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MONITORED NATURAL ATTENUATION: USEPA RESEARCH PROGRAM – AN EPA SCIENCE ADVISORY BOARD REVIEW

REVIEW BY THE ENVIRONMENTAL ENGINEERING COMMITTEE (EEC) OF THE EPA SCIENCE ADVISORY BOARD (SAB)

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

May 17, 2001

OFFICE OF THE ADMINISTRATOR
SCIENCE ADVISORY BOARD

EPA-SAB-EEC-01-004

The Honorable Christine Todd Whitman
Administrator
U.S. Environmental Protection Agency
1200 Pennsylvania Avenue, NW
Washington, DC 20460

Subject Monitored Natural Attenuation: USEPA Research Program – An EPA Science Advisory Board Review

Dear Governor Whitman:

The Natural Attenuation Research Subcommittee of the EPA Science Advisory Board's (SAB) Environmental Engineering Committee reviewed EPA's research program for monitored natural attenuation (MNA) of contaminants in groundwater, soils, and sediments. The Subcommittee evaluated the Office of Research and Development's (ORD) research in terms of its scientific quality and its effectiveness and utility for promoting sound decisions regarding the use of MNA as a remedy at specific sites. The major elements of ORD's research program on MNA, which goes back to the 1970s, focus on: chlorinated solvents; fuels and fuel additives, inorganic compounds, soils and contaminated sediments. The Subcommittee approached this review using science and engineering disciplines related to the fate of contaminants in the subsurface. Although also of importance, the Subcommittee did not address questions relating to social science, diffusion of technology, or waste reuse issues. In its review, the Subcommittee made extensive use of the recent report, *Natural Attenuation for Groundwater Remediation (2000)*, prepared by the Committee on Intrinsic Remediation of the National Research Council (NRC).

The Subcommittee finds that the EPA has established a scientifically sound research program which has contributed substantially to an improved understanding of MNA and its applications. In the process EPA has exercised considerable noteworthy leadership in the larger technical community. However, a great deal remains to be learned about the science underlying MNA and its application to contaminants and media. Given the pressure to apply this remedy to more and more varied situations, EPA's current research program is not commensurate with the need to provide a sound scientific basis for decision making. The Subcommittee will briefly explain its reasoning in this letter; the attached report addresses the findings and recommendations in depth.

EPA and NRC definitions of MNA have changed over time as understanding of the processes involved and clean-up goals has evolved. For the purposes of this report, the Subcommittee considers

MNA to be a remediation approach based on understanding and quantitatively documenting naturally occurring processes at a contaminated site that protect humans and ecological receptors from unacceptable risks of exposure to hazardous contaminants. The Subcommittee stresses that, MNA is a "knowledge-based" remedy because, instead of imposing active controls, as in engineered remedies, scientific and engineering knowledge is used to understand and document **naturally** occurring processes. The intricacies of definition are discussed at greater length in section 2.1.1 of the attached report.

A review of any research program must be undertaken in the context of the intended application. MNA is increasingly used in the Superfund, Resource Conservation and Recovery Act (RCRA), and Underground Storage Tank (UST) programs. The Superfund program, for example, uses MNA as a remedy at more than 25% of contaminated groundwater sites. The Subcommittee found that understanding the behavior of BTEX compounds at those UST sites where they are the sole contaminants of concern is maturing scientifically and has been accepted as an adequate remediation approach. However, the science base for other applications is less well developed. The Subcommittee notes that, in any MNA application, long-term monitoring and documentation are required to ensure that the risks of exposure are, in fact, being reduced to acceptable levels. Such monitoring is needed because of the system uncertainties and also to conform with the EPA's Quality System.

Moreover, part of the context for this review is the public concern about possible misapplication of natural attenuation. Some view this technique as a "do nothing" approach. For example, a feature article (*Environmental Science & Technology*, Volume 34, Issue 15, August 1, 2000, pages 346-353) quotes a prominent environmental scientist as saying that natural attenuation is a,"low-cost, ineffective approach that delays the inevitable need to clean up the site." Clearly, some stakeholders believe that natural attenuation may be an ineffective approach to remediating contaminated sites, and that its adoption does not preclude the ultimate need to actively clean-up contaminated sites.

Where the public's concern is based on an immature science base, inadequate site-specific analysis, or inadequate monitoring, the concern is shared by the Subcommittee. When properly employed, MNA is not a "do-nothing" alternative, rather it is an effective knowledge-based remedy where a thorough engineering analysis informs the understanding, monitoring, predicting, and documenting of the natural processes. In order to properly employ this remedy, EPA needs a strong scientific basis supported by appropriate research and site-specific monitoring implemented in accordance with the Agency's Quality System.

Although the public's perception of MNA is generally negative, public acceptance may improve when there is a reliable scientific basis for distinguishing those sites at which the contaminants are controlled by processes that destroy or strongly immobilize the contaminants from sites at which MNA is not an appropriate remedy. The compelling evidence needed to support proper evaluation of the remedy requires that the processes that destroy or immobilize contaminants are well understood and that their effectiveness at the site is documented. The NRC (2000) report provides a specific strategy for providing convincing evidence during the decision-making process, which is consistent with the spirit of the EPA's guidance as stated in the 1998 *Technical Protocol*.

Specifically, the Subcommittee found that the Agency's present research program is well-established and scientifically sound. EPA research has contributed substantially to an improved understanding of MNA and its applications. However, a great deal remains unknown and the EPA's present research program is incommensurate with support of the widespread application of this remedy. Significant additional focused research is needed to support the evaluation of MNA for application to chlorinated solvents, fuel additives, inorganic compounds, and contaminated sediments or to soils and sediments.

There is a critical need for more research. To support the proper use of MNA for applications other than BTEX, the EPA should enhance the science base underlying natural attenuation to ensure that decision-making strategies are developed based on appropriate and sound science. The Subcommittee's report provides research recommendations to strengthen the science base through the EPA research program, subsequently implement appropriate decision-making strategies, and support the improvement of EPA guidance on MNA. The details of the Subcommittee's recommendations are found in Chapters 3 and 4 of the attached report.

We would like to acknowledge the support of the staff of the Office of Research and Development's National Risk Management Research Laboratory and also the cooperation and support of staff from the Office of Solid Waste and Emergency Response. We appreciate the opportunity to review these documents, and look forward to receiving the response of the Assistant Administrator for Research and Development to the issues raised.

Sincerely,

/s/
Dr. William Glaze, Chair
EPA Science Advisory Board

/s/
Dr. Hilary I. Inyang, Chair
Environmental Engineering Committee
EPA Science Advisory Board

/s/
Dr. Domenico Grasso, Chair
Natural Attenuation Research Subcommittee
Environmental Engineering Committee
EPA Science Advisory Board

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ABSTRACT

MNA is a knowledge-based remedy where a proper engineering analysis informs the understanding, monitoring, predicting, and documenting of the natural processes. The EPA Science Advisory Board reviewed the Environmental Protection Agency's research program for monitored natural attenuation (MNA) of contaminants in groundwater, soils, and sediments; evaluated ORD's research in terms of its scientific quality and its effectiveness and utility for promoting sound decisions about the use of MNA as a remedy at specific sites; and assessed the applicability and limitations of the EPA's guidance as expressed in the1998 *Technical Protocol* on MNA. In its review, the Subcommittee made extensive use of the recent *Natural Attenuation for Groundwater Remediation (2000)* published by National Academy Press.

MNA is widely used for the remediation of contaminated sites. Scrupulous attention to site-specific studies is required to document that processes that destroy or immobilize contaminants are well understood and sufficiently documented to ensure an acceptable remedy.

Specifically, the Subcommittee found that the Agency's present research program is well-established and scientifically sound. EPA research has contributed substantially to an improved understanding of MNA and its applications. However, a great deal remains unknown and the EPA's present research program is incommensurate with support of the widespread application of this remedy. Significant additional focused research is needed to support the evaluation of MNA for application to chlorinated solvents, fuel additives, inorganic compounds, and contaminated sediments or to soils and sediments.

The Subcommittee's report provides recommendations to strengthen the science base through the EPA research program on chlorinated solvents, fuel additives, inorganics, and sediments. The improvement in the science basis should lead to improvement of frameworks and guidance.

Keywords: natural attenuation, groundwater, soil, sediments, monitoring, research, technical protocols, chlorinated solvents, MTBE, arsenic, lines of evidence

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1. EXECUTIVE SUMMARY

The Office of Research and Development (ORD) requested that the EPA Science Advisory Board (SAB) review the EPA's research program for monitored natural attenuation (MNA) of contaminants in groundwater, soils, and sediments; evaluate ORD's research in terms of its scientific quality, effectiveness and utility for promoting sound decisions about the use of MNA as a remedy at specific sites; and assess the applicability and limitations of the EPA's guidance as expressed in the 1998 *Technical Protocol*. The Environmental Engineering Committee's Natural Attenuation Research Subcommittee conducted this review, making extensive use of the recent report, *Natural Attenuation for Groundwater Remediation (2000)* from the National Research Council (NRC).

The Subcommittee approached this review using science and engineering disciplines related to the behavior of contaminants in the subsurface. It did not address questions relating to social science, diffusion of technology, or waste reuse. General advice on those issues can be found in SAB reports including the following:

a) Review of the SAB Report "Toward Integrated Environmental Decision-Making" (EPA SAB-EC-LTR-00-004)

b) Commentary Resulting from a Workshop on the Diffusion and Adoption of Innovations in EPA-SAB-EEC-COM-01-001)

c) Commentary and Recommendations on Overcoming Barriers to Waste Utilization (EPA-SAB-EEC-COM-00-006)

DEFINITION

EPA and NRC definitions of MNA have changed over time as understanding of the processes involved and protections needed has improved. For the purposes of this report, the Subcommittee considers MNA to be a remediation approach based on understanding and quantitatively documenting naturally occurring processes at a contaminated site that protect humans and ecological receptors from unacceptable risks of exposure to hazardous contaminants. The Subcommittee stresses that, MNA is a "knowledge-based" remedy because, instead of imposing active controls, as in engineered remedies, scientific and engineering knowledge is used to understand and document **naturally** occurring processes to clearly establish a causal link. Monitoring and documentation are vital to demonstrate that the risks of exposure are being reduced to acceptable levels. The intricacies of MNA definition are discussed at greater length in section 2.1.1 of this report.

This research program is important because MNA is being increasingly used on a wider variety of contaminants and there concerns about misapplication. Misapplication could result, for example, from an insufficient understanding of the relevant processes or inadequate attention to the long-term monitoring and documentation required by the Agency's Quality System. Although MNA is frequently used in the Superfund, RCRA, and UST programs, the public is concerned about the misapplication of natural attenuation, which often is viewed as a “do nothing” approach. To the extent that the public's concern is based on inadequate site-specific analysis, the concern is shared by the Subcommittee.

The Subcommittee approached this research review from the perspective that MNA should not be a “do nothing” alternative. Properly employed, it is a knowledge-based remedy in which a proper engineering analysis informs the understanding, monitoring, predicting, and documenting of the natural processes, rather than manipulating them.

During the course of this review, the Subcommittee agreed with and endorsed the overall strategy that NRC (2000) provides for deciding whether or not MNA protects human health and the environment. According to NRC (2000), MNA should be selected only when a cause-and-effect relationship is established between loss of contaminant and destruction or immobilization processes. NRC (2000) prescribes a three-part strategy for implementing their approach for MNA decision making:

a) develop a site conceptual model that identifies what destruction or immobilization processes are responsible for protecting human health and the environment;

b) obtain site-specific information that documents the cause-and-effect relationship between contaminant loss and the destruction and immobilization process; and

c) implement a long-term data acquisition and evaluation program that documents that these processes are sustained and are consistent with design objectives.

The first key element of the NRC's strategy is the “footprint” concept. Footprints are documentation of products of destruction or immobilization reactions consistent with the proposed conceptual model. The second key element is “level of effort”. When uncertainty is high, those considering MNA must expend more resources to gather and interpret information that documents whether or not the destruction or immobilization processes are effective at the site. EPA's research efforts ultimately must be directed towards reducing uncertainty, which will make MNA decision-making more reliable and resource effective.

EPA has been a major contributor to the body of knowledge addressing MNA. ORD has conducted research in this area almost as long as EPA has been an Agency and has thereby contributed substantially to an improved understanding of MNA and its applications. However, a great deal remains unknown and the EPA's present research program is incommensurate with the support of the widespread application of this remedy.

To better understand and evaluate MNA and the range of circumstances for which MNA may be considered a reliable remedy, the EPA must enhance the science base underlying natural attenuation applications to ensure that decision-making strategies are based on sound science and to support the improvement of EPA's guidance on MNA. An overview of the Subcommittee's findings and research recommendations follows, organized by major charge topic (chlorinated solvents, fuels and fuel additives, inorganic compounds, and contaminated sediments). Chapter 2 provides additional background and the complete charge. Chapter 3 details the response to the charge.

1.1 Overview of Findings and Research Recommendations for Chlorinated Solvents

Recently, the application of MNA to chlorinated solvents has received considerable interest. While MNA will not be effective for solving chlorinated solvent remediation needs at most locations (NRC, 2000), MNA may provide effective management where contamination of chlorinated solvents coincides with fuel hydrocarbons, leading to extensive reductive dechlorination.

EPA's 1998 *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater* 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 accumulated products. Much of the uncertainty results from the difficulty in obtaining accurate field information to account for all relevant processes and quantify reaction rates. Other factors that contribute to uncertainties about the application of MNA to chlorinated solvents include high-concentration source areas, synergistic/antagonistic interactions among chlorinated solvents and other chemicals, and degradation by mechanisms other than reductive dechlorination.

Based on these findings, the Subcommittee made the following research recommendations to support evaluation of MNA at chlorinated solvent sites.

a) Develop and conduct laboratory and field research that will elucidate when and why site conditions allow complete degradation of chlorinated solvents.

b) Develop methods of quantifying natural attenuation rates when different biodegradation processes are occurring in different parts of the plume.

c) Conduct field and laboratory experiments to determine how reductive dechlorination behavior of chloromethanes, chloroethanes, and chlorinated benzenes compare to chlorinated ethenes.

d) Investigate factors that control source dissolution and biodegradation in or near the source area and properly integrate them into the MNA framework.

e) Evaluate whether mechanisms other than dechlorination can be significant contributors to the natural attenuation of chlorinated solvents.

1.2 Overview of Findings and Research Recommendations for UST

The use of MNA for the remediation of UST sites at which fuel hydrocarbons (chiefly benzene, toluene, ethyl benzene, and xylenes -- BTEX) 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. Fuels contain hydrocarbons other than BTEX; some of these compounds may be relevant to understanding the MNA of fuels and fuel additives. When present in UST source zones and down gradient plumes, the solubility, high mobility, and apparent persistence of methyl-tertiary-butyl ether (MTBE), an additive to fuels (and other oxygenates) introduces significant uncertainty about the effectiveness of MNA at UST sites when compared to BTEX-only sites.

Based on its review, the Subcommittee recommends that EPA undertake research initiatives in the following areas to support evaluation of MNA at UST sites:

a) determine the biodegradability of MTBE and other oxygenates under various field conditions;

b) improve the predictability of dissolution rates for MTBE and other fuel components and their fluxes exiting source zones;

c) develop an information database on indirect measures of MTBE natural attenuation to support previous and ongoing site assessments; and

d) determine whether hydrocarbons in gasoline not on the Target Compound List should be considered in remedial risk analyses.

1.3 Overview of Findings and Research Recommendations for Inorganics

The Subcommittee also considered EPA's research program as it relates to the use of MNA for hazardous inorganic contaminants, of which arsenic and heavy metals are most critical. Although immobilization is the primary attenuation process operative for arsenic and metals, it is not fully understood; this uncertainty makes it very difficult to apply MNA to arsenic and metals. No footprinting or monitoring guidance is currently available for employing MNA for metals and arsenic. At present, it is difficult to reconcile laboratory and field data for arsenic and metal reactions in soil.

Current and proposed ORD research addresses some of the critical questions required for understanding natural attenuation of arsenic. Although a framework addressing the natural attenuation of inorganics is urgently needed, the processes that affect speciation, fate, and transport of arsenic and metals are not sufficiently understood.

Based on its review, the Subcommittee recommends that, notwithstanding present research gaps, the EPA should begin to develop a conceptual scientific framework for MNA of metals and arsenic to support regulatory decisions. More specifically, EPA should:

a) further elucidate attenuation mechanisms governing the immobilization of arsenic and other metals;

b) evaluate the effect changes in geochemical conditions have on the re-mobilization of once immobilized contaminants;

c) understand the fate and behavior of metals in co-mingled organic/inorganic plumes; and

d) develop guidelines for obtaining field and analytical data needed for an MNA remedy, demonstrating sufficient understanding of permanence of the immobilization processes, using models reconciling laboratory and field data, and incorporating uncertainty analysis.

1.4 Overview of Findings and Research Recommendations for Sediments

The application of MNA to contaminated sediments has received much less attention than MNA for contaminated soil and groundwater. Of the relevant work completed to date, most has focused on freshwater sediments. Sediments dynamics involve important phenomena not relevant to groundwater or most soil settings. 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. Any of these can affect biodegradation and other attenuation processes acting within the sediment bed. These phenomena create unique challenges for monitoring and for addressing the issue of permanence.

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* (1998) does not explicitly address the role of MNA in contaminated sediment management. Management of contaminated sediments involves interacting with many levels of government and therefore is administratively complex and challenging.

Based on these findings, the Subcommittee recommends that EPA:

a) Expand its research program to develop a scientific basis for understanding cause and effect attenuation mechanism in sediments that can be validated using footprint analyses. The approach should consider permanence of the remedy as paramount.

b) Expand its research program to develop monitoring methods to quantify attenuation mechanisms, contaminated sediment transport processes, and bioaccumulation to support footprint documentation and analysis of permanence.

c) Redefine research projects associated with the *Contaminated Sediment Management Strategy* to include MNA and develop additional research specific to MNA in fresh water, coastal, and marine aquatic sediment environments.

1.5 Overview of Findings and Recommendations for Issues Beyond the Charge

In the course of its review, the Subcommittee reached consensus on a number of issues relating not just to the EPA's MNA research program, but to the field application of this remediation technology. While these comments are outside the charge for the review and touch upon policy, the Subcommittee provides them here because they fall within the context of the Subcommittee's findings and recommendations on the MNA research program.

The decision-making strategy in *Natural Attenuation for Groundwater Remediation* (NRC, 2000) describes an approach for establishing a cause-and-effect connection that is essential for proper use of MNA. This strategy is related to, but not the same as, two previously published sets of evidence for documenting attenuation processes in the field (NRC, 1993; EPA, 2000). The strategy from NRC (2000) includes and expands on the previously published sets of evidence.

Although the Subcommittee underscores that the guidelines in NRC (2000) supersede the other sets of evidence, it recognizes that these sets are both valuable and influential. The Subcommittee emphasizes that whatever set of evidence is adopted, it must be supported by a strong scientific research base. This presumption forms the framework within which this review was conducted.

The Subcommittee strongly endorses the NRC (2000) recommendation that EPA should lead an effort to develop National guidelines for natural attenuation, and, that the national guidelines and all future natural attenuation methodologies should be peer reviewed. Such peer review would be consistent with the EPA's own peer review policy.

The Subcommittee encourages the EPA to freely exchange scientific and technical information with industry and other outside groups.

2. INTRODUCTION

This chapter of the report provides the background, context, and charge for the review. Because of the complex nature of the charge, definition and application of MNA, many over-arching issues relevant to all the charge questions are discussed in Chapter 2. Specific responses to charge questions can be found in Chapter 3.

2.1 Background

MNA is a commonly considered remedy at hazardous-waste sites and, When properly applied, MNA offers the potential to significantly reduce the costs of site remediation. The Office of Research and Development (ORD) conducts research on MNA in support of EPA regulatory programs. This EPA Science Advisory Board (SAB) review is the first peer review of ORD's natural attenuation research program.

The research program should be understood in the context of its application. In the case of MNA, the results of laboratory research must be moderated and validated by field experience. Field experience is very site-specific and generalities are difficult to frame. The Subcommittee therefore provides an introductory chapter discussing background issues that are cross-cutting and relate to all the charge issues.

A firm understanding of contextual MNA applications is necessary to frame the requirements of a responsive research program. Although many definitions of MNA pervade the literature, for the purpose of this report, the Subcommittee adapted a succinct definition that subsumes the salient elements and concepts that are broadly held in the scientific community. This chapter briefly reviews EPA's MNA programs in risk reduction and research, providing an appropriate historical and regulatory backdrop for the report. Chapter 2 concludes with significant issues relating to the appropriate application of MNA in the field, i.e., lines and types of evidence, mass flux, and cause and effect.

2.1.1 What is MNA?

MNA is a remediation approach based on understanding and quantitatively documenting the **naturally** occurring processes at a site protecting humans and ecological receptors from unacceptable risks of exposure to hazardous contaminants. In short, MNA is a “knowledge-based” remedy. Instead of imposing active controls, as in engineered remediations, MNA involves understanding and documenting naturally occurring processes that reduce risks of exposure to acceptable levels and clearly establish a causal link. The technology of MNA is scientific and engineering knowledge.

The term “natural attenuation” also appears in several regulatory contexts. For over a decade, EPA has recognized the role of natural attenuation in site clean-up stating that, "In limited cases, natural attenuation, which can involve either the dispersion or actual biodegradation of contaminants, may be the most appropriate remedy for a site." This is consistent with the usage of the term in the Office of Emergency Response and Remediation (OERR) document: *Guidance on Remedial Actions for Contaminated Ground Water at Superfund Sites* (USEPA, 1988a and b). Two years later, EPA described natural attenuation more broadly in the Preamble to the 1990 Final *National Oil and Hazardous Substances Pollution Contingency Plan* (USEPA, 1990). Here, EPA recognized natural attenuation as a possible remedy for groundwater and defined natural attenuation as use of "biodegradation, dispersion, dilution, and adsorption” to "effectively reduce contaminants in the groundwater to concentrations protective of human health [and the environment] in a time frame comparable to that which could be achieved through active restoration.”

More recently, the 1997 Office of Solid Waste and Emergency Response (OSWER) interim policy directive requested that the term “monitored natural attenuation (MNA)" be used to emphasize that long-term monitoring is an important component of a remedy where natural processes are to be relied upon to achieve cleanup objectives. EPA also wished to distinguish using MNA as a remedy from situations where "natural attenuation" processes occur as part of a no-action alternative. In the latter case, natural attenuation is not being relied upon to reduce future risks below present levels. The ORD's National Risk Management Research Laboratory documents and this report of the SAB's Natural Attenuation Research Subcommittee use the term MNA in order to be consistent with EPA's terminology.

Under proper circumstances, natural processes can transform certain contaminants found in groundwater and soils into products that are not harmful or that are strongly immobilized. Natural processes alone have been used as a remedy for contamination at many waste sites.

In 2000, the National Research Council (NRC) issued *Natural Attenuation for Groundwater Remediation* (NRC, 2000). This two-year study:

a) assessed current knowledge on the processes affecting natural attenuation,

b) clarified what natural attenuation is likely to achieve,

c) defined an evaluation and monitoring strategy needed for natural attenuation,

d) evaluated the degree to which existing documents provide sufficient guidance for decision-making on natural attenuation, and

e) recommended that EPA lead an effort to create national guidelines for natural attenuation.

Natural Attenuation for Groundwater Remediation (NRC, 2000) found that,

a) under proper conditions, natural attenuation processes can cause the destruction or transformation of contaminants in the environment,

b) natural attenuation is an established remedy for only a few types of contaminants,

c) rigorous requirements are needed to ensure that natural attenuation potential is analyzed properly, and

d) natural attenuation should be accepted as a formal remedy for contamination only when the processes needed to achieve remediation goals are documented to be working and are sustainable.

The NRC (2000) report *de facto* restricted the acceptable (or eligible) natural attenuation processes to biodegradation and strong immobilization. This is a more restrictive definition than that used by EPA (next paragraph) and reflects NRC's finding that, while other processes occur and can contribute to natural attenuation, the processes that destroy or strongly immobilize contaminants are more reliable in reducing risks. Their pre-eminent position stems from two related factors. First, biodegradation and immobilization are active risk-reducing processes that can be documented. Second, these processes are viewed by engineers, scientists, and the public as valid means to reduce risks. Some stakeholders have been concerned about the broad use and, perhaps, misuse of MNA. MNA is increasingly used in the Superfund, Resource Conservation and Recovery Act (RCRA), and Underground Storage Tank (UST) programs. The Superfund program, for example, uses MNA as a remedy at more than 25% of contaminated groundwater sites.

Some view this technique as a “do nothing” approach. For example, a feature article (*Environmental Science & Technology*, Volume 34, Issue 15, August 1, 2000, pages 346-353) quotes a prominent environmental scientist as saying that natural attenuation is a,“low-cost, ineffective approach that delays the inevitable need to clean up the site.” Clearly, some stakeholders believe that natural attenuation may be an ineffective approach to remediating contaminated sites, and that its adoption does not preclude the ultimate need to actively clean-up contaminated sites.

2.1.2 MNA and EPA Risk Reduction Programs

Major regulatory programs with an interest in MNA remedies at contaminated sites include OSWER's Resource Conservation and Recovery Act Corrective Action, Superfund, and Underground Storage Tanks (UST) programs. Their interest has largely been in the removal of organic contaminants from **groundwater** and prevention of contaminant migration off site. This is the subject addressed most directly by *Natural Attenuation for Groundwater Remediation* (NRC, 2000).

Risk reduction through the natural attenuation of metals and a range of contaminants in **aquatic sediments** is currently a topic of great interest to regulators, the regulated community, and public stakeholders. OSWER and the Office of Water (OW) are concerned with contaminated sediments and metals, the latter as they relate to contaminated sites under Superfund and RCRA programs and the former as they relate to the overall goal of clean water. OSWER is currently developing guidance for management of contaminated sediments, including dredging, capping, and natural recovery. OW's programs are presently focused more on risk assessment activities, with a specific goal to identify safe or acceptable contaminant levels in sediments.

2.1.3 MNA in the EPA Research Program

ORD conducts research in support of EPA risk assessment and risk reduction programs. The *Strategic Plan for the Office of Research and Development* (USEPA, 1996) sets forth ORD's vision, mission, and long-term research goals. ORD uses the risk assessment/risk management paradigm to provide a foundation for the development of research strategies on high priority research topics, one of which is waste research, particularly for contaminated sites.

Based on extensive communications among program and research offices, ORD developed *The Waste Research Strategy* (USEPA, 1999), which incorporates MNA The Environmental Engineering Committee of the SAB reviewed the draft strategy in 1997 (USEPA SAB, 1998a).

In the context of this review, the Subcommittee sees ORD's role in advancing the proper use of MNA as the reduction of uncertainty by elaborating the applicability and limitations of key attenuation processes and by creating proper frameworks for evaluating sites for which natural attenuation is proposed. Today, uncertainty regarding underlying processes is high for certain key contaminants, and methods to gather and interpret information documenting destruction or immobilization inadequate. By expanding knowledge about natural attenuation processes and how to obtain field documentation, EPA research will improve the likelihood that MNA will be properly selected only when it effectively lowers exposure risks.

2.1.4 Content and Background of ORD's MNA Research Program

ORD research on MNA ranges from studies of basic processes in various media, to field pilot studies, and to projects that are carried out at full scale in the field. In addition to its research, ORD is also responsible for providing technical assistance and technology transfer activities to facilitate the proper use of its natural attenuation research results in EPA's operating programs.

The foundations of ORD's research on natural attenuation in groundwater date back to the work of McNabb and Dunlap in the 1970s (USEPA, 1973). This work was among the first to demonstrate that naturally occurring subsurface microorganisms are capable of degrading synthetic organic chemicals. ORD researchers have maintained leading roles in several aspects of what is now called MNA.

2.1.4.1 Fuels - ORD's first significant research on natural attenuation as a site remedy took place at the Coast Guard Air Rescue Facility in Traverse City, Michigan, in the mid 1980s. ORD scientists assisted the Coast Guard with clean up of a release of aviation fuel that had migrated off site and contaminated a large number of private water wells before exiting into Lake Michigan. Combining soil-microcosm studies with modeling indicated that, if the source of contamination could be terminated at the boundary of the Coast Guard facility, naturally occurring biodegradation processes would reduce the levels of the benzene, toluene, ethylbenzene, and xylene (BTEX) to below drinking water standards in a reasonable period of time.

An additional significant accomplishment of ORD's fuels research, conducted in collaboration with the U.S. Air Force, was the development of a protocol (Wiedemeier et al., 1995) for assessing the natural attenuation of fuels in groundwater.

Although its research on natural attenuation of BTEX is largely complete, ORD currently is conducting research on a fuel oxygenate, methyl tertiary butyl ether (MTBE). However, because MTBE in gasoline is being phased out over the next several years, ORD is also considering studying other oxygenates, such as ethanol, likely to be used as additives.

2.1.4.2 Chlorinated Solvents - One of ORD's earliest studies of the natural attenuation of chlorinated solvents took place at a trichloroethylene (TCE) release site at St. Joseph, Michigan, in the early to mid 1990s. Groundwater samples collected as part of the site characterization contained significant quantities of *cis*-dichloroethene, vinyl chloride, and ethene which are products of the reductive dechlorination of TCE. Because the source of the plume was known to contain only TCE, the presence of these products was strong evidence that natural biodegradation was occurring.

ORD's research on the natural attenuation of chlorinated solvents has resulted in the document, *Technical Protocol for Evaluating the Natural Attenuation of Chlorinated Solvents in Ground Water* (USEPA, 1998). This document was produced in collaboration with the U.S. Air Force and the U.S. Geological Survey. The *Protocol* summarizes ORD's recommendations for MNA of chlorinated solvents in groundwater and is specifically referenced in the OSWER directive on natural attenuation. The *Protocol* was subject to both internal and external technical peer review. The Regional and Program offices also provided policy review to ensure that its recommendations were consistent with EPA's policies for site remediation.

ORD continues to conduct research on natural attenuation of chlorinated solvents.

2.1.4.3 Inorganics and Metals - Research related to the natural attenuation of inorganics, including metals, in groundwater evolved from studies on the transport and fate of chromium at the U.S. Coast Guard facility at Elizabeth City, North Carolina, which began in the very early 1990s. Site characterization studies showed that significant amounts of mobile and toxic Cr(VI) were being transformed to largely insoluble and much less toxic Cr(III). Geochemical conditions at the site were sufficiently reducing to make it unlikely that a reverse reaction would occur. The capacity of the system and the rates of transformation were not sufficient to recommend natural attenuation as a sole site remedy, but they were the basis for the subsequent and successful installation of a permeable reactive barrier.

The issue paper *"Natural Attenuation of Hexavalent Chromium in Ground Water and Soils"* (USEPA, 1994) provided early guidance on methods and approaches to assess natural attenuation of chromium at field sites.

Natural attenuation research for inorganics is at an earlier stage of development than research on fuels. ORD is currently conducting research on natural attenuation of chromium and arsenic. These two contaminants are among the most commonly occurring inorganic problems at waste sites. Furthermore, arsenic is of concern to the EPA's drinking water programs.

2.1.4.4 Sediments - ORD's research program on contaminated sediments is relatively new, including studies of contaminated sediments at two Superfund sites. ORD is also analyzing data from sites where natural attenuation has been proposed or where monitoring of natural processes has occurred over a period of years. Analyses include changes in chemical concentration, as well as more direct measures of changes in toxic effects on ecoreceptors. ORD research on biodegradation of polynuclear aromatic hydrocarbons (PAHs) in soil may contribute more broadly to knowledge of natural attenuation of hydrophobic organic compounds in sediments.

2.2 Context

The Subcommittee referred to the recently published NRC report, *Natural Attenuation for Groundwater Remediation* (NRC, 2000) in evaluating ORD's MNA research program. The Subcommittee agrees with and endorses the overall guidance that NRC provides for deciding whether or not MNA is an appropriate remedy for protecting human health and the environment.

2.2.1 The NRC's Strategy

Although not explicitly stated, NRC (2000) recognized that MNA is a "knowledge-based" remedy. Instead of imposing engineered conditions that sequester, destroy or remove contaminants from a site, MNA relies on understanding and documenting the naturally occurring processes that destroy or strongly immobilize the contaminants. Because MNA is based solely on knowledge, MNA should be selected only when a cause-and-effect relationship between loss of contaminant and the destruction and/or immobilization processes is documented at the site today and for as long as the contamination source persists.

NRC (2000) prescribes a three-part strategy for implementing their approach to MNA decision-making:

a) develop a site conceptual model that identifies what destruction or immobilization processes are responsible for protecting human health and the environment;

b) obtain site-specific information that documents the cause-and-effect relationship between contaminant loss and the destruction and immobilization process; and

c) implement a long-term data acquisition and evaluation program that documents that these processes are sustained and are consistent with achieving remediation design objectives.

The first key element of the NRC's strategy is the "footprint" concept. Footprints are documentation of chemical and/or physical character of the site consistent with the proposed conceptual model. The footprint should include the products of the parent contaminant destruction or immobilization reactions or depletion of reactants. Finding one or several footprints produced at rates commensurate with the loss of target contaminants is strong documentation that cause-and-effect is established.

The second key element of the NRC's strategy is "level of effort". When uncertainty is high, those considering MNA must expend more resources to gather and interpret information that properly documents whether or not the destruction or immobilization processes are effective at the site.

Uncertainty can derive from two primary sources: reaction mechanisms and site heterogeneity.

For <u>some</u> contaminants, the destruction or immobilization reaction mechanisms are not well understood. The biodegradation of MTBE is a contemporary example. In such a case, the site evaluation may require fundamental studies that demonstrate that destruction processes actually take place and to identify reliable footprints.

For <u>all</u> contaminants, significant uncertainty is introduced when the site is complex or difficult to sample. Site heterogeneity and the related confounding reactions make it difficult to obtain unambiguous documentation. In this case, the plan for site characterization and monitoring must be properly designed to obtain the most useful information.

EPA's research efforts ultimately must reduce both types of uncertainty. By expanding the fundamental understanding of natural destruction and immobilization processes and creating and demonstrating effective methods for site characterization and monitoring, EPA research will lead to more reliable MNA decision-making process.

2.2.2 Evidence

The decision-making strategy in *Natural Attenuation for Groundwater Remediation* (NRC, 2000) describes an approach for establishing the cause-and-effect connection that is essential for proper use of MNA. This strategy is related to, but not the same as, two previously published sets of evidence proposed for documenting attenuation processes in the field (NRC, 1993; EPA, 2000). The strategy from NRC 2000 subsumes and expands on the previously published sets of evidence.

Although the Subcommittee underscores that the guidelines in NRC (2000) supercede the other sets of evidence, it recognizes that these sets are both valuable and influential.

The older NRC report, *In Situ Bioremediation: When does it work?* (NRC, 1993) recommended that *in situ* bioremediation be evaluated with "three lines of evidence."

a) observed loss of contaminant,

b) evidence that biodegradation is feasible for the setting, and

c) evidence from the field that the biodegradation potential actually is realized.

According to EPA, estimates of rates of natural attenuation and the processes responsible for it are often based on "types of evidence," which collectively provide a basis for concluding that natural attenuation is operative and effective. ORD's overview document (EPA, 2000) describes the three types of evidence as:

a) historical chemical and/or biological data for the contaminants of concern that demonstrate a clear and convincing trend of decreasing contaminant mass, concentration, and/or toxicity over time at appropriate monitoring or sampling points;

b) hydrologic, geochemical, biological, or mineralogical data that can be used to demonstrate indirectly that specific types of natural attenuation processes are active at the site and the rate at which such processes will reduce contaminant concentrations to desired levels; and

c) data from field or laboratory microcosm studies conducted with actual contaminated site media which directly demonstrate the occurrence of a particular natural process at the site and its ability to degrade or otherwise reduce the risk of exposure from the contaminants of concern.

Although similar, the NRC's (1993) three lines of evidence are not precisely the same as the three types of evidence articulated by EPA (2000). The following table compares the three lines of evidence with the three types of evidence in summary fashion. The table provides comments on how these sets of evidence fit within the guidelines of NRC (2000).

NRC (1993) Line of Evidence	**EPA (2000) Type of Evidence**	**Comments Relating to NRC (2000) Strategy**
1. Observed loss of contaminant	1. Historical chemical and/or biological data for the contaminants of concern	NRC 1993 line and EPA type of evidence are essentially the same. These are connected to footprints, which must be produced at a rate commensurate with the loss of the contaminant.
2. Evidence that biodegradation is feasible for the setting	3. Data from field or laboratory microcosm studies conducted with actual contaminated site media.	This NRC 1993 line of evidence is addressed partly by the EPA's third type of evidence. This line of evidence is part of establishing a site conceptual model that proposes feasible destruction or immobilization reactions and their footprints. When the process is not well-understood, the site evaluations may need to perform laboratory studies to establish a feasible process.
3. Evidence from the field that the biodegradation potential actually is realized.	2. Hydrologic, geochemical, biological, or mineralogical data	EPA type of evidence helps fulfill NRC 1993 line of evidence. EPA type of evidence also corresponds directly to NRC 2000 footprints
	3. Data from field or laboratory microcosm studies conducted with actual contaminated site media.	EPA type of evidence helps fulfill NRC 1993 line of evidence. EPA type of evidence complements, but does not substitute for footprints.

2.2.3 Mass Flux, Cause-and-Effect, and Sustainability/Permanence

The processes that destroy or immobilize contaminants must occur at rates that prevent the transport of the contaminants to human and ecological receptors today and for the life of the contaminant source. In many cases, the duration of an MNA remedy will be measured in decades, and the rates must be sustained during the entire time.

Although concentrations are often used as monitoring and design parameters, a mass budget or mass flux analysis is required to provide unequivocal evidence of destruction or immobilization. Proper estimation of the rates of destruction and immobilization reactions generally requires measurements of the mass flux of contaminants and footprint materials into and out of the plume (NRC, 2000). Consistency between mass flux of contaminants and other footprint parameters is strong evidence that postulated processes are responsible for loss of the contaminant. If all appropriate mass fluxes can be sustained in the future, the MNA remedy is likely to be sustainable as well.

In summary, measurements of mass flux of the contaminants and footprint parameters – not just concentrations -- are necessary to document cause-and-effect and to assess long-term sustainability/permanence. Site-characterization and monitoring plans should be proactively designed to accommodate mass-flux estimates.

2.3 Charge for this Review

ORD requested that the SAB review its research program for monitored natural attenuation of contaminants in groundwater, soils, and sediments, in terms of its scientific quality and its effectiveness and utility for promoting good decisions about the use of MNA as a remedy at specific sites. The final Charge for the review was agreed to March 27, 2000. More specifically, ORD asked the SAB to address the following questions.

a) *Is the research that supports the Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater (included in review materials) complete? Does the work that is currently in progress or planned (as described in the review materials) address the important remaining questions? What additional research would the SAB recommend that ORD undertake to promote prudent decisions on the use of MNA as a remedy for sites where groundwater is contaminated by chlorinated solvents?*

b) *Does the SAB believe that the approach to MNA that is described in the Protocol for Chlorinated Solvents can be adapted to make prudent decisions about the use of MNA at UST sites. What additional research on the transport and fate of MTBE and other fuel oxygenates in groundwater, beyond that described in the reports and project descriptions, would the SAB recommend that ORD undertake?*

c) *Does the SAB believe that ORD's current and proposed research (as described in the review materials) to better understand the processes governing the natural attenuation of inorganics such as arsenic and other metals in soils and groundwater addresses the important issues that must be understood in order to incorporate MNA in site remedies for sites contaminated by metals? What additional research would the SAB recommend that ORD undertake?*

d) *NRMRL is beginning to conduct research on MNA for contaminated aquatic sediments. The contaminants of concern are persistent organic compounds (e.g., PCBs, DDT, PAHs, etc.) and inorganics (e.g., arsenic, mercury, etc.). The most likely attenuation mechanisms include dilution, dispersion, coverage by clean sediments, and biodegradation (or biologically-mediated alteration for inorganics), many of which will not destroy the contaminant or irreversibly sequester it. Given the potential dominance of non-degradative processes, what are the dominant processes that should be evaluated to better understand the potential for the use of MNA for remediation of contaminated sediments? Does the SAB have advice on how to approach the issue of permanence for MNA of contaminated sediments?*

The Subcommittee held public conference call meetings on January 26, February 24, May 1, and May 30, 2000. These were followed by a face-to-face meeting August 14-15, 2000 in

Washington, DC and a publicly announced conference call on October 25, 2000. In invited expert, Dr. Cynthia Evanko of GeoSyntech Consultants in Atlanta, Georgia participated in the face-to-face meeting because press of other duties prevented panelist Dr. David Major from attending and their technical backgrounds were similar. The Subcommittee reviewed products of EPA research on natural attenuation, on-going research programs, and planned research.

To support the Subcommittee, ORD provided a number of documents which are listed in Chapter 5. These documents were supplemented by briefings at the meeting and by responses to questions posed by the Subcommittee on the conference calls and at the face-to-face meeting.

After discussion on the conference calls, the Subcommittee and ORD agreed that an extensive answer was not warranted for the last question, “Does the SAB have advice on how to approach the issue of permanence for MNA of contaminated sediments?” The Subcommittee's comments on contaminated sediments are included in Section 3.4.

The EPA Science Advisory Board encourages compliance with the EPA's Quality System. Because the Board has advised the EPA on this issue (EPA-SAB-EEC-LTR-98-003 and EPA-SAB-EEC-LTR-99-002) and there is no special reason to think this research program should be exempted from those requirements or that additional requirements should be imposed upon it, the Subcommittee did not address compliance with the EPA's Quality System in this review.

The Subcommittee formed four two-person teams to draft responses to the charge questions on chlorinated solvents, fuel oxygenates, metals and sediments. Initially, each team consisted of an academician and practitioner in the subject area. Due to press of other duties, there was some attrition from the initial teams, resulting, in one case, in a single Subcommittee member drafting the initial text for one response. The teams presented their preliminary findings and recommendations to the Subcommittee by email and orally on conference call. After receiving the constructive input of other Subcommittee members, each team revised draft materials reflecting the consensus of the Subcommittee on those issues as understood by the team.

Under the overall guidance of the Subcommittee Chair (Dr. Grasso), the Designated Federal Officer assembled these materials into SAB report format for review by the Chair and one other Subcommittee member not on one of the teams. The Designed Federal Officer (DFO) made the suggested edits and circulated the first draft report to the Subcommittee, EPA, and public about ten days before the August 14-15 meeting. Both improvements to the existing text and further changes were proposed at the meeting, especially concerning the context for the Subcommittee's report and issues beyond the charge. A second public draft was made available August 24. Dr. Grasso briefed the Environmental Engineering Committee on the progress of the review at the EEC's publicly announced September 20, 2000 conference call. A small writing group consisting of Drs. Grasso, Hughes, and Rittmann used comments from the Subcommittee and the public together with their notes of the face-to-face meeting to prepare a third public draft which incorporated all the changes the Subcommittee had requested. This draft was circulated to the Subcommittee and the public the week of October 16, 2000. The Subcommittee held a public conference call meeting to consider approval of the draft on October 25, 2000, with additional edits made at a non-public conference call writing session on November 6. The revised Subcommittee draft was forwarded to the Subcommittee (to confirm that the requested changes had been successfully made), the EPA and the public (for information), and the Environmental Engineering Committee for consideration at its December 5-7, 2000 face-to-face meeting. After approval by the EEC, the revised draft was forwarded to the Executive Committee of the SAB for consideration at its February 1, 2001 public conference call meeting where it was approved pending certain changes to be made to the satisfaction of the discussants. The final discussant communicated his satisfaction on March 27, 2001.

3. RESPONSE TO THE CHARGE

The Subcommittee congratulates ORD for being a leading proponent in expanding understanding of monitored natural attenuation. ORD's research efforts have contributed in no small measure to an improved understanding of MNA and its applications.

This Chapter is organized by charge questions. Section 3.1 presents the Subcommittee's response to the first set of charge questions, Section 3.2 the response to the second set, and so forth. Chapter 4 provides the Subcommittee's advice on issues beyond the charge.

3.1 EPA's *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater*

Recently, the application of MNA to contaminants other than BTEX has received considerable interest. Due to the widespread detection of chlorinated solvents in groundwater, the potential use of MNA at these sites is being considered with increasing frequency. NRC's report, *Natural Attenuation for Groundwater Remediation*, cautions that the MNA will not be effective for solving chlorinated solvent remediation problems at most locations (NRC, 2000). However, MNA may provide effective management of hydrocarbon (i.e., BTEX) and chlorinated solvent contamination at sites at which contamination of chlorinated solvents coincides with fuel hydrocarbons, leading to extensive reductive dechlorination.

This section reviews the EPA's *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater*. It addresses the following question(s):

> *"Is the research that supports the Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater complete? [This is addressed in 3.1.2.2] Does the work that is currently in progress or planned (as described in the review materials) address the important remaining questions? [This is addressed in 3.1.3] What additional research would the SAB recommend that ORD undertake to promote prudent decisions on the use of MNA as a remedy for sites where groundwater is contaminated by chlorinated solvents"?[This is addressed in 3.1.4]*
>
> — ORD Charge Question #1 (March 27, 2000)

Summary of Major Findings

1. 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 accumulated products.

2. Significant uncertainty results from the difficulty in obtaining accurate field information to account for all the relevant processes and quantify the reaction rates.

3. Other factors that contribute to uncertainties in MNA for chlorinated solvents include:
   a) 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;

   b) synergistic/antagonistic interactions among chlorinated solvents and other chemicals; and

   c) degradation by mechanisms other than reductive dechlorination. 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 accumulated products. While it is instructive to use the categories of chlorinated solvents sites (i.e., types I, II, III as defined in the *Protocol*), they are not appropriate for use in decision-making because extensive site characterization and data acquisition are required to determine if MNA is appropriate.

Summary of Major Research Recommendations

The EPA should undertake broad initiatives in the following areas to support the appropriate evaluation of MNA at chlorinated solvent sites and reduce uncertainty –

1. Develop and conduct laboratory and field research that will elucidate when and why site conditions allow complete degradation of chlorinated solvents.

2. Focus research programs on how fluxes of electron donors and acceptors from source areas interact to control dechlorination rates at MNA sites. This work may involve establishing a data base of field sites that have been comprehensively characterized to document dechlorination reactions.

3. 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).

4. De-emphasize simple categorization of chlorinated solvent sites (i.e., Type I, II, or III) and eliminate scoring systems.

3.1.1 Summary of Current EPA Research and Thinking

EPA’s *Protocol* for chlorinated solvents presents a methodology for data collection and analysis to evaluate MNA at chlorinated solvents sites. The *Protocol* in particular (a) identifies key field methods and parameters that are needed for evaluating the appropriateness of MNA at chlorinated solvent sites; and (b) develops a conceptual framework for the intrinsic bioremediation of the chlorinated solvents under conditions when fuel hydrocarbons are present.

The EPA *Protocol* has motivated better characterization of chlorinated solvent sites and has prompted the regulatory and regulated communities to collect data on important field parameters that typically would not have been measured or analyzed during site assessments. Additionally, the *Protocol* provides an approach that can be used to evaluate natural attenuation along with other remedial options. The majority of field characterization and data collection procedures described in the *Protocol* are well documented and supported by an extensive body of knowledge available in the general literature.

3.1.2 Analysis of the Present State of MNA Knowledge at EPA

3.1.2.1 General Comments

Overall, the EPA *Protocol* should be viewed as a <u>framework</u> for MNA studies at chlorinated sites rather than a step-by-step manual or protocol. This viewpoint is shared by the authors of *Natural Attenuation for Groundwater Remediation* (NRC, 2000), who reviewed 14 protocols, including the EPA chlorinated solvent protocol, and concluded that "None of the protocols meets all of the characteristics defined by the committee."

Chlorinated-solvent degradation depends on the environmental conditions present at the site, particularly the presence or absence of a carbon source that can serve as an electron donor for dechlorination. To implement the concept that an electron donor is required for reductive dechlorination, EPA’s *Protocol* identified three types of plume behavior (Type I, II, or III). Type I and Type II plumes, as defined in the *Protocol*, differ in the source of organic carbon. Type I plumes have anthropogenic carbon (i.e., BTEX) as an electron donor, while Type II plumes have high contributions of native organic matter. Type I and Type II plumes support dechlorination activity but Type II usually has lower rates and extent of biodegradation of the highly chlorinated solvents, according to the *Protocol*. Type III plumes, which are subject only to advection, dispersion, sorption, and abiotic reactions, have minimal levels of organic matter, are aerobic, and do not support dechlorination.

While it is instructive to use these categories of sites for initial assessments of MNA potential, they are not appropriate for use in decision-making. Extensive site characterization and data acquisition are required to determine if MNA is appropriate. For example, degradation products must be acceptable, sufficient electron donor material must be present to sustain degradation, and evidence of adequate electron donor-electron acceptor contact must be established, among others.

The EPA protocol employs a numerical scoring system as a screening tool. However, the NRC (2000) recommended that numerical scoring systems should be abandoned and observed that,

> "Ultimately, site closure decisions depend on the professional judgment of individual regulators. Investigators and regulators sometimes employ and advocate minimalist criteria or rules of thumb to make quick decisions on natural attenuation without using detailed technical protocols to show cause and effect. However, such rules should not be substituted for experienced professional assessments based on a conceptual model and understanding of cause and effect that are consistent with all of the data.. In particular, it is important to avoid creating a climate in which regulators feel pressured to apply simple rules. In general, providing guidelines for documenting cause and effect is one of the most critical roles of a natural attenuation protocol."

3.1.2.2 Is the research that supports the *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater* complete?

The Subcommittee believes that several areas of research must be addressed to support and further develop EPA guidance in this area. These areas include a better understanding of biodegradation processes, degradation rates, and the impact of source zones on the processes occurring. Each is discussed in the remainder of this section.

Extent of Chlorinated Solvents Reduction (CS) - In a recent multiple plume study, McNabb et al. (1999) reported that CVOC (chlorinated volatile organic compound) sites could be roughly divided into equal thirds based on extent of reductive dehalogenation, i.e., no evidence of reductive dehalogenation (no *cis*-1,2-DCE or vinyl chloride production), weak evidence of reductive dehalogenation (*cis*-1,2-DCE, but no vinyl chloride plume), and strong evidence of reductive dehalogenation (vinyl chloride plumes present). The authors concluded that

> "the presence of a vinyl chloride plume indicates that reductive dechlorination may be playing a role in reducing the extent of CVOC plumes at approximately one-third of the sites. In contrast, the presence of a cis-1,2-DCE plume in the absence of a vinyl chloride plume appears to indicate reductive dechlorination rates that are insufficient to effectively reduce the extent of CVOC plumes; little evidence exists to suggest that plume lengths and plume growth rates are substantially affected by reductive dehalogenation in these circumstances."

Similarly, a review by Bradley (2000) concluded that "*in the majority of groundwater systems reductive dechlorination apparently stops at DCE or VC.*"

The EPA protocol uses the presence of degradation products as a key criterion to classify sites, but the classification system does not distinguish among the products that are present. Because sites at which dechlorination reactions ultimately stop at DCE are combined with sites at which VC is present, this scheme is ineffective in identifying those sites at which reductive dechlorination is not likely to achieve remediation goals. Moreover, should the degradation rate of vinyl chloride be much greater than that of *cis*-1,2-DCE, then one might not observe much vinyl chloride. Research is needed to identify factors that control the extent to which chlorinated solvents are reductively dechlorinated.

To date, most research on the natural attenuation of chlorinated solvents has focused on PCE, TCE, DCE, and vinyl chloride. While PCE and TCE and their breakdown products are the chlorinated solvents most frequently found in groundwater, it is not rare to encounter others. The chloromethanes, chloroethanes, and chlorinated benzenes are all common ground-water contaminants, but their natural attenuation has not been studied to the same extent as the chlorinated ethenes.

Rates of Chlorinated Solvent Biodegradation - Evaluating whether the plume is stable or expanding is important in determining risk. Therefore, research that helps determine whether a chlorinated-solvent plume achieves a quasi-steady state condition is needed. These efforts require modeling, and that modeling should incorporate the advice contained in the SAB's *Resolution on the Use of Mathematical Models by EPA For Regulatory Assessment and Decisionnmaking* (USEPA SAB, 1989). Any modeling must be well-grounded in the mechanisms of processes occurring, and attention must be given to site-specific rate constants and the estimation of parameters. The *Protocol* does not adequately emphasize the need for estimating **field-based natural attenuation rates** for the chlorinated solvents. Of particular importance in the determination of degradation rates for chlorinated solvents is the recognition that considerable spatial heterogeneity in the kinetics of individual processes may exist. Determining or estimating this variability in rates is required for the analysis of plume stability and is not adequately incorporated into the current protocol.

The EPA *Protocol* describes two methods (Wiedemeier et al., 1996 and Buscheck and Alcantar, 1995) for estimating a biodegradation rate at a given site but the practical usefulness of these methods for chlorinated solvents is limited. The tracer method described in Wiedemeier et al. (1996) cannot be readily applied to chlorinated solvent sites without identifying an appropriate tracer that could be used in the analysis. Additionally, the Buscheck and Alcantar method is applicable only for steady-state plumes. There is no scientific research that establishes a reliable method for predicting whether a chlorinated solvent plume is stable or at steady state, without extensive monitoring of the plume over extended periods.

Source Terms and Their Impact on Natural Attenuation - The presence of sufficient mass of electron donors to accommodate reductive dechlorination reactions is critical to insuring sustained biodegradation rates. Consequently, it is important to understand and quantify mass flux of chlorinated solvents and available electron donors from source areas and understand their subsequent transport and retardation characteristics. At present, the EPA research program does not sufficiently address these issues.

The EPA *Protocol* focuses on biodegradation as the primary process influencing the natural attenuation of chlorinated solvents. There is recent evidence, however, that DNAPLs and source strength play a important role in observed dechlorination. In fact, McNabb et al. (1999) suggested that "CVOC transformation rates through dehalogenation exert less impact on plume length than source strength and groundwater velocity", and conclude that "*plumes with weaker source strength and slower groundwater velocities may be better candidates for the application of natural attenuation remedies*".

Degradation Reactions Other than Reductive Dechlorination - Certain chlorinated solvents (including TCE) can be biotransformed through aerobic, cometabolic reactions (NRC, 2000). Recent evidence generated by the EPA suggests that other chlorinated solvents might be transformed by oxidative reactions. If reactions other than reductive dechlorination are important in MNA, they must be thoroughly documented by additional studies.

3.1.3 Does the work that is currently in progress or planned (as described in the review materials) address the important remaining questions?

The research currently in progress is described in a project summary provided to the Subcommittee by EPA (Task Number 3674). The project summary does not provide sufficient information to evaluate the proposed research in detail. The project description indicates that the *Protocol* will be "revised" and tested at two or three sites. This research project will assist in addressing some of the uncertainties associated with the natural attenuation of chlorinated solvents but does not appear to be comprehensive enough in scope or depth to address other issues described herein.

3.1.4 What additional research would the SAB recommend that ORD undertake to promote prudent decisions on the use of MNA as a remedy for sites at which groundwater is contaminated by chlorinated solvents?

The following Subcommittee specific research recommendations appear in priority order.

a) Develop and conduct laboratory research to identify what factors control the extent of observed dechlorination and to determine how electron donor – acceptor interactions control rates of dechlorination.

b) Develop methods for quantifying natural attenuation rates when different biodegradation processes are occurring at different locations in the plume.

c) Conduct field and laboratory experiments to determine how the reductive dechlorination behavior of chloromethanes, chloroethanes, and chlorinated benzenes compares to chlorinated ethenes.

d) Investigate factors that control source dissolution and biodegradation in or near the source area and integrate them into the MNA framework.

e) Evaluate whether reactions other than dechlorination can be significant contributors to the natural attenuation of chlorinated solvents.

3.2 The Use of MNA at UST Sites as it Relates to MBTE and Other Oxygenates

This section evaluates EPA's research program as it relates to MNA and USTs. It addresses the following question(s):

> *"Does the SAB believe that the approach to Monitored Natural Attenuation (MNA) that is described in the Protocol for Chlorinated Solvents can be adopted to make prudent decisions about the use of MNA at UST sites? [This is addressed in 3.2.2.3] What additional research on the transport and fate of MTBE and other oxygenates in groundwater, beyond described in the reports and project descriptions, would the SAB recommend that ORD undertake?" [This is addressed in 3.2.4]*
>
> -- ORD Charge Question #2 (March 27, 2000)

Summary of Major Findings

1. The use of MNA for the remediation of 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.

2. 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.

3. 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.

4. Because fuels contain hydrocarbons other than BTEX, these hydrocarbons may be relevant for the assessment of MNA remedies. For example, New York State Department of Environmental Conservation, Interim Procedures for Inactivation of Petroleum-Impacted Sites (draft), January 2, 1997, Appendix O, Table O.3 suggests that allowable exposures to 1,3,5-trimethylbenzene are only five times greater than allowable exposures to benzene. Because trimethylbenzene is less soluble and less volatile than benzene, it may dominate the toxicity of weathered gasoline.

Summary of Major Research Recommendations

The EPA should undertake broad initiatives in the following areas to support the appropriate evaluation of MNA at UST sites.

1. Determine the biodegradability of MTBE and other oxygenates under various field conditions (for example, various electron acceptor conditions and mixtures of hydrocarbon substrates) quantifying related uncertainties.

2. Improve the predictability of dissolution rates for MTBE and other fuel components and their fluxes exiting source zones.

3. 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.

4. Determine whether hydrocarbons in gasoline not on the Target Compound List should be considered for remedial risk analyses.

3.2.1 Summary of Current Research and Thinking

MNA of fuel hydrocarbons is an accepted approach to remediate certain UST sites in the United States.

The development of MNA as an alternative remediation strategy has been the direct result of interest in the observed formation and migration of petroleum plumes from UST sites. A large base of information exists regarding attenuation processes for BTEX compounds, and protocols for the use of MNA for these contaminants have been developed.

Hydrocarbons other than BTEX may be relevant for the assessment of MNA remedies at fuels sites. For example, New York State Department of Environmental Conservation, Interim Procedures for Inactivation of Petroleum-Impacted Sites (draft), January 2, 1997, Appendix O, Table O.3 suggests that allowable exposures to 1,3,5-trimethylbenzene are only five times greater than allowable exposures to benzene. Because trimethylbenzene is less soluble and less volatile than benzene, it may dominate the toxicity of weathered gasoline.

The compounds of most concern at UST sites are BTEX and oxygenates (MTBE in particular). Considerable information exists on the MNA of BTEX compounds, and MNA of BTEX is generally recognized as an established practice in subsurface restoration (NRC, 2000). Less is known about MNA‘s effectiveness in managing oxygenate contamination, and MTBE is therefore a focus of this section.

Conceptual Model of Contaminated Sites - The release of petroleum hydrocarbons from UST sites results in the contamination of the vadose zone, underlying groundwater, or both. The Subcommittee's charge is limited to the remediation of contaminated groundwater. Naturally occurring transport and fate processes can result in the reduction of the total mass of contaminants present in the subsurface and the concentration of contaminants within the contaminant plume.

The most common scenario for UST sites is the release of gasoline or related fuels (e.g., diesel and aviation fuels) to the subsurface. Gasoline and other fuels are composed of a number of individual compounds with a mixture density less than water. The concentrations of contaminants entering groundwater is a function of source composition (i.e., the fraction of various chemical species), the aqueous solubility of individual species, and their activity in the Non-Aqueous Phase Liquids (NAPL) solution. Johnson et al. (2000) report the following equilibrium concentrations of BTEX and MTBE that would result from typical gasoline mixtures in contact with water.

COMPOUND	**CONCENTRATION (mg/L)**
Benzene	18
Toluene	25
Ethyl benzene	3
Xylenes (total)	20
MTBE (RFG)	4,700
MTBE (oxyfuel)	6,300

(RFG refers to reformulated gasoline)

Over time, the composition of the contaminant source changes, as it becomes depleted of the more soluble fractions (such as MTBE), decreasing the equilibrium concentrations observed. Also, mass transfer limitations often reduce the actual concentrations observed near source areas below that which would be predicted by equilibrium.

BTEX compounds are oxidized by microorganisms and biodegradation processes consume electron acceptors (O_2, NO_3, Fe (III), and $SO_4{}^{2-}$). The groundwater near the source can become strongly anaerobic – resulting in the observation of iron reduction, sulfate reduction and methanogenesis, if the oxidation of BTEX is significant enough to deplete O_2 and NO^-_3 The dispersion of oxygen carrying groundwater and re-aeration from the vadose zone eventually restore aerobic conditions to waters at some distance down gradient from the contaminant source. This spatial transition of redox conditions implies that contaminants (i.e., BTEX and MTBE) often are exposed to a wide range of microbial reactions and communities during their transport. Numerous studies have been conducted to evaluate the biodegradability of BTEX under a variety of electron acceptor conditions. Certainly, all BTEX compounds are degraded under aerobic conditions. It appears that all can be degraded anaerobically, although the occurrence of anaerobic benzene degradation is still an active research question.

In comparison to BTEX, far less is known about the biodegradability of MTBE and other fuel oxygenates. Under aerobic conditions, MTBE degradation has been linked to bacterial growth (at slow rate) and to co-metabolism catalyzed by oxygenase enzymes. Although Wilson et al. (2000) present evidence that anaerobic MTBE degradation may occur, considerable research will be needed to fully assess the potential for anaerobic MTBE degradation

Since MTBE and BTEX compounds are among the most soluble constituents of fuels, the time associated with their removal from source zones is less than other, more hydrophobic chemicals. Thus, constituents other than BTEX and MTBE may be the most long-lived contaminants in source zones and be the most persistent components of associated contaminant plumes. Little is known about the anaerobic metabolism of these constituents.

3.2.2 Analysis of the Present State of MNA Knowledge at EPA

3.2.2.1 Identification of important issues and assessment of status of EPA knowledge and effort.

For improved knowledge, the most pressing need is in the area of MTBE biodegradation. There is sparse information on MTBE mineralization. More research is sorely needed to predict the potential for MTBE biodegradation. For example, the range of aerobic organisms capable of MTBE biodegradation has not been assessed. If organisms possessing metabolic capability for MTBE biodegradation are absent, bioaugmentation may become a viable alternative to achieve degradation. Also, the observation of slow growth rates and slow acclimation by aerobic bacteria utilizing MTBE has heightened concern that rapidly migrating plumes may expand at rates faster than MTBE-degrading populations can respond. Additional concerns include: the effect of other organic contaminants on MTBE biodegradation; the potential for MTBE metabolism under anaerobic electron acceptor conditions; the potential accumulation of hazardous intermediate products (e.g., tert-butyl alcohol); and the effect of source aging on MTBE dissolution rates.

3.2.2.2 Assessment of protocol(s) for incorporation of required and appropriate scientific knowledge and approach.

The following research recommendations derive from the dearth of knowledge in understanding fate processes affecting MTBE and the current criteria outlined in EPA's *Protocol.*

Site Assessment - The level of MTBE addition to gasoline has varied with time and by region of the U.S. Thus, assessing the extent of MTBE within a source zone is more complicated than similar assessments for BTEX or other compounds that are routinely found in fuel within certain concentration ranges. This results in the need to improve the analysis of site history in the preliminary conceptual modeling that takes place as part of site characterization. MTBE is more mobile than BTEX; thus, the analysis and transport of preferential flow paths, and the location of down gradient monitoring wells must be considered more carefully than for BTEX alone. A stable BTEX plume does not imply that an MTBE plume has stabilized. For example, the release of BTEX may have preceded the release of MTBE. While sufficient time may have elapsed to stabilize the BTEX plume, the MTBE plume may still be expanding. The advice contained in the SAB's *Resolution on the Use of Mathematical Models by EPA For Regulatory Assessment and Decision-making* (EPA-SAB-EEC-89-012) may be useful in conducting this work (USEPA SAB, 1989).

Evaluating MTBE Biodegradation - Beyond plume stability, the strategies for geochemical footprinting of biodegradation activity (e.g., electron acceptor consumption, product formation, and inorganic carbon) are required. Currently, it is unclear what footprints are associated with MTBE biodegradation, because little is known about MTBE metabolism. Based on theoretical stoichiometric calculations, the complete mineralization of MTBE by aerobes would consume 2.8 mg of O_2 per mg of MTBE. Similar calculations result in the predicted consumption of 4.3 mg of NO^-_3 or 4.1 mg of SO_4^{2-} during the compete oxidation of 1 mg of MTBE by nitrate reduction or sulfate reduction, respectively. Methanogenesis would produce 0.7 mg of methane from 1 mg of MTBE. At this time, the applicability of these ratios as footprints of MTBE biodegradation has not been evaluated.

Due to the number of studies that have shown BTEX degradation, microcosm studies are no longer frequently needed to confirm BTEX metabolism. In the case of MTBE, microcosm studies should be required to demonstrate the MTBE-degrading microorganisms are present and that degradation is feasible.

3.2.2.3 Does the SAB believe that the approach to Monitored Natural Attenuation (MNA) that is described in the Protocol for Chlorinated Solvents can be adopted to make prudent decisions about the use of MNA at UST sites?

The Subcommittee does not advocate the use of protocols *per se*. However, in the Subcommittee's view MNA can be appropriately and successfully applied at many UST sites containing BTEX compounds. 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. However, the presence of fuel oxygenates in UST source zones, and subsequently the down-gradient plume, introduce uncertainty in the effectiveness of MNA to provide an acceptable level of protection at UST sites – compared to BTEX only sites.

3.2.3 What additional research would the SAB recommend that ORD undertake to promote prudent decisions on the use of MNA in situations involving UST, MTBE, or other oxygenates?

The most pressing need is to develop an understanding of the biodegradation of MBTE and, possibly, other oxygenates. In comparison to BTEX, little is known about the biodegradability of MTBE and other fuel oxygenates. In particular, research will be needed to fully assess the potential for anaerobic MTBE degradation. More specifically, the EPA should:

a) Determine the biodegradability of MTBE and other oxygenates under various field conditions (for example, various electron acceptor conditions and mixtures of hydrocarbon substrates) quantifying related uncertainties.

b) Improve the predictability of dissolution rates for MTBE and other fuel components and their fluxes exiting source zones.

c) 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.

3.3 MNA of Hazardous Inorganics in Soils and Groundwater

This section evaluates EPA's research program as it relates to the use of MNA for hazardous inorganic contaminants, of which arsenic and heavy metals are most critical. It addresses the following questions:

> *“Does the SAB believe that ORD’s current and proposed research to better understand the processes governing the natural attenuation of inorganics such as arsenic and other metals in soils and groundwater addresses the important issues that must be understood in order to incorporate MNA in site remedies for sites contaminated by metals? [This is addressed in new section 3.3.3] What additional research would the SAB recommend that ORD undertake?”[This is addressed in 3.3.4]*

— ORD Charge Question #3 (March 27, 2000)

Summary of Major Findings

1. Immobilization, the primary attenuation process operative for arsenic and metals, is not fully understood, which makes the application of MNA to these inorganics more challenging.

2. No footprinting or monitoring guidance is currently available for employing MNA for metals and arsenic.

3. Currently, it is difficult to reconcile laboratory and field data for arsenic and metal reactions in soil.

4. 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.

Summary of Major Research Recommendations

To provide the technical community with an understanding of when and how MNA can be appropriately applied to arsenic and heavy metals that is similar to the level of understanding which exists for BTEX, EPA should continue research to elucidate mechanisms of immobilization and to evaluate the permanency of immobilization at field sites. More specifically, EPA should:

1. further elucidate attenuation mechanisms governing the immobilization of arsenic and other metals;

2. evaluate changes in geochemical conditions responsible for the re-mobilization of once immobilized contaminants; and

3. perform studies to understand the fate and behavior of arsenic and metals in co-mingled organic/inorganic plumes.

The Subcommittee further recommends that EPA should develop guidelines for:

1. field and analytical data needed for MNA to provide a basis for establishing footprints and monitoring criteria

2. demonstrating permanence of the immobilization process;

3. using models to reconcile laboratory and field data; and

4. incorporating uncertainty analysis in mathematical models to extrapolate laboratory results to the field with an understanding of the limitations of model predictions..

Notwithstanding present scientific gaps, the EPA should begin to develop a framework for MNA of metals and arsenic. As the framework evolves, additional unforeseen issues requiring solution will arise.

3.3.1 Summary of Current EPA Research and Thinking

EPA acknowledges two transformation processes that can attenuate inorganic contaminants using reactive mechanisms:

a) immobilization in a form resistant to transport, and

b) transformation of soluble species to ones with low toxicity or bioaccumulation potential.

The first process, immobilization, has served as the focal point for ORD research. EPA has subdivided its approach to understanding immobilization reactions into three different categories:

a) contaminant flux,

b) contaminant attenuation capacity, and

c) geochemical buffering capacity.

EPA's definition of immobilization centers around solid-phase partitioning. Although many other processes may play a role in immobilization, solid phase partitioning is thought to be the primary mechanism.

Notwithstanding the insufficient availability of kinetic and thermodynamic data for most reaction processes that sequester or immobilize inorganic contaminants, there is a dire need to develop a framework within which to evaluate the potential for natural attenuation of inorganic contaminants. To address this problem, EPA has initiated a multi-faceted research program focused on developing better measurement techniques for in-situ and solid phase contaminant speciation, as well as collection/assessment of quantitative thermodynamic and kinetic data.

More specifically, current EPA research addresses:

a) the identification of natural attenuation processes, focusing on the geochemical parameters that exert the greatest influence on arsenic partitioning to soils and sediments and evaluating the role of iron and sulfur on arsenic speciation and mobility;

b) the development of reliable sampling and *in situ* measurement methods, focusing on chemical speciation of arsenic and mercury;

c) obtaining reliable rate estimates of the time frame for natural attenuation for metals and arsenic;

d) developing laboratory methods to assess solid phase contaminant speciation for arsenic;

e) developing protocols for assessing the role of biota in arsenic and metals attenuation; and

f) development of tools for estimating aquifer attenuation potential for metals and arsenic.

3.3.2 Analysis of the Present State of MNA Knowledge at EPA

3.3.2.1 ORD's Currently Identified Research Needs – Although the EPA's current research program focuses on appropriate issues for the proper application of MNA to inorganics, the EPA's <u>proposed</u> research program focuses primarily on arsenic, and does not address data gaps for other inorganic contaminants.

Because the scientific understanding of inorganics immobilization processes is not fully developed, EPA should expand its research efforts to develop a better understanding of immobilization/mobilization processes relating to not only arsenic, but also other heavy metals in natural systems. The results of this research can be used to establish footprint and monitoring criteria for MNA of arsenic and metals. Permanence is the most critical element in this analysis because, if the immobilization isn't permanent, the contaminants may re-mobilize and become a secondary source. It is important to evaluate the stability of inorganics attenuated by soil surface and matrix processes under a variety of pH, redox, and aging conditions. Research should focus more heavily on the permanence of MNA reactions under expected long-term geochemical conditions, rather than on the buffering capacity of the aquifer.

Because extrapolation of laboratory studies to field conditions is often very difficult, the consistency of field and laboratory studies should be evaluated and guidelines for consistency should be established with acceptable criteria. This is especially true for metals and other inorganics, because they can be found in a great variety of forms and species.

Sites contaminated with metals commonly involve co-mingled wastes. Therefore, understanding interactions between organic and inorganic contaminants is critically important. These interactions can alter the geochemical behavior of individual contaminants when they are present in mixtures.

While there are deficiencies in the kinetic and thermodynamic databases for inorganics, there is a critical need for direction in the evaluation of MNA remedies for inorganic contaminants. Existing MNA protocols (Wiedemeier et al., 1998) for organics are not directly applicable to inorganics. Therefore, EPA should evaluate whether there are sufficient data available to develop an initial framework for MNA evaluations for inorganics while contaminant-specific research needs continue to be identified and addressed.

In considering whether sufficient data are available to develop a framework, EPA should have as an <u>initial</u> goal, a flexible framework (not a protocol) that would be applicable for arsenic and other metals. In this framework, EPA should emphasize the use of mathematical models for extrapolating the results from the laboratory to the field and incorporating uncertainty in the projections and develop monitoring and footprint criteria to validate and support natural attenuation processes for inorganics. The framework should describe the behavior of arsenic and other inorganics as related to categories such as redox sensitive, cationic versus anionic species, soils versus groundwater, alkaline (calcareous) versus acidic (glaciated) environments, oxidative versus reducing conditions.

3.3.3 Does the SAB believe that ORD's current and proposed research to better understand the processes governing the natural attenuation of inorganics such as arsenic and other metals in soils and groundwater addresses the important issues that must be understood in order to incorporate MNA in site remedies for sites contaminated by metals?

Because much less is known about the application of MNA to metals as compared to BTEX compounds, which have been studied for decades, significantly more research on the application of MNA to sites contaminated with metals is required before the technical community will have a similar understanding of when and how MNA can be appropriately and confidently applied to such sites.

ORD's current research program addresses some, but not all, of the important issues that must be understood to incorporate MNA as a remedy at sites contaminated by metals. For example EPA is appropriately working to elucidate mechanisms of immobilization and to evaluate the permanency of immobilization at field sites. The Subcommittee has identified additional important research issues in section 3.3.2. These include addressing issues related to footprinting criteria, demonstration of permanence, models, and uncertainty analysis.

The proposed research program focuses on arsenic. This does not begin to address the behavior of metal contaminants in natural systems, especially assessing permanence of immobilization. The Subcommittee encourages EPA develop a flexible framework (not a protocol) for arsenic and metals which emphasizes the use of mathematical models to extrapolate laboratory results to the field incorporating uncertainty analysis.

Given the size of the present research program, it is unrealistic to believe that the EPA can provide a better understanding of the processes governing the natural attenuation of inorganics. Yet these processes must be understood if the technical community is to base decisions about MNA at sites contaminated with metals on an understanding comparable to that for BTEX. Both time and resources for research are needed to gain that understanding.

3.3.4 What additional research would the SAB recommend that ORD undertake to promote prudent decisions on the use of MNA as a remedy for sites where arsenic or other metals are present in groundwater or soil?

In general, the research needs relating to inorganics must be better articulated and prioritized. The lack of priorities in the research strategy may otherwise result in an overall lack of understanding of the underlying processes. As understanding advances, the priorities should be re-evaluated and revised. More specifically, the EPA should:

a) further elucidate attenuation mechanisms governing the immobilization of arsenic and other metals;

b) evaluate changes in geochemical conditions responsible for the re-mobilization of once immobilized contaminants; and

c) perform studies to understand the fate and behavior of arsenic and metals in co-mingled organic/inorganic plumes.

The Subcommittee further recommends that EPA should develop guidelines for:

a) field and analytical data needed for MNA to provide a basis for establishing footprints and monitoring criteria

b) demonstrating permanence of the immobilization process;

c) using models to reconcile laboratory and field data; and

d. incorporating uncertainty analysis in mathematical models to extrapolate laboratory results to the field.

Notwithstanding present scientific gaps, the EPA should begin to develop a framework for MNA of metals and arsenic. As the framework evolves, additional unforeseen issues requiring solution will arise.

3.4 The Use of MNA to Evaluate Aquatic Sediments

This section evaluates EPA's proposed research on MNA for aquatic sediments and specifically addresses the following questions:

> *NRMRL (National Risk Management Research Laboratory) is beginning to conduct research on MNA for contaminated aquatic sediments. The contaminants of concern are persistent organic compounds (e.g., PCBs, DDT, PAHs, etc.) and inorganics (e.g., As, and Hg, etc.). The most likely attenuation*

mechanisms include dilution, dispersion, coverage by clean sediments, and biodegradation (or biologically-mediated alteration for inorganics), many of which will not destroy the contaminant or irreversibly sequester it.

a) Given the potential dominance of non-degradative processes, what are the ***dominant processes*** *that should be evaluated to better understand the potential for the use of MNA for remediation of contaminated sediments? [This is addressed in 3.4.2.1 Section on Dominant Processes]*

b) Does the SAB have advice on how to approach the issue of ***permanence*** *for MNA of contaminated sediments? [This is addressed in 3.4.2.1 section on Sustainability/Permanence]*

— ORD Charge Question #4 (March 27, 2000)

Summary of Major Findings

1. The application of MNA to contaminated sediments has received much less attention than MNA for contaminated soil and groundwater. Of the relevant work completed to date, most has focused on freshwater sediments.

2. 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.

3. 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.

4. The *Contaminated Sediment Management Strategy* (1998) does not explicitly address the role of MNA in contaminated sediment management.

5. Management of contaminated sediments involves many levels of government and is, therefore, administratively complex and challenging.

Summary of Major Research Recommendations

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

2. Develop monitoring methods to quantify attenuation mechanisms, contaminated sediment transport processes, and bioaccumulation to support footprint documentation and analysis of permanence.

3. Redefine the research projects associated with the *Contaminated Sediment Management Strategy* (1998) to include MNA and develop additional research specific to MNA in fresh water, coastal, and marine aquatic sediment environments.

4. Improve collaboration with DOD and DOE for managing contaminated sediments and with affected industries to develop comprehensive research programs.

3.4.1 Summary of Current EPA Research and Thinking

The development of remedial approaches, including MNA, for use in contaminated sediments has received much less attention than those implemented for contaminated soil and groundwater. Work in contaminated sediments completed to date has focused mostly on freshwater sediments, resulting in limited information on coastal, estuarine, and marine sediments. For example, the EPA's *Contaminated Sediment Management Strategy* (1998) is limited to estimates of the top five centimeters of contaminated freshwater sediments "underlying our nation's surface water" and does not fully address non-freshwater sediments. Considerable effort will be required to establish appropriate implementation of MNA at contaminated sediments sites. Although information on contaminant attenuation in soils and groundwater can serve as a basis for understanding certain processes of attenuation in contaminated sediments, the dynamic and heterogeneous nature of sediment systems introduces complexities not found in soils or groundwater.

3.4.2 Analysis of the Present State of MNA Knowledge at EPA

The Subcommittee reviewed two EPA documents that describe research activities on contaminated sediments: a) *EPA's Contaminated Sediment Management Strategy* (1998), available from the US EPA's website and b) "Review of EPA's Natural Attenuation Research" (2000), prepared for this review.

The first document describes a variety of ORD's past and current research programs on contaminated sediments relating to: standardized test methods on sediment toxicity and contaminant bioaccumulation, chemical analysis of contaminants, bioavailability and trophic transfer of contaminants, fate of contaminants in sediments, routes of biological exposures, and sediment quality criteria. The document also states that ORD will conduct laboratory and field research to determine when MNA is appropriate by studying factors that control the rates of recovery of benthic communities under various environmental conditions and stresses. Results from these research programs would be relevant to and have direct bearing on the evaluation of MNA use in contaminated sediments.

Research programs described in the *Contaminated Sediment Management Strategy* (EPA, 1998) plan to use the National Sediment Inventory (NSI) database to target sediment remediation sites and to consider natural attenuation as a cleanup approach. However, EPA does not appear fully to have considered contaminated sediments in developing its *Protocol* for evaluating MNA and chlorinated solvents (EPA, 1998). The *Strategy* was to prescribe the EPA's direction and policies on contaminated sediment issues, and an updated research strategy on contaminated sediments is under development. The updated strategy should allow ORD to fully incorporate the concept of MNA into its research program unique to contaminated sediments.

The second document, *Review of EPA's Natural Attenuation Research* (2000) describes three current projects and one future project:

a) monitoring natural recovery at 1 PCB-contaminated site and 1 PAH-contaminated site,

b) providing funding to the National Academy of Science on remediation of PCB-contaminated sediments,

c) performing data analysis on MNA, and

d) developing a simple conceptual model on chemical fluxes at the sediment interface.

The descriptions of these projects were too brief to assess their objectives, goals, extent, and potential impact. When the results of the NRC report on PCB contaminated sediments are published, EPA should consider the report as a source of information for MNA of aquatic sediments to be incorporated into EPA's future consideration of MNA in a manner similar to this Subcommittee's incorporation of the NRC (2000) report.

3.4.2.1 Identification of important issues and assessment of status of EPA knowledge and effort

Dominant Processes – A number of processes are capable of influencing contaminant attenuation in sediments. Certainly, the processes that dominate attenuation will be site specific. Therefore, an over-arching recommendation of the Subcommittee is that future research focus on how best to use site-specific information to determine which process(es) dominate attenuation at a particular location.

Within the list of possible processes that will be important in many sediment-MNA applications, the Subcommittee recommends that particular emphasis be placed on the following (no order of prioritization implied):

a) processes that immobilize or destroy contaminants. These include processes such as aging of organic material, biotic or abiotic destruction reactions, and sediment consolidation;

b) the role of episodic and sustained events on sediment bed stability (transport, scouring, and deposition);

c) the potential for bioaccumulation, trophic transfer in food webs, bioturbation/biomixing to significantly influence contaminant fate and transport in sediments near the water-sediment interface;

d) quantification of diffusive rates of contaminants into, through and out of sediments; and

e) bioaccumulation and trophic transfer of contaminants in aquatic organisms in and near contaminated sediments.

Sustainability/permanence – MNA in sediments will require long time periods before all risk associated with contamination is ameliorated. Thus, the issue of permanence (i.e., the long-term sustainability of MNA as an effective remedy) is an important concern. For the most part, the crucial role of sustainability is shared with MNA in groundwater or soils. However, the potential impact of a severe episodic event heightens concern about the sustainability/permanence of MNA as a remedy in sediments. A massive dislocation of contaminants can catastrophically undermine sustainability/permanence of a MNA remedy. In addition, sustained burial processes might impede certain degradation processes, such as aerobic biodegradation.

Contaminants can also be transported and dispersed by mobile aquatic organisms through bioaccumulation causing ecological impact and possibly eventual trophic transfer to sensitive species and humans. All of these factors add more uncertainty to MNA remedies for contaminated sediments as compared to MNA remedies for contaminated soil and groundwater. Therefore, MNA of contaminated sediments is likely to require more for remedial actions and more extensive monitoring during MNA.

The Subcommittee took these factors into consideration in preparing the following advice on the issue of sustainability/permanence:

a) Determine the extent of ancillary remedial actions. For example, the removal of heavily contaminated areas, capping, etc. in conjunction with MNA.

b) Develop methods to rigorously evaluate the stability of the contaminated sediment bed as an initial component of site assessment. This may involve an analysis of current and projected waterway uses.

c) Describe an approach for monitoring sediment MNA compounds that follows the NRC (2000) strategy and uses state-of-the-art methodologies. This approach should be submitted for peer review and public comment, and should be tested at field sites.

Collaboration - Sediment management involves local, regional, state, federal, and international agencies. Principal federal agencies responsible for managing contaminated sediments are US EPA and the Department of Defense (DOD), including the DOD's Army Corps of Engineers (COE). For example, the EPA and the COE have jointly administered the dredged materials disposal provisions of the Clean Water Act (CWA) and the Marine Protection, Research and Sanctuaries Act (MPRSA) for over 20 years. Facilities of DOD and the Department of Energy (DOE) have on-site sediments contaminated with radionuclides, PCB's, metals and other toxics; these facilities use “Federal Facilities Agreements” to coordinate implementation of remedial actions at their facilities (EPA's *Contaminated Sediment Management Strategy*, 1998).

The development of effective MNA approaches to contaminated sediments will require close collaboration. There should be an overarching plan to coordinate activities among agencies to leverage resources and improve the consistency and applicability of MNA remedies for sediments. EPA is also encouraged to collaborate with affected industries.

3.4.2.2 Assessment of protocol(s) for incorporation of required and appropriate scientific knowledge & approach

It is improper to apply existing protocols to contaminated sediments without considering factors unique to sediments, such as sediment mobility, bioturbation/mixing, and periodic events.

3.4.3 What additional research would the SAB recommend that ORD undertake to promote prudent decisions on the use of MNA at sites with contaminated aquatic sediments?

3.4.3.1 Methods Development

A fundamental concern in the application of MNA to sediments is the potential for sediment transport. Critically needed are a strategy for and methods to delineate site boundaries, assess sediment stability, and evaluate contaminant concentration and criteria for attenuation footprints when the sediment bed may be affected by sediment transport.

3.4.3.2 Biodegradation and Bioaccumulation

Research is needed on the interactions of biodegradation and bioaccumulation processes with sediment dynamics. Unique sediment processes not fully addressed by research on groundwater MNA include:

a) episodic events that can alter distributions of electron donors and acceptors;

b) bioturbation/biomixing, which can alter distributions of the contaminants and microorganisms;

c) deposition (or scouring) of organic colloids that serve as an ultimate electron donor; and

d) high sulfate concentrations in salt water, which can shift the ecological balance toward sulfate reduction.

3.4.3.3 Physical/Chemical Processes

a) Mobility and Speciation of Contaminants.

The mobility of immobilized metals is of concern. In salt water, chloride could play a major role in metal complexation (e.g., with the central metal ion, Hg) and increase metal mobility. Conversely, colloidal contaminants may have their mobility retarded by high salt concentrations.

b) Sorption

The colloidal nature of sediments may accentuate sorption of hydrophobic organic contaminants (e.g., PAHs and PCBs) because of the large surface area and high organic content of the colloids). The role of colloids and the heterogeneous nature of organic matter distribution in enhancing sorption of contaminants requires additional study.

3.4.3.4 Effect of Remedial Actions

If MNA is to be considered after a remedial action (e.g., the removal of heavily contaminated portions or capping), the effects of the remedial action on the chemistry, biology, and physics of contaminated sediments must be evaluated. The effects include: 1) potential disturbances on reaction conditions and aquatic life when dredging is used; and 2) changes on reaction conditions and mass transfer in the sediment and at the sediment/water interface when capping is used.

4. COMMENTS BEYOND THE CHARGE

In the course of its review of EPA's research program on MNA, the Subcommittee reached consensus on a number of issues relating not just to research, but to the application of this remediation technology. While these comments are outside the charge for the review and touch upon policy, the Subcommittee provides them here within the context of the Subcommittee's findings and recommendations on the MNA research program.

Because of variability in site conditions, contaminants, and receptors, each site must be considered individually. Although natural processes destroy or strongly immobilize some contaminants at some sites, these processes are not necessarily active and adequate at other sites having similar contamination. Therefore, natural attenuation is an appropriate remedy for a specific site only when adequate monitoring now and in the future confirms that risks are declining to acceptable levels at the site.

The NRC's *Natural Attenuation for Groundwater Remediation* (NRC 2000) and *OSWER Directive 9200.4-17P: Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites* (EPA, 1999) recognize the need for sufficient site-specific analysis before a remedy is selected and subsequent monitoring to document whether the remedy has achieved the stated objectives. The Subcommittee endorses the NRC's (NRC, 2000) finding that, "natural attenuation should be accepted as a formal remedy for contamination only when the processes are documented to be working and are sustainable." Generic decision-making schemes of the sort currently used by the EPA, which are not based on formal and thorough statistical analyses of large samples of cases, should be prohibited.

As a means to reduce the likelihood that generic decision-making occurs, the Subcommittee agrees with the NRC (2000) recommendation that all ad hoc scoring systems be eliminated from protocols. This does not foreclose the possibility that accumulated monitoring data may, in the future, allow formal statistical analyses that will have rich enough specifications, adequate precision and accuracy, and sufficient out-of-sample predictive capability to be helpful in decision-making. It does, however, emphasize that no existing scoring systems come remotely near this standard.

The EPA already has in place many policy and guidance documents to help practitioners make appropriate decisions about MNA. In addition to the OSWER Directive, these include the EPA's Quality System requirements and guidance documents, especially the *Guidance for the Data Quality Objectives Process for Hazardous Waste Sites* (G-4HW) (EPA, 2000). This guidance is applicable to MNA.

Decisions about MNA are technically challenging and MNA is sometimes selected and implemented in ways that are inconsistent with EPA policy and good science. From their individual professional experiences, the Subcommittee members and consultants know of sites where natural attenuation was implemented as a remediation method without adequate site-specific analysis. Similarly, of those who spoke to the Subcommittee identified only one site at which monitoring wells were designed to provide the necessary data to document the progress of site clean-up through natural attenuation.

The public is concerned about the misapplication of natural attenuation (MacDonald, 2000). Many view natural attenuation as a "do nothing" approach that saves responsible parties money while transferring risk to the local community. Some of this concern may stem from poorly implemented public involvement processes (NRC, 2000). To the extent that the public's concern is based on inadequate site-specific analysis and insufficient follow-up, it is shared by the Subcommittee. However, MNA should not be a "do nothing" alternative. If properly employed, it is a knowledge-based remedy where the engineering informs the understanding, monitoring, predicting and documenting the natural processes rather than in manipulating them.

While the Subcommittee was formed to address charge questions relating to research on the fate of contaminants in the subsurface, it recognizes that the social sciences may also contribute to a better understanding of decision-making on MNA. As the SAB Report, *Review of the Peer Review Program of the Environmental Protection Agency* (EPA-SAB-RSAC-00-002) states, ". . . flawed decision-making on the implementation of environmental control technologies (which may include considerations and approaches that are nested in the social science framework) can result in a poor program even if the technological options are intrinsically effective."

The Subcommittee underscores that MNA is a valuable option for remediation of sites contaminated with hazardous materials. It has the potential to reduce cleanup costs while avoiding dangerous exposures to humans and sensitive environmental receptors.

The Subcommittee urges the EPA to take a two pronged approach to preserve MNA as an efficacious option for cleaning up contaminated sites. The first is consistent implementation of existing policies, including the OSWER *Directive* and the EPA's *Quality System* (SAB, 1998 and 1999). The second is additional research and development of technical guidance. Both are needed. No policy or protocol can substitute for the understanding of basic processes developed through research, and research alone cannot ensure that practitioners will, in fact, make the best use of the knowledge gained.

Policy and practice can be linked to knowledge gained through research using guidance documents. The NRC report (NRC, 2000) recently reviewed over a dozen existing guidance documents, including EPA's and found that the existing body of natural attenuation guidance is limited in several important areas. The Subcommittee endorses the NRC's finding that rigorous guidance is needed to ensure that natural attenuation potential is analyzed properly.

NRC (2000) recommended that EPA lead an effort to develop national guidelines for protocols on natural attenuation and that the national guidelines and all future natural attenuation protocols should be peer reviewed. Such peer review would be consistent with the EPA's own peer review policy, i.e., “major scientifically and technically based work products related to EPA decisions normally should be peer reviewed.” The Subcommittee endorses NRC (2000) recommendations on national guidelines.

Publication and dissemination of research results is especially valuable for MNA, for which knowledge is the essential benefit of EPA's research. EPA encourages its scientists to publish the results of their work in the peer-reviewed literature. Prior to publication, ORD requires that publications undergo internal and external peer review in accordance with the EPA’s *Peer Review Handbook* (USEPA, 1998b), and that the Quality Assurance Manager reviews the document.

EPA's efforts to conduct research and develop protocols relevant to MNA will benefit from the EPA's current efforts to cooperate with other interested organizations including industry, other governmental bodies, and the public. The Subcommittee encourages the EPA to freely exchange scientific and technical information with industry and other outside groups.

5. DOCUMENTS PROVIDED FOR REVIEW

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Ground Water Issue for September 1999 and October 1994

GLOSSARY

As	Arsenic
Biomixing	Bioturbation and biomixing have been used interchangeably to refer to the physical and biological activities of aquatic organisms at or near the sediment-water interface, which cause the sediment to become mixed.
Bioturbation	Bioturbation and biomixing have been used interchangeably to refer to the physical and biological activities of aquatic organisms at or near the sediment-water interface, which cause the sediment to become mixed.
BTEX	Benzene, toluene, ethylbenzene, and xylene
COE	U.S. Army Corps of Engineers
Cr	Chromium
CS	Chlorinated Solvents
CVOC	chlorinated volatile organic compound
DCE	dichloroethene
DDD	an intermediate degradation product of DDT
DDE	another intermediate degradation product of DDT
DDT	a pesticide no longer used or produced in the United States because of its tendency to persist in the environment
DNAPLs	Dense Non Aqueous Phase Liquids
DOD	Department of Defense
DOE	Department of Energy
EPA	U.S. Environmental Protection Agency
Hg	Mercury
MNA	Monitored Natural Attenuation
MTBE	Methyl-tertiary-butyl ether, an additive to fuels
NAS	National Academy of Science
NRC	National Research Council
NRC Report	*Natural Attenuation for Groundwater Remediation (2000)*
NRMRL	USEPA National Risk Management Research Laboratory
NSI	National Sediment Inventory
OERR	Office of Emergency Response and Remediation (Superfund)
ORD	Office of Research and Development
OSWER	Office of Solid Waste and Emergency Response
OW	Office of Water
PAHs	Polycyclic aromatic hydrocarbon
PCBs	Polychlorinated biphenyl
pH	a measure of acidity
Protocol	*Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water*
RCRA	Resource Conservation and Recovery Act
RTDF	Remediation Technologies Development Forum

SAB	EPA Science Advisory Board
TCE	Trichloroethane
TNT	Trinitrotoluene
TZ	surface water transition zone
UST	underground storage tanks
VC	vinyl chloride

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APPENDIX A: Summary of Elements of the EPA Quality System and an Introduction to the Data Quality Objectives Process

The Agency's quality **policy** is consistent with ANSI/ASQC E-4 and is defined in EPA Order 5360.1 CHG 1 (1998), the Quality Manual and the organizational components designed for policy implementation as described by the Agency's **Quality System** (EPA QA/G-0). The quality system provides the framework for planning, implementing, and assessing work performed by the organization for carrying out required quality assurance and quality control.

EPA has a comprehensive system of tools for managing its data collection and use activities to assure data quality. The **management tools** used in the organizational level of the EPA Quality System include Quality Management Plans and Management System Reviews. The **technical tools** used in the project level of the EPA Quality System include the Data Quality Objectives Process, Quality Assurance Project Plans, Standard Operating Procedures, Technical Assessments, and Data Quality Assessment.

At the management level, the **Quality System** requires that organizations prepare **Quality Management Plan** (QMP). The QMP provides an overview of responsibilities and lines of authority with regards to quality issues within an organization. Therefore, not only does ETV have a QMP, but the verification partners and subcontractors are required to develop and implement their own QMPs. The ETV program calls these documents **Quality and Management Plans.**

Organizations with **QMPs** review their own performance and develop Quality Assurance Annual Report and Work Plans (QAARWP) that provide information on the previous yearís QA/QC activities and those planned for the current year. The QAARWP functions as an important management tool at the organizational level as well as at the Agency-wide level when QAARWP supplied information is compiled across organizations.

At longer multi-year intervals EPA conducts periodic **Management System Reviews** for organizations. An **MSR** consists of a site visit; a draft report that details findings and recommended corrective actions, consideration of the reviewed organization's formal response to the draft report and the authoring of a final report.

At the project level, the data life cycle of planning, implementation and assessment becomes important. The data life cycle begins with systematic planning. EPA recommends that this required planning be conducted using the **Data Quality Objectives (DQO) Process**. The DQO process is a strategic planning approach based on the scientific method that is used to prepare for a data collection activity. It provides a systematic procedure for defining the criteria that a data collection design should satisfy, including when to collect samples, where to collect samples, the tolerable level of decision errors for the study, and how many samples to collect.

EPA has prepared *Guidance for the Data Quality Objectives Process* (QA/G-4). This guidance document applies to projects where the objective of the study is to collect environmental data in support of an Agency program, and, the results of the study will be used to make a specific decision. DQOs are qualitative and quantitative statements that clarify study objective(s), define the most appropriate type of data to collect, determine the most appropriate conditions from which to collect the data, and specify tolerable limits on the decision errors which will be used as the basis for establishing the quantity and quality of data needed to support the decision. The QA/G-4 provides guidance on using a systematic planning process to develop DQOs; it is based on a graded approach.

Briefly, the seven steps in the DQO process are:

1. State the problem
2. Identify the decision
3. Identify the inputs to the decision
4. Define the study boundaries
5. Develop a decision rule
6. Specify tolerable limits on decision errors

APPENDIX B: ROSTERS

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