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Next Generation – Monitored Natural Attenuation and Enhanced Attenuation – Chlorinated Solvents

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ABSTRACT: Monitored Natural Attenuation (MNA) is a necessary part of the remedial action at most chlorinated solvent sites. As a result, site owners, stakeholders, and regulators are identifying and responding to MNA's technical challenges. For example, many contaminated plumes are not in anaerobic settings, making it unlikely the predominant mechanism embodied in existing protocols and guidance documents, reductive dechlorination, will be viable. This is the case for many of the chlorinated solvent sites at Department of Energy (DOE) facilities. The DOE is conducting a project to explore the possibility of other mechanisms contributing to the attenuation of chlorination solvents in the environment. The project is exploring three key areas: mass balance as a way to evaluate the significance of the different processes occurring at a site, sustainable enhancements as a way to increase the attenuation capacity of a site so that it is sustained allowing remediation goals to be met, and characterization and performance monitoring methods that will support the first two areas in a manner that will support transition to legacy management.

INTRODUCTION

Transition from active treatment of chlorinated solvent plumes into efficient-effective MNA or Enhanced Attenuation (EA) is a crucial step in responsible environmental management. Chlorinated solvents represent many of the largest and most challenging plumes at DOE sites. To facilitate and accelerate implementation of MNA and EA for these sites, the DOE Office of Environmental Management (EM) is sponsoring a project in collaboration with the Interstate Technology and Regulatory Council (ITRC), an organization of 43 state regulator agencies. The three-year effort is intended to identify promising science and technology development topics and fund targeted field research supporting these topics. In parallel, input on direction and progress will be gathered from regulators, end users and stakeholders. These interactions are key to ensuring the project's end product will be consistent with end user needs and regulatory policy. Specifically, the project is focused on encouraging the use of MNA and other sustainable enhancement methods in accordance with the principles embodied in the 1998 Environmental Protection Agency (EPA) protocol and 1999 EPA Office of Solid Waste and Emergency Response Directive. Central to the DOE project is a technical working group (TWG) with national interdisciplinary representation. During the first year of the project, the TWG published a document that examined the historical experience in implementing MNA and the scientific advancements since the EPA protocol and directive became publicly available (DOE, 2003). Included in the document were central research concepts and specific-integrated research and development (R&D) targets that

focus and guide the project's research studies. During the second year of the project, research projects that support the R&D targets were initiated and the 16 R&D targets were synthesized into three central concepts for development: mass balance framework, EA, and innovations in characterization and monitoring (C&M) that support the first two concepts to facilitate transition to legacy management.

This paper presents a summary of the work in these three areas and the supporting research. Three documents providing greater detail on these three areas will be published by the DOE by the end of 2005 and will be available through the Office of Scientific and Technical Information. There are two papers in these proceedings that provide more detail on the mass balance framework (Quantifying Mass Balance in Support of Monitored and Enhanced Natural Attenuation by Chapelle, et al.) and EA (Enhancements to Natural Attenuation Processes: New Approaches to Plume Management by Early, et al.). There are also two papers presenting specific research results supporting these efforts: Push-Pull Tests to Determine In Situ Site-Wide Natural Attenuation Capacity and Microbial Activity at Savannah River CMP Pits and C-Area by Raes, et al. and Electron Shuttles in Redox Processes: Characterization, Quantification, and Remediation Optimization by McLoughlin and Pirkle. Results from other sponsored research will be reported throughout the next several years.

At a site with active attenuation processes, the development of a contaminant plume (Figure 1) can be roughly described in four stages: expanding, stable, shrinking and exhausted. The general requirements for environmental strategies that rely on attenuation are that the plume pose minimal risk (often by meeting a concentration standard at an agreed location) and the plume not expand. Thus, a key element in implementing MNA and EA is documenting that the plume is stable, shrinking or exhausted. Plume stability can be conceptualized as a balance between the delivery to and removal of contaminants from any groundwater system.

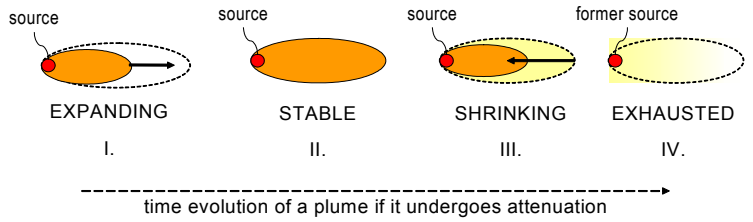

FIGURE 1. Four stages describing development of a contaminant plume (adapted from Newell and Connor 1998)

MASS BALANCE CONCEPT

Mass balance is a simple accounting process that keeps track of loading, accumulation, destruction, creation, and the releases. Complexity is added when one must account for loss or gain of material within the system due to the attenuating mechanisms acting upon the contaminants and their resulting daughter products. These attenuating mechanisms are described as the "Natural Attenuation Capacity (NAC)" of the system. The NAC is defined as the sum of all the physical, biological, and chemical processes serving to disperse, biodegrade, chemically transform, immobilize, or permanently sequester contaminants in a groundwater system. Figure 2 represents a mass balance for a contaminated system. Depending on the size of the system, different processes may be active in distinct sectors of the system. Thus, the calculation of the

NAC becomes a greater challenge.

When a system is balanced with the NAC greater than the loading so that the contaminant flux or concentration to the receptor meets agreed upon criteria, the system can be placed in a state of MNA. When a system is unbalanced with the loading greater than the NAC, the concept of EA is a potential method to bring the system back into balance and into a state of MNA.

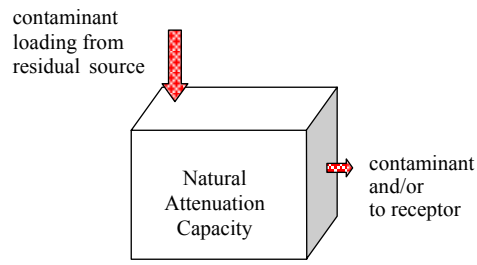

FIGURE 2. Mass balance example for contaminants in a subsurface system.

QUANTIFYING THE MASS BALANCE

There are two distinct philosophies for calculating a mass balance - the empirical method and the deterministic method. The empirical method is consistent with the three lines of evidence as described in the 1998 EPA protocol. This method uses site-specific historical monitoring data and gives the most accurate description of the past and present behavior of the hydrologic system. The empirical method measures fluxes of contaminants moving through different transects of the hydrologic system directly using properly designed monitoring well networks (Figure 3). A main limitation of using the empirical method is that one cannot use it to predict future behavior of the system. This approach cannot be used in situations where active remediation was initiated quickly and is currently operating. It can not be used as a tool to determine how much source removal is needed or when to turn off active remediation and transition to MNA. It can not be used to evaluate potential EA options (unless a long period of post enhancement monitoring is planned).

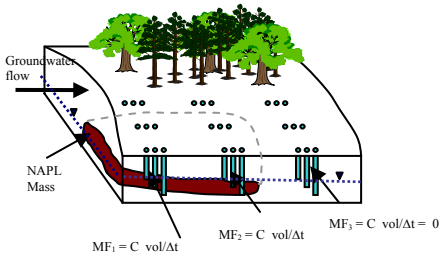

FIGURE 3. The empirical method of describing the mass balance of a system.

Alternatively, a deterministic method can be used to assess contaminant loading and attenuation (Figure 4). This method has the advantage that when sufficient hydrologic, geochemical and biological data are available, it is possible to project future behaviors of the hydrologic system and contaminant life cycle. The deterministic method can be used to assess mass balance and plume stability. A main disadvantage of the deterministic method is that it is difficult to measure all or most of the relevant hydrologic, geochemical, and biological parameters with any certainty. Nevertheless, the time-dependent formulation of the mass-balance equation, makes it

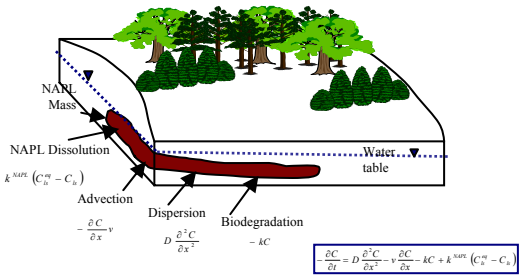

FIGURE 4. The deterministic method of describing the mass balance of a system.

possible to estimate the future behavior of the contaminant plume and the time to complete remediation associated with different management strategies.

An alternative to either individual method is to combine the two. Even though fundamentally different, they are not mutually exclusive. By applying them systematically, these methods can be synergistic, as depicted in Figure 5. The empirical method is entirely based on site-specific monitoring data. It provides a mass balance at a single point in time. Thus, it is capable of giving the most accurate description of past and present conditions providing sufficient data have been collected. On the other hand, the deterministic method is based on universal, quantifiable physical and chemical processes that apply to all sites. Because the mass balance equations developed are time-dependent, this raises the possibility that the deterministic method can provide estimates of the future behavior of sites. The accuracy of these predictions is constrained by the quality of the site data. As such, the deterministic method is capable of providing the most accurate description of future conditions providing sufficient data have been collected.

The ultimate goal of blending these two methods is to provide a framework to answer the central questions faced by those implementing MNA: Are natural processes sufficient to stabilize and shrink the contaminant plume? When can I turn off a pump-&-treat system and transition to MNA? How much source treatment will be needed to support transition to MNA? If natural processes are not sufficient, can these processes be enhanced and how much enhancement will be needed?

ENHANCED ATTENUATION: THE MISSING LINK

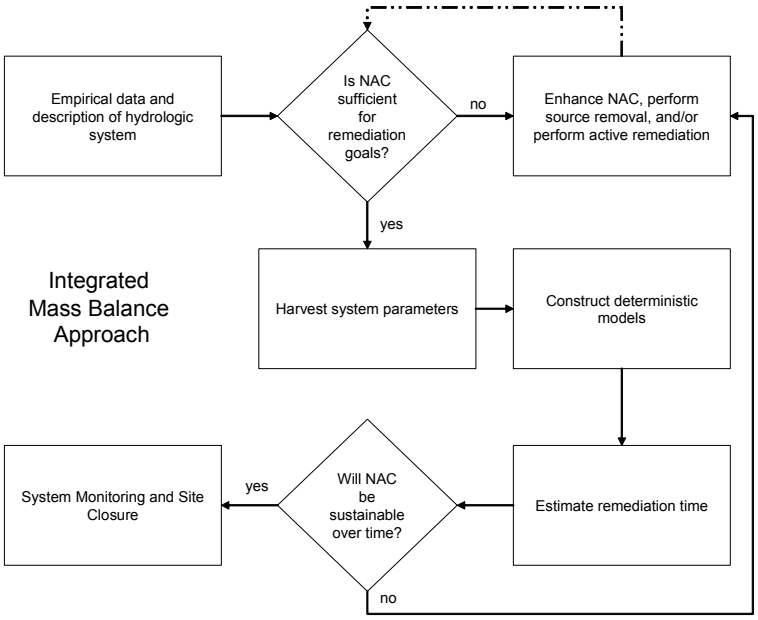

FIGURE 5. Integrating empirical and deterministic methods.

EPA has defined MNA (EPA, 1999) as:

"The term 'monitored natural attenuation' ...refers to the reliance on natural attenuation processes (within the context of a carefully controlled and monitored clean-up approach) to achieve site-specific remedial objectives within a time frame that is reasonable compared to that offered by other more active methods. The 'natural attenuation processes' that are at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favorable conditions, act

without human intervention to reduce mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater." (EPA, 1999; pg. 3)

Elsewhere in this directive the following statements appear:

- *"EPA prefers those processes that degrade or destroy contaminants." (pg. 3)*
- *"EPA expects that source control and long-term performance monitoring will be fundamental components of any MNA remedy." (pg. 3)*
- *"While MNA is often dubbed 'passive' remediation…, its use at a site does not preclude the use of 'active' remediation…" (pg. 4)*
- *"…by definition, a remedy that includes the introduction of an enhancer of any type is no longer considered to be 'natural' attenuation." (pg. 4)*

From this definition and the additional statements in the directive it is clear that any actions that involve human interaction cannot be called MNA. However, there is the question, are there actions that can be taken that are limited in their duration and disturbance to the environment that will result in a sustained, increased attenuation capacity of the natural system? If the answer is yes, they cannot be called MNA. They also cannot be called "active" treatments because they have a different purpose. The term that has been identified is "Enhanced Attenuation". Enhanced attenuation enables one *through intervention to sustainably manipulate natural attenuation processes so that they operate more effectively than without intervention and thereby result in an increased reduction in mass flux of contaminants sufficient to meet regulatory requirements.* This then leads to defining a *sustainable enhancement as an intervention action that continues until such time that the enhancement is no longer required to reduce contaminant concentrations or fluxes.* If we look at treatment options for chlorinated solvents as a continuum, Figure 6, enhanced attenuation processes are placed between the more passive engineered processes and MNA.

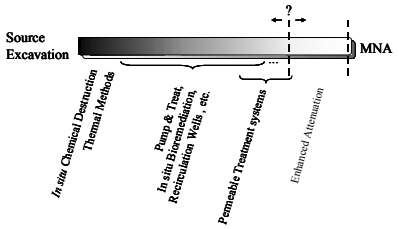

FIGURE 6. Remediation technology and strategy continuum.

Technology classes that can be captured under the EA umbrella can be looked at as either reducing source loading or increasing attenuation capacity, as shown in Figure 7. Many of the technologies are already in existence, but their focus has been towards active treatment. An example of how a relatively new technology that is classified as a biostimulation technology would meet the definition of EA would be at a site that does not have sufficient NAC to reach its' remediation goals with MNA but the estimates are that if the NAC could be increased by factor X for a 2 to 3 year period the remediation goal would be

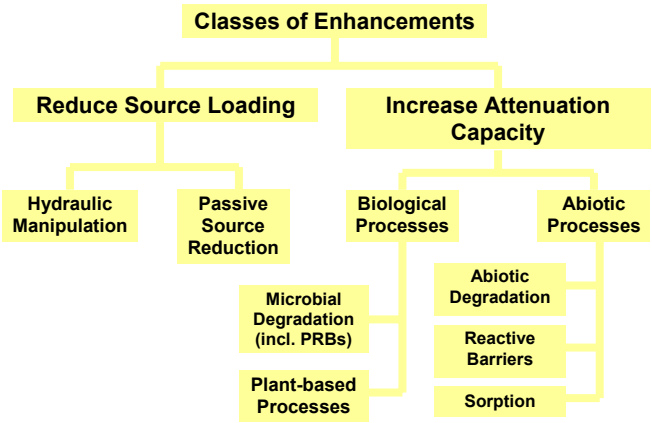

FIGURE 7. Classes of Enhanced Attenuation technologies.

met. By injecting molasses as a one time injection, the NAC would be increased by factor X and that capacity be sustained for the needed 2 to 3 years, then the molasses injection would be considered an EA process. However, if it is estimated to require 15 to 20 years to reach the remediation goal, molasses, while an excellent active biostimulation option for this site, would not be an EA process. The existing evidence indicates that a one time addition of this substrate would not be able to sustain the needed NAC for the required period of time. In this instance, the site owner could select active remediation or consider alternative electron donors to implement EA.

The goal in developing EA as a technology class is to provide site owners with an accepted method to take an intervention action that will result in natural attenuation as the last action in the remediation process.

CHARACTERIZATION AND MONITORING: TOOLS AND STRATEGIES TO SUPPORT MNA AND EA

Several avenues are being explored as associated with characterization and monitoring for MNA and EA. All the development activities revolve around the concept that the waste unit is a system and monitoring must be optimized. The emphasis of the optimization is to monitor those parameters that are essential – the key indicators of performance of the system. The resulting developmental activities are: expanded strategy for characterization and monitoring, direct measures of microbiological degradation, sentinel concepts for monitoring, engineered weak spots for monitoring, and non-traditional strategies for monitoring. We will look at each of these briefly.

Expanded strategy for characterization and monitoring. As the attenuating processes that contribute to NAC of chlorinated solvents are expanded beyond reductive dechlorination, the process of characterization and monitoring could become an expensive endeavor. In an effort to mitigate that possibility, a four phased approach that expands both characterization and monitoring into two phases each has been developed, Figure 8. *Screening characterization* answers the question is MNA potential viable, *decision characterization* identifies the attenuation processes that are significantly contributing to the NAC, *process monitoring* verifies whether the NAC is sufficient or if EA should be evaluated and it defines the envelop in which the system must operate to

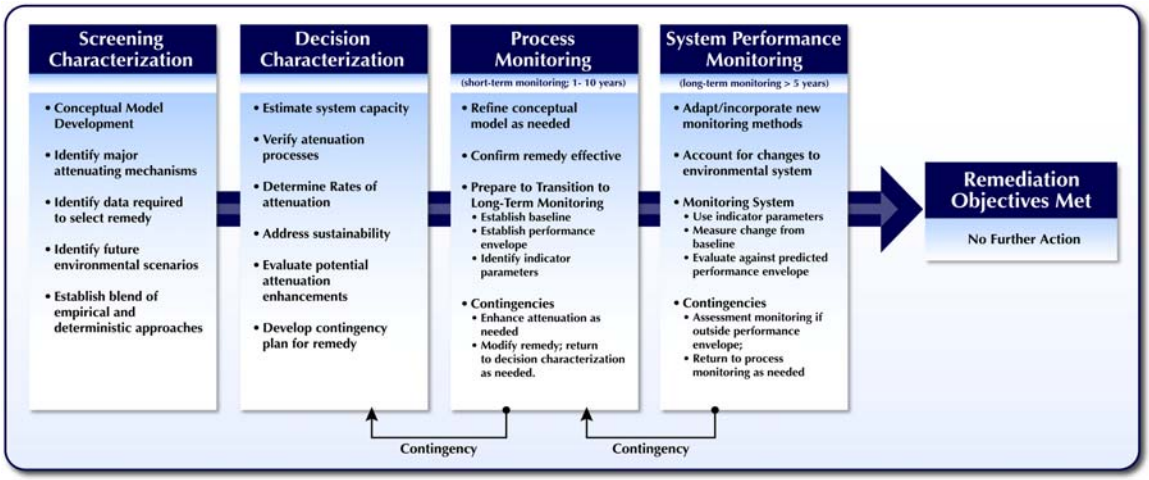

FIGURE 8. Four phased approach to characterization and monitoring for MNA and EA of chlorinated solvents.

meet the remediation goals, and *system performance monitoring* is the long-term monitoring that may continue for decades and will verify that the system is operating as expected. To reduce costs, advances in the tools used will be necessary.

Direct measures of microbiological degradation. At present indirect methods, as outlined in the EPA lines of evidence approach, are used to determine if reductive dechlorination is occurring. Because these are indirect measures, there is always a certain level of uncertainly associated with conclusions made from their interpretation. In the last half dozen years, significant progress has been made in developing molecular based methods to measure both the quantity and level of activity of the microorganisms responsible for degradation of particular chemicals by specific mechanisms. Because of the advances by the medical community in the use of molecular methods for diagnostic purposes, the costs of these tools are steadily decreasing. The environmental community can reap the rewards by taking advantages of the medical community's efforts. If costs can become comparable to costs for present day characterization methods, the uncertainty related to characterizing microbial processes associated with MNA will be decreased.

Sentinel methods and engineered weak spots for system performance monitoring. The traditional method for long-term monitoring is sampling a series of monitoring wells for the contaminants of concern for an extended period of time. Depending on the size of the plume and the agreement reached with the regulating agency, this can become a costly proposition. Another option is to use tools that act as sentinels for unexpected occurrences. This can be as simple as a remotely deployed sensor that only signals to home-base when an off-normal occurrence occurs, such as power loss or excedence of a preset value. Engineered weak spots are also possible options. By engineering or identifying the natural spot in the system most susceptible to failure, one can monitor that point rather than the entire system, thus minimizing expenditures while maximizing results.

Non-traditional strategies for system performance monitoring. A major concern by some site owners is that the costs for long-term monitoring will become prohibitive. One idea being investigated is the use of non-traditional methods for long-term monitoring. Can data mining or neural networks be used to evaluate historical site data to develop non-traditional methods for monitoring? Is it possible to use remote data, such as precipitation, vegetation health/abundance, river/surface water level, or biomarkers to indicate whether a system is within its' acceptable performance window? Success in this area has the potential to significantly cut long-term monitoring costs for large facilities or those with multiple receptors.

The goal of the characterization and monitoring efforts is to develop tools and strategies that will support evaluating MNA in terms of a mass balance and monitoring EA processes.

SPONSORED RESEARCH SUPPORTING THE KEY DEVELOPMENT AREA

Fourteen research studies are being funded that support the three key areas of the project. These studies are being conducted by researchers at universities, in industry, and at federal facilities. A few of the projects are straightforward with completion possible in

the timeframe of our project. On the other end of the spectrum there are a few studies developing cutting edge technologies where advances are expected over the timeframe of our project. We knew this when we selected the studies. The goal is to advance the science and our understanding of MNA and EA that would support the technical directions of this project.

Several researchers are working to develop molecular based tools for reductive dechlorination of PCE/TCE by *dehalococcoides* and aerobic co-metabolism of PCE/TCE by JS666. One research team is investigating the significance of anaerobic oxidation as an attenuating mechanism. Several teams are investigating diverse characterization tools. One of particular interest to the project team is the use of the Push-Pull test as a method to measure in situ the NAC of a contaminant plume. Upgrades to existing models used for making decisions on whether MNA is viable are being undertaken by several teams, as well as development of a framework similar to a taxonomic key that will provide a tool for customizing the characterization process based on site conditions.

SUMMARY

Initial response by regulators, stakeholder groups, and end users indicate the ideas being developed in this project are welcome. However, this does not guarantee success. There is much work to be done. The mass balance concept while very appealing and simple in concept will be a challenge to develop the mathematical formulations that will allow the varying attenuation processes to be calculated on a consistent basis. Good progress is being made on developing the concept of Enhanced Attenuation and defining the appropriate technologies. This work will continue. The TWG will work to flesh out the four-phased approach to characterization and monitoring and will develop a few of the non-traditional approaches to characterization and monitoring that would be well suited for MNA and EA.

This project will be complete at the end of 2006. The 14 research teams will complete their studies at the end of May 2006. The TWG will document technical guidance that integrate the three key areas and the results of the research studies with the goal of advancing the implementation of MNA and initiating the use of EA for chlorinated solvents. The TWG is working in collaboration with ITRC in developing the concept of EA. The goal of the ITRC team is to write a tech-reg for EA followed by developing a training course on the subject.

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