

Solving Closure Challenges: Applying Attenuation Processes to Metals and Radionuclides - 11234

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ABSTRACT

Attenuation-based remedies for metals and long-lived radionuclides rely primarily on immobilization of contaminants as stable and/or nontoxic species. This stabilization and toxicity reduction can result from natural processes, geochemical gradients, or biogeochemical manipulation. Except for a few radionuclides, the original contaminant remains in the subsurface so that documentation of the sustainability, or permanence, of stabilization and detoxification is crucial to assessing performance.

The Interstate Technology & Regulatory Council (ITRC) has developed a technical and regulatory guidance to facilitate implementation of new EPA policy and guidance for monitored natural attenuation (MNA) of metals and radionuclides. The document addresses issues identified in a web-based survey of state regulators and provides examples of state protocols and stakeholder issues related to the application of MNA as a remedy. Significant uncertainties in MNA cleanup efficacy and timelines may conflict with stakeholder expectations. Current federal and state regulatory policy and guidance is summarized and factors crucial to regulatory acceptance are presented.

A decision framework in this guidance document provides a consistent basis for states, stakeholders, federal agencies, and site owners to evaluate and implement attenuation-based remedies for metals and radionuclides. In the framework, an enhanced attenuation strategy supports instances where actions may be needed to support long-term sustainability of the MNA mechanisms. The outcome of these efforts is a process that will encourage regulatory cooperation and expedite cleanup.

INTRODUCTION

Until recently, there has been little regulatory guidance to support attenuation-based remedies for groundwater contaminated with metals and radionuclides. This has contributed to inconsistent application of those remedies and generally discouraged their consideration. The net result is that many sites face intractable closure problems. The U.S. Environmental Protection Agency (EPA) recently issued a three-volume technical guidance set that specifically addresses MNA of inorganic contaminants. In addition, EPA has just prepared a new directive that explains its policy towards applying MNA to inorganic contaminants.

Techniques for removing or containing metal or radionuclide contaminants in groundwater are often inefficient and quite costly below certain concentrations – concentrations that may still be above regulatory criteria. Dealing with this dispersed low-level contamination may be especially

challenging at many cleanup sites. In addition, intrusive remedial techniques may cause other environmental consequences and may expose workers to unacceptable risks. Understanding how and where attenuation processes may be effective in remediating a waste site is therefore a significant issue for these sites.

Integration of attenuation-based technologies into the remediation of metals and radionuclides contamination in groundwater may be a complex undertaking at many sites. While attenuation of organic compounds is predominantly based on biotic processes, attenuation of metal and radionuclide contaminants is predominantly based on abiotic processes that can be influenced by microbial processes. For metal and radionuclide contaminants in the subsurface, the interaction of groundwater with the soils and sediments in the saturated zone becomes very important because in large part, the properties of the soils and sediments will strongly control the attenuation processes. The role of co-contaminants may add to the complexity of the problem and the solution. Evaluating and incorporating attenuation-based technologies into treatment processes may require a new perspective and approach for many regulators and environmental professionals.

Attenuation of metals and radionuclides involves more interdependent sets of processes than attenuation of organic compounds. This can mean that sites contaminated with metals or radionuclides, even at very low levels, face the challenge of continued remediation and management for many years – even decades. These long periods of time result in extraordinary costs when using conventional treatments or at sites where complete cleanup and removal may not be achievable within economic constraints or technical feasibility.

Although elevated levels of metals and radionuclides do occur in nature, the majority of this contamination is a result of anthropogenic activities. Metal and/or radionuclide contamination can come from a wide variety of activities. Examples include:

- Metals mining and ore processing;
- Primary metals industries;
- Industrial processes (manufacturing, casting, plating, electronics manufacturing, metals recycling, cement kilns, and utility operations);
- Spent munitions (Department of Defense facilities);
- Waste deposition from production of nuclear weapons (more than 20,000 Department of Energy facilities)
- Nuclear power generating facilities;
- Disposal (landfills, lagoons, wastewater residuals);
- Agricultural applications of pesticides and herbicides (e.g., arsenic and lead);
- Dispersal from mobile sources along transportation corridors.

ATTENUATION PROCESSES

EPA's definition of natural attenuation includes both organic and inorganic contaminants. The applicable attenuation processes are generally quite different for metals and radionuclides and result in contaminants remaining in the environment. Unlike organic contaminants, metals and radionuclides are not destroyed by those processes. These processes affect most metals and radionuclides by changing their valence state, which in turn affects their solubility and therefore

mobility. For example, hexavalent chromium can be chemically or biologically reduced to the less soluble and less toxic trivalent chromium. In the case of radionuclides, radioactive decay leads to less of the contaminant over time. However, radionuclide half-lives vary considerably and many decay rates are too slow to be considered for a reasonable remedial timeframe. In addition, the primary transport mechanism for inorganics is through groundwater, while organics have a variety of mobile phases and exposure routes.

Regardless of the operative geochemical process of attenuation, metal and radionuclide contaminants will remain in place with any natural attenuation approach to site remediation. However, MNA can provide an effective site remedy through the stabilization and sequestration of the contaminant of concern from mobile and bioavailable states, thereby effectively mitigating exposure to sensitive human and ecological receptors. Spatial and temporal changes in site geochemistry, which may result in mobilization of previously stabilized metal and radionuclide contaminants, must be accounted for when considering MNA as a remedial alternative. Since MNA of metal and radionuclide contaminants will inevitably leave the contaminant in place, MNA is generally only acceptable for sites that intrinsically have low potential for contaminant migration.

With the exception of radioactive decay, the dominant attenuation mechanisms for metals and radionuclides involve chemical reactions that cause partitioning of the contaminant to immobile forms. The geochemistry of aquifers concerns chemical reactions involving minerals and constituents dissolved in groundwater. At a given point, most aquifers are at near-steady-state conditions geochemically, meaning the reactions are very slow and only subtle changes in pore water composition and mineralogy occur with time. Faster reactions occur locally where there are changes in aquifer mineralogy or an influx of water with a significantly different composition than the pore water of the aquifer, e.g., a contaminant plume entering an aquifer.

Contaminant plumes can induce a variety of reactions when they enter an aquifer. The nature of the reactions depends on the chemical composition of the contaminant plume, the chemical composition of the natural aquifer pore water, and the mineralogy of the aquifer matrix. Attenuation mechanisms for metal and radionuclide contaminants are reactions that cause the contaminants to partition from being dissolved in the mobile pore water to being bound on or within immobile solids in the aquifer. In other words, attenuation is achieved by the contaminant transferring from a mobile to an immobile form. Yet, these are not the only reactions which must be considered.

Contaminant attenuation reactions or mechanisms are part of a network of potential reactions that are interrelated. The partitioning of a contaminant between pore water and aquifer solids is a balance between forces that tend to pull the contaminant into the pore water and those that tend to pull the contaminant into the solid. The forces that pull the contaminant into the pore water are summed up by the concept of aqueous speciation. The forces that pull the contaminant into the solid phase are attractions of two types. One is between the dissolved contaminant ion and other ions that cause a mineral to form that contains the contaminant (precipitation or co-precipitation). The other is between the contaminant ion and the surface of a mineral (adsorption or absorption).

Chemical reactions adhere to thermodynamic and kinetic principles and can be predicted if the right information is known. Equilibrium thermodynamics reveals what reactions are possible or what chemical conditions are required for reactions to be possible. However, some reactions in the environment proceed so slowly they are not observable despite thermodynamic predictions that conditions are favorable for their occurrence. These are sometimes referred to as being kinetically controlled. Rates of kinetically controlled reactions are predictable for simple systems based on laboratory studies, but the subsurface is not a simple system. Variables such as temperature, surface area of minerals, and the presence in solution of constituents that inhibit reactions make reaction rate predictions difficult. In some cases reaction rates can be measured directly in the field, but often can not. Reaction kinetics is an important aspect to geochemical reactivity in the subsurface. In many instances thermodynamically favorable processes are known not to occur on time scales relevant site-specific consideration. This is particularly true for environmental redox processes. Biotic mediation of most redox processes in groundwater environments is ultimately the determining factor for the rate at which a given chemical processes will occur in the subsurface environment. The pertinent message is that although a certain process is predicted to be thermodynamically favorable, this does not immediately translate to the rate at which that processes will occur.

An understanding of waste site evolution is fundamental to evaluation of the permanence of attenuation of metals and radionuclides caused by natural or engineered processes. A contaminant plume is a transient perturbation of natural conditions within an aquifer. For most plumes these perturbations are significant because the chemical compositions of contaminant-bearing fluids are significantly different than the natural groundwater. The contrast between the geochemical conditions within the plume and the natural geochemical conditions of the aquifer dictate that conditions in the subsurface will evolve as the plume moves. Hence, at any given location, natural attenuation mechanisms will also evolve with time.

There are four principal mechanisms by which metal and radiological contaminants are attenuated in the subsurface environment. They are as follows:

- Sorption - Desorption
- Precipitation - Co-precipitation - Dissolution
- Dilution - Dispersion
- Radiological decay

Metal solubility, sorption, and bioavailability depend primarily on metal speciation. Metal speciation, in turn, is determined by the site-specific geochemical conditions. The ambient geochemical conditions of the groundwater aquifer solids which affect metal speciation include pH, Eh, alkalinity, natural organic matter, and chelating ligands (e.g., carbonate, phosphate, organic chelators, etc.). These geochemical conditions are often established by the dominant biogeochemical processes (e.g. aerobic vs. iron/sulfate reducing conditions) and are expected to collectively govern metal speciation in groundwater. For example, groundwater with elevated concentrations of natural organic matter is associated with low Eh (reducing conditions), which may lead to the reduction of metals, such as arsenic or chromium, which are susceptible to redox processes.

The extent to which these processes are relevant to a particular contaminant is site specific and can depend greatly on the nature of the subsurface material and aqueous geochemical conditions, and the nature and extent of the contaminants present (mixed plume situations). Different background biogeochemical processes may create geochemical gradients along which metal speciation is expected to change.

The processes described above operate either individually or in concert to govern the attenuation of metal contaminants. Multiple processes may operate concomitantly to influence the fate of metal contaminants, particularly at mixed-plume locations. Complications arise when changes in geochemical conditions function to decrease the solubility of one metal, but increase the solubility of another. An example of this is plumes containing both arsenic and chromium. Oxidized arsenic(V) species are typically lower in solubility and have a greater propensity for sorption onto aquifer solids, especially iron (hydr)oxides. In contrast, reduced arsenic(III) species are more mobile in groundwater. Alternatively, chromium is virtually immobile in its reduced chromium(III) form, whereas oxidized chromium(VI) is highly soluble and more toxic than chromium(III). Thus, geochemical site conditions, such as a geochemical gradient of declining Eh, may promote chromium attenuation and concurrently mobilize arsenic.

It is important to understand overall geochemistry of the contaminated site and its evolution through time. A comprehensive understanding of site conditions allows qualitative prediction of the behavior of multiple contaminants within a plume and the effects of natural or artificial changes in geochemical conditions. Ultimately, the success or failure of MNA at any particular site will be determined by the operative physico-chemical processes and by the rate and extent of these processes. Thus, site evaluation for MNA will necessitate collection of site-specific data that define the processes controlling contaminant transport.

DECISION FRAMEWORK

In 2007, EPA published the first two of a three-volume series (three-volume MNA set) called “Monitored Natural Attenuation of Inorganic Contaminants in Ground Water” [1,2]. The third volume was published in 2010 [3]. This three-volume MNA set represents a technical resource for site managers to facilitate evaluation for the potential effectiveness of MNA as a remedial approach for metals and radionuclides in groundwater.

The first volume of the three-volume MNA set [1] titled “Technical Basis for Assessment”, contains the technical requirements for assessing the potential applicability of MNA as part of a groundwater remedy for plumes with inorganic contaminants. Included in these technical requirements is a tiered approach for site characterization to evaluate the potential for MNA as an effective remedial approach. The objective of this tiered approach is to provide site managers with a logical framework to screen sites for MNA that is cost effective because it prioritizes the data required for site evaluation. Conceptually, a tiered approach seeks to progressively reduce uncertainty as site-specific data are collected, thereby effectively managing project resources.

The framework in Figure 1 provides logic for integrating EPA’s tiered process into the remediation process and for transitioning from energy intensive (labor, materials, costs)

remediation technologies to attenuation-based approaches. Each part of the framework must be considered sequentially, but that does not mean extensive work or additional data are always required. For example, much of the data required for Tier I are the traditional data collected to delineate contaminant plumes and in many cases will already exist. The primary objective of progressing through the tiered evaluation steps is to reduce uncertainty in the remedy selection.

Successfully working through the MNA framework and meeting remedial goals will often be an iterative process. The tiered analysis process provides a means of organizing the data collection effort in a cost-effective manner that allows the ability to eliminate sites at intermediate stages of the site characterization effort. The framework can be exited at any time in the remediation process and thus the point of exit will be based on where one is within the process. For example, if the use of a source treatment allows the identified remedial goals to be met, then there is no reason to continue working through the framework and evaluating all the steps. One can also enter the framework at any time in the remediation process. It is assumed that sufficient characterization has been conducted to indicate whether contamination is present at a level that requires action.

The following tiers and related questions make up the framework:

- Tier I - Assess System Hydrology, Groundwater Chemistry, and Contaminant Distribution
(Is the Plume Stable or Shrinking?)
- Tier II - Evaluate Mechanism(s) and Rate(s) of Attenuation
(Do Attenuation Rates Support a Reasonable Timeframe?)
- Tier III - Mechanism Stability and Capacity
(Is the System Capacity Sufficient? Is the Contaminant Stability Sufficient?)
- Tier IV - Design Performance Monitoring Program and Contingency Plan(s)
(Can Regulatory Criteria be Met?)

The final step is to evaluate the performance of the MNA remedy by monitoring. Monitoring the system ensures that the attenuation mechanisms controlling the system will be sustainable over the time needed to have the plume diminish so that remediation goals are met. A combination of decreasing contaminant concentrations and trends of decreasing contaminant flux from the source(s) through the distal portion of the plume(s) may be the ultimate best indicator of long-term acceptable performance.

The decision framework sets forth a process that will produce conceptual site models that take a systems approach to remediating a site rather than a series of disparate parts. Metal- and radionuclide-contaminated sites, in particular, benefit from this approach because the contaminants, except for short-lived radionuclides, are not destroyed but remain in the system unless physically removed. Thus, actions taken in one sector of the contaminant plume will have an impact on contaminant fate and transport in downgradient sectors of the plume. The process depicted by the decision framework should facilitate investigations that will be conducted in a more timely and cost efficient manner and will result in remediation technology choices that work in concert to restore groundwater to beneficial use.

As noted in the decision framework in Figure 1, multiple decision points could potentially direct the user to evaluate enhancement options. The process of evaluating enhanced attenuation

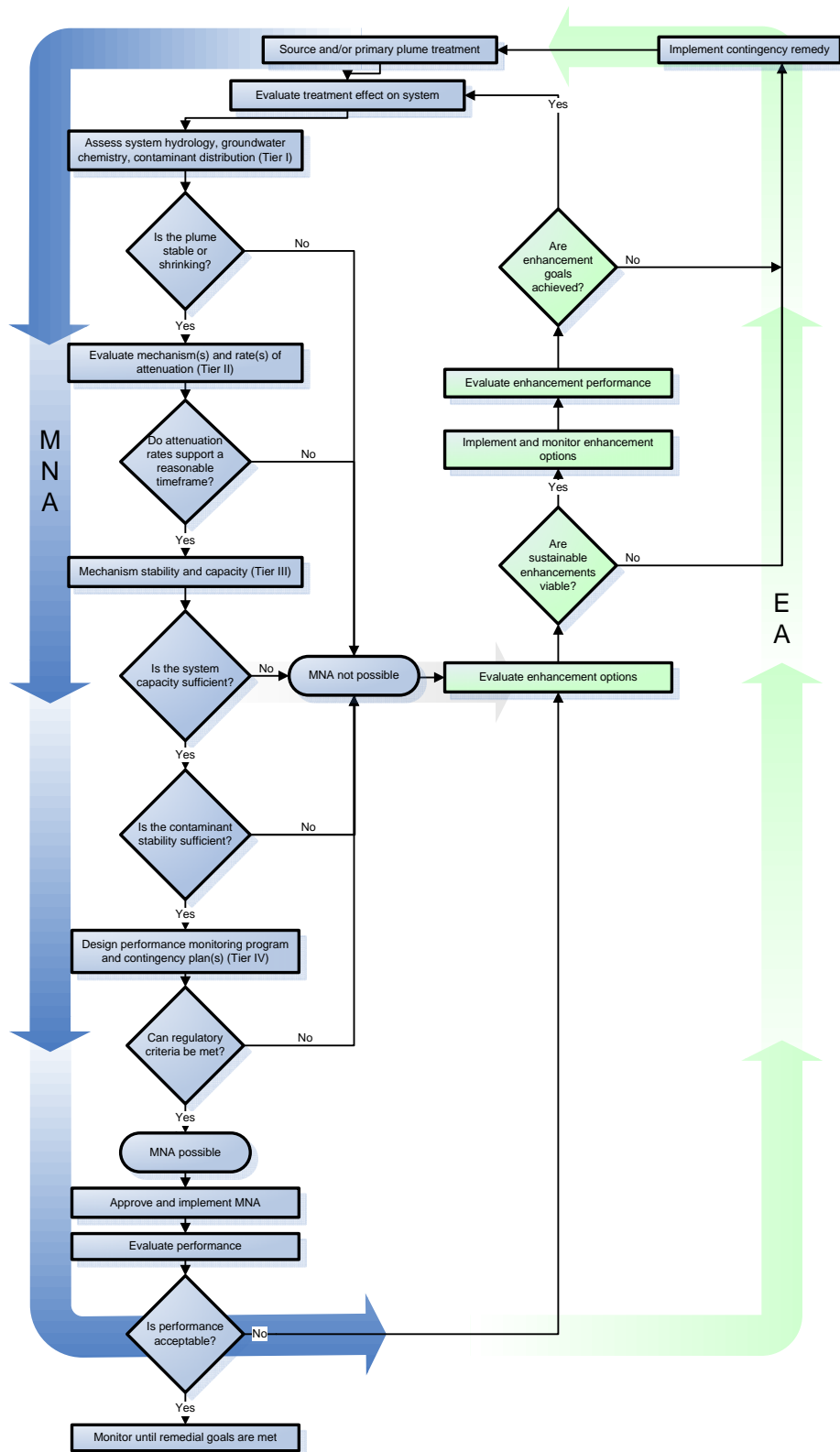


Fig. 1. Decision framework for applying MNA to groundwater plumes contaminated with metals or radionuclides

options moves up the right-hand side of the decision framework. Enhanced attenuation is defined as any type of intervention that might be implemented in a source-plume system to increase the magnitude of attenuation by natural processes beyond that which occurs without intervention. Enhanced attenuation is the result of applying an enhancement that sustainably manipulates a natural attenuation process. Sustainability in this context refers to the ability of a system to maintain attenuation mechanisms through time. Regardless of the sector of the plume (e.g., the source, aqueous plume, or dilute fringe) being remediated, enhancement options work by increasing attenuation capacity, reducing source loading and/or increasing stability.

REGULATORY PERSPECTIVES

As stated in the National Research Council report [4], “natural attenuation is an established remedy for only a few types of contaminants,” which do not include metals and radionuclides. This is still largely true, because MNA of metals and radionuclides was not considered an available remedy when many of the current regulations were written. However, federal and state regulations and guidance are now beginning to include some provisions pertinent to utilizing MNA.

With or without associated engineered remedies, MNA as a remedy has been accepted throughout the regulated community for organic groundwater constituents as a viable process for many years. Several policy and guidance documents exist to support attenuation of organics and to provide consistency in application and documentation. EPA’s initial policy [5] also emphasized the application of MNA to petroleum compounds and chlorinated solvents; metals and radionuclides were only briefly mentioned.

Different federal and state remedial programs may have somewhat different remedial objectives. For example, the CERCLA and RCRA Corrective Action programs generally require that remedial actions:

- prevent exposure to contaminated groundwater, above acceptable risk levels;
- minimize further migration of the plume;
- minimize further migration of contaminants from source materials; and
- restore ground-water conditions to cleanup levels appropriate for current or future beneficial uses, to the extent practicable.

Different, and often multiple, divisions of state government may have jurisdiction over remedial efforts at different contaminated sites. In RCRA-authorized states, the RCRA-equivalent state regulations can be considered applicable or relevant and appropriate requirements (ARARs) under CERCLA or may be applied directly. These state regulations apply in lieu of federal regulations, and while most state solid and hazardous waste regulations are based on the federal requirements, some states have developed regulations more stringent than the federal program. State regulations, therefore, include the basic list of RCRA metals, but may also specify additional metals. States also develop and promulgate regulations and standards to protect groundwater and surface water from toxic levels of certain metals. These water regulations and standards are consistent with, and sometimes more stringent than, federal regulations in the Clean Water Act.

To determine the specific approach for its new guidance document, ITRC conducted a web-based survey of state regulators and stakeholders to determine the existing state of knowledge and acceptance regarding the application of attenuation processes as a remedy at sites with groundwater contaminated with metals and/or radionuclides. ITRC evaluated results from the survey and found that there appears to be a lack of knowledge with respect to the technical and regulatory aspects of attenuation for radionuclides. Further, responses to the survey suggested a greater level of uncertainty in understanding the importance of the various attenuation mechanisms associated with radionuclides than those associated with metals. However, respondents appeared comfortable with their knowledge associated with attenuation of metals and the importance of the various attenuation mechanisms. Survey findings also indicated a lack of governing policies and guidelines for evaluating the viability of attenuation-based remedies for sites with metals and/or radionuclide contamination and revealed a variability among states which have developed policies. ITRC took these apparent competencies and deficiencies into consideration while developing its document and determining its scope and focus.

MNA of metals and radionuclides in groundwater involves more complex and interdependent processes than does MNA of organic compounds, however, many of the factors that must be considered by regulators are the same. Most state and federal regulatory programs have incorporated MNA of organic compounds into their policies because practical experience and knowledge of the processes involved have reached a level where the perceived risk is tolerable. Regulatory acceptability of MNA of inorganics lags behind because a similar base of knowledge and practical experience has been lacking.

In general, in order for MNA to be considered as a remedial option, regulators must have:

- confidence in the technology prior to full-scale application,
- adequate site characterization,
- an adequate performance monitoring plan, and
- a commitment to long-term stewardship.

TRIBAL AND STAKEHOLDER ISSUES

Concerns of stakeholders regarding attenuation include community participation, long-term monitoring and maintenance, future site use, health and safety, and specific tribal issues. Tribes are different from public stakeholder groups because tribes have government-to-government relationships with Federal, state, and local governments. Each tribe is a unique entity culturally, governmentally, and socially and tribes will have concerns specific to their own interests that may not be present in public stakeholder groups.

APPLYING MONITORED NATURAL ATTENUATION

The more complex a site, the greater the level of geochemical expertise will be required. However, using information collected during a typical site characterization effort will provide much of the information needed to begin developing a robust conceptual site model and to begin the evaluation of whether MNA will be a viable option at a remedial site.

The traditional data sets collected in many waste site investigations can provide a wealth of information regarding the potential of incorporating MNA into a remedial strategy. It is important to understand subsurface conditions prior to the introduction of the waste materials, which is done by evaluating upgradient conditions and/or conditions ahead of the reach of the contaminant plume. Information from such data sets aids in understanding the conditions the site will naturally return to once the plume has passed through the source area and thus the potential attenuation capacity and long-term sustainability of attenuation mechanisms at the site.

CONCLUSIONS

MNA can be a viable remedy for groundwater contaminated with metals and radionuclides and may be capable of satisfying regulatory requirements at many contaminated sites. It may also often result in significant cost savings compared to more active remedies. MNA is not, however, a “do-nothing” remedy, but rather may require intense characterization in order to understand the attenuation processes involved and to justify reliance on them.

MNA of metals and radionuclides does not yet enjoy the same level of acceptance by regulators and stakeholders as natural attenuation of organics, primarily because the contaminants are not destroyed, but remain in the subsurface. With new guidance and a framework for applying that guidance now available, they will be able to better understand if attenuation mechanisms can be sustained over time, i.e., if contaminants will be stable under natural background conditions. Greater regulator and stakeholder acceptance is anticipated as these new policies and guidance begin to be applied.

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