A Decision Flowchart for the Use of Monitored Natural Attenuation and Enhanced Attenuation at Sites with Chlorinated Organic Plumes

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A DECISION FLOWCHART FOR THE USE OF MONITORED NATURAL ATTENUATION AND ENHANCED ATTENUATION AT SITES WITH CHLORINATED ORGANIC PLUMES

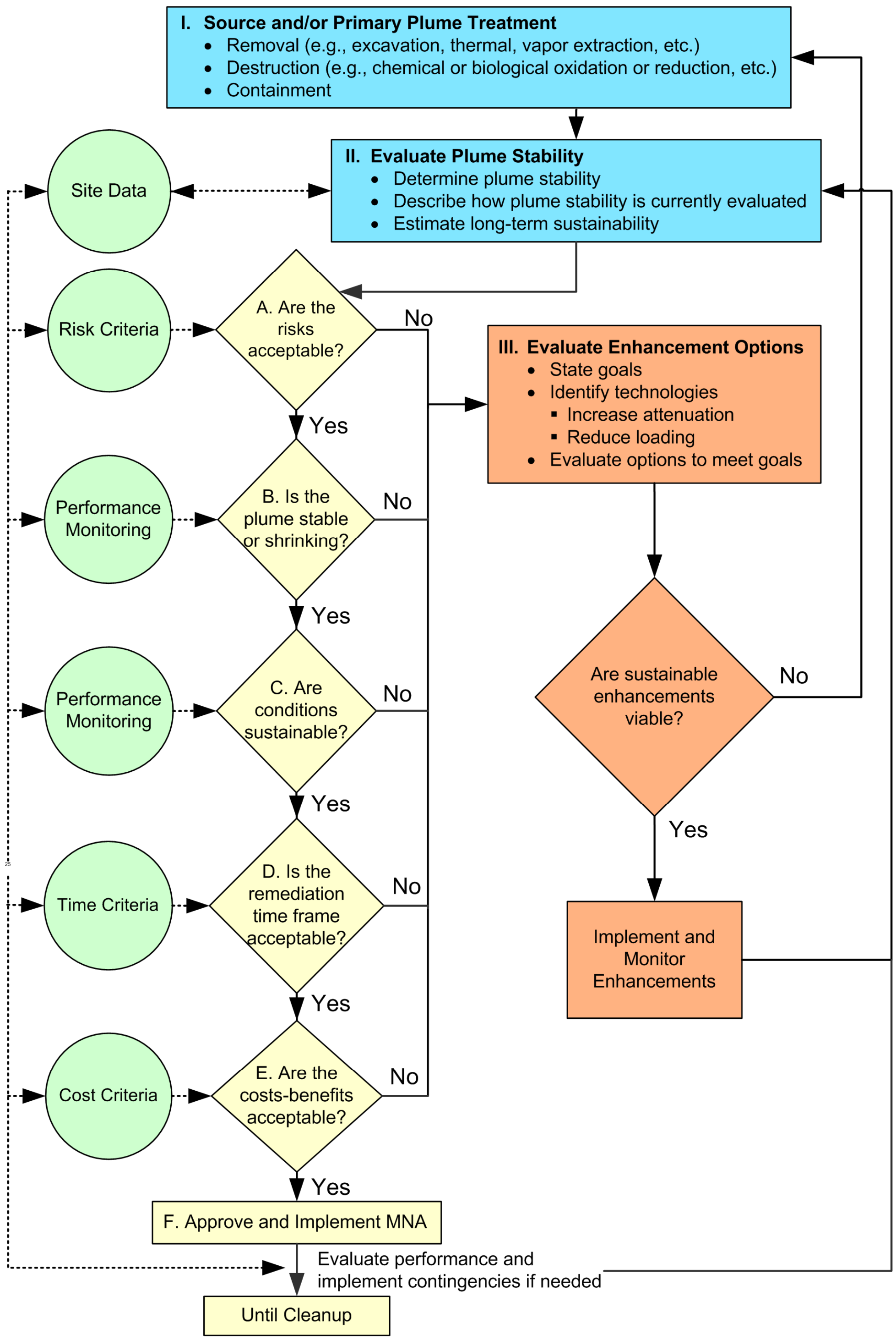


Figure 1. Decision flowchart for the use of monitored natural attenuation (MNA) and enhanced attenuation for chlorinated organic plumes.

INTRODUCTION

The overarching goal of Decision Flowchart for the Use of Monitored Natural Attenuation (MNA) and Enhanced Attenuation (EA) shown in Figure 1 is to encourage a decision process that is both innovative and disciplined, enabling users to identify and implement appropriate remedial alternatives. The flowchart provides a mechanism for transitioning sites through the remediation process and represents a decision framework for not only the regulator, but also the site manager. The decision flow process is not cumbersome or technically complicated, and the goal of site remediation can be documented with an efficient scientific process. It is important to note that this Decision Flowchart can also be used to determine site remedial change from MNA to active remediation through EA technologies.

Over the past 20 years, MNA for chlorinated organics has advanced rapidly, supported by improved scientific information and clear policy developments. The U.S. Environmental Protection Agency (EPA) formally recognized regulation of the use of natural attenuation for chlorinated solvents and the use of the term "MNA" with issuance of two documents, a protocol (EPA 1998) and a directive (EPA 1999). These encouraged the use of MNA in combination with other actions, as needed, to achieve remediation goals. In cases where natural attenuation mechanisms are not sufficient to achieve remediation goals because of risk/exposure to receptors, plume growth, or long time frames to achieve remediation goals, additional actions (i.e., alternative approaches) are needed. In addition, targeted approaches are necessary to overcome the reason(s) that MNA alone is not adequate for site remediation. Innovative strategies that will couple active remediation techniques with natural attenuation and the consideration of EA are discussed in the context of the Decision Flowchart.

> EA is a plume remediation strategy to achieve groundwater restoration goals by providing a "bridge" between source-zone treatment and MNA and/or between MNA and slightly more aggressive methods. EA provides an organized, scientific, and disciplined approach to implement treatment technologies at appropriate sites and at appropriate times. Various remediation technologies can be designed to reduce the source flux and/or increase the attenuation capacity/rate in the plume to ensure the plume will stabilize and shrink in a suitable time frame.

Natural attenuation processes occur in most soil and groundwater systems and act, to varying degrees, on all contaminants. A decision to rely on natural attenuation processes as part of a site-remediation strategy depends not only on the occurrence of natural attenuation, but also on its effectiveness in meeting site-specific remediation goals. Meeting these goals typically requires that there is low risk, plume stability/depletion, and documentation of accepted and sustainable attenuation processes. Plume stability and sustainability depend on the balance between contaminant loading into the plume and contaminant attenuation within the plume. This "mass balance" is a simple and powerful idea that is critical to conceptualizing natural attenuation remedies, designing enhancements, developing characterization and monitoring strategies, and developing regulatory decision frameworks that encourage broader use of MNA/EA with clarified technical responsibility.

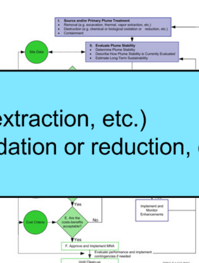
MNA typically relies on attenuation processes "without human intervention" and has been described as "watchful waiting." MNA remedies move toward remediation goals at an "acceptable" rate and limit the collateral damages sometimes associated with active remedies (e.g., resource use or physical/chemical ecosystem disruption). EA is an active remedy that involves human intervention but maintains the explicit goals of stabilizing and shrinking the plume, reducing risks, and/or achieving remedial goals within an accelerated time frame.

The general structure of the Decision Flowchart (Figure 1) is familiar and consistent with existing guidance documents and protocols. As depicted, the process encourages implementation of MNA according to the existing protocols with additional emphasis on mass balance based assessment of plume stability and with additional documentation of sustainability. This latter requirement—applicable, for example, to sites that may have co-disposed hydrocarbons that serve as electron donors to facilitate attenuation—represents an additional level of documentation and rigor to supplement current protocols. Importantly, if a site is approaching MNA but does not meet the requirements of MNA (i.e., it does not pass the requirements on the left side of the figures), the Decision Flowchart provides an additional potential option of EA. In this case, the scientist/engineer determines whether there is a sustainable action that will modify the risk, plume stability, remediation time frame, etc. and allows for implementation of that action. This additional loop within the Decision Flowchart, entitled "III. Evaluate Enhancement Options," should encourage a smoother, more efficient, and defensible transition to MNA from traditional source treatment (e.g., aggressive physical, thermal, or chemical removal or intensive treatments with chemical and/or microbial methods) and traditional plume treatment (e.g., pump and treat or active bioremediation).

Section III of the flowchart describes EA in more detail, and Sections II A–II E provide specific requirements to be considered in evaluating the mass balance to optimize long-term plume stability/reduction.

It should be noted that the decision process is iterative. If enhancements are not viable, then traditional treatment continues. If enhancement is viable, then it is implemented and monitored to document that the desired change was achieved so that the site can transition into traditional MNA or to identify that the desired change was not achieved such that further traditional treatment is required. The selection of the preferred response action or the decision to transition from active to natural or enhanced attenuation typically requires an analysis of a short list of remedial alternatives, collaboratively developed by technical specialists working with the site owner along with regulators and stakeholders.

I. SOURCE AND/OR PRIMARY PLUME TREATMENT



I. Source and/or Primary Plume Treatment
- Removal (e.g., excavation, thermal, vapor extraction, etc.)
- Destruction (e.g., chemical or biological oxidation or reduction, etc.)
- Containment

When a source/primary plume is present, essentially all regulatory guidance recommends, and regulators require source/primary plume treatment. Based on current trend analysis, many chlorinated organic contaminated sites will require the use of several technologies that combine aggressive and passive technologies to reach cleanup goals.

Two key issues to consider for source and plume treatment in the context of the EA evaluation process are how to integrate the source area remedy with a current or future EA/MNA remedy and how to develop an understanding of the effects of the source area remedy on aquifer conditions that affect the entire plume remedial efforts.

The first objective is to develop a decision process that provides knowledge of when to stop operation of the active remedy in the source zone and transition and implement into other appropriate EA/MNA remedies. In addition, a site manager needs to be able to decide whether it is appropriate to implement an EA/MNA approach for a different area of the plume while the source area remedy is still operating. Appropriate decisions for both aspects of this issue can be made as long as an adequate performance assessment program is in place. Performance metrics that would help determine when the action is complete or can no longer be equally effective with the same level of effort should be identified early in the process.

The second issue for consideration with regard to source area remediation in the context of an EA/MNA evaluation is the potential collateral effects of the technology on the aquifer. Rather than approaching site remediation as a series of isolated steps, consideration should be given to potential collateral effects on possible later attenuation goals. The evaluation of these collateral effects can be performed using a "subsurface ecology assessment" approach[1]. This assessment can be defined by evaluating three major areas: hydrological impacts, microbial population changes, and electron donor/electron acceptor activity changes.

Hydrological Impacts

Remedial processes that directly or indirectly impact groundwater flow may impact the existing risk management conditions (such as diverting or increasing flow to a receptor or discharge point) or other attenuation processes (such as decreasing flux of biologically available electron donor/acceptor). Examples of hydrological impacts include the following:

- hydraulic or physical containment of the source, which may change groundwater flow characteristics
- biomass growth and gas generation due to bioremediation, which may reduce porosity locally

Microbial Population Changes

Remedial processes may create conditions that inhibit or enhance biological processes. Examples include the following:

- Pump and treat can introduce oxygen into the subsurface that will benefit aerobic processes but inhibit the growth of strict anaerobes.
- Thermal treatment may reduce the activity of chloro-respiring microorganisms, delaying the onset of reductive dechlorination.

[1] The subsurface ecological assessment concept recognizes the interrelatedness of the living and geochemical components of the subsurface environment. A subsurface ecological assessment is an evaluation of the direct impact on subsurface conditions, or potential change in conditions, associated with a remedial technology and how those conditions will directly or indirectly impact biotic-biotic and biotic-abiotic interactions.

- It was previously thought chemical oxidation would cease biological activity, but recent work (Chapelle, Bradley, and Casey 2005; Rowland et al. 2001; Rowland and Golden 2003) has shown that aquifer conditions following chemical oxidation may be favorable for future reductive dechlorination.
- Geochemistry changes, such as pH, conditions, sulfide/sulfate, etc., may occur.

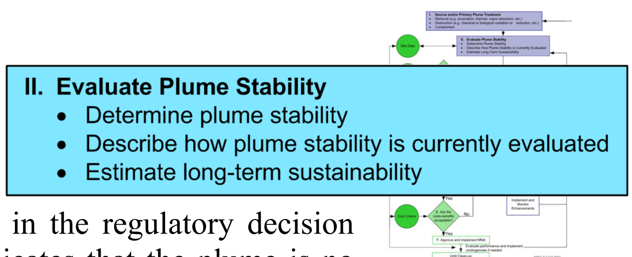
Electron Donor/Acceptor Activity Changes

Processes that change the availability of oxidizable or reducible chemical species may impact future remedy implementation. Examples include the following:

- Injection of oxidizing agents such as peroxide or permanganate can change redox conditions and introduce new electron acceptors to the local and down gradient aquifer.
- Residual co-solvents from a flushing operation can act as electron donors for reductive dechlorination.

The above considerations should help regulators and site managers provide an evaluation of conditions which are included in Section I of the Decision Flowchart.

II. EVALUATE PLUME STABILITY



Determine Plume Stability

The question of plume stability is a key factor in the regulatory decision process. Generally speaking, plume stability indicates that the plume is no longer expanding in size, nor is its footprint moving. It is also useful to consider a more academic definition of plume stability such as the following from The U.S. Department of Energy's (DOE) *Decision-Making Framework Guide for Evaluation and Selection of Monitored Natural Attenuation Remedies at Department of Energy Sites* (DOE 1999), which is based on contaminant attenuation and mass flux:

> Plume [stability] occurs when the perimeter of the plume attains sufficient size or location such that attenuative mechanisms equal or exceed the mass flux at that boundary.

Describe How Plume Stability Is Currently Evaluated

Traditionally, various documents such as EPA's *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water* (EPA 1998) cite "lines of evidence" to assess the degree to which natural attenuation is occurring and whether it could be a suitable remedy. Although geochemical, biochemical, and microbiological evidence may exist, most regulatory agencies consider a stable or shrinking plume to be the critical line of evidence for determining whether MNA alone is an appropriate remedy.

Determining plume stability can be difficult, particularly if data resolution is low throughout space and time. Currently, most regulations require the comparison of concentration data (i.e., mass per volume) to regulatory standards as opposed to evaluation of mass flow or mass flux (i.e., mass per area per time). When used in combination, both concentration data and mass flux may provide a truly scientific approach acceptable to regulators to support transitioning between technologies and ensure that compliance is maintained and measured via a concentration standard.

Assessing plume stability relies on the emplacement of a representative monitoring network to provide the spatial and temporal data necessary to evaluate whether the plume is stable, shrinking, or expanding. EPA's *Performance Monitoring of MNA Remedies for VOCs in Ground Water* (EPA 2004) offers in-depth discussion regarding monitoring for plume stability.

Assessment of plume stability may also include the following:

- assessment of in situ attenuation rates
- mass balance assessment to evaluate the natural attenuation capacity and how it will be affected by implementation of a particular remedy in the near- and far-source regions of the plume

Estimate Long-Term Sustainability

Until recently, most evaluations of plume stability focused on the question of current stability as indicated by spatial and temporal trends in existing monitoring data. With the advent of evaluation mechanisms of the MNA remedy, the importance of understanding the likelihood of achieving future long-term plume stability/reduction is starting to be considered by responsible parties and regulatory agencies as a necessary component for acceptance of an MNA remedy. Evaluation of long-term plume stability/reduction can start with the mass balance evaluation on attenuation mechanisms vs. mass loading.

In cases in which biodegradation is an active attenuation mechanism, it is important to determine how sustainable it will be over the expected life of the plume (i.e., whether there will there be sufficient electron donor to sustain an adequate biodegradation rate for continuous plume stability). Ultimately, the mass balance should demonstrate whether the plume is likely to remain stable, shrink in size, or expand over the long term. In the "real" world of site remedial efforts, it will be difficult in many cases to estimate electron donor sustainability. Performance measures will capture the ongoing remedial efforts and should provide adequate information for the site manager to establish ongoing sustainability.

It is important to collect relevant natural attenuation data as early and often as possible, such as during site characterization. Monitoring programs should be designed with the long-term evaluation of plume stability in mind and should include collection of necessary data from the start. Software such as Groundwater Services, Inc.'s Mass Flux Tool Kit (www.gsi-net.com/Software/massfluxtoolkit.htm) and DOE's Biobalance model may provide valuable insights during the mass balance/sustainability evaluation. Key factors that should be considered in the mass balance/sustainability evaluation include the following:

- organic substrate

- groundwater flow/replenishment
- sequence of electron acceptors
- geochemistry

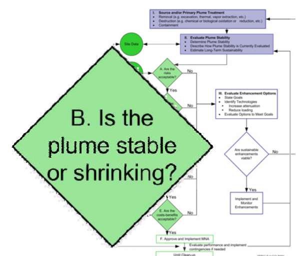
The following paragraphs describe details of each decision point in Section II of the flowchart.

A. Are the Risks Acceptable?

ITRC's *Natural Attenuation of Chlorinated Solvents in Groundwater: Principles and Practices* (ITRC 1999) states, "Natural attenuation should not be considered as the remedy or a portion of the remedy when natural attenuation will not be protective of human health and the environment or alternative remediation technologies can more reliably and cost-effectively treat the contaminants to minimize risk."

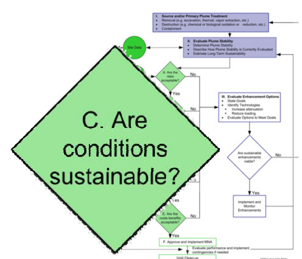
The main concern is whether or not the current risk to a receptor requires some additional remediation before MNA can be implemented or whether the risk precludes consideration of an MNA remedy altogether. Even then, MNA may not be acceptable due to public/community pressure or perception or the existence of unacceptable residual risk throughout the plume.

B. Is the Plume Stable or Shrinking?



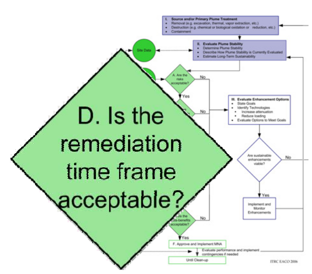
This decision point is a yes/no response based on the actual evaluation of plume stability for the site. Obtaining regulatory agency concurrence is an essential step in documenting plume stability.

C. Are Conditions Sustainable?



This decision point is a yes/no response based on the evaluation of long-term plume stability for the site. Obtaining regulatory agency concurrence is an essential step in documenting long-term plume stability.

D. Is the Remediation Time Frame Acceptable?



In some cases, remediation time frame may be driven by public/community concerns, political pressure, and/or requirements of the regulatory agencies, irrespective of the cost-benefit analysis. Therefore, for an MNA remedy to be successful, input from key parties such as the following should be carefully considered:

- responsible party(s)

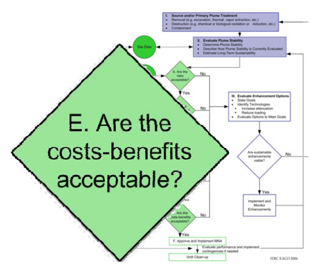
- resource agencies
- local governments
- impacted community/public
- environmental groups/advocates

Many states allow for a “reasonable” time frame for cleanup to reach restorative standards, as long as current risks to human health and the environment are considered acceptable. However, what is considered a “reasonable” time frame is subjective and varies among state regulators.

The key to developing an acceptable time frame is to involve the concerned parties in remedial discussions at an early stage. An important step is to communicate the reality of how long remedial methods are likely to take before contaminant concentrations reach acceptable levels. Once the parties involved understand the realistic time frames, a more productive discussion can occur.

Meeting acceptable remediation time frames may require consideration of other risk-reduction strategies either preceding or in tandem with the MNA remedy. More importantly, it may require establishing interim remediation goals to measure MNA remedy success.

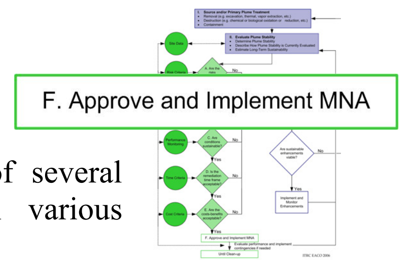
E. Are the Cost-Benefits Acceptable?



Another aspect of evaluating the appropriateness of an MNA remedy is consideration of the cost-benefits. The interplay among remediation time frame, reliability, achieving regulatory standards, performance goals, and cost-effectiveness must be considered when comparing an MNA remedy to other alternatives. Many states have specific requirements aimed at balancing these factors. The desire for faster cleanup, even at greater cost, may be driven by the need to mitigate unacceptable risks or by community/political involvement. In some cases, an alternative may result in faster cleanup at a lower lifetime cost. Specific regulatory requirements and site-specific drivers regarding remediation time frame, reliability, and cost-effectiveness should be thoroughly reviewed and discussed with the regulatory agency. The key questions to address include the following:

- Is an alternative remedy (or combination of remedies) faster, more reliable, or more cost-effective?
- Is faster or more reliable cleanup warranted even if it costs more (i.e., due to unacceptable risks, community/political pressure, etc.)?
- Can enhancements be used to cost-effectively reduce the remediation time frame and support the MNA remedy?

F. Approve and Implement MNA



The decision to approve and implement MNA should be viewed as part of the total remedy, and it is important to stress that <u>creative approaches</u> to the use of MNA may include a combination of several treatment technologies and/or enhancements implemented in various locations of the entire plume.

OR

Assuming the plume has been demonstrated to be stable under current conditions and all indications are that stability can be managed into the future, then regulatory concurrence will be needed to implement the MNA remedy.

OR

If the previous five decision steps resulted in "Yes" answers, then MNA is the appropriate remedy. When natural attenuation is the remedy, it is important to monitor the system to ensure that the attenuation mechanisms identified as controlling the system will be sustainable over the time needed to have the plume diminish so that remediation goals are met and will remain below those values over time.

If the attenuation mechanisms cannot be maintained so that the plume continues to diminish over time, then contingency plans that will take the responsible parties back into the flow diagram must be enacted.

III. EVALUATE ENHANCEMENT OPTIONS

State Goals

EA is built on the foundation that the goal of the attenuation processes is equal to or greater than the rates of the contaminant loading. The overall goal of the enhancement(s) is to achieve a mass balance between contaminant loading and natural attenuation processes, such that the plume stabilizes and/or shrinks over time. To be effective, the enhancement must demonstrate sufficient longevity to ensure that the plume shrinks and the enhancement is no longer required to reduce contaminant concentrations or fluxes.

Enhancements are the specific technologies that constitute an EA strategy remedy and are designed to enhance natural attenuation processes or reduce loading of contaminants at the source or downgradient in the plume. Enhancements have several fundamental requirements:

- The enhancement achieves or maintains the stability of the plume and results in plume shrinkage over time,
- the enhancement results in an increased rate of the attenuation processes,
- the enhancement can be monitored and validated, and

- the enhancement has sufficient longevity to maintain a reduction in flux for a period that achieves regulatory requirements.

Identify Technologies

An enhanced attenuation technology either reduces loading from the source or increases the attenuation capacity within the plume (e.g., reduce infiltration, source containment, increase biological or abiotic reactions within plume, permeable reactive barriers, etc.). Most of these technologies are presently used for active treatment. To be considered for inclusion in an EA strategy, a technology—singly or in a treatment train—must meet the requirements above. Detailed information about these technologies can be found in the DOE publication *Enhanced Attenuation: Approaches to Increase the Natural Treatment Capacity of a System* (SRNL 2006b) and from the ITRC's Enhanced Attenuation: Chlorinated Organics Team technical and regulatory guidance document to be published in 2008.

Evaluate Options to Meet Goals

After identifying possible EA technologies, each will be evaluated to determine whether it will meet the specific goals for the site. Feasibility study approaches, as outlined in the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) process, or decision analysis approaches, such as cVOC Decision Tool, provide formats to document the analysis. As there may be several goals associated with the decision of selecting a specific EA treatment and the relative importance of these goals may vary by involved party, including those parties in the evaluation process is recommended.

Are Sustainable Enhancements Viable?

This decision point is a yes/no response based on the evaluation of the EA options for the site. Obtaining regulatory agency concurrence is an essential step. This process involves subjective as well as objective decisions.

Implement and Monitor Enhancements

The goals of monitoring EA are as follows:

- Ensure the sustainability of the EA remedy,
- confirm mass flux reductions,
- confirm protection of human health and the environment through reduced risk,
- confirm that the regulatory milestones have been achieved, and
- allow the opportunity to reconsider the appropriateness of the current remedial response (i.e., have conditions at the site shifted such that the current site response should be reconsidered).

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