *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation*, the U.S. Air Force *Technical Protocol for Evaluation Natural Attenuation of Chlorinated Solvents in Groundwater*, and the U.S. Navy document *Technical Guidelines for Evaluating Monitored Natural Attenuation,* are reviewed elsewhere such as NRC (2000b). It was beyond the available resources for this review to do a detailed search and review of the numerous DOD published sources and DOE Internet sites for information relevant to natural attenuation.

Many of the Records of Decision (RODs) and case studies that are captured via computerized literature reviews on the subject "natural attenuation" or are used in publications and Internet sources as examples of the use of monitored natural attenuation are for DOD facilities, especially fuel spills at Air Force bases.

A cursory, computerized literature review indicated several DOD documents by J. C. Pennington and others pertaining to the application of natural attenuation of explosives in groundwater, including the document *Draft Protocol for Evaluating, Selecting, and Implementing Monitored Natural Attenuation at Explosives-Contaminated Sites*.(a)

Numerous other DOD sources that may contain information on natural attenuation likely exist. These would include the Defense Environmental Network and Information eXchange (DENIX) environmental information system. The DENIX system is an Internet resource for all of DOD containing environmental news, policy and guidance, legislation and regulations, training information, and reference materials. Natural attenuation is periodically a subject in the monthly, e-mail newsletter "*Fielding Environmental Solutions*" which is prepared the U.S. Army Environmental Center (USAEC). A recent issue of the newsletter describes a study by the USAEC, U.S. Army Industrial Operations Command (currently the Operation Support Command), and the U.S. Army Tank-automotive and Armaments Command to evaluate natural attenuation as a remediation option at sites contaminated with petroleum hydrocarbons, solvents or metals. A standardized methodology was developed to assess the feasibility of screening and applying natural attenuation as a remediation option. Based on this methodology, a list of the top 20 sites where natural attenuation was most feasible was developed.

(a) Pennington, J. C., R. Bowen, J. M. Brannon, M. Zakikhani, and D. W. Harreison. 1999. *Draft Protocol for Evaluating, Selecting, and Implementing Monitored Natural Attenuation at Explosives-Contaminated Sites*. WES/TR/EL-99-10, U.S. Army Engineer Waterways Experiment Station, Vicksburg.

Appendix E

Other Sources of Technical Information on Natural Attenuation

Appendix E

Other Sources of Technical Information on Natural Attenuation

E.1 Software Tools for Screening Natural Attenuation

In addition to MNAtoolbox, several other software tools exist for screening and evaluation of natural attenuation of contaminants at a contaminated site. These software tools were not reviewed for the purpose of preparing this white paper, but are mentioned here for the sake of completeness. The focus of these software tools is typically on organic contaminants.

- BIOCHLOR

  Aziz, C. E., C. J. Newell, J. R. Gonzales, P. Haas, T. P. Clement, and Y. Sun. 2000. *BIOCHLOR: Natural Attenuation Decision Support System. User's Manual; Version 1.0.* EPA/600/R00/008, prepared National Risk Management Research Laboratory, Ada, Oklahoma by Groundwater Services, Inc., Houston, Texas; U.S. Air Force Center for Environmental Excellence, Brooks Air Force Base, Texas; and Battelle Pacific Northwest Laboratory, Richland, Washington.

  BIOCHLOR is a screening model that simulates remediation by natural attenuation of dissolved solvents at chlorinated solvent release sites. The software is programmed as an Excel spreadsheet and based on the Domenico analytical solute transport model. The software has the ability to simulate one-dimensional advection, three-dimensional dispersion, linear adsorption and biotransformation via reductive dechlorination (the dominant biotransformation process at most chlorinated solvent sites). BIOCHLOR includes the following three models: 1) solute transport without decay, 2) solute transport with biotransformation modeled as a sequential first-order decay process, and 3) solute transport with biotransformation modeled as a sequential first-order decay process with two different reaction zones. The software package may be downloaded from the following EPA Internet site: http://www.epa.gov/ada/csmos/modeldscr.html

- BIOPLUME III

  Rafai, H. S., C. J. Newell, J. R. Gonzales, S. Dendrou, B. Dendrou, L. Kennedy, and J. T. Wilson. 1998. *BIOPLUME III: Natural Attenuation Decision Support System,* *User's Manual Version 1.0.* EPA/600/R98/010, prepared for EPA National Risk Management Research Laboratory, Ada, Oklahoma by Groundwater Services, Inc., Houston, Texas; U.S. Air Force Center for Environmental Excellence, Brooks Air Force Base, Texas; and Zei MicroEngineering, Inc., Annandale, Virginia.

BIOPLUME III is a two-dimensional, finite difference model for simulating the biodegradation of hydrocarbon in groundwater. The model is based on the two-dimensional solute transport code USGS-MOC. It may be used to model two-dimensional contaminant transport under the influence of oxygen, nitrate, iron, sulfate, and methanogenic biodegradation. The software has the ability to simulate advection, dispersion, sorption, ion exchange, first order decay, and biodegradation. The software package may be downloaded from the following EPA Internet site: http://www.epa.gov/ada/csmos/modeldscr.html

- BIOSCREEN

Newell, C. J., R. K. McLeod, and J. R. Gonzales. 1996. *BIOSCREEN: Natural Attenuation Decision Support System. User's Manual. Version 1.3.* EPA/600/R96/087, prepared for EPA National Risk Management Research Laboratory, Ada, Oklahoma by Groundwater Services, Inc., Houston, Texas in cooperation with the U.S. Air Force Center for Environmental Excellence, Brooks Air Force Base, Texas.

BIOSCREEN can be used to model three-dimensional contaminant transport for dissolved phase hydrocarbons in the saturated zone under the influences of oxygen, nitrate, iron, sulfate, and methane limited biodegradation. The software has the ability to simulate advection, dispersion, adsorption, first-order decay, and instantaneous reactions under aerobic and anaerobic conditions. In addition to providing guidance on input data and analysis of output, the user's guide discusses the relative importance of different electron acceptors in the natural attenuation of fuel hydrocarbons, the preferred reactions as controlled by energy potential, the distribution of electron acceptors at sites, and the kinetics of aerobic and anaerobic reactions. The software package may be downloaded from the following EPA Internet site: http://www.epa.gov/ada/csmos/modeldscr.html

- Fate 5

Fate 5 is a groundwater natural attenuation calibration software tool. It is developed by Groundwater Services, Inc. (Houston, Texas) based on a calculation engine developed by Shell Development Company of Houston, Texas. It was designed for use with the Tier 2 RBCA (Risk Based Corrective Action) spreadsheet system. The software has the ability to simulate advection, dispersion, adsorption, and chemical decay. A product summary *for Fate 5* is given at the following Internet site: http://www.gsi-net.com/RBCATools/Fate_5/AboutFate5.htm

- RT3D

Clement, T. P. 1997. *RT3D (Version 1.0). A Modular Computer Code for Simulating Reactive Multi-Species Transport in 3-Dimensional Groundwater Systems*. PNNL-11720, Pacific Northwest National Laboratory, Richland, Washington.

Clement, T. P., Y. Sun, B. S. Hooker, and J. N. Petersen. 1998. "Modeling Multi-Species Reactive Transport in Groundwater Aquifers." *Groundwater Monitoring and Remediation Journal*, 18(2):79-92.

RT3D is a FORTRAN 90-based software package for simulating three-dimensional, multi-species, reactive transport of chemical compounds in a groundwater aquifer. RT3D was developed for use in design of accelerated in situ bioremediation systems and for evaluation of natural attenuation, but RT3D application can be extended to other in situ remediation technologies as well. The software provides pre-defined reaction kinetics modules for common *in situ* bioremediation scenarios. RT3D also has the flexibility to simulate any reaction kinetics via a user-defined reaction package implemented as a FORTRAN dynamic link library (DLL). RT3D uses the standard MODFLOW code from the U.S. Geological Survey to define the hydraulic flow conditions. User-friendly interfaces for RT3D are provided in the following three popular groundwater modeling packages: U.S. Department of Defense Groundwater Modeling System (GMS), Environmental Simulation's Groundwater Vistas, and Waterloo Hydrogeologic's Visual Modflow.

RT3D (version 1.0) development was supported by the DOE Office of Technology Development, Subsurface Contamination Focus Area. The software package and documentation may be downloaded at no cost from the following PNNL Internet site: <http://bioprocess.pnl.gov/rt3d.htm>

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