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Monitored Natural Attenuation of Chlorinated Solvents - Moving Beyond Reuctive Dechlorination

by

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Abstract

Monitored natural attenuation (MNA), while a remedy of choice for many sites, can be challenging when the contaminants are chlorinated solvents. Even with many high quality technical guidance references available there continue to be challenges implementing MNA at some chlorinated solvent sites. The U.S. Department of Energy, as one organization facing such challenges, is leading a project that will incorporate developing concepts and tools into the existing toolbox for selecting and implementing MNA as a remediation option at sites with chlorinated solvents contamination. The structure and goals of this project were introduced in an article in the Winter 2004 issue of *Remediation* (Sink et al.). This article is a summary of the three technical areas being developed through the project: mass balance, enhanced attenuation, and characterization and monitoring supporting the first two areas. These topics will be documented in separate reports available from the US Department of Energy Office of Scientific and Technical Information at www.osti.gov.

Introduction

Remediation of chlorinated solvent contaminated sites is a significant challenge for many site owners. Once in the subsurface, the chemical properties of chlorinated solvents result in persistent, long-lived plumes in many geohydrologic settings. Source treatment is typically a good first step when remediating a site. For many sites, particularly those where the contaminants were released to the environment decades ago, substantial solute plumes have formed. Thus, source treatment alone may not result in the remedial goals being met in a timely manner or before potential receptors are impacted. There are many technical options for "treating" the residual contaminants remaining in the source after source treatment and the solute plume; there is no "one size fits all" treatment option that will result in remedial goals being met in a timely manner. A cursory review of Records of Decision and various other technical documents available on public webpages indicate that treatment trains addressing the source, the main portion of the solute plume, and the distal solute plume are in fact being employed. Although various technologies are being identified for the source and solute plume, almost all sites are recommending monitored natural attenuation (MNA) as a ground water remedy for the distal portion of the solute plume. The question becomes, will the mechanisms of natural attenuation be sufficient to result in remedial goals being met in an acceptable timeframe?

A survey of 191 sites indicated that most parties use the U.S. Environmental Protection Agency (EPA) *Technical protocol for evaluating natural attenuation of chlorinated solvents in ground water*, (EPA 1998) as the basis for characterization to determine if MNA is a viable remedial approach for their chlorinated solvent contaminated sites (McGuire et al. 2003). The natural attenuation mechanism that the EPA (1998) document emphasizes is reductive dechlorination, which for many, but not all, sites is believed to be the predominant attenuating mechanism (McGuire et al. 2003). Many of the large chlorinated solvent plumes within the U.S. Department of Energy (DOE) complex, however, do not have the classic geochemical characteristics that result in reductive dechlorination being the predominant attenuation mechanism. The implementation of MNA at sites where mechanisms other than reductive dechlorination dominate is not well supported by the current protocols.

One challenge for DOE, and others, is to identify, quantify, and document which attenuation mechanisms are active in a system. This is then followed by determining if any or all of those mechanisms in combination with source and/or enhanced sustainable treatments will result in the remedial goals being met in an acceptable timeframe. For those systems where MNA is viable, the challenge will be to develop monitoring programs that reliably monitor the attenuation mechanisms, ensure they are sufficiently robust to maintain a shrinking plume, and are designed in a fashion that results in reasonable costs.

To address the issues described above, the U.S. DOE Office of Environmental Management (EM) in 2003 initiated a three-year technically-based project to identify promising science and technology development topics and fund targeted research, henceforth referred to as the project. The final product of the project will be a published technical guidance for selecting and implementing the new concepts. Specifically, the project is focused on encouraging the use of MNA and other sustainable enhancement methods in accordance with the principles embodied in the U.S. EPA's 1998 *Technical protocol for evaluating natural attenuation of chlorinated solvents in ground water* (EPA 1998) and the 1999 U.S. EPA Office of Solid Waste and Emergency Response Directive *Use of monitored natural attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites* (EPA 1999) by exploring three concepts: 1) using a mass balance framework to evaluate plume stability in terms of loading and attenuation, 2) defining and developing concepts for sustainable actions to make the overall attenuation response more robust, and 3) developing a new paradigm and associated tools to support characterization and monitoring for MNA and enhanced sustainable processes.

In 2004 the Interstate Technology and Regulatory Council (ITRC) identified enhanced, sustainable remedies as a topic of interest and formed a team, led by state regulators, to work in partnership with DOE to co-develop this topic. Jointly the two organizations will develop technical-regulatory guidance on enhanced attenuation.

Background and History of MNA Protocols and Guidance Documents

The 1990s saw the publication of technical guidance and protocol documents relating to MNA for both hydrocarbons and chlorinated solvents. These documents were published by various national organizations, as depicted on Exhibit1. Of note are the U.S. EPA's 1998 *Technical protocol for evaluating natural attenuation of chlorinated solvents in ground water* (EPA 1998) and the Office of Solid Waste and Emergency Response Directive *Use of monitored natural attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites* (EPA 1999). As previously stated McGuire et al. (2003) reported that the US EPA 1998 technical protocol is the most widely used guidance document for characterizing chlorinated solvent contaminated sites where MNA may be applicable. Although not shown on Exhibit 1, state agencies have been developing and publishing guidance documents to aid in the evaluation of natural attenuation processes for chlorinated solvents. Among the states to have published such documents are Minnesota (1999) and Wisconsin (2003). The natural attenuation mechanism that is the main focus of these documents is reductive dechlorination and for many sites this will be the dominant mechanism.

According to EPA (1998):

> *The term "monitored natural attenuation," as used in this Directive* (OSWER Directive 9200.4-17P)*, 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 other methods. The "natural attenuation processes" that are at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil and ground water. These in-situ processes include biodegradation, dispersion, dilution, sorption, volatilization, and chemical or biological stabilization, transformation, or destruction of contaminants. Monitored natural attenuation is appropriate as a remedial approach only when it can be demonstrated capable of achieving a site's remedial objectives within a time frame that is reasonable compared to that offered by other methods and where it meets the applicable remedy selection program for a particular OSWER program. EPA, therefore, expects that monitored natural attenuation typically will be used in conjunction with active remediation measures (e.g., source control), or as a follow-up to active remediation measures that have already been implemented.

As this definition states, a variety of natural attenuation mechanisms are included in MNA. Nonetheless this guidance document focuses heavily on reductive dechlorination. This may be partially explained by a statement in the OSWER Directive (1999), "The scientific understanding of natural attenuation processes continues to evolve. EPA recognizes that significant advances have been made in recent years, but there is still a great deal to be learned regarding the mechanisms governing natural attenuation processes and their ability to address different types of contamination problems." Reductive dechlorination is a robust destructive mechanism for chlorinated solvents when the setting has sufficient electron donors and low levels of competing electron acceptors. Because reductive dechlorination plays such a dominant role in the destruction of chlorinated solvents at a significant number of sites, much effort has gone into understanding the process and the responsible microorganisms. Through ongoing scientific research there is a growing awareness and understanding of other natural attenuation mechanisms, as well. Tools are being developed to directly measure the organisms responsible for and characteristics related to a variety of biological attenuation mechanisms.

There are several disadvantages of MNA stated in the OSWER directive (EPA 1999) including:

- *Site characterization is expected to be more complex and costly;*
- *Long-term performance monitoring will generally be more extensive and for a longer time;* and
- *Hydrologic and geochemical conditions amenable to natural attenuation may change over time and could result in renewed mobility of previously stabilized contaminants (or naturally occurring metals), adversely impacting remedial effectiveness*.

The first two bullets could potentially price MNA out of implementation. Does it have to lead to this result? Can existing paradigms related to how to characterize and monitor contaminant plumes be shifted so that the same or greater level of protection of the environment occur with acceptable costs? Are new tools available or being developed or are there tools that can be adapted from other technical fields that will support data collection under these new paradigms?

The third bullet relates to the ability to predict future plume behavior and to mitigate negative changes. As the driving forces behind the various attenuation mechanisms are better understood, this information can be incorporated into the models used to predict long-term behavior of a system, resulting in more robust models. As models are only predictions of behavior, can these models be used to identify those conditions or processes that, if changed, would have the greatest negative impact to remedial effectiveness? If so, long-term performance monitoring could be designed to monitor the most influential conditions, minimizing the negative effects of such changes through early detection. Also, by understanding which conditions or processes are likely to change, it may be possible to design remedies that are more sustainable so the attenuation mechanism continues to function at the needed rate.

The OSWER Directive (EPA 1999) also states "A related consideration for site characterization is how other remediation activities at the site could affect natural attenuation." A conceptually simple way to evaluate the impact of engineered treatments on the system is the use of a mass balance, as depicted in Exhibit 2. However, putting analysis of mass balance into practice for complex hydrogeologic settings is anything but simple. A significant challenge is in obtaining data for the various attenuation mechanisms that are in consistent units so they can be evaluated using a mass balance approach. By developing tools to evaluate different mechanisms on an equivalent basis, characterization and monitoring methods and tools can be developed or modified to gather data that can be most directly interpreted to provide that equivalent basis. While providing the basis of how to approach implementing MNA for a contaminated site, review of the OSWER Directive (EPA 1999) and the EPA technical protocol (EPA 1998) provided the project team insights into areas for scientific advance.

Project Technical Emphasis

To address the questions posed above, the three technical areas developed in the project are discussed in this article. They combine technical targets identified by the project team (Chapelle et al. 2004), the areas for scientific advancement identified by reviewing the EPA documents (EPA 1998 and 1999), and results of a survey of the implementation of MNA (McGuire et al. 2003), summarized by McGuire et al. in the Winter 2004 issue of this journal. First is the use of mass balance as an approach to explicitly evaluate plume behavior and stability in terms of loading and attenuation (Looney et al. 2005). Second is the definition and development of concepts for taking sustainable actions to make the overall attenuation processes more robust (Early et al. 2005). The term coined for these concepts is "enhanced attenuation." Third is the development of a new paradigm and associated tools and techniques to support characterization and monitoring for MNA and enhanced attenuation (Gilmore et al. 2005). These three topics have been pursued independently but integrated to support each other. For example to complete a mass balance to determine if MNA is a viable remedy, the attenuation processes must be measured. Characterization methods are being developed and tested that will support efficiently and reliably collecting the pertinent data on a system basis.

Mass Balance Approaches

Simply stated, the mass balance approach is an accounting process that keeps track of loading (or inputs), accumulation/reduction, destruction/creation, and release (outputs). There are several approaches for performing a mass balance; however, regardless of the approach, the first step is developing a clear and agreed-upon definition of the target plume volume or mass around which the mass balance will be calculated. Once agreement is reached, the process of determining the balance between contaminant loading and the attenuation capacity of a given vadose-groundwater system can begin. For purposes of this article, the term attenuation capacity is used to indicate the total of all reduction and destruction processes.

A contaminant plume goes through four stages: expanding, stable, shrinking, and exhausted, as shown in Exhibit 3. Important factors to the development of environmental strategies that rely on attenuation are that the plume poses minimal risk and that the plume will not expand. Thus, the first question to be answered using a mass balance where MNA is being considered must be, is the attenuation capacity greater than the contaminant loading? Another way to ask this same question is, are the natural processes sufficient to stabilize and shrink the contaminant plume?

Two divergent philosophies exist for quantifying plume stability or the “stage” of the plume. These are the empirical and deterministic philosophies. Exhibit 4 provides a summary of these two philosophies.

Though divergent in philosophy, case studies written over the past decade have demonstrated that the empirical and deterministic approaches to evaluating the viability of MNA are not mutually exclusive. Improved decision support and efficiency may result from combining these methods based on the specific challenges at a given site. Typically, the empirical approach is used to quantify the mass loading and attenuation capacity. This is the most effective way to demonstrate the efficiency of ongoing attenuation processes in accordance with current regulatory guidance. In addition, monitoring well networks installed for the empirical approach can provide estimates of the parameters needed for deterministic models. These models can provide estimates of contaminant behavior over time, including evaluations of whether it will be necessary to employ an enhancement and/or active source treatment.

A required component in the selection process of MNA as a ground water remedy is that the timeframe for the natural attenuation processes to decrease the contaminant load must be at equivalent to or better than, active treatments. This requires an understanding of how the footprint of the solute plume will look over time. One approach involves the use of an integrated Mass Flux (iMF) as a measure of the system's ability to attenuate the loadings resulting in remedial goals being met (typically concentration goals at a receptor location). The iMF is the total quantity of a migrating substance that moves through a planar transect that is within a system of interest and is oriented perpendicular to the direction of movement. The iMF measured at a transect at the entry plane to a system is the loading, and likewise, at the exit plane is the discharge. This term has units of mass per time (e.g., Kg/yr, g/day) and is an extension of the traditional engineering definition of flux (e.g., $Kg/yr/m^2$) in which the transect area is accounted for to allow a mass balance calculation of plume- or system- scale behavior. The goal of using flux-based measures is not to replace concentration goals, but to determine if designing and monitoring a system in terms of an iMF will provide early detection of when a system is headed for failure (i.e., exceeding the limiting concentration goal).

Wiedemeier (1999), Suarez and Rafai (2002) and others suggest that alternative interpretation approaches applied to traditional field measurements may be a powerful and appropriate tool for assessing iMF within a plume. In turn, these fluxes can be used to calculate degradation rates and mass balances. Their recommendations are already incorporated into various MNA-related training classes and guidance documents and the concepts set the groundwork for a mass balance view of plume stability and for using field data as a key element in quantifying the mass balance. Through this project the potential to build on these concepts using alternative well geometries (e.g. horizontal wells or trenches) for sampling, new field methods such as the push-pull test, and new sensor technologies are being explored.

Enhanced Attenuation

The EPA states the following in the OSWER Directive (EPA 1999):

> *While MNA is often dubbed "passive" remediation because natural attenuation processes occur without human intervention, its use at a site does not preclude the use of "active" remediation or the application of enhancers of biological activity (e.g., electron acceptors, nutrients, and electron donors). However, by definition, a remedy that includes the introduction of an enhancer of any type is no longer considered to be "natural" attenuation.*

From this statement and others within this Directive it is clear that any actions that involve human interaction cannot be called natural attenuation. However, one must ask 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?" The key to these actions is that they must result in a **sustainable** increase in the attenuation capacity of the system. Because these actions require intervention they would not be considered a MNA remedy. One the other hand, they would not be considered "active" treatment, in the traditional sense, because they have a different purpose. We typically think that the goal of "active" treatment is to "quickly" remove contaminants. Sustaining natural attenuation processes is not part of the usual design considerations. For enhanced attenuation, actions resulting in sustainable natural attenuation processes are the primary goal. Thus, there may be "active" treatments that when designed with a different needs-based goal will fit into the category of enhanced attenuation.

It is stated in the OSWER Directive (EPA 1999) that "EPA expects that MNA will be most appropriate when used in conjunction with other remediation measures (e.g., source control, groundwater extraction), or as a follow-up to active remediation measures that have already been implemented." Enhanced attenuation processes would be implemented along these same lines. They are not primary actions, but instead are secondary actions used to support the use of MNA when the natural attenuation mechanisms are not sufficient to reach remediation goals. Through the use of mass balance the impact of various enhancement options on the attenuation capacity of the system can be evaluated for implementation.

Enhanced attenuation is defined herein as *enabling sustainable manipulation of natural attenuation processes through intervention so that they operate more effectively than without intervention and thereby result in a reduction in mass flux of contaminants that is sufficient to meet regulatory requirements*. This leads to the definition of 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*. Enhanced attenuation can be thought of as a bridge between source/active treatments and MNA. Enhanced attenuation technologies typically address either reducing the loading of residual source material or increasing the attenuation capacity in the aqueous portion of a plume. Exhibit 5 is a graphical depiction of the effect of enhancements on natural attenuation processes. Examples of specific technologies that can be enhancements when designed to meet the definition of enhanced attenuation are shown in Exhibit 6. Caps, cover systems, barometric pumping, and biostimulation are familiar technologies conventionally designed for active treatment that can be designed to meet the goals of enhanced attenuation.

Two methods to reduce loading have been identified. The first, hydraulic manipulation, is typically accomplished using standard engineering methods that divert water from a system (e.g., caps, covers, French drains). Non-standard approaches to hydraulic control include alternative covers, (e.g. using plants and grasses to increase evapotranspiration), engineered phytotranspiration systems, and passive drain or siphoning walls to decrease the hydraulic gradient in the area of concern reducing contaminant movement away from that area. Several new concepts that involve hydraulic manipulation are (1) the use of a constant head moat that integrates engineering controls in the form of a trench/French drain closed loop system and plant based methods to promote an inward hydraulic gradient, and (2) use of large-scale hydrological modifications to divert electron acceptors that compete with the contaminants of concern for the available supply of electron donors (either indigenous or added). Setting up permanent, sustainable, and easily documented changes in large-scale hydrology is relatively straightforward. Properly designed and implemented, these traditional concepts provide hydrologic control for as long as the hydraulic control is in place. A benefit of hydraulic manipulation is that the methods are robust and can be operated without detailed knowledge of the underlying attenuation processes.

The second method to reduce loading involves the use of passive methods for removing residual source contaminants. Regardless of the source treatment actions, residual source material remains after the source treatment action is complete in almost every instance. These residuals are typically difficult to degrade or extract thus making active methods for removal expensive due to the time and energy that must be spent. Passive methods, while less aggressive than active methods, take advantage of system characteristics. Because they do not require energy to operate, these methods have a lower cost and are easily sustainable. Barometric pumping, one example of this form of enhancement, takes advantage of natural variations in pressure between the subsurface soil gas and the atmosphere to remove residual contaminants in the vadose zone (Rossabi, 1994). It may also be used to passively inject air to stimulate aerobic processes in the subsurface. While reducing loading this last use of barometric pumping also passively increases the attenuation capacity of the aerobic biological processes.

Two methods have also been identified to increase attenuation capacity. The first, biological processes are preferred for MNA. As an enhancement our interests are in methods that manipulate the system in a sustainable manner so the biological processes will be sufficient to handle the loading so the discharge meets the remedial goals. Biostimulation is one biological method being used in active bioremediation. The difference between the traditional use of this method and its use as an enhanced attenuation approach is sustainability. In traditional applications, multiple applications of nutrients are conducted to reach remediation goals without incorporation of the concept of sustainability to the rate of reapplication. As an enhanced attenuation approach, the objective is to manipulate the system so that, ideally, a single application of the nutrients would be required resulting in a sustainable attenuation capacity at an acceptable level. Whether a biostimulation process can be sustainable may be dependent on how long the enhanced attenuation rate is needed. Potential new biological processes are bioaugmentation; wetlands, either natural or engineered; and plant-based methods. All three of these new processes are beginning to see use. They are complex and there are still many unknowns related to how they work. A greater understanding of the sustainability of added microorganisms and their impact on the natural system are two factors that will contribute to bioaugmentation gaining mainstream application. Geochemical conditions within wetlands, as well as the indigenous plants, play a large factor in the degree to which contaminants will be attenuated. Recent research on various plants is providing evidence that biological degradation of some chlorinated solvents can occur within the roots zones. In addition, such systems tend to increase the amount of electron donors present. Understanding how these systems work can provide the basis for enlarging existing systems or creating such systems in distal portions of plumes to increase the attenuation capacity of the existing systems.

The second method of increasing attenuation capacity uses abiotic processes. These can be separated into two classes, pure abiotic and biologically mediated abiotic reactions. Common attenuation processes that are considered to be purely abiotic methods are the common physical processes of adsorption, advection, and diffusion. Because they do not destroy the contaminant, they are less preferable mechanisms for MNA. Although it only occurs in select hydrogeologic environments, truly abiotic degradation can occur via a reaction between reduced iron bearing minerals such as pyrite, magnetite, and green rust (Lee and Batchelor 2002a, 2002b, 2003; and Ferrey et al. 2004). A growing body of literature is suggesting that the biologically-mediated abiotic processes may, in select cases, be important in the natural attenuation capacity of a system. One such process is the reaction between iron sulfide minerals that form during the reduction of iron and sulfate and chlorinated compounds. The advantage of this reaction is that it can easily be engineered and does not result in the formation of vinyl chloride during degradation. Increased understanding of these biologically-mediated abiotic processes may lead to their incorporation into evaluations of the attenuation capacity of a system. This may also lead to the development of methods to create sustainable environments to enhance the attenuation capacity using these processes.

The goal in developing enhanced attenuation 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 step in the remediation process. Members of the ITRC whom the project team are collaborating with are very interested in exploring and developing the concepts and technologies for sustainably increasing the attenuation capacity of a system so natural attenuation processes remain an integral part of the remediation approach. This is important because many feel that it is not feasible or fiscally responsible to actively treat all sites until remedial goals are obtained. To support development of enhanced attenuation a research study was funded through the project to investigate a method to enhance abiotic dechlorination using electron shuttles.

Characterization and Monitoring

The EPA's OSWER directive (EPA 1999) states:

> *As with other remediation methods, selection of MNA as a remediation method should be supported by detailed site-specific information that demonstrates the efficacy of this remediation approach.*
>
> *Site characterization is expected to be more complex and costly.*
>
> *In general, the level of site characterization necessary to support a comprehensive evaluation of MNA is more detailed than that needed to support active remediation.*
>
> *Furthermore, largely due to the uncertainty associated with the potential effectiveness of MNA to meet remediation objectives that are protective of human health and the environment, EPA expects that source control and long-term performance monitoring will be fundamental components of any MNA remedy.*

Long-term performance monitoring will generally be more extensive and for a longer time.

The importance of characterization and monitoring for MNA is apparent in the above statements, as understanding and measuring the processes that control the attenuation capacity of the system is paramount to evaluating and documenting success. This project has funded several research studies associated with tools to support characterization and monitoring for MNA to support greater understanding of natural attenuation processes. The project team is also exploring what could result in a paradigm shift in how to approach characterization and monitoring. Most interest in MNA has focused on upfront characterization to determine if MNA is viable. Less focus has been placed on monitoring; it is commonly addressed after the remedy is selected and is commonly an extension of measuring the parameters collected during characterization. The traditional approach to characterization involves collection of groundwater samples, usually via a detection monitoring well network, that was used to define the extent of the solute plume. These groundwater samples are typically analyzed for the contaminants of concern, their degradation products, and select geochemical parameters. For sites where the empirical approach can be employed, this method of characterization works well. However, for complex sites where a deterministic or a combined empirical/deterministic approach is required, methods that provide more definitive data on the types of attenuation processes would be useful and may be required. Wiedemeier et al. (2005) describe some of these data and rank them in order of importance.

For sites where attenuation processes in addition to or instead of reductive dechlorination are necessary to support MNA, characterization may become more complex if it is necessary to identify the active attenuation processes and determine their contribution to the overall natural attenuation capacity of the system. Long-term performance monitoring conducted in the traditional manner using detection monitoring well networks may result in increased lifecycle costs.

Development of a four-phased approach to characterization and monitoring (Exhibit 7) supports both the mass balance and enhanced attenuation aspects of this project. This phased approach is consistent with the five phase process for chlorinated solvents described by the state of Minnesota (1999) and the four phased approach described by EPA for MNA of metals and radionuclides (EPA 2004). These approaches utilize a systematic process to identify and quantify the most important mechanisms having the greatest impact or potential impact (in the case of selecting an enhancement) on the natural attenuation capacity of the system. They define and recommend programs to monitor those key attenuation processes.

The four-phased approach developed by the project facilitates timely application of the correct methods and tools. This approach emphasizes the need to begin planning for the monitoring phases earlier in the remediation process and thus leads to a more cost-effective approach to monitoring system design and implementation. As shown in Exhibit 8 this approach can be integrated into the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) process.

Characterization Phases

Characterization falls into two distinct phases: *screening* and *decision*. Although each phase has specific goals, the overall goal of characterization is to determine if MNA is an appropriate remedial approach. If MNA is not appropriate for a site, then the characterization phases are also designed to determine what combination of enhancements, source removal, or engineered solutions are necessary.

As used herein, the screening characterization phase is consistent with the "site characterization and developing and screening of alternatives" associated with the CERCLA process. Information supporting an MNA decision through the mass balance approach includes : 1) the extent and location of the primary source; 2) the contaminant loading; and 3) an estimate of the attenuation mechanisms. At some sites, the screening characterization phase will be straightforward, particularly where one or two primary attenuating mechanisms provide enough attenuation capacity. At the other extreme, the screening phase may show that MNA is not appropriate.

The decision characterization phase is a more detailed effort intended to enable complete evaluation of the natural attenuation processes to support selection of MNA and is similar to the CERCLA treatability study process. During this phase, a more detailed estimate of the system mass balance is determined in terms of attenuation capacity and contaminant loading. The attenuating mechanisms, their rates, and an estimate of sustainability are identified. This phase provides the information that can be included in the "detailed analysis of alternatives" under CERCLA to make a decision to either 1) to select MNA as a remedy; 2) to consider enhanced attenuation in conjunction with MNA; or 3) to reject MNA and use another remediation technique. In some cases this phase is the most difficult because a "preponderance" of evidence is often required to support the MNA decision.

Monitoring Phases

Characterization will transition to a two-phased monitoring approach once a remedy has been selected. The first phase of monitoring, process monitoring, will be used to verify that the remedy is working as intended. In this phase, attenuation capacities and rates determined in the characterization stage are confirmed in order to validate the planned remedy. The goal of this phase is to collect data as efficiently as possible to allow a transition to the systems performance-monitoring phase. Process monitoring is likely to be data intensive, however, in order to support multiple lines of evidence as outlined by EPA (1998). This phase has two objectives: 1) establishing a baseline for the plume conditions including the range or "performance envelope" within the plume; and 2) identifying select "indicator" parameters that can be used in place of comprehensive suites of parameters for monitoring. Once both objectives are met system performance monitoring can begin. The exact timing of the process-monitoring phase within the CERCLA process cannot be rigidly defined. This phase theoretically begins with the signing of the Record of Decision. The exact duration depends on the time to meet the two objectives mentioned earlier in this paragraph.

Systems performance monitoring is designed to assess the long-term function of the remedy. It is the primary activity in long-term stewardship. The basis of this phase is to monitor indicator parameters and compare them to established baseline conditions to determine if plume conditions are within the established "performance envelope." This concept is equivalent to the assessment monitoring described in the Resource Conservation and Recovery Act (RCRA 1976). Contingency plans for both detailed assessment monitoring and enhanced attenuation should be prepared in case one of these components fails to perform as expected. Like the process-monitoring phase, the exact timing of this phase within the CERCLA process cannot be rigidly defined.

In many applications, the systems performance-monitoring stage will be the longest in duration. Thus, it is important to make the monitoring process as efficient as possible. This is typically done by reducing the number and frequency of observations/samples. To accomplish this efficiency, the focus of system performance monitoring should be on the system (plume and environmental setting) as a whole. Measured flux or documented stresses to the system can be more useful than point measurements in wells. System performance monitoring can usually be most efficient by focusing on indicator parameters, particularly spatially integrated indicator parameters.

Ongoing Activities

Work on the mass balance approach, enhanced attenuation and characterization and monitoring continues at this time. Currently 14 research teams are conducting studies that support various aspects of these three key topics, as summarized in Exhibit 9. These research teams consist of scientists and engineers from academia, private industry, national laboratories, and federal agencies. The results of these studies will be combined with the development efforts in the three topic areas to produce a technical guide to implementing these concepts and tools. The work on the molecular tools will lead to methods of direct measurement of the biological attenuation processes to support the calculation of rates of degradation and mass balance for the system. Similarly, the activities associated with attenuation mechanisms other than reductive dechlorination will support calculating a mass balance for the system. Understanding these additional mechanisms may provide avenues for enhancement at sites where a boost in the attenuation capacity is needed to include MNA in the final remedy. One of the development efforts on the models provides a tool to incorporate flux into conceptual model development and initial selection of remedial alternatives. Another of the modeling efforts incorporates additional degradation mechanisms into an existing 3-dimensional transport model. These efforts also support calculating a mass balance of a system. The decision tools provide guidance on designing both characterization and long-term or system performance monitoring programs. One is very similar to a taxonomic key in that based on general site characteristics, the likely attenuation processes are described and general guidance on how to approach the characterization effort is provided. The second decision tool uses neural networks in the evaluation of characterization data collected during the first three phases, as outlined in Exhibit 7, to support the selection of the system performance monitoring parameters. Finally, the field measurement tools provide various tools to support characterization and monitoring. Tools supporting passive flux monitors, as well as an oxygen sensor that can reliably measure low levels of dissolved oxygen in water, are being tested. Use of push-pull tests to support calculation of a system mass balance is also included in the field measurement tools. As this work is ongoing it is premature to identify which studies will bear fruit. The studies were selected because they addressed technical challenges associated with moving MNA forward for all sites contaminated with chlorinated solvents.

Though simple in concept, both mass balance and integrated mass flux, face challenges for implementation. How accurately must quantification of the source be so that one can have confidence in mass flux calculations? How does one go about measuring integrated mass flux in ground water? What are the limitations of the integrated mass flux approach? For complex sites, is it possible to calculate a mass balance with any degree of accuracy? In an attempt to address some of these issues, members of the project are in the midst of developing case studies of real world sites that will be evaluated using various approaches to calculating a mass balance. In addition, case studies are being developed to provide examples of how technologies can be considered enhanced attenuation technologies. These case studies will look at several of the less familiar technologies, such as alternative caps and wetlands.

Implementing the Results

An integral part of the project is the collaboration with ITRC. The Enhanced Attenuation Chlorinated Organics (EACO) Team was formed because of the ITRC interest in the concepts identified as important by the project. For the past two years these team's have been jointly developing the three concepts of mass balance, enhanced attenuation, and characterization and monitoring, with the ITRC emphasizing the development of enhanced attenuation. The EACO team will develop a technical-regulatory guidance document and subsequent training associated with that document to facilitate dissemination of the work of these two teams. All products of the DOE team will be available for use by the ITRC. The technical-regulatory guidance document is planned for publication in 2008 with training to follow.

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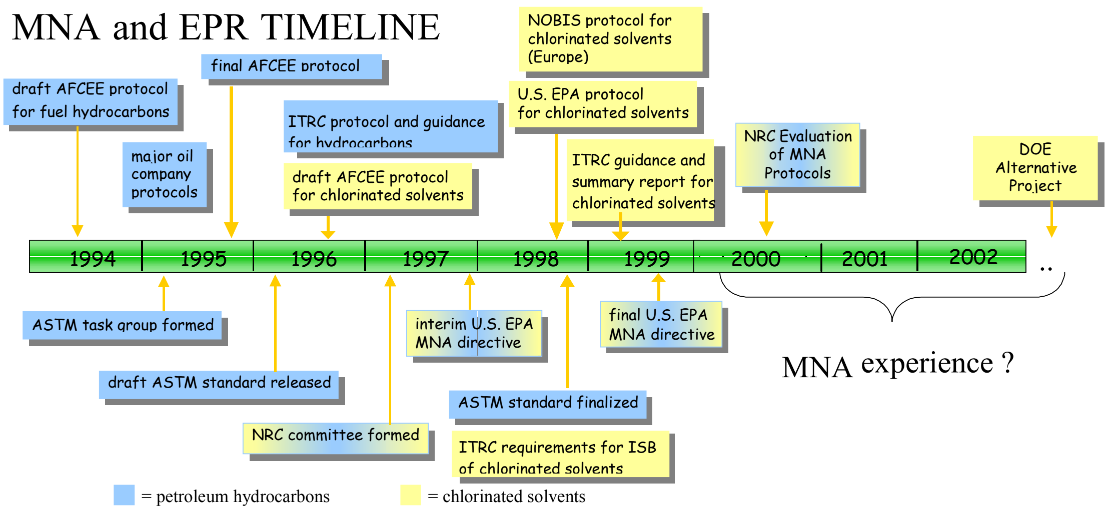
Exhibit 4. Comparison of empirical and deterministic philosophies to approaching a mass balance

Approach	Empirical	Deterministic
Definition	Relying on or derived from observation or experiment.	A process that assumes that "events proceed in a fixed predictable fashion".
Input needs	Historical contaminant concentration data and bulk geochemical information	Hydrologic, geochemical, and microbiological data
Timeframe of Evaluation	Past and present	Past, present, and future
Typical Methods for Evaluation	Transects and statistical methods	Simple to complex computer models
Strengths	With sufficient data, the NAC can be defined inexpensively and with a high degree of certainty.	With sufficient data, a projection of how a system will respond to active or enhanced attenuation treatments.
Weaknesses	1) Requires a relatively long period of undisturbed historical data. Not amenable to changing conditions. 2) Not effective in evaluating sites where active remediation was initiated quickly and is currently operating. 3) Cannot be used to predict future viability of MNA or when to turn off active systems and transition to MNA.	1) Some of the needed data is difficult to measure with certainty. 2) Obtaining data may be costly.

Exhibit 9. Summary of funded research studies support of key technical topics of MNA/EA for Chlorinated Solvents Project

Research Study Topic Area	# of Projects in Topic Area	Mass Balance	Enhanced Attenuation	Characterization and Monitoring
Molecular Tools	4	•		•
Attenuation processes other than reductive dechlorination	3	•	•	
Models	2	•	•	
Decision Tools	2			•
Field Measurements	3	•		•



(modified from Wiedemeier and Barden, 2005)

Exhibit 1. History of the development of MNA protocols and guidance documents.

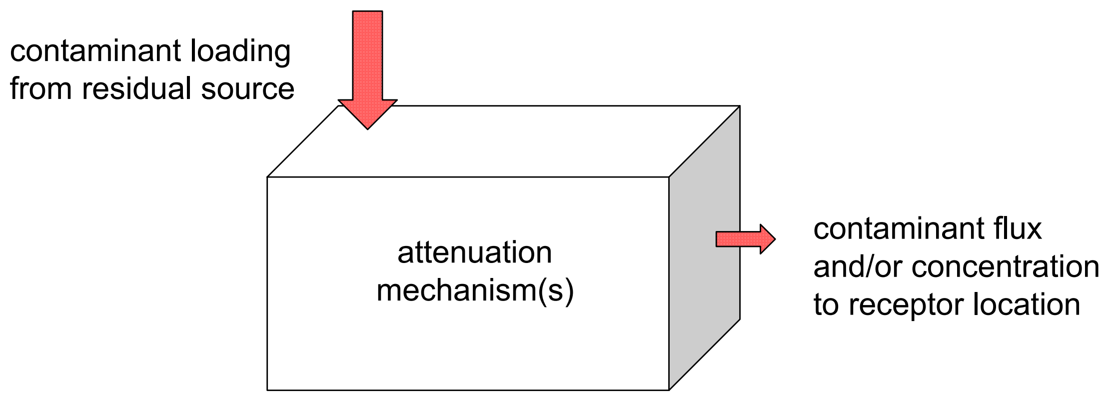


Exhibit 2. Example of a steady state mass balance for water in a subsurface system.

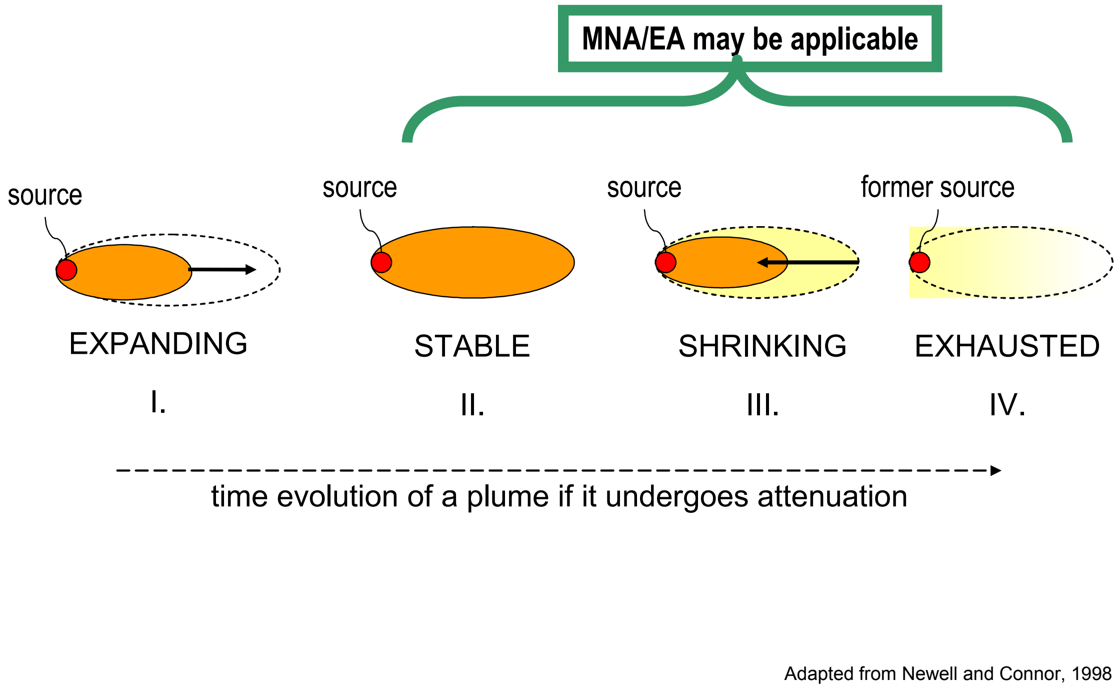


Exhibit 3. The four stages of a plume.

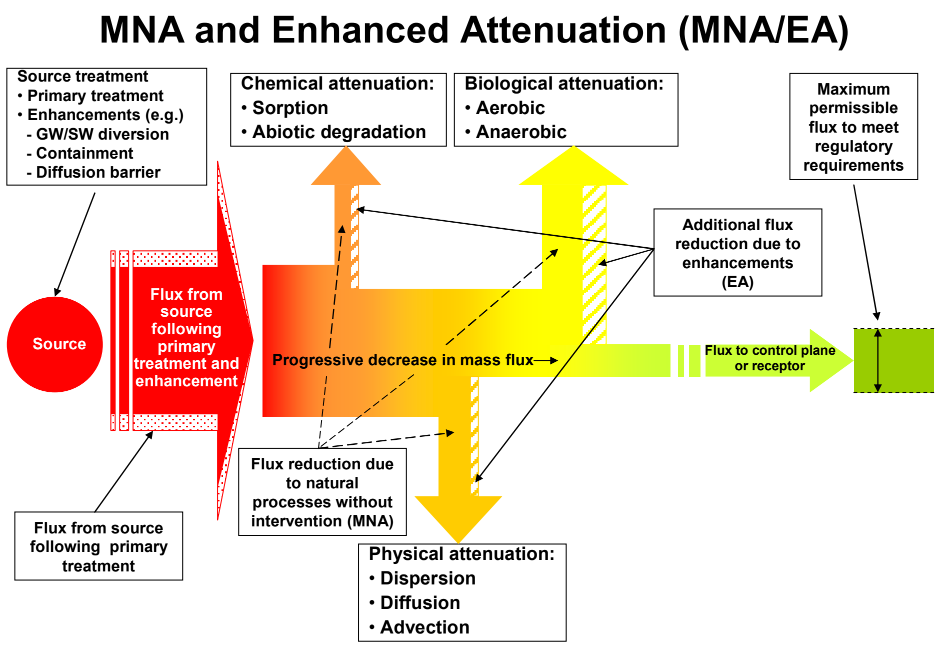


Exhibit 5. Enhancements to natural attenuation processes increase the attenuation capacity of the system. The cross hatching associated with the arrow immediately to the right of the source circle indicates reduction in loading due to implementing an enhancement at the source. The cross hatching associated with the multiple arrowed component representing the plume indicates the increase in attenuation from the various attenuation mechanisms identified.

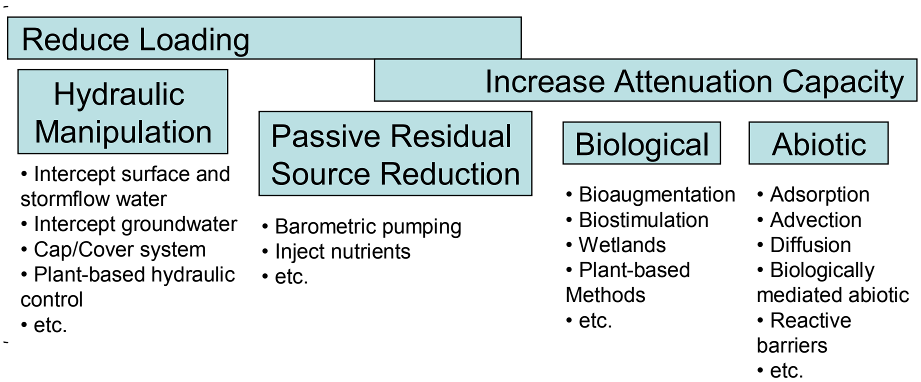


Exhibit 6. Examples of technologies that can be deployed under the concept of Enhanced Attenuation.

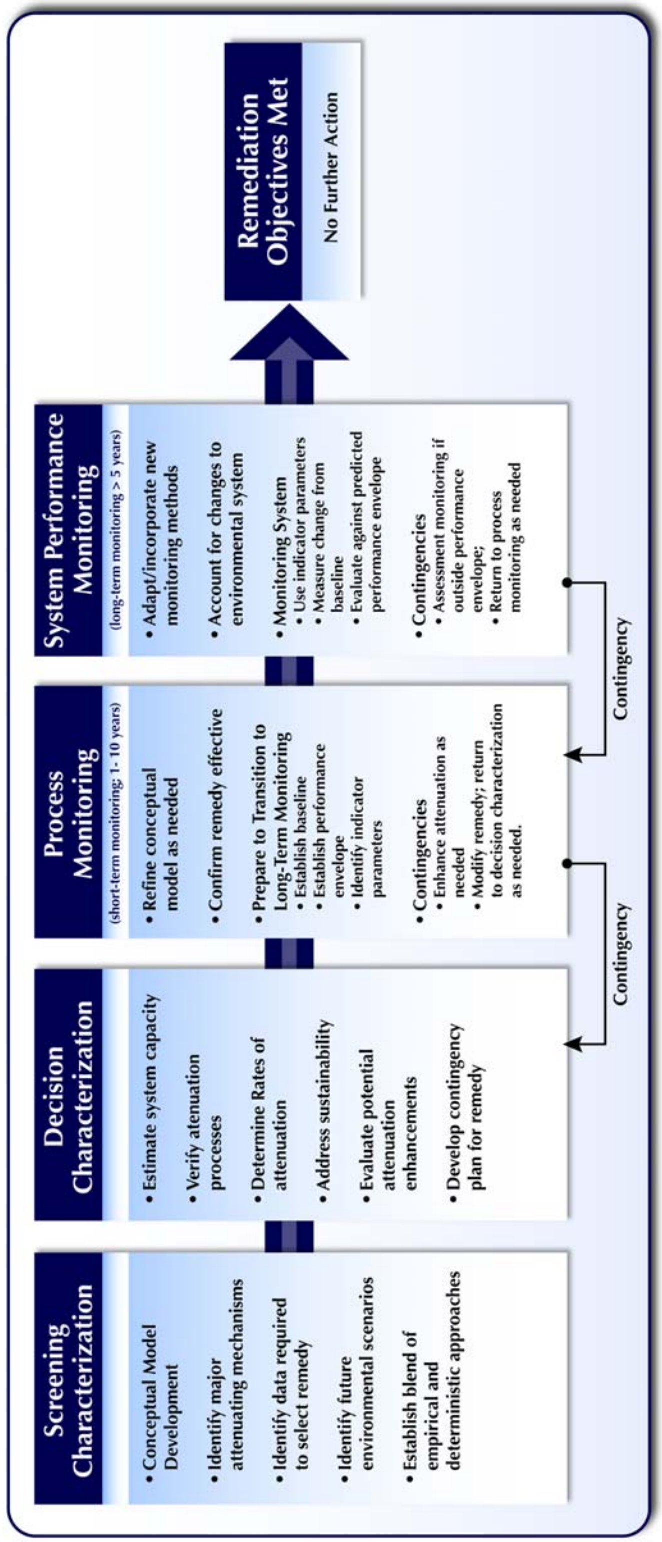


Exhibit 7. Phased approach to characterization and monitoring of Monitored Natural Attenuation.

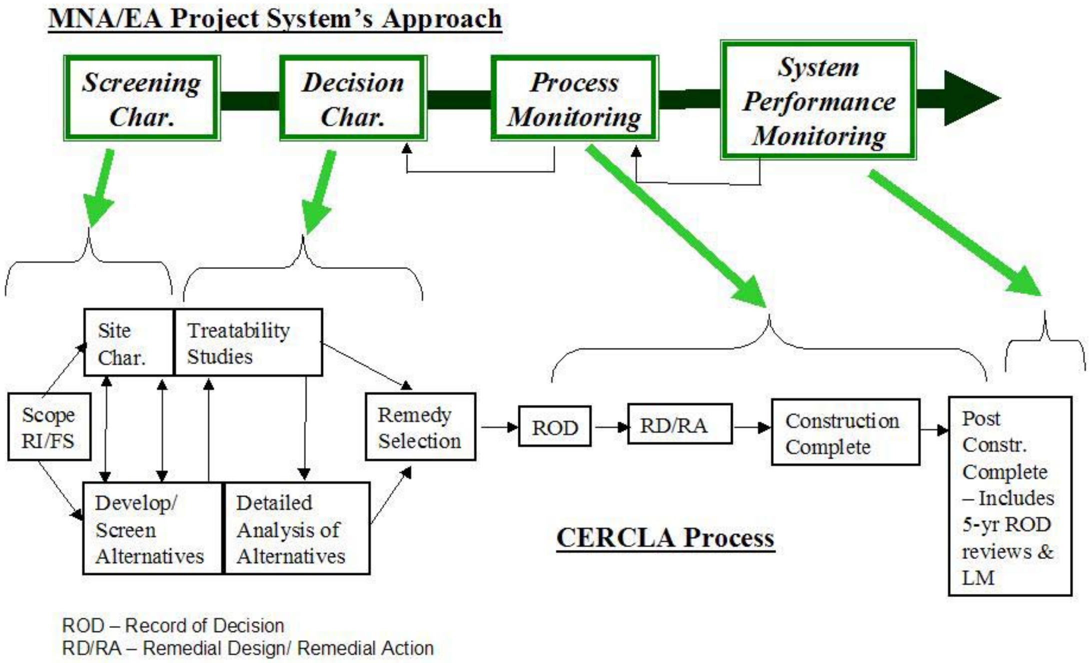


Exhibit 8. Correlation of the MNA/EA Project 4 phased system approach with the CERCLA process.