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# Guidance for Monitoring Passive Groundwater Remedies Over Extended Time Scales

September 2021

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# Summary

Passive remediation can be appropriate where natural processes and actions such as institutional controls mitigate exposure to contaminated groundwater, achieving remedial action objectives and protectiveness of human health and the environment. Monitored natural attenuation (MNA) is a prevalent passive remediation strategy supported by a regulatory framework and monitoring design guidance. However, long-term passive remedies are usually selected in combination with at least one active remedy, such as source removal, in situ treatment, or pump-and-treat, functioning as a complementary method for achieving remediation objectives and meeting the applicable statutory and regulatory requirements. However, MNA and existing monitoring guidance primarily target situations where the remedial action objectives are met within a few decades. When time scales for passive remediation extend to many decades (50 years or more), a corresponding change in monitoring strategy is needed to adapt to the extended time scale. This document provides guidance for implementing an extended-scale monitoring (ESM) approach appropriate for long-duration passive remediation. Extended-scale is defined in this document with respect to time (i.e., a long duration of remediation) and a large enough physical scale such that downstream receptors will not be impacted within the remediation timeframe.

ESM applies to slow-moving groundwater contaminant plumes and emphasizes monitoring primarily for potential exposure pathways. For this approach, the primary monitoring objective is to demonstrate that the plume diminishes before reaching the receptor zone or point of compliance and/or a receptor does not receive concentrations above the compliance limit. While the overall objectives of protecting human health and the environment are the same as for plumes where remediation can occur over a shorter time period, the time scales between decisions are longer and the dynamics of plume evolution are slower. To this end, a scenario-based strategy is described for different plume and source conditions, defining a containment and receptor zones. The containment zone is the area where the risk of exposure to groundwater contamination can be mitigated (e.g., through institutional controls) during the remediation cannot be mitigated and compliance concentration standards must be met. Within the containment zone, slow plume migration may occur, leading to concentrations that exceed compliance standards. However, where distance to the receptor zone is large relative to plume migration and attenuation rate, this approach can be protective of the receptor zone.

Selection of a long-duration passive remedy needs to be based on sufficient understanding of contaminant sources, hydrogeology, and contaminant plumes. A strong technical basis, supported by predictive analysis, is recommended to substantiate that contamination is expected to stay within the containment zone during the active remediation and attainment phase of the remedy, and diminish to meet compliance standards within the extended timeframe prior to reaching the receptor zone (e.g., many decades or even centuries). The ESM approach is based on verification of plume behavior and not on detailed plume dynamics. Monitoring is conducted to confirm expected behavior with an emphasis on exposure pathways to verify that plumes remain contained in areas where the protectiveness objectives can be met. ESM should not be adopted if there is significant risk of the plume extending beyond the containment zone. Given the slow movement within the containment zone, less frequent sampling is required relative to approaches used for conventional-scale remediation.

The guidance provided in this document can facilitate the development of site-specific monitoring plans that consider local site conditions and in the selection of specific monitoring techniques most appropriate to the site for long-duration plumes. The nature of an ESM plan is not to fully understand the dynamics of plume behavior, but rather to verify that the plume is staying within the containment zone and to verify that the plume is behaving as predicted, consistent with the conceptual site model. Alternatives to standard monitoring techniques such as well-based sampling and analysis may also be appropriate for some aspects of ESM. A portfolio of approaches is described in this document, including sampling methods currently under development that may reduce costs associated with long-term monitoring.

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# Acronyms and Abbreviations

ARAR	applicable or relevant and appropriate requirement
CERCLA	Comprehensive Environmental Resource, Conservation, and Liability Act
COC	contaminant of concern
CSIA	compound-specific isotope analysis
CSM	conceptual site model
DET	diffusive equilibration in thin films
DGT	diffusive gradients in thin films
DOE	U.S. Department of Energy
DQO	data quality objective
DST	Decision Support Tool
EPA	U.S. Environmental Protection Agency
ESM	extended-scale monitoring
FOCS	fiber optic chemical sensors
ITRC	Interstate Technology & Regulatory Council
LOD	limit of detection
LOQ	limit of quantitation
MAROS	Monitoring and Remediation Optimization System
MCL	maximum contaminant level
MNA	monitored natural attenuation
NAS	Natural Attenuation Software
NRMRL	National Risk Management Research Laboratory
OSWER	Office of Solid Waste and Emergency Response
PFAS	per- and polyfluoroalkyl substances
PFM	passive flux monitor
POCIS	polar organic chemical integrative sampler
RAO	remedial action objective
ROD	Record of Decision
SADA	Spatial Analysis and Decision Assistance
SMART	specific, measurable, achievable, relevant, and time-bound
SMARTe	Sustainable Management Approaches and Revitalization Tools – electronic
SOMERS	Scientific Opportunities for Monitoring at Environmental Remediation Sites
SPE	screen printed electrode
TI	technical impracticability
ТРН	total petroleum hydrocarbon
VOC	volatile organic compound
VSP	Visual Sample Plan

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# 1.0 Introduction

Groundwater monitoring data are used for site characterization and remedy selection; remedy management, implementation, and remedy decision support; and compliance demonstration during remediation or remedy closure (NRC 2013). Regardless of the intended purpose, it is important that an environmental monitoring program be tailored to meet the site monitoring objectives for the stage of the remediation process (Bunn et al. 2012). Without careful and adaptive planning, monitoring objectives may not be met or are met with unnecessary costs. Thus, a careful monitoring design that is tailored to the site remediation and monitoring requirements is needed.

An overall framework for monitoring design and implementation is presented in Bunn et al. (2012). Focused on U.S. Department of Energy (DOE) sites, the SOMERS (Scientific Opportunities for Monitoring at Environmental Remediation Sites) approach identifies monitoring objectives based on the stage of remediation, selecting diagnostic monitoring approaches that provide data to support remediation decisions. SOMERS describes the importance of the conceptual site model (CSM) and its refinement over the course of remediation as a core element to support monitoring design. This document expands on some of the SOMERS concepts, centering on the CSM as a critical tool for long-term monitoring, and presents guidance that relies on natural attenuation referred to as extended-scale monitoring (ESM).

# 1.1 Monitored Natural Attenuation in Groundwater in an Extended Scale Context

Monitored natural attenuation (MNA) is a prevalent passive remedy supported by a regulatory framework and monitoring design guidance when remedial objectives can be achieved and documented with sufficient lines of evidence. MNA is often used after active remediation techniques have been terminated (e.g., pump-and-treat). Multiple guidance documents for the design of MNA monitoring programs are available (ITRC 2007, 2010; Wilson 2012), providing information on spatial and temporal monitoring intensity is directly related to meeting the MNA remedy performance objectives included in the Office of Solid Waste and Emergency Response (OSWER) guidance (USEPA 1999c). The objective of MNA is to contain contamination within a containment zone separate from receptors. Within this zone, natural processes such as degradation (biotic and abiotic), dilution, and sediment interactions (e.g., sorption and ion exchange) retard contaminant transport and reduce dissolved phase concentrations (USEPA 1999b).

Contaminated groundwater remedies need to meet applicable or relevant appropriate requirements (ARARs) based on federal and state regulations. ARAR waivers are possible for some site conditions under federal and state regulations (ITRC 2017), although interim remedies can be identified that do not necessarily achieve all ARARs. A technical impracticability (TI) ARAR waiver (or TI waiver) is one type of ARAR waiver that can be invoked when technology or site conditions preclude the achievement of ARARs. TI waivers can be granted either pre- or post-remedy selection (USEPA 2012; ITRC 2017). A TI waiver process requires public comment on a proposed plan and it must be issued in a final Record of Decision (ROD) or ROD Amendment. A TI decision, including the alternative remedial strategy, must be incorporated into a ROD or be incorporated into a modification or amendment to an original document. TI waivers may involve establishing a groundwater management or containment zone that is as small as possible, while passive or active measures are applied to meet site objectives based on the ARAR waiver designation. Typically, extended monitoring periods are needed for TI waiver applications to verify compliance with ARAR waiver designations and to ensure protectiveness. For MNA and TI waivers, monitoring is used to evaluate plume conditions associated with maintaining protectiveness and meeting ultimate remedy or ARAR waiver objectives. Passive remediation has unique monitoring needs because plume behavior is typically driven by less dynamic forces (i.e., natural gradient) than those applied during active remediation and monitoring may be needed over long time periods. Passive remedies may also include verifying that the groundwater plume is contained within a particular zone. However, such containment strategies are only recommended when plume movement and contaminant flux are efficiently and persistently slowed by natural conditions (Rügner et al. 2006).

Monitoring locations and measurement frequency are important aspects of a monitoring plan that support passive remedies. Sentinel well monitoring locations are usually placed between a known area of groundwater contamination and a receptor zone to provide advanced warning of contaminant movement to a downstream receptor. While standard rules-of-thumb guidance for monitoring frequency are appropriate for plumes that naturally attenuate within decades, these guidelines may not be applicable at large sites and/or long-duration plumes (e.g., 50–100 years or more) where the rate of change in plume conditions is slow. For example, the New Jersey Department of Environmental Protection (NJDEP) describes a process for determining the monitoring frequency of sentinel wells as the groundwater velocity divided by half the distance between the source and the nearest receptor (NJDEP 2012). If the distance to the nearest receptor is 5 miles and the groundwater velocity averages 0.2 ft/day, then the recommended monitoring frequency for sentinel wells is once every 180 years. In contrast, the state of Wisconsin (WDNR 2014) recommends a minimum annual sampling frequency irrespective of plume size or velocity. Neither of these generic recommendations represents an acceptable monitoring frequency for large, long-term plumes. On one end, annual sampling agnostic of plume characteristics is potentially excessive, whereas sampling once every 180 years does not meet or demonstrate the requisite protectiveness intended by regulatory sampling and monitoring requirements.

A specific monitoring application that has not been well described in existing guidance documents or literature is the monitoring of large, slow-moving or persistent plumes, here termed "extended-scale monitoring," or ESM. This document considers ESM for situations where the plume characteristics are such that active or passive remedy approaches cannot meet cleanup objectives in a time scale that is manageable using current remediation technologies (e.g., within 30–50 years). This situation may be driven by site complexities, as discussed in the recent Remediation Management of Complex Sites document (ITRC 2017), which describes related technical and nontechnical challenges that can impede remediation and prevent a site from achieving federally and state-mandated regulatory cleanup goals within a reasonable time frame. The technical challenges include geologic, hydrologic, geochemical, and contaminant-related conditions as well as large-scale or surface conditions.

The Interstate Technology & Regulatory Council (ITRC) provides guidance and a framework for the use of adaptive site management approaches for complex site conditions (ITRC 2017). The ESM approach is intended to complement this guidance by presenting a design that emphasizes monitoring large, long-duration plumes with limited or no short-term exposure potential. Importantly, relative to monitoring objectives during characterization or initial active remediation process or performance monitoring, long-term monitoring objectives need to change to reflect the scale, time frame, protectiveness, and cleanup targets associated with long-term passive plume management. Hence, the intent of this document is to provide guidance that complements existing MNA guidance for long-duration situations (e.g., longer than  $\sim$ 50 years). This includes other long-duration passive monitoring needs such as a long-term TI waiver management situation where exposure pathways (i.e., contact with the plume) can be effectively controlled during the long remediation time period.

Typically, MNA is used following active remediation, and only after source control measures have been implemented. Although the MNA approach may follow active remediation measures, if the long-term exposure to potential receptors is low, then MNA may be implemented without the use of an active remedy. The ESM approach is also only applicable to long-term plumes (greater than ~50 years). If there is significant uncertainty associated with the CSM, or if there is significant stakeholder resistance, then the site is not a good candidate for this passive remedial approach.

## 1.2 Slow-Moving Plumes

Under natural conditions, groundwater travels downgradient, transporting dissolved contaminants toward areas of discharge (rivers, lakes, etc.). The rate of contaminant migration, however, is dependent on the hydraulic conductivity, hydraulic gradient, and porosity, which in turn is dependent on aquifer material (e.g., unconsolidated sediments or fractured rock). An average groundwater velocity of 1 foot per day or greater is considered a high groundwater velocity, whereas a slow groundwater velocity may be as low as 1 foot per year or 1 foot per decade (Alley et al. 1999).

Within the context of ESM, a slow-moving plume is one in which groundwater velocities are low and natural attenuation processes are rapid enough to prevent the migration of contaminants past the site boundaries or containment zone. Natural attenuation is typically most applicable to sites with relatively dilute contaminant plumes (<100 times the cleanup goal) (Fruchter 2002). For both MNA and ESM, evidence is needed to demonstrate that natural processes are decreasing the contaminant mass and mobility. Examples of natural attenuation processes include biodegradation, dispersion, dilution, sorption, volatilization, and chemical or biological stabilization, reduction, and chemical precipitation (USEPA 1999c).

U.S. Environmental Protection Agency (EPA) guidance specifically requires MNA to achieve sitespecific cleanup objectives within a reasonable time frame, but the length of time is not defined. The time that is needed for MNA to remediate a contaminated site depends on the types and amounts of contaminants, on the size and the depth of the contaminated area, on the type of soil, and on the conditions present at the site. It is possible that decades to hundreds of years are needed to achieve cleanup goals by naturally occurring processes. If natural attenuation meets relevant selection criteria and site remediation objectives, and contaminants remain within the containment zone over the remediation time period, then the groundwater velocity and plume change are sufficiently slow for application of ESM.

## 1.3 Document Organization

This document is structured to describe the ESM approach and monitoring tool resources to provide a new cost-effective paradigm for monitoring long-duration plumes. Section 2.0 is an overview of the criteria and conditions relevant to developing an ESM approach. Scenarios where this type of monitoring would be appropriate are presented in Section 3.0. Section 4.0 describes monitoring strategies appropriate for the idealized scenarios described in Section 3.0. Section 5.0 provides information on supporting monitoring tools and approaches. Conclusions and recommendations for integrating the ESM approach into remedy planning and decisions are presented in Section 6.0. Appendix A presents example cases where ESM might be a viable remedial option, while Appendix B contains a description of software packages that can be used to support ESM design.

# 2.0 Extended-Scale Monitoring Considerations

Many groundwater contamination sites will have plumes that move too quickly or are too close to receptors to make an ESM approach appropriate. Sites where ESM may be feasible must meet the following specific criteria:

- A robust CSM with minimal uncertainty quantified through predictive assessments and supported by site characterization data
- A cleanup remedy involving a passive remediation approach (though the ESM approach could be linked to other monitoring applied for active remedies in a subsection of the overall plume)
- A predicted long remediation management duration (more than ~50 years)
- An absence of complete exposure pathways (i.e., contact with the plume) or the ability to control exposure pathways during the long remediation time period
- An agreement by the site regulators and stakeholders to integrate the ESM approach into the selected remedy

A primary objective of verifying that plumes remain contained in areas where they meet protectiveness objectives and ultimately reach remedial action objectives (RAOs) is *imperative* for implementing an ESM approach. If there is uncertainty about the rate at which a plume is moving, or considerable risk if the plume moves faster or farther than expected, then an ESM approach is <u>not</u> appropriate. This section discusses considerations for developing an ESM monitoring approach.

For plume remediation management that spans more than  $\sim$ 50 years, the monitoring approach needs to be commensurate with plume management needs, compliant with associated requirements, and cost-effective. Situations leading to long-duration plume remediation management stem from remediation difficulties due to factors that may include large plume size, continuing primary or secondary sources, subsurface or surface conditions that inhibit remediation effectiveness, and/or slow natural attenuation processes (ITRC 2017).

Long remediation time periods may be acceptable depending on the plume setting (e.g., distance to receptors and a slow migration rate along exposure pathways) and if elements such as institutional controls can be employed to provide protection of human health during the remediation management period. The development of an ESM approach for passive remediation of long-duration plumes is described in more detail in the following sections.

# 2.1 Monitoring Objectives

Monitoring objectives reflect remediation management needs and compliance targets, consider plume dynamics, and include consideration of the stage in the life cycle of the remedy (Bunn et al. 2012). Thus, monitoring objectives should consider the factors important for complex sites (ITRC 2017), as well as factors unique to large, long-duration plumes where exposure pathways can be effectively contained throughout the long remediation time period.

Groundwater provides a pathway for potential contaminant migration to receptors (e.g., surface water or downgradient wells) and may also be the medium targeted for compliance as the remediation goal. Contaminant migration and plume behavior depend on physical, chemical, and biological properties of the saturated zone, contaminant properties, and hydraulic conditions. Concentration and/or flux of

contaminants are monitored to verify containment and demonstrate regulatory compliance. The specific objectives for implementation of MNA (USEPA 1999c) are listed in Table 2.1.

This guidance promotes the use of hierarchical monitoring objectives for ESM. The primary objectives are related to evaluating exposure pathways to verify protectiveness. Secondary objectives are related to confirming plume behavior with respect to meeting final remediation objectives. For long-duration plumes, this approach to prioritizing monitoring objectives is appropriate due to the slow plume dynamics. It is functionally an approach that focuses on verifying that plumes remain contained in areas where the protectiveness objectives can be met.

#### Table 2.1. Monitoring Objectives Identified in MNA Guidance

MNA Objective <sup>(a)</sup>		
1. "Demonstrate that natural attenuation is occurring according to expectations"		
2. "Detect changes in environmental conditions (e.g., hydrogeologic, geochemical, microbiological, or other changes) that may reduce the efficacy of any of the natural attenuation processes"		
3. "Identify any potentially toxic and/or mobile transformation products"		
4. "Verify that the plume(s) is not expanding (either downgradient, laterally or vertically)"		
5. "Verify no unacceptable impact to downgradient receptors"		
6. "Detect new releases of contaminants to the environment that could impact the effectiveness of the natural attenuation remedy"		

7. "Demonstrate the efficacy of institutional controls that were put in place to protect potential receptors"

8. "Verify attainment of remediation objectives"

(a) Direct quotes from the "Performance Monitoring and Evaluation" subsection within the "Implementation" section of the EPA OSWER Directive 9200.4-17P (USEPA 1999c).

To provide confidence in natural attenuation processes and the ability to maintain protectiveness, information supporting these objectives includes monitoring to:

- Track contaminant movement.
- Quantify source flux into the downgradient plume.
- Assess remedy processes and performance.
- Provide information for contaminant movement prediction.
- Verify subsurface conditions related to remediation or long-term plume behavior.
- Maintain regulator and stakeholder trust.

Even within a single, hydraulically connected groundwater zone, there is rarely a homogeneous distribution of groundwater flow. Variations in flow regimes are caused by the inherent heterogeneity of rocks and sediments, which when combined with complex biogeochemical processes affect contaminant transport and remedy effectiveness. This complexity is further compounded during monitoring, where limited spatial and temporal data is used to interpret 3D realizations of behavior. MNA is generally not applied to complex sites where adequate monitoring is infeasible (USEPA 1999c). Reliance on standard monitoring well sampling and analysis for contaminant concentrations in groundwater may not be appropriate for all situations and may be costly over the life cycle, especially for long-term monitoring. However, because the use of monitoring wells is a traditional approach already established at most sites, significant efforts may be needed to justify alternative approaches to understand contaminant conditions and behavior in the subsurface.

For plumes that require long-duration remediation management, the rate of change in plume conditions must be slow, commensurate with the conditions driving plume longevity (e.g., slowly declining primary or secondary contamination sources, slow transport and attenuation rates). ESM selection criteria are important to consider when developing monitoring objectives appropriate for the plume conditions. In addition, monitoring objectives are linked to the selected remedy management approach to provide necessary information for management decisions and to demonstrate compliance with regulatory requirements (ITRC 2017). Monitoring objectives also need to consider other possible data needs that support adaptation of monitoring over time or other aspects of the remediation process.

#### 2.1.1 Data Quality Objectives

Data quality objectives (DQOs) define a process for identifying the type, quantity, and quality of data required to evaluate environmental risks and support decision-making. A monitoring strategy for verifying the maintenance of remedial actions for contaminated groundwater for ESM can be designed by following a DQO process (USEPA 2000). The DQO process is an iterative seven-step planning process for environmental data collection that defines the purpose of data collection, clarifies what data are required to satisfy the purpose, and specifies the performance requirements for the quality of information to be obtained from the data (USEPA 2000).

DQOs are to be specific, measurable, achievable, relevant, and time-bound (SMART), as defined by Doran (1981). DQOs as detailed by EPA guidelines are explicit, fully articulated specifications for data collection. Objectives can be either functional or absolute. Absolute objectives are generally metric based, whereas functional objectives define steps needed to achieve an absolute objective (ITRC 2011). For example, the objective of reducing groundwater contaminant concentrations to below a regulatory limit is considered an absolute objective. A functional objective demonstrates the achievement of an absolute objective, such as a demonstration that risks to human health have been reduced to an acceptable level. Ultimately, there is only one absolute objective for ESM: to passively monitor and verify the contaminants of concern (COCs) remain within the containment zone.

Functional objectives include monitoring of the contaminant plume and hydraulic conditions to verify expected migration, and sentinel well monitoring to prove downgradient absence of contaminant. One important aspect regarding functional objectives is cost effectiveness, or the concept of return on investment from monitoring and data collection requirements. In this regard, the functional objective of monitoring data must enable broad quantification of plume movement and render unnecessary the requirement of additional monitoring for detailed plume dynamics – a practice that can result in significant expense for very little additional information.

Physical and geochemical heterogeneities and contaminant subsurface behavior often present the largest sources of uncertainty at environmental remediation sites. Thus, the SMART protocol typically focuses on defining absolute and functional objectives based on the current understanding of the CSM and the need to design data collection to effectively support decision-making under varying plume conditions (NRC 2005). Functional ESM objectives must be clearly articulated and verifiable to adequately evaluate the containment system. These objectives can then be addressed though a data collection program designed following the DQO process.

The Comprehensive Environmental Resource, Conservation, and Liability Act (CERCLA 1980) requires that cleanup objectives, referred to as remedial action objectives (RAOs), be established and achieved within a reasonable time frame. These objectives can be either absolute or functional and be either interim or final. For containment-based remedies and long-term MNA, RAOs are not usually considered final because of the uncertainty associated with long cleanup time frames. In such cases, long-term objectives

need to be defined as measurable and accountable, building milestones into the monitoring plan based on the current understanding of the CSM.

A monitoring strategy for verifying the maintenance of containment-based remedial actions under an ESM plan follows the DQO process to develop data collection plans and update the CSM. Data collection efforts are prioritized to address the major uncertainties in the CSM, commonly associated with physical, geochemical, and hydrologic conditions and plume dynamics among others. Data collection may be used in conjunction with and in support of modeling efforts in an integrated system monitoring approach (Bunn et al. 2012), with the collected data serving as model inputs or verification of model outputs.

# 2.2 Quantitative Conceptual Site Model

A CSM is a comprehensive pictorial, graphical, and written summary of what is known or hypothesized on relevant site features and events as well as the physical, chemical, and biological processes that control contaminant transport and its potential impact to human health and the environment. The CSM is an iterative tool that is updated over the life cycle of the site investigation and cleanup, justifying characterization approaches, prioritizing site actions, and providing the technical basis for remedy decisions. A quantitative CSM not only provides descriptive site information on contaminant distributions, but also quantitative information on how the distribution resulted based on features, events, and processes. Principal categories of information in a CSM include the following:

- Site history
- Regulatory framework,
- Geology, hydrogeology, and surface hydrology
- Contaminant sources and release mechanisms
- Mechanisms and rates of attenuation
- Contaminant fate and transport
- Remedial actions
- Potential receptors and exposure pathways

Information needed to develop CSMs that support ESM may be available in the site remedial investigation, remedy selection process, initial remediation performance data, and/or information collected in support of an ARAR or ARAR waiver. Numerical modeling and data trend analyses provide information for quantifying the plume and exposure pathway conditions needed to meet performance assessment objectives and compliance requirements. For example, numerical modeling can predict contaminant migration paths and arrival times, which helps inform decisions on sampling location, well placement, and sample frequency.

SOMERS (Bunn et al. 2012) describes the importance of the CSM and its refinement over the course of remediation as a core element to support monitoring design. Additionally, adaptive management is widely recognized as an important aspect of quality monitoring programs. So, while it may seem that SOMERS and adaptive management are contradictory to the concept of minimal CSM refinement, it is expected that refinement should not be necessary, will occur infrequently, or only need to occur for aspects of the plume that result in significantly faster migration or arrival than predicted. For example, the size of the plume in the CSM does not need to be refined after every round of sampling as long as the leading edge of the plume is migrating at an acceptable rate with respect to predicted behavior. This is to balance the

costs associated with CSM refinement to prevent the collection of data associated with refining aspects of the CSM that are not relevant to plume confinement.

The CSM, contaminant and hydraulic trend analyses, and predictive modeling provide critical and necessary inputs for establishing ESM objectives addressing exposure pathways and plume dynamics. Further, it is expected that there will be a high degree of confidence in the CSM (i.e., low uncertainty) before beginning an ESM program that reflects highly predictable plume behavior that has been confirmed by monitoring data so that deviations from expected behavior can be quickly identified. Hence, substantial CSM refinement should <u>not</u> be needed over the duration of an ESM program because the nature and extent of contamination is sufficiently characterized for decision-making. Although expert judgment may be needed to identify if the CSM has sufficient detail to support ESM, an external (third-party) review is recommended to identify potential data gaps and uncertainties that should be addressed prior to ESM implementation. The review process can accelerate stakeholder acceptance and ease the transition to less-intensive monitoring.

Any uncertainties and data gaps can be addressed when adequate contingencies are provided as decision rules. If a problem statement for ESM is that "large, dilute groundwater plume is migrating toward the river located at a distance of 10 km with an estimated travel time of 150 years," then this represents the conditional "if" element of a decision rule (see DQO process in Section 4.0). Hence, a decision rule may read "if the contaminant concentration in groundwater exceeds the regulatory limit by a factor of 10 within 1 km of the river, then additional samples will be collected downgradient to better define plume extent." This provides the justification for collecting additional data and identifies a trigger for additional action.

To evaluate the applicability of MNA, especially for metals and radionuclides, site-specific, subsurface attenuation mechanisms and rates of attenuation need to be quantified (USEPA 2007; ITRC 2010). The basis for evaluating reaction mechanisms and determining system attenuation capacity includes information on subsurface chemistry, mineralogy, microbiology, and contaminant speciation, since the attenuation of metals and radionuclides usually occurs with a change in valence state. Attenuation capacity can be supported with laboratory studies that verify immobilized contaminant stability, as well as predictive analyses that support long-term attenuation. To this end, the ITRC (2010) technical guidance document is recommended as it provides a decision framework to determine if attenuation-based remedies can be successfully implemented at a site.

For the long-duration plumes targeted for ESM, the CSM needs to predict plume migration and identify exposure pathways. Associated tasks include compiling and synthesizing information about the site setting and site hydrogeologic and biogeochemical conditions that relate to estimates of plume behavior and exposure pathways, as well as documented cases of natural attenuation that have taken place over the lifespan of many contaminated sites (Newell et al. 2013). Predictive modeling is a key element in monitoring design for integrating analysis of source flux, attenuation rate, and transport along exposure pathways, and estimating plume migration over time. Trend and hydrologic system analyses can be conducted to estimate source flux (Lemke et al. 2004; ITRC 2017), attenuation rate (Ávila et al. 2014; Stefania et al. 2018), and evaluate expected transport rate along exposure pathways (Ghasemizadeh et al. 2012). Collectively, this quantitative CSM information is used to identify monitoring techniques, locations, and frequencies.

## 2.3 Monitoring Network

The monitoring network consists of wells or other information/data sources for meeting monitoring objectives. The selection of monitoring techniques, layout of the monitoring network, and monitoring frequencies are the key factors that affect monitoring costs and cost effectiveness. For an ESM approach, the primary objective for the monitoring network and technique selection is to verify plume containment as predicted by the CSM. Secondary considerations relate to locations and techniques to evaluate progress toward ultimate remediation objectives.

One important consideration in development of the monitoring network is subsurface heterogeneity. The ESM approach assumes that the impact of microscale physical and biogeochemical heterogeneities have limited impact at the macroscale over the expected domain and extended period of plume management. Since an ESM approach will employ a limited number of monitoring locations, ensuring that the selected monitoring locations provide data that are representative of the subsurface conditions over a macroscale is an important aspect of network design. If any macroscale heterogeneities are identified that might affect plume behavior, the monitoring network within the containment zone needs to capture the impacts and verify them against predictive assessments. Some sampling techniques may be influenced or biased by heterogeneities more than others. Sampling protocols should be designed to account for large-scale influences on plume migration over the anticipated ESM timeframe.

## 2.4 Monitoring Frequency

For long-duration plumes with slower rates of plume change, the frequency of sampling and data collection needed is likely much lower than that required for plumes with short remediation time periods. In addition, the ESM focus on evaluating exposure pathways to verify protectiveness should inherently require a lower frequency than evaluating plume dynamics. Other shorter duration/timeframe activities used to support or validate remediation objectives (e.g., implementation of land-use controls), may continue to require a higher monitoring frequency than the ESM plume sampling and monitoring requirements.

## 2.5 Regulatory Considerations

As discussed by the ITRC (2017), there are multiple strategies for managing a long-duration plume, including the potential use of ARAR waivers, though regulators expect an active remediation component (source control, in situ treatment, etc.) to be included as part of the remedy solution inclusive of timeframes and remediation objectives. For regulatory planning purposes, it may be useful to consider and incorporate concepts of ESM early in the discussion of remediation decisions to develop an overall remedy approach and implementation process (i.e., monitoring and institutional control plan) that is most appropriate for cost-effective management of the contamination risks at a site that has a long-duration plume.

## 2.6 Stakeholder Considerations

Stakeholder considerations and interactions for the ESM of long-duration plumes are expected to be similar to those described in the Remediation Management of Complex Sites document (ITRC 2017). The long-term nature of the plume and associated planning activities to initiate, evaluate, and adapt plume management throughout the duration of the remedy are especially relevant to ESM. Clearly setting monitoring objectives and identifying how monitoring components meet objectives are foundational communication elements between the site, regulators, and stakeholders. Though not specifically required, one meaningful way to enlist regulator and stakeholder support is to encourage active participation in the DQO process when developing the ESM plan (Section 4.0).

# 3.0 Scenarios for Extended-Scale Monitoring

Extended-scale plumes are defined as having a long duration of remediation and an extensive spatial scale such that potential receptors are a significant distance away relative to the slow migration rate. These factors enable selection of a passive remedy for which there is good confidence that protectiveness can be maintained throughout the long remediation time period. Several scenarios, generally representing different types of plume dynamics and plume conditions, may result in extended-scale plumes; each presents a unique site situation and considerations for the types of monitoring elements that are appropriate. These scenarios are briefly described below and considered in examples of monitoring approaches in Appendix A. For each scenario, there is at least one plume and source condition within a containment zone where exposure can be contained throughout the remediation time period. Plume migration during the remediation time period may occur along one or more exposure pathways toward a receptor zone that is outside the containment zone. For the ESM approach, a primary objective and key element of monitoring is to control exposure by verifying that the plume will not reach the receptor zone at concentrations above the regulatory limit.

## 3.1 Requirements

Implementation of ESM is only appropriate when the correct combination of conditions (e.g., plume, source, pathway, receptors, and timeframe) are met. The characteristics listed below are conditions that may allow for an ESM approach.

- The rate of plume change is slow such that travel times to downstream receptors are ~50 years or more. The slow rate of change leads to contamination being present over long time periods with an expectation that the slow system dynamics result in (1) the plume not reaching receptors and (2) the plume footprint eventually becoming stable or diminishing within the containment zone. For ESM scenarios, the slow rate of plume change generally corresponds to differences in plume concentration and extent that are meaningfully quantifiable over decade time scales, and there is low risk of the plume reaching the receptor zone over shorter time scales (e.g., between monitoring events).
- The contaminant source flux, if present, is stable to declining such that the resulting plume dynamics are diminishing or transitioning toward diminishing conditions, although this transition may occur over a long time period and plumes may be present over a large footprint but within the containment zone. Sources may be present over a long time period at or below the threshold for acceptable plume conditions within the containment zone (i.e., evolving toward concentration goals within the containment zone). For ESM scenarios, the source conditions are not expected to have rapid changes that cause unacceptable plume conditions. Additionally, changes in source conditions should be quantifiable over decades to verify conditions, with low risk of a continuing source, such as a rapid increase in source flux creating a significant expansion of the plume over shorter time scales (e.g., annually).

Due to the extended temporal and spatial scales of the contamination issue, initial site characterization and monitoring data coupled with a predictive assessment are used to support a remedy decision for longterm passive remediation management of the site and the corresponding applicability of ESM. Contaminants or plumes that are significant distances from receptors are not prescriptively considered for ESM; the process for consideration must wholly reflect initial site data collection and assessment including a CSM, plume/source conditions, and plume/source trends to establish the basis and conditions that may be considered for an ESM scenario. The predictive assessment will include a forecast of plume/source behavior that provides a basis for interpreting future monitoring results. Collectively, this information establishes expectations to justify the long-term passive remediation management approach and to provide confidence that evaluation of decade-scale changes is appropriate for use over the extended (i.e., many decades) time period of remediation management. In addition, this information will be evaluated to identify monitoring parameters and locations that are "diagnostic" for evaluation of plume/source behavior and verification of expectations from predictive assessments. Thus, diagnostic monitoring can be applied to focus ESM efforts. Where necessary, a phased approach to monitoring can be applied to augment the initial site data and refine the selection of diagnostic monitoring parameters and locations such that monitoring locations and frequencies can potentially be reduced over time.

Implementation of long-term passive remediation management will include a containment zone that provides protectiveness in locations where contamination is expected to be present during the remediation management period. Thus, the primary risk that needs to be addressed during the remediation period is migration along an exposure pathway that reaches a receptor at concentrations above the site-specific objectives (compliance limit) for protection of human health and the environment.

The characteristics listed above lead to an ESM approach that applies decade-scale time frames and is focused on diagnostic parameters and locations. Determination of the appropriate monitoring approach requires considering the site-specific characteristics, properties, physical setting, and contaminant conditions that relate to plume behavior, remediation management time frame, and risk.

## 3.2 Predictive Assessment Support

An important aspect of monitoring is the evaluation of plume and source behavior compared to expectations from the CSM and associated predictive assessments (e.g., numerical modeling). During remedy selection and shorter-term active (or passive) remediation, a close coupling of monitoring as feedback to refining the CSM and updating predictive assessments is warranted and is typically applied as part of remedy optimization and adaptive site management. Currently, predictive assessments are used to establish a range of expected plume behavior as part of evaluating whether a long-term passive remedy is appropriate and will be protective of human health and the environment. Once the long-term remedy is selected on that basis, there is no expectation of closely coupling monitoring with CSM refinement or updating the detailed predictive assessments. Rather, over long time periods, the expectation for ESM is that monitoring data are compared to predicted behavior as quantified by trend analysis and predictive assessments. This comparison can be used to verify anticipated containment or serve as a trigger for a CSM update and/or additional sampling.

Thus, verification of plume behavior is conducted by comparing monitoring data to trend analysis or numerical modeling prediction intervals for individual wells or groupings of wells. When the observations are within the expected range of concentrations are conclusively (1) within the relevant range of expected concentration (e.g., 2-sigma), and (2) continuing to be protective of receptors (at the time of the monitoring event and as forecast by CSM/predictive assessments), then no major adjustments of the remediation approach are needed. Additionally, monitoring data could be used to trigger actions or invoke a contingency plan, the first step of which could be to refine the CSM and re-evaluate predictive assessments. Thus, updates to CSM and predictive assessments are not emphasized in ESM based on the premise that selection of a long-term passive remediation approach has sufficient technical evaluation to (1) justify the long-term passive remediation management approach, (2) provide confidence that evaluation of decade-scale changes is appropriate for use over the extended (i.e., many decade) time period, and (3) support use of monitoring based on plume behavior verification and triggers for contingency actions rather than the need for detailed efforts to continually refine the CSM.

## 3.3 ESM Scenarios

Idealized ESM scenarios are briefly described below and considered as templates for monitoring under extended time scales (see hypothetical example sites in Appendix A). Site-specific objectives must be determined to drive the development of an appropriate monitoring plan.

- <u>A detached plume that is translating and diminishing</u>. A plume after source treatment or after an active treatment (e.g., after pump and treat or a focused area of in situ treatment) may be deemed suitable for long-term passive remediation because, although translating along a flow path, it is diminishing and will not affect receptors (Figure 3.1). Even though this scenario differs from the shrinking plume scenario described in MNA guidance because it can continue to move downgradient within a large, containment area, it can still meet passive remediation objectives with monitoring along a flow path during the remediation period.
- <u>A slowly diminishing continuing source and associated plume</u>. If a source cannot be fully treated and/or removed, it may persist but diminish slowly over time and thereby cause the plume to ultimately diminish depending on the attenuation processes at the site (Figure 3.2). With a diminishing source, if any continued plume expansion will not affect receptors prior to the plume diminishing/stabilizing, it may be a candidate for passive long-term remediation and/or use of ARAR or other waivers (e.g., TI waiver).
- <u>A "plume" with noncontiguous contaminated zones</u>. A plume or contaminated area with either multiple discrete primary or secondary source areas or areas that have different remediation potentials can result in noncontiguous contaminated zones (Figure 3.3). These zones may be managed as a single unit if their collective behavior can be managed relative to meeting compliance and protection of receptors while they passively diminish over a long period. In this case, collective monitoring evaluations with respect to compliance and performance assessment is appropriate.
- <u>A composite plume of co-mingled contaminant plumes/sources within the same footprint</u>. Any of the above scenarios may entail multiple contaminant plumes or source areas (or both) that may be of similar or disparate sizes depending on the contaminant transport and source characteristics (Figure 3.4). These multiple plumes can potentially be managed in composite with primary consideration of compliance and the protection of receptors, making allowances for variation in needs with respect to contaminant transport rates and source characteristics. Decisions and management for small "internal" plumes may be adjusted based on the presence of a larger plume that is the primary risk for compliance and protection.
- <u>A plume where hydrogeologic factors affect plume behavior over time</u>. Any of the above scenarios may be influenced by physical changes over the duration of the long remediation time period that affect plume behavior. Management and associated monitoring need to account for changes and how they relate to meeting compliance and protection objectives.



Figure 3.1. Conceptual depiction of a detached plume that is translating and diminishing. Over time the plume size and position change progressively through Conditions 1, 2, 3, and 4. (Each condition represents a conceptual change in plume configuration and location over time.)



Figure 3.2. Conceptual depiction of a diminishing source and associated plume. In this figure, the plume and source change over time progressively through Conditions 1, 2, and 3 where the plume may expand temporarily and then decline as the source declines over time.



Figure 3.3. Conceptual depiction of noncontiguous contaminated zones that can potentially be managed as a composite "plume" (dotted line).



Figure 3.4. Conceptual depiction of a composite plume/source scenario with co-mingled contaminants that can potentially be managed as a composite with respect to protection of the receptor zone.

Each plume scenario has characteristics that relate to setting monitoring objectives and selecting a monitoring design. The type of monitoring that is appropriate for one scenario may be different from another scenario. Thus, for a specific site, considering the CSM and relating it to an anticipated scenario for the lifetime of the remediation and monitoring period is an important step to set the stage for developing monitoring objectives and the monitoring design.

# 4.0 Implementation Approach

The idealized scenarios describe diminishing plumes (contiguous and noncontiguous) with or without continuing sources. Hence, plume dynamics may also be controlled by the source flux and potential interactions with other contaminants. ESM supports plume remediation management of these zones as a single unit, focusing on the collective behavior relative to protection of receptors and meeting compliance objectives. However, data interpretation may be more complex under continuing sources and in the presence of co-located plumes. For all scenarios, the following requirements must be met:

- Plume movement and source flux changes are slow, such that travel times to downstream receptors are ~50 years or more and differences in plume concentration and extent and source flux are meaningfully quantifiable over the measurement time scales.
- A structured conditional and time-phased sampling approach is used, guided by predictive assessment results for plume migration (see Figure 4.1).
- Metrics are used that are diagnostic of plume condition:
  - Data that verify receptors are not affected
  - Data that quantify the plume migration rate and that the plume is not farther downgradient than it is expected to be at a given time (i.e., inconsistent with predictive assessments)
  - Data that verify hydraulic conditions (e.g., hydraulic heads and hydraulic boundary conditions) and that features that control the migration and attenuation of the plume and source flux are within bounds used for predictive assessments
  - Data that verify limited to no potential for vertical contaminant migration into lower aquifers through aquitards or fault traces
  - Data that demonstrate the plume and source flux are diminishing as needed to meet remediation objectives

The frequency of data collection and analysis to meet monitoring objectives is determined based on the rate of plume or source change and how frequently information is needed to support decisions or remediation status reviews. While monitoring objectives could be addressed through traditional hydraulic and contaminant monitoring at wells, the alternative approaches in this document, as well as considerations of the frequency and extent of monitoring, offer opportunities for more cost-effective long-term monitoring.



Figure 4.1. Generalized process for monitoring long-duration plumes for different plume configurations and source flux conditions.

## 4.1 Data Quality Objectives for ESM

Key elements of an ESM approach can help with developing site-specific monitoring designs based on the relevant site-specific DQOs, monitoring objectives, and site interim and end-state objectives. DQOs define a process for identifying the type, quantity, and quality of data needed to evaluate environmental risks and support decision-making (USEPA 1999a).

ESM emphasizes monitoring primarily for exposure pathways. For this approach, the primary monitoring objective is to demonstrate that the plume diminishes before reaching the receptor/point of compliance zone and/or the receptor does not receive concentrations above the compliance limit (considering that there is a containment zone to prevent exposure within the plume during the remediation period). In some cases, the presence of a persistent source may also drive the need for a monitoring objective to demonstrate that the plume/source condition reaches concentration objectives assigned within the plume area (e.g., objectives defined by ARAR or other waivers). Although remedy completion verification monitoring (e.g., well-by-well analysis) is needed at the end of the remediation period, it is not specifically addressed in this guidance. This guidance is focused on the long-duration monitoring period leading up to remedy completion verification.

The frequency of data collection and analysis to meet monitoring objectives is determined based on the rate of plume or source change and how frequently that information is needed to support decisions or remediation status reviews. While monitoring objectives could be addressed through traditional hydraulic and contaminant monitoring at wells, the alternative approaches in this document, as well as considerations of the frequency and extent of monitoring, offer opportunities for more cost-effective long-term monitoring.

A contaminant plume addressed with an ESM approach is likely to be relatively remote, have contamination sources located miles from receptors, take decades to reach containment boundaries, and may include groundwater plumes of several square miles in size. Designing a monitoring strategy to meet the challenges of an ESM approach can be addressed under the current DQO guidance, with consideration given to the special challenges of scale. The following sections discuss the considerations for developing an ESM program using the systematic seven-step iterative DQO planning process for environmental data collection (USEPA 2000).

#### 4.1.1 Step 1. State the Problem

The main outputs of step 1 of the DQO process are a description of the problem through data collection and a CSM, formation of a planning team, and identification of relevant resources. Under an ESM program, the problem statement explicitly addresses the scale and time issues confronting the monitoring strategy design. The problem statement will acknowledge the vast complexity of the potentially affected subsurface, the number of characterization boreholes and monitoring wells, and the number of samples required to verify plume containment. The problem statement will also characterize the general plume scenario (detached, diminishing, etc.).

The CSM proceeds from a basic characterization of expected plume transport. Under ESM, the CSM addresses processes that will occur over decades, including contaminant degradation rate, but also chemical degradation products and radiological ingrowth, if applicable. In addition, secondary release mechanisms after initial reductions, such as secondary sources and other potential contaminant reservoirs, need to be identified. Seasonal and decadal variations in groundwater conditions need to be described, as well as the possible effects of climate change, land and surface water use, and receptor types and locations. Importantly, potential changes in regulations and action levels should be considered, particularly as they may determine contaminants of interest and their acceptable concentration limits.

#### 4.1.2 Step 2. Identify the Decision

The outputs of step 2 are decision statements linking the principal study question to potential actions. For passive remediation strategies, the decision statement is to contain the plume within the defined containment zone. In all cases of decision identification, a series of alternative actions should be proposed that correspond to possible study outcomes. For example, if it is determined that a detached plume is translating faster than predicted by the CSM, active remediation strategies may be recommended to inhibit the advance. Should cleanup to highest use prove to be impracticable, a TI waiver may be a potential consideration.

Step 2 considers the full range of actions that might be available at various locations and receptors. Actions might vary by location, and given the slow plume movement characteristic of ESM, intermediate actions may only be used temporarily. Available actions may change over the ESM time scale, and boundary, land use control, regulatory, and receptor and location changes may need to be considered as part of the DQO process. Alternative actions can be specified so that data needs for their implementation can be identified.

#### 4.1.3 Step 3. Identify Inputs to the Decision

The outputs of step 3 are a list of data inputs to the decision and their sources, including measurement needs. For ESM, data inputs may include contaminant plume concentrations and dimensions, and supporting hydrological and geochemical inputs needed to model future plume movement. Previous modeling and historical data on the site contamination are also potential data inputs.

Step 3 also involves setting the action level for alternative actions. This is the threshold measurement or modeled value required to make an informed decision on alternative actions. For ESM, this means identifying acceptable levels of deviation from monitoring results, including considerations of percent detections, historical maximum concentrations, coefficients of variation, and mass flux calculations. The action level basis is likely to be based on concentration limits downstream of the plume, though unexpectedly high flux measurements may reach the action level. Indicator, tracer, or surrogate measurements may also provide inputs to the decision statement. The overall decision statement for ESM does not change, since routine measurements (e.g., interval from 5 to 10 years) provide consistent and defensible reassurance that no alternative action is required.

Since ESM is executed over decades, the requirements for record keeping and databases may also evolve over time. Analytical method development, new analytical capabilities, sensors and sampling methods, including those developed by regulatory agencies may provide inputs for the decision statement at a significantly reduced cost. Step 3 is to be periodically re-evaluated as new technologies develop.

#### 4.1.4 Step 4. Define the Study Boundaries

The outputs of Step 4 are definitions of the scope of investigation, including the geographical limits, subsurface strata, and contaminants of interest, including degradation products. This step also sets the sampling time intervals and specifies the initial monitoring network. ESM geographical boundaries are defined as a containment zone that extends from the source plume to the nearest downgradient receptor within the receptor zone. The slow movement of contaminant and spatial separation from receptors provide reduced risk and added time for decisions.

Monitoring well locations depend on the plume migration as predicted by the CSM. Moreover, these locations may change as plumes advance or recede. The optimal sampling network (number and location of wells) may be refined at the end of the initial monitoring phase, using the initial sampling data. Sentinel wells are sampled further downgradient but still at a sufficient distance from receptors.

Sampling designs consider how the boundaries and scope of monitoring and compliance might change over several decades. Future receptor conditions may change due to changes in population density, receptor location, site use, the local economy, and climate change. Current and possible future action levels under all potential alternative actions need to be considered. Compliance requirements of the various alternatives, including a TI waiver, may also affect sampling designs based on cleanup goals that are practicably achievable.

#### 4.1.5 Step 5. Develop a Decision Rule

The outputs of Step 5 are decision rules in the form of if-then statements reflecting the actions that should be taken given various measurement outcomes. For example, if a contaminant is measured at a sentinel well above a threshold concentration, then more intensive sampling may be recommended to determine that active remediation is required and ESM is no longer applicable. The "if statement" may be based on a statistical parameter (mean, median, etc.) that properly characterizes the COC. The concentration at which action is prescribed surpasses the limit of detection (LOD) to minimize the possibility of false positives. One important decision rule in an ESM approach is the use of sentinel wells and a contingency plan for action if contaminants reach the sentinel well zone. A decision rule for declaring an ESM site sufficiently clear of COCs to cease monitoring is also recommended.

Step 5 defines how measurement data will be applied to make decisions. The specific statistical tests that might be applied and their required inputs are identified early in the planning to ensure that the correct measurements are made. Mean concentration is likely to be a parameter of choice for diminishing plumes, since a sharp concentration gradient is not likely to exist. A unique sampling strategy may be recommended for noncontiguous or composite plumes, where focus is directed at the primary plume of interest. Planners should estimate the number of samples that must be collected for a decision from preliminary estimates of plume size and the size and number of affected strata. The need for accurate information on plume transport is to be weighed against the costs and resources required for a decision. Given the large time scales and slow COC movement in ESM, action levels should be set to a relatively high limit (or require multiple exceedances) to reduce the possibility of a false positive leading to unnecessary action.

Step 5 requires anticipating possible changes in action levels over decadal time frames, changes in regulatory agencies and staff, and the possibility of new alternative actions. Planners should dry run potential measurement results within the candidate statistical tests for decisions to understand how, for example, non-detects will be treated and how data from different methods or laboratories will be combined over time. Such tests will inform the selection of statistical tests or parameters, such as the mean or median or some percentile concentration, or other rules developed for decisions based on monitoring data.

#### 4.1.6 Step 6. Specify Limits on Decision Error

The outputs of step 6 are specifications of tolerable limits on decision errors. A decision error is the selection of action/inaction based on the inherent uncertainty of the measurement data, where the alternative decision would have otherwise been made. In active remediation or MNA, step 6 involves the selection of a baseline condition that is assumed unless measurements provide overwhelming evidence to the contrary (null hypothesis). The site manager is also to determine the "gray area" where the

consequences of a decision error are minor. In an ESM approach, the gray area extends up to the edge of the containment area. Any unexpected contaminant transport within the containment zone has no immediate effect on receptors. Limits on the decision error will likely be based primarily on sentinel well measurements.

ESM measurements are largely spatially focused, as the temporal delay between sampling events is quite large. In both a detached plume scenario and a diminishing source and plume scenario, detailed analysis of the plume location and concentration gradient is unnecessary. The only objective is to verify containment within the containment zone. Only a radical deviance in measured concentration from predicted CSM values warrants action. In this case, the associated sampling or measurement error is likely well below the threshold for a decision error. Noncontiguous and composite plumes are non-homogeneous and have more error associated with sampling. However, due to the long distances between plume and receptor, decision error should be limited. If an order of magnitude difference is observed between measured and CSM values, and the measured values are above the limit of quantitation (LOQ), then an action level may be reached. However, normal measurement error is not likely to be a significant contributor.

Unlike ESM monitoring wells, sentinel wells are considered the last line of analysis before the receptor zone. Any contamination above natural background levels may indicate undesirable plume movement. Grab sample values near the LOD are not necessarily actionable due to associated measurement errors. Concentrations near the LOQ are cause for immediate action, especially if monitoring well data indicate massive plume movement. Passive sampler technology is highly recommended for sentinel well monitoring as the devices accumulate COCs over a period of time, decreasing the incidence of samples near LOQ and LOD.

If measured concentrations of COCs are significantly higher than predicted, the CSM may be updated accordingly. Only significant deviation should result in action, with a potential reconsideration of ESM implementation. Unlike active remediation strategies near receptors, ESM allows for adequate response time, as any consequence is buffered by the long distance between receptor and source.

#### 4.1.7 Step 7. Optimize the Design for Sampling

Outputs of step 7 are cost-effective sampling designs for the collection of data necessary to support decisions. ESM sampling requires expert judgment, as it subjectively targets anticipated contaminant locations as modeled by the CSM. Over time, the number of sampling wells may diminish, as statistical methods can be used to identify redundant wells. This is especially true for detached plumes, where contaminants may progress beyond the initial monitoring wells and diminish. ESM optimization is primarily spatially focused, as sampling cycles only occur every 5-10 years. The goal is to broadly characterize plume movement (or lack thereof) and compare to the CSM, thus verifying COC containment. Detailed analysis of plume movement or size is neither necessary nor cost effective.

Sample optimization extends beyond spatial placement. It also applies to sampling frequency, measurement or analysis techniques, and constituents monitored. Analysis may be conducted by a hybrid of field and laboratory testing, combining their respective traits of low cost and high accuracy. Measurements of surrogate species, or adoption of new technologies, has potential to characterize general contaminant movement at reduced costs, especially over long periods of time. Various sampler types (grab, passive, etc.) can be used to estimate the relative error of measurements and validate results. The accuracy of measurements is not the primary concern of ESM sampling. The objective is simply to verify that the contaminant is not moving toward the receptor zone at an unsafe rate. In this manner, careful selection of the monitoring frequency, the methods used and the locations to monitor can result in an optimized sampling approach.

In step 7, an informed and flexible strategy is needed to allow updates to sampling designs over time as site knowledge is gained, groundwater assumptions are verified, and technologies or regulatory constraints change. Such an approach may rely on multiple lines of evidence and predictive analyses. Factors that affect groundwater conditions and receptor populations over decades, such as climate change, changes in land and water use, and receptor populations, need to be identified with appropriate decision rules that require changes in sampling design or alternative actions.

## 4.2 Sentinel Wells

Sentinel wells are sampling points located upgradient of the receptor zone and downgradient of expected plumes, which are meant to demonstrate receptor protection. They are expected to detect only background levels of contaminant, thus proving the absence of COCs. Sentinel wells also provide evidence that the expected plume movement is not radically different than predicted by the CSM. In the context of ESM, sentinel wells are likely one component of a groundwater monitoring system. Typically, a site may include wells used for different purposes such as performance, compliance, and sentinel monitoring. At a fundamental level, the use of sentinel wells indicates that what is happening in the plume is of minimum concern, and that the remedy continues to be protective of human health and the environment provided no COCs are reaching the sentinel wells.

To accurately inform site managers, sentinel wells need to be sited, constructed, and monitored with an appropriate sampling frequency to measure the metric that demonstrates receptor protection. Measured verification of plume containment is a functional objective that proceeds from the absolute objective of restricting contaminant movement to the containment zone. Sentinel wells are important tools for achieving this functional objective and to prove regulatory compliance. Plume penetration to an ESM sentinel well indicates absolute objective failure and the need for an action decision.

At active remediation sites, sentinel wells are placed in a "target area," which is defined by plotting the distance that groundwater is estimated to travel toward a receptor and/or supply wells within 2 to 5 years (e.g., NYDEC 2010; MDEQ 2008). For ESM settings, the target area may be defined based on containment boundaries. As the sole purpose of sentinel wells is to verify receptor protection, they should be spaced far downgradient while still allowing sufficient time for action in the unlikely event that a contaminant is detected above background level. The large distance between plume source and receptors, and the slow plume migration rates, associated with ESM allow this additional spacing between plume and target area. Predictive analyses can be used to identify the depth and pathway of maximum plume concentration (AMEC 2019); the sentinel well should extend to this depth to allow analysis at highest possible concentration.

Sentinel well locations in ESM should not be moved upgradient as plumes diminish or attenuate, as their sole purpose is to demonstrate receptor protection. They may be moved iteratively downgradient over extended time periods as plumes advance. Sentinel wells represent the last line of analysis before receptors, and any increase in contaminant concentration may illustrate containment failure. Sentinel wells, therefore, must be placed sufficiently far downgradient to minimize the possibility of false positives caused by moderately high contaminant concentrations compared to CSM projections.

# 4.3 ESM Monitoring Phases

ESM monitoring can be divided into two phases. In Phase 1, plume and source flux behavior must be verified by comparing against expected behavior, which can be accomplished with three to five sampling events. Plume behavior illustrated by these snapshots is then compared to predictions, and predictions are updated as needed. This can be accomplished by comparing data to trend analyses or numerical modeling prediction intervals for individual wells or groupings of wells. Water level information, precipitation data,

and other hydraulic boundary condition data important to the site hydraulic conditions are collected coincident with contaminant data to evaluate hydraulic conditions for interpretation of plume transport conditions. Note that this verification of plume behavior is not as rigorous as monitoring for shorter-term MNA.

After the initial monitoring is completed, Phase 2 sampling shifts to diagnostic monitoring locations chosen from predictive assessments and the initial monitoring phase. These locations can include the initial wells from Phase 1, but are expected to focus mainly on a small number of wells along the exposure path transect and sentinel wells. If sources are present, source flux monitoring with accumulation devices is also continued to verify that these fluxes are diminishing and are within the expected range for estimating plume behavior. After the plume reaches a maximum and begins to recede, monitoring intervals can be increased and the downgradient diagnostic locations at the maximum plume extent can be dropped from the monitoring network. The need to retain sentinel wells is considered based on the confidence in understanding the plume and source flux behavior.

#### 4.3.1 Phase 1: Synoptic Sampling of the Existing Well Network

In Phase 1, the existing well network can be used to provide "snapshots" of the plume (i.e., sampling from the full well network in a single sampling event). Based on expected plume behavior and rate of plume migration, these snapshots occur every 5 to 10 years contingent on an optimized well network that demonstrates extended times between sampling events do not pose a risk to receptors or negatively impact site management decisions. If a source is present, monitoring can be deployed in or just downgradient of the source zone to monitor flux to groundwater. If the contaminated area contains multiple discrete primary or secondary source areas or multiple plumes with different remediation potential, remediation management of these zones is accomplished as a single unit, focusing on the collective behavior relative to protection of receptors and meeting compliance objectives. Interpolating data into a single plume is not appropriate, but other analyses can be applied, such as overall mass-based trends or individual well trends.

Because data collection is infrequent, constituents for standard groundwater sample analysis of the plume(s) include all COCs and other groundwater chemistry information needed to assess plume behavior. Site-specific monitoring plans can identify the need for siting wells that can identify plume extents versus wells that confirm receptor protection. Accumulation samplers (e.g., passive samplers) or other alternative approaches can target specific COCs or all COCs, as appropriate. Three components of the initial monitoring phase are summarized below.

- **Plume migration verification.** Groundwater should be sampled using the optimization monitoring network once every three to five years over the next 15 to 25 years. Monitoring results should be presented and compared with expected conditions in a Five-Year Report. If plumes are co-located and/or non-contiguous, the focus is on the plumes representing the highest and nearest-term risk, with targeted verification of other plumes.
- Source flux quantification. For scenarios where sources still exist, source flux behavior must be verified by comparing against predictions and expected behavior. Determination of source flux can be quantified from data collected from accumulation devices or calculated from groundwater velocity and concentration data. Similar to the process for verifying the plume migration rate, three to five samples using the optimization monitoring network are needed over the next 15 to 50 years to verify diminishing source behavior.

• Hydraulic conditions and cross-gradient verification. Water level information, precipitation data, alluvium-bedrock aquifer communication, aquitard permeability, and other hydraulic boundary condition data important to the site hydraulic conditions can be collected coincident with contaminant data as input for evaluating both vertical and transverse plume transport, source flux conditions, and groundwater flow conditions.

Note that this verification of plume behavior is not as comprehensive (spatially or temporally) as monitoring for shorter-term MNA but provides a timeseries of data that supports plume migration rates into the first few decades of the ESM program. Analysis of contaminant trends includes individual well trend analysis, well-to-well transect trend analysis, and full plume analysis using mass-based concentration approaches. The first part of this workflow (Phase 1) is shown in Figure 4.1, but is also applicable to Phase 1 and Phase 2 objectives.

#### 4.3.2 Phase 2: Extended-Scale Monitoring

After Phase 1 ends, sampling shifts to diagnostic monitoring locations selected based on the predictive assessments as modified by the initial monitoring phase. These new well locations focus mainly on a small number of wells along exposure path transects. The diagnostic locations are based on the expected maximum extent of the plume, but locations may also need to consider key hydraulic features at the site (aquitards, high permeability zones, etc.), and locations selected based on their use for verifying compliance with protection of receptors (sentinel wells).

The number of wells for each downgradient diagnostic location (e.g., how many wells within Conditions 2 and 3 in Figure 3.1 through Figure 3.4) depends on the uncertainty of plume migration (e.g., due to heterogeneity) and the confidence needed in confirming plume configuration versus conditions at a single diagnostic location. Monitoring during this phase includes the collection of plume snapshots at each monitoring interval (e.g., every 10 years) from the initial well network and the new diagnostic locations. Some of the initial well network locations can be removed if a smaller set of wells provides sufficient information to track the plume (e.g., transect wells along the axis of the plume may be sufficient). Source flux monitoring with accumulation devices is also continued to verify that source flux conditions are diminishing and are within the expected range for estimating plume behavior. After the plume reaches a maximum extent and begins to recede, monitoring intervals can be increased and the downgradient diagnostic locations at the maximum plume extent can be dropped from the monitoring network. The need to retain sentinel wells is considered based on the confidence in understanding the plume and source flux behavior.

During this phase, well monitoring based on alternative approaches (see Section 5.2) can also be deployed in the downgradient diagnostic wells. Alternative monitoring data can be collected along with the standard sampling-based concentration measurement at the downgradient locations. Combined, these data are used to assess the degree to which the leading edge of the plume will reach sentinel wells significantly earlier than expected, if ever. In particular, passive samplers can be helpful at sentinel locations to evaluate if contaminants are present within a designated time interval (ideally 5- or 10-year intervals coinciding with other upgradient monitoring activities). However, passive samplers cannot be left in place over the long time intervals between sampling, as fouling and depletion of sorption capacity limit their time in-place and need to be retrieved. Water level measurements taken during sampling evaluate hydraulic conditions (relative to expected conditions), and hydrologic data such as precipitation and river stage information can also be compiled, if appropriate.

Components of the diagnostic monitoring occurring during Phase 2 are summarized below. The workflow for the second phase of monitoring is indicated in Figure 4.1.

- **Diagnostic and sentinel well location identification**. After verifying the plume migration rate, identify diagnostic and sentinel locations for continued monitoring downgradient of the initial plume location(s) to verify the approximate maximum extent of the plume(s) and sampling frequency. Identify any individual contaminated zones that are migrating more than anticipated or that may reach the receptor zone. Based on this information, select diagnostic and sentinel locations within or downgradient of the initial well network.
- **Diagnostic well monitoring.** Monitor diagnostic locations every 5 to 10 years (depending on the expected plume migration rate) using standard sampling and analysis or alternative methods (e.g., passive flux) in downgradient locations.

**Sentinel well monitoring.** Monitor sentinel locations that demonstrate receptor protection. This might be done with traditional groundwater sampling, or with alternative methods. For example, the use of accumulation devices in sentinel wells can provide lower detection limits and a time-integrated sample. Sentinel wells should be evaluated nominally at 10-year intervals (depending on expected plume migration rate and results from diagnostic locations).

- Source flux monitoring. Monitor source flux every 5 to 10 years (depending on the estimated source inventory and liquid volume) using standard sampling and analysis and complementary monitoring techniques until the source term diminishes.
- Monitoring well network update. Monitor relevant downgradient locations until any individual contaminated zones of concern begin to recede. At the same time, monitor sentinel locations that demonstrate receptor protection. Passive devices, or other alternative methods, may be options for sentinel well monitoring. Monitoring of sentinel wells should occur at 10-year intervals, depending on expected migration rate. After the plume(s) begins to recede, decrease the monitoring frequency to every 10 years at most and remove non-sentinel wells as they become unnecessary.

The number of wells for each downgradient diagnostic location depends on the uncertainty of individual plume migration (e.g., due to heterogeneity). Monitoring during this phase includes collection of trend data for the selected plumes at a frequency based on the expected rate of migration from the initial well network plus the new diagnostic locations. Initial well network locations for individual plumes shown to be declining during Phase 1 can be dropped from the network or monitored very infrequently to verify objectives are being met. Source flux monitoring is also continued for plumes with uncertainty to verify that source flux conditions are diminishing and are within the expected range for estimating plume behavior. After the contamination begins to recede, monitoring intervals can be increased and the downgradient diagnostic locations at the maximum plume extent can be dropped from the well network. The need to retain sentinel wells is considered based on the confidence in understanding the plume and source flux behavior.

During this phase of monitoring, alternative monitoring techniques can also be deployed in the downgradient diagnostic wells to provide an integrated measure of contaminant mass arriving at a monitoring location. These data are collected along with the standard sampling-based concentration measurement at the downgradient locations. Combined, these data help interpret the degree to which the leading edge of the plume has reached a specific well. Passive devices can be particularly useful at sentinel locations to evaluate if contaminants are present within a designated time interval (ideally 5- or 10-year intervals coinciding with other upgradient monitoring activities) as the time-integrated nature of passive samples can result in lower detection limits. Water level measurements are taken at sampling times to check hydraulic conditions and fundamental available hydrologic data like precipitation and river stage information are compiled, if appropriate.

The conceptual designs of an ESM approach are primarily for the monitoring elements associated with use of groundwater wells. Based on site-specific conditions, additional elements derived from information in Section 5.0 can be incorporated or used to replace the following examples (e.g., use of geophysical plume monitoring) if plume characteristics can be assessed with these alternative monitoring techniques.

## 4.4 Additional Considerations

The four scenarios are intended to serve as examples of plume situations and associated general monitoring approaches to help sites develop an appropriate site-specific ESM plan. This section provides additional considerations for implementing ESM.

#### 4.4.1 Five-Year Review Requirements

With ESM, contaminants remain in place, with the expectation that concentrations decline below regulatory limits before reaching receptors, verified by infrequent sampling. Section 121 of CERCLA, however, requires a 5-year review for any contaminants that remain in place following a remedial action to evaluate the implementation and performance of a remedy (USEPA 2001). If a CERCLA 5-year review requires sampling, the sampling can consist of lower cost diagnostic monitoring that verifies no significant deviations from the CSM (review of hydraulic gradient data, limited monitoring at sentinel wells, sensor measurements of indicator species, etc.). More extensive monitoring can occur at 10- or 15-year intervals. ESM monitoring campaigns could also be aligned to coincide with the 5-year reviews.

It may be necessary to conduct diagnostic monitoring at select wells to support a 5-year review if there is lower confidence in expected plume behavior. Under these circumstances, sampling a few diagnostic wells could meet the 5-year review requirement. If plume movement is predictable and well-controlled, then a 5-year review can be conducted with existing data, supplemented with data from a limited number of diagnostic well locations.

#### 4.4.2 Long-Term Data Management and Interpretation

ESM sites will need to be managed over long-time scales that range from many decades to hundreds of years. Significant technological advances are anticipated over these time frames that may impact data collection and interpretation, including the following:

- Field measurement of relevant hydraulic, concentration, and flux data (e.g., sensors)
- Data storage, including databases and computer hardware/software
- Data interpretation, including software used for processing data and visualizing plume behavior
- Modeling software and associated computer hardware/software
- Reporting mechanisms and associated computer hardware/software

A management plan is needed to track and update technological advancements with time. For instance, databases and computer models cannot be viewed as being developed, used, and then archived for future use because they may become obsolete. Thus, the management plan should include use of non-proprietary, portable database elements, if possible, and actions to periodically examine data formats and make necessary updates. Numerical models that have been used for predictive analyses should be archived, but the archive should also include separate information about the model configuration that can be used to recreate the model in the future with new modeling software, if needed.

The long duration time scale of ESM requires multiple individuals within agencies to implement and manage the remedy and associated monitoring activities. Thus, planning and documentation need to include clear description of procedures for transfer of information to successors. Strategies presented in ITRC (2017) are a resource for these activities. Planning and documentation also include provisions for periodic review and discussion among site decision-makers and stakeholders and identification of successors for these participants. These efforts to preserve continuity and the legacy of site knowledge are equally important as the efforts to maintain databases and data interpretation as technology changes.

#### 4.4.3 Monitoring Only at Sentinel and/or Diagnostic Locations

If there is low risk from a plume, reliable controls for the containment zone (see Figure 3.1 through Figure 3.4), and a solid defensible basis that future plume behavior is well understood and will not affect receptors, then monitoring only at a limited number of sentinel and/or diagnostic-location wells may be sufficient. Wells may be located downgradient and/or within the plume to meet the primary ESM objective of demonstrating protection of receptors. The limited monitoring network and infrequent monitoring for this scenario is designed based on the predicted plume behavior and with monitoring at sufficient time intervals to support remedy management needs. The monitoring plan for this scenario should identify trigger values for measurements to determine if any changes in the monitoring approach are needed over time or to identify when remedy closure actions should be initiated. Well locations are determined based on the primary objective of showing that the plume is not migrating or changing in a way that could affect receptors and to substantiate ongoing natural attenuation.

For ESM adoption, decision-makers and stakeholders need to agree that the risk from the plume is managed effectively by the containment zone restrictions and that the likelihood of unexpected plume behavior along an exposure pathway is low. Use of sentinel and/or diagnostic-location wells does not provide direct information about the entire plume, rather focusing on demonstrating that the plume is not moving to areas of concern. For instance, if a plume is diminishing but will do so over a long period of time, monitoring data from downgradient sentinel/diagnostic wells are used to confirm this condition by demonstrating that contamination is not moving downgradient and receptors are protected. However, this approach does not monitor the rate at which the plume is diminishing. Potentially, a diagnostic location within the plume can be used either in combination with downgradient wells or alone as an indicator of the plume condition to demonstrate protection of the receptor and to provide data indicating when remedy closure actions should be initiated.

Thus, for some low-risk situations, a small network of wells may be sufficient to demonstrate the protection of receptors and guide remedy management. In these cases, it may be useful to monitor every 5 to 10 years so that there are periodic data for plume management that may also serve to accommodate regulatory expectations for updating plume maps with some degree of frequency (e.g., in conjunction with the 5-year review requirement). If appropriate, the site could select longer monitoring intervals depending on the plume conditions, risk, and administrative situation of the site or collect additional data on any changes in hydraulic conditions. Closure requirements may also require more frequent sampling to obtain a more statistically significant data set, motivating an exit from an ESM approach (USEPA 2013).

#### 4.4.4 Managing Changing Hydraulic Conditions

Over the many decades of monitoring during an ESM program, regional or local groundwater conditions may change. For instance, climate change or other factors could impact the system within the extended time scale. In Sections 4.1 through 4.4, recommended monitoring included collection of information on hydraulic conditions because they are an important control for contaminant transport. An initial assessment of the possibility for changes in hydraulic conditions can be made at the onset of ESM. Based on this assessment, identification of trigger values for hydraulic monitoring data may be needed to

indicate if plume behavior is outside of the expected range of behavior used for developing the ESM plan. In this case, a trigger value causes possible updating of the CSM and re-evaluation of the monitoring plan based on the new hydraulic conditions and associated plume behavior predictions. ESM assumes that there is no need for closely coupled, high-frequency feedback of monitoring data with interpretations of plume behavior or adjustment of monitoring or remediation management. While hydraulic condition changes do not occur rapidly, or significantly increase the risk from plume migration, they must be evaluated carefully within the monitoring framework of the ESM approach.

#### 4.4.5 Managing Unexpected Behavior

As described in Section 2.0, one of the criteria for implementing ESM is a high degree of confidence in the expected behavior of the contaminant plume. If implemented correctly, it is unlikely that the leading edge of the plume will reach sentinel wells significantly earlier than expected, if ever. However, groundwater transport can occur at unexpected rates or along unanticipated flow paths. The ESM plan can identify uncertainty bounds to allow for a range of anticipated plume behavior and identify contingency plans for further evaluation if unexpected behavior occurs.

Long-term monitoring data can exhibit variation due to seasonal impacts to precipitation and groundwater levels. Some variation may be due to errors in sampling and analysis, but the variation may be the result of changing conditions, such as hydraulic condition changes, extreme weather, or seismic events. If contaminant concentrations show a statistically significant increase, or if predicted plume migration demonstrates a significant deviation, then more frequent sampling under ESM may be required. Trigger criteria for more intensive sampling should be identified in a contingency plan prior to implementing ESM but are expected to be based on groundwater concentrations and risk of exposure to downstream receptors.

A contingency plan identified in the site remedy decision document will function as a response in the event that the ESM fails to perform as anticipated. Flexibility for adjusting the monitoring frequency over the life of ESM should be included in the monitoring plan. In the same way that ESM is designed to decrease monitoring frequency in accordance with monitoring data that support a slow-moving, naturally attenuating plume, monitoring frequency can be increased if unexpected conditions are observed. Sufficient data will need to be collected to address any uncertainty, update the CSM, and address all stakeholder concerns.

Risk at ESM sites can be managed by appropriate locations of sentinel wells, sampling protocols, and contingency plans. If uncertainty is reduced after re-evaluation, then monitoring frequency can once again be decreased. However, if uncertainty remains, then long-term monitoring requirements need to be re-assessed to determine if ESM is still appropriate for the site.

# 5.0 Sampling Methodology

A key tenet of an ESM approach is the optimization of data collection to verify plume conditions. Due to the long monitoring period associated with an ESM approach, the lifetime costs for collection of just a few extra samples per monitoring event can be significant, especially on large sites that have complex plumes where mobilization and analytical costs may be substantially high. For example, one groundwater sample analyzed for a full suite of constituents can have an estimated cost that ranges between \$1000 – \$5,000 per sample (including collection, analytical, administrative, and data management costs). Extrapolated over 100 years, and assuming a sampling frequency of once every 5 years, the cost for collecting one extra sample from one additional well during each event could plausibly range from \$20,000 [strictly limited to key COC(s)] up to \$100,000 for the full suite of target analytes.

The monitoring conducted over the extended time frame of an ESM program only targets the data necessary to verify the approach and demonstrate compliance. The scenarios presented in Section 4.0 identified four basic data needs for verifying that the extended-scale approach is working and appropriate, with:

- Data that indicate receptors are not affected
- Data that verify the rate of contaminant movement and location expected at a given time
- Data that verify hydraulic conditions and features that control the migration of contaminants are within predicted bounds
- Data that demonstrate contaminants are diminishing as needed to meet remediation objectives, including concentrations, source flux, spatial extent, or natural attenuation parameters

There are two fundamental considerations to minimizing costs over the lifespan of an ESM program while still meeting the monitoring objectives. The first is to minimize the number of samples collected. The second is to collect samples and data that have a low-cost burden compared to samples collected using traditional fully purged groundwater well sampling methods. To this end, two considerations are presented to support the ESM approach: (1) sample collection optimization and (2) alternative measurement methods. In Section 5.1, optimization approaches collection are discussed, whereas Section 5.2 discusses potentially less costly monitoring alternatives that might be used in lieu of, or in conjunction with, bulk water sample collection/analysis.

Due to the long monitoring time frames, technologies will likely change substantially throughout the duration of the monitoring program. The following sections provide a basis for considering alternative approaches. More detailed descriptions of the current state-of-the-art for these monitoring approaches can be found in other reference material (e.g., Delepine-Lesoille et al. 2017; Barrias et al. 2016).

The nature of an ESM plan is not to fully understand the dynamics of plume behavior, but rather to verify that the plume is staying within the containment zone, and to verify that the plume is behaving as predicted consistent with the current CSM. This means that a standard monitoring tool may be implemented in a nontraditional manner. For example, active groundwater well sampling is often used for plume delineation; but in an ESM, the active monitoring may only be used for occasional verification monitoring or in response to an indication of plume movement by another method (i.e., passive sampler or geophysics).

This section provides a description of complementary tools and methods that can be implemented in a monitoring plan to reduce monitoring costs. For example, use of an in-ground sensor for a surrogate

geochemical indictor may be used in conjunction with active groundwater sampling.<sup>1</sup> Active groundwater sample collection can be deployed infrequently, as long as the sensor does not indicate presence of the plume.

# 5.1 Optimization of Sample Collection

To achieve efficient and effective targeted plume monitoring as part of an ESM, there are optimization techniques that can help reduce monitoring frequency without limiting the amount of information obtained on plume movement. These include the use of sentinel wells, use of intelligent sample design, and application of statistical software in the sample design (Li and Chan Hilton 2005; Luo et al. 2016).

#### 5.1.1 Sample Design

CERCLA, as amended, requires monitoring to ensure that any remedial action is protective of human health, welfare, and the environment. This premise is also fundamentally consistent with the Resource Conservation and Recovery Act (RCRA) objectives. Though nuanced in naming convention (e.g., remedial design and remedial action under CERCLA vs. corrective measure and corrective action under RCRA), sampling has a role in substantiating that any action is protective and functioning as established in legal documents, such as a ROD under CERCLA, or a Final Decision and Response under RCRA. Fundamentally, sampling is used to measure progress toward meeting a cleanup objective while providing justification for either a continuation or an adaptive change in procedures during implementation of cleanup priorities.

As described in Section 4.0, an ESM monitoring program can begin with an initial phase of monitoring the existing well network every 5 to 10 years for 15 to 50 years to verify plume behavior. Following the initial phase, as the plume translates and migrates downgradient, additional wells may be needed. The sample collection frequency and spatial density should be site specific and negotiated, with the objective of collecting sufficient data to verify that contaminants remain within the containment zone. For such an approach to be successful, careful consideration must be given to the development of sampling plans.

Several investigators have examined how sampling can be optimized, through monitoring well placement, modified sampling intervals, and an overall reduction in the number of wells, while not sacrificing needed compliance, performance, and sentinel monitoring (USEPA 2005). Ling et al. (2003) provided a review of groundwater monitoring optimization studies, introducing a groundwater monitoring methodology to improve existing monitoring plans. The authors use three standalone methods: (1) spatial redundancy reduction, (2) well siting for new sampling locations, and (3) sampling frequency determination (Ling et al. 2003). This approach eliminated redundant wells, identified new locations for an inadequately delineated plume, and provided better recommendations regarding the sampling frequency for each location. The approach described by Ling et al. (2005) aligns well with ESM implementation. The characterization and active-remedy performance monitoring phases that occur prior to ESM implementation of ESM may not provide sufficient well coverage that function as diagnostic and sentinel well locations (see Section 4.0). These locations may be identified immediately upon adoption of ESM, or after the initial three to five verification sampling events used to formulate a longer-term monitoring plan.

Software packages can also be implemented to assist with sample design optimization (Appendix B). For example, the Visual Sample Plan (VSP) software was developed for DOE specifically for sample plan optimization. While not specific to groundwater, VSP assists in the development of cost-effective, statistically defensible sampling plans, and is applicable to any 2D plan. The statistical-based approach

<sup>&</sup>lt;sup>1</sup> A surrogate is a chemical or physical analog or indicator that is not the target COC. Additional information is provided in Section 5.2.2.

provides an assessment of sampling frequency, the number and location of wells needed, and the probabilistic determination of exceeding threshold concentrations at well locations. Similarly, the Monitoring and Remediation Optimization System (MAROS) software provides a strategy for formulating appropriate long-term groundwater monitoring programs that can be implemented at lower costs (Appendix B). The MAROS software package is a decision support tool based on statistical methods applied to site-specific data. Since neither VSP nor MAROS consider the system hydrogeology, professional review is required to assure that monitoring requirements include the flow system. Other approaches explicitly consider site hydrogeology, such as the stochastic method presented in Sreekanth et al. (2017), which integrates a groundwater model into an uncertainty approach to identify a robust monitoring network.

By accounting for relevant current and historical site data, as well as hydrogeologic factors and the location of potential receptors, an optimization plan can be developed to efficiently achieve the termination of redundant monitoring wells. The extended spatial and temporal scales encountered with an ESM approach make computer-aided design useful in achieving regulatory and stakeholder acceptance of an optimized sample collection plan.

# 5.2 Alternative Sampling Options

A traditional approach to monitoring contaminant concentrations in groundwater is to collect water samples at regular intervals and measure contaminant concentrations through laboratory analysis. However, the next generation of monitoring at DOE sites may use an integrated systems-based approach (Bunn et al. 2012; Otero et al. 2009) that supports alternative paths to closure by demonstrating system behavior, documenting trends, and identifying relationships among monitored variables, remedy performance, and remedial goals. Similarly, alternative sampling or analysis methodologies could be implemented in an ESM plan to realize greater cost savings. As noted by Bunn et al. (2012), unique approaches that avoid costly reliance on monitoring concentrations at specific locations should be considered and potentially integrated with the site land use. Monitoring strategies that are effective for short-duration remedies may be inefficient and costly for long-term management.

#### 5.2.1 Sampling

A key aspect of sampling plan development is to collect representative samples (USEPA 2005). To obtain representative groundwater samples, traditional approaches require purging prior to sample collection, either multiple well bore volumes or until parameters stabilize and incur costs associated with purged water disposal. Hardware such as pumps, hoses, and purge tanks are also required.

A dual rate pumping system to purge and equilibrate wells has recently been demonstrated to potentially decrease labor associated with groundwater sampling. Sampling times and wastewater volumes may be reduced without sacrificing sample quality (Wang et al. 2019). This is important when collecting samples over multiple decades. While cost differentials may appear minimal on a per-well or per-sample basis, measurable cost savings can be realized when implemented over long timeframes.

Other whole-water collection methods may lower sample collection costs. For the goals of minimizing monitoring costs and sample variability, low-flow small volume purge and passive no-purge collection methods may also provide a representative sample. A program can transition from high purge to low flow by performing both sample methods a couple of times to demonstrate differences and perform cost comparisons.

#### 5.2.2 Surrogates and Geochemical Indicators

Surrogate species and geochemical indictors can be used to monitor and assess contaminant presence or migration for cost effective analysis (McHugh et al. 2015). They could be used as a proxy for a COC, or as an indicator of when to sample for the COC. For example, a change in dissolved oxygen or dissolved metals concentration could indicate that a plume is reaching the monitoring well. Or, if the COC was codisposed with other conductive compounds, a change in specific conductance of the groundwater may indicate a change in contaminant concentration. Examples of other indicators include fecal indicators (Ferguson et al. 2012) and gross radioactivity (Mendoza et al. 2007), as well as other simple parameters such as conductivity (Galhardi and Bonotto 2016), temperature, and the oxidation-reduction potential. For ESM, the primary goal of monitoring is to demonstrate that the contaminant plume is moving at (or slower) than the expected rate.

Similar to measuring an indicator species, tracers can also be added to the leading edge of a plume to provide a surrogate species for analysis (Robinson et al. 2020; Klammler et al. 2016). In this approach, a tracer could be added as a small volume of concentrated solution or injected as a larger, more dilute plume. Tracers can also be used to estimate the flux of contaminants, velocity of groundwater, or hydraulic conductivity (LeBlanc et al. 1991; Novakowski et al. 2006). The tracer needs to have long-term stability and be non-reactive to be useful in the timeframe of consideration. Additional considerations for the use of tracers include the potential for a temporary change in hydraulic conditions, tracer diffusion, and regulatory permission for tracer injection.

#### 5.2.3 Sensors

Technology development often outpaces regulatory acceptance of new technology for monitoring purposes. However, technological advancement has the potential to continually reduce monitoring costs over long-term monitoring periods. The cost for sampling (per mobilization, per well) and use of state-of-the-art laboratory analytical methods can result in high analytical costs on a per-well basis. Significant savings can be realized if labor and analytical requirements are replaced with sensors capable of quantifying COCs, COC proxies, or analytes indicative of performance, compliance, or sentinel metrics. Low-cost sensors have limited contaminant selectivity and should only be deployed in well-characterized sites. The commercial manufacture of sensors is expected to reduce future costs (USEPA 2003). Production of disposable sensors with much lower costs than laboratory testing may occur within ESM time scales (Hayat and Marty 2014).

All sensors incorporate two essential elements: a receptor that interacts with the analyte of interest and a transducer to communicate an associated signal. Sensors can be chemical, electrochemical, or biosensors, depending on the receptor element (Moretto and Kalcher 2014). Chemical sensors may relate a change in color (Li et al. 2019), sensor mass or resonant frequency, time of flight, etc. to COC concentration. Electrochemical sensors have an electrode that is placed in the sample or adsorbs contaminant and experiences a resultant change in conductive properties. Electrodes are often formed from polymers that can selectively accumulate analyte, increasing the LOQ. Biosensors typically involve an enzyme or biomolecule that reacts with certain COCs, generally pesticides (Andrianova et al. 2016). Some sensors discussed in the literature are hybrids, measuring a reaction with biological or chemical elements impregnated into an electrode (Noori et al. 2020). In addition, sensor limitations may exist, only operating, for example, within a specific pH range or depth (Cuartero and Crespo 2018).

Ongoing research and development will continue to result in chemical sensors that are robust, reliable, cost-effective, and widely available (Swager and Mirica 2019). Future work is likely to be directed at screen printed electrodes (SPEs), which relate contaminant concentration to amperometric (current), potentiometric (voltage), or conductometric (resistive) measurements (Arduini et al. 2017). Large scale

manufacturing of small sensors incorporating working, reference, and counter electrodes is likely to significantly decrease the cost and time associated with groundwater sampling. These sensors are small, fast, low cost, and provide a wide linear response to contaminant concentrations. SPEs can be tailored to accurately measure a wide variety of contaminants by incorporating biological sensing elements (enzymes, bacteria), nanomaterials, and different polymers within the electrode assembly. Research in SPEs has confirmed their ability to accurately detect and quantify volatile organic compounds (VOCs), heavy metals, pesticides, and radionuclides (Li et al. 2012).

Although most biosensors are used for monitoring glucose in diabetic patients, biosensors have been developed to measure polychlorinated biphenyls, heavy metals, uranium (Quesada-González et al. 2018), and inorganic phosphate in environmental media. Biosensors are especially relevant for use with aromatic pesticides, as these inhibit several enzymes. However, analysis of specific pesticides is often limited as the enzymes have low selectivity.

Another sensor technology that holds promise involves the use of nanomaterials. Nanomaterial-enabled sensors have been used to detect pesticides, metals, and pathogens. The small size and large surface area of nanomaterials make them especially well-suited for portable sensor use (Irshad et al. 2013). Nanomaterial-enabled sensors have been developed to detect triazine and neonicotinoids (pesticides) as well as mercury, cadmium, lead, and chromium (Li et al. 2013; Willner and Vikesland 2018). Willner and Vikesland (2018) describe the use of nanomaterial-enabled sensors as having the promise of a "facile, low cost, field-deployable technology." Nanomaterials may also be doped into electrochemical sensor electrodes to increase selectivity or detection limits (Rico et al. 2009).

Fiber optic chemical sensors (FOCS) represent another emerging class of in situ sensors.<sup>1</sup> They are lightweight, robust, inexpensive, and can be operated remotely (Yin et al. 2018). Fiber optic sensors can be either extrinsic (fiber only carries light to a detector) or intrinsic (the fiber is the detector). An intrinsic fiber optic chemical sensor undergoes a physical change in response to the presence of the target chemical. This physical change results in a quantifiable change in the light transmission properties of the fiber. Extrinsic FOCS deliver light to a sensing element and measure the attenuation, adsorption, fluorescent, or other response. Fiber optic chemical sensors have been developed for VOCs and metals, and are commercially available for measurements of dissolved oxygen (Wang and Wolfbeis 2016). The solid-state components and low power demand of a fiber optic chemical sensor should allow for long performance lifetimes.

#### 5.2.4 Groundwater Flow Characterization

Measurements of groundwater head elevation, and the calculated gradient, can be a powerful tool in understanding the dynamics of a site. The gradient can be used to estimate the groundwater flow direction and, coupled with aquifer hydraulic properties, it can be used to estimate the groundwater velocity. As noted in Section 4.0, monitoring of groundwater flow conditions is an important aspect of confirming stable hydrologic conditions or identifying significant changes that impact the CSM.

Measurements of the depth to groundwater from a surveyed top-of-casing reference point (traditionally taken manually using an electronic water level meter) are ideally collected at the same time at all monitoring wells (Ahmadi and Sedghamiz 2007). Such synoptic measurements provide a snapshot in time of the water level elevations (hydraulic head distribution) and can be used to determine hydraulic gradients during various seasons and years. Data interpretation relies on the CSM because the hydrogeologic unit(s) targeted by each individual well screen must be considered to determine which well data can be combined for a 2D (map) view of hydraulically connected units.

<sup>&</sup>lt;sup>1</sup> <u>https://clu-in.org/characterization/technologies/focs.cfm</u>

Water level data collection may benefit from frequent, sensor-based monitoring. For locations or sites where mobilization costs are significant and/or routine access is prohibitive, sensor-based monitoring programs can leverage remote data collection and transmission capabilities to collect and transmit data to a responsible agent, thereby limiting the need for hands-on measurement and data collection. Importantly, this approach can provide valuable details that may be missed by infrequent, manual measurements. Inspection of water level data from a sensor network may provide insights into the dynamic response of water levels to precipitation events, evapotranspiration, pumping stresses, and remedial actions, and may indicate unexpected issues with subsurface infrastructure (Quinn and Johnson 2005). However, the frequency of water level data collection should be weighed against the volume of data generated and stored. For example, hourly measurements at a single well for 100 years can generate nearly 1 million data records. For slow-moving, slow-changing plumes targeted in an ESM approach, seasonal water level measurements may be adequate.

#### 5.2.5 Passive Monitoring

Passive sampling refers to the use of a device that accumulates and traps the analyte of interest over time without pumping or purging (Imbrigiotta and Harte 2020). Some designs reach equilibrium with the surrounding water, while other designs take up the contaminant at a rate proportional to the concentration, providing a time-averaged concentration. Time-averaged systems include diffusive gradients in thin films (DGT) and the polar organic chemical integrative sampler, where contaminants diffuse through a gel and adsorb to a resin over a period of hours to weeks. Continual measurements may be taken by diffusive equilibration in thin films (DET), where an electrode covered in a gel relates conductivity to contaminant concentration within the gel at equilibrium. Other equilibrium systems are physically removed for analysis, providing a single measurement reflecting conditions over the last few days of deployment. Some passive monitors use a combination of contaminant uptake and tracer loss to determine contaminant flux. Passive samplers for liquid contaminants have been developed for metals, organic compounds, and radionuclides (Puschenreiter 2017; Forsberg et al. 2006; Murdock et al. 2001), and have been deployed in groundwater, surface water, wastewater streams, and even in air.

Passive samplers have two primary attributes that make them potentially beneficial to an ESM approach. The first attribute is that passive samplers can provide a low-cost sample collection approach, as they measure a time-integrated average concentration rather than a point-in-time measurement, with the potential to replace traditional purge-based sampling and low-flow purge methods without a loss in data quality (Vrana et al. 2005; ITRC 2006).

The primary driver for the increased use of passive sampling is the cost reduction associated with sample collection. Deployment and collection involve lowering the sampler into place and pulling it up - a matter of minutes compared to the hours associated with traditional pumped sampling. In addition, passive samplers are cost-effective because they require less hardware (e.g., pumps, hose, purge tanks), no power, and limited generated waste (Stroo et al. 2014).

The second attribute, in addition to cost savings, is that passive samplers allow time-integrated measurements of contaminant concentration. Because passive samplers accumulate contaminants over time, they provide a time-averaged concentration. This has several benefits, including increased temporal coverage, lower detection limits, uncertainty reduction associated with vertical heterogeneity, and mass flux estimates. Normal grab (pumped) samples are subject to both spatial and temporal variations, potentially missing or over representing episodic events. Passive sampling has the capacity to measure time-averaged concentrations over a period of weeks or months.

Because passive samplers do not induce flow within the well-bore, they can provide samples that, in some instances, may be more representative of the average concentration within the formation. In locations with

significant heterogeneities, active sampling provides a sample that is biased toward the portions of the aquifer with higher hydraulic conductivity (which are not necessarily the portions with the highest contaminant concentrations). A passive sample collects analyte under ambient gradient conditions, providing a measurement (potentially) more representative than an active sample. While ambient vertical flow may still exist in wells, and lead to a biased passive sample, this can be minimized by conducting vertical profiling of lateral inflow as part of the hydrologic characterization. Passive sampler depth placement within the borehole can be selected to minimize any bias from vertical flow.<sup>1</sup> Additionally, the relatively low cost of passive samples allows for multiple samples to be located vertically within a well, providing a better vertically integrated interpretation of the concentration.

Passive samplers can also detect contaminants that are at or below the detection limit of conventional techniques. Because passive samplers accumulate contaminants over time, longer exposure periods can result in larger mass uptake and correspondingly lower detection limits relative to whole water samples. While this is dependent on the analytical technique as well as the passive sampler design and performance, detection limits of up to10 times lower have been reported for passive samplers relative to grab samples (Hageman et al. 2019). Passive samplers often must be calibrated with the COC using expected flow rates to provide accurate measurements and determine the minimum and maximum deployment time periods.

While passive sampling provides some potential benefits, it also has limitations (Stroo et al. 2014). Specifically, not all passive samplers can be used for all analytes; certain passive samplers are not able to collect sufficient sample volume for analyses; some passive samplers may not fit in standard size well; and the methods (e.g., sorptive) of some passive samplers produce a calculated concentration rather than a measured concentration.<sup>2</sup> In addition, data obtained with passive samplers cannot be easily compared to historical samples collected with traditional methods. Diffusive transport and sorption of certain contaminants within a passive system can vary greatly with pH or ionic strength of solution, and these parameters are subject to change over long time periods (Fatin-Rouge et al. 2006). In DGT, organic complexes formed with metal ions may lower sorption to the resin and result in inaccurate concentration estimates. Biofouling can also affect pesticide uptake rates in accumulation devices (Harman et al. 2012). With these limitations in mind, DGT and DET are useful tools in sentinel wells where they can be used to detect contaminants above background levels.

Passive sample methodology is still being developed for a wide range of contaminants. Extended longterm passive monitoring (~1 year) is not currently used because biofouling, sampler saturation, and physical degradation can greatly diminish accuracy (Harman et al. 2012). For shorter time periods, such sampling is not uncommon for metal ions and some radionuclides, and results are often strongly correlated to grab samples (Martin et al. 2003). Passive sampling technology is more advanced for monitoring organic compounds and has been successfully deployed for VOCs and per- and polyfluoroalkyl substances (PFAS) (Nicolle et al. 2009; Kaserzon et al. 2019). Passive sampling is low in cost and labor, produces minimal waste, and can potentially provide insight into groundwater systems at higher spatial (vertical) and temporal resolution.

#### 5.2.6 Mass Flux and Mass Discharge

Passive flux monitors (PFMs) are a unique adaptation of passive samplers that provide estimates of contaminant flux and groundwater velocity. PFMs accumulate contaminants over a period of days or weeks while simultaneously releasing tracer compounds. The mass change for each species is used to calculate groundwater velocity and COC movement on a mass/time/area basis. When employed in

<sup>&</sup>lt;sup>1</sup> <u>https://clu-in.org/characterization/</u>

<sup>&</sup>lt;sup>2</sup> <u>https://www.serdp-estcp.org/Tools-and-Training/Environmental-Restoration/Monitoring-and-Characterization</u>

sufficient numbers, PFMs can provide a detailed temporal and spatial view into contaminant and groundwater movement (Verreydt et al. 2010). This application of passive sampling technology could be readily applied to ESM programs for both source term and diagnostic monitoring wells, though extended time periods of analysis are not currently recommended as fouling and alcohol biodegradation are inevitable (Bondehagen 2010).

PFMs are composed of a permeable tube filled with high-affinity sorbent for a specific COC. While now patented as Enviroflux<sup>™</sup>, PFMs were developed through funding provided by several government agencies (Campbell et al. 2006). Most devices use several alcohols of varying molecular weight and branching as tracer compounds. These tracers elute from the device at rates proportional to the groundwater flux. Analysis of vertical PFM sections is conducted at the end of sampling to determine COC accumulation and tracer loss. At least 32% of the initial alcohol must be retained at the end of sampling to provide useful results – incorporating several tracers is common to ensure adequate retention.

PFMs can be deployed for more than 2 months, allowing a time-integrated estimate of COC concentration even when present at trace levels. Vertical sectioning and positioning multiple units within wells can facilitate accurate determination of flux at different depths. The technology provides high-resolution analysis for CSM development, initial site analysis, and validation of remedial strategy. Conditions of low flux, or diminished contaminant flux over distance, indicate successful natural attenuation in an ESM setting (NRC 2005). In an ESM application, PFMs could be used to verify mass flux rate at the leading edge of a plume, as for a detached or non-contiguous plume, or used to verify the reduction in mass flux from a diminishing source scenario.

#### 5.2.7 Geophysical Monitoring

Geophysical monitoring encompasses a wide array of technologies (including electrical, magnetic, vibrational, radiation, and electromagnetic) used to measure properties of the earth. Geophysical measurement techniques have been applied to groundwater problems for different purposes, including plume location, vadose zone source, and treatment zone (Robinson et al. 2020; Johnson et al. 2015; Fernández de Vera et al. 2017; Kos 1997). Cross-borehole electrical resistivity tomography (ERT) has proven to be particularly useful in imaging sub-surface features along a transect (Englert et al. 2016; Perri et al. 2020), while surface methods can be better suited to 3D visualization (Márquez Molina et al. 2015; Meyerhoff et al. 2014) although the resolution of surface-based geophysics tends to diminish with increasing depth (e.g., seismic, electromagnetic methods). While trace level contaminants probably would not have enough response to be detected with ERT, if the contaminants were comingled with a species that did provide the necessary response (i.e., conductive salts), ERT methods may provide sufficient measurement resolution (Balbarini et al. 2018).

Geophysical monitoring can be costly but is powerful because of the large areas it can survey. It is even more powerful when comparing changes in response rather than quantifying the absolute magnitude (i.e. concentration) of a response. These properties indicate that geophysical techniques could be applied in an ESM program to verify plume size, shape, or velocity, eliminating the need for confirmatory measurements within the source zone. Similarly, geophysical measurements (in the saturated or vadose zone) could be used in a diminishing source zone scenario to verify that a source term was diminishing at the expected rate.

#### 5.2.8 Compound Specific Isotope Analysis

Detailed analysis of pollutant sources, concentrations, and degradation pathways can be obtained by compound-specific isotope analysis (CSIA). One drawback of CSIA is that samples need to be collected using traditional well sampling methodologies: mobilization, well purging with stabilization of

parameters, sample collection, and laboratory analysis. This methodology typically combines chromatography with isotope ratio mass spectrometry to measure isotopic ratios of elements in organic compounds (<sup>13</sup>C/<sup>12</sup>C, <sup>15</sup>N/<sup>14</sup>N, <sup>37</sup>Cl/<sup>35</sup>Cl, <sup>2</sup>H/<sup>1</sup>H). These measurements can be used to infer the extent of transformation and verify contaminant degradation in both time and space. CSIA is well established for organic legacy compounds such as chlorinated solvents, and is well suited for measurements over prolonged time scales (Elsner and Imfeld 2016). Isotope analysis has proven successful at elucidating the relative contributions of COC degradation, dilution, and sorption (Audí-Miró et al. 2015). Such detailed analysis comes at a cost, however, as nanogram quantities of contaminant are required, resulting in large sample volumes (>10 L) for micropollutants. Measurements also may require pre-enrichment, which can cause isotope fractionation, co-enrichment of organics, and inaccuracies, though more selective enrichment methods have recently been developed (Bakkour et al. 2018). Hence, CSIA may be best used to assess the attenuation capacity of the aquifer and the appropriateness of the ESM approach.

#### 5.2.9 Gas-Phase Sampling

While it is anticipated that most contaminant plumes where ESM may be a viable approach will not include VOCs as the primary COC, there may be applications where gas-phase sampling is needed; for example, in a slowly diminishing primary or secondary source and associated plume, or a persistent semi-volatile source where the break-down products are more volatile. Active collection of gas-phase samples could be cheaper than collection of groundwater samples, particularly if purge water disposal costs are high.

Adamson et al. (2012) discusses issues associated with long-term monitoring programs for contaminant plumes in groundwater and conducted a field validation program to evaluate three different vapor-phase sample collection methods: (1) headspace samples, (2) passive vapor diffusion samplers, and (3) field vapor headspace analysis of groundwater samples. While the authors concluded that gas diffusion samplers placed in the screened interval was the only effective gas-phase technique, they also noted that head space samples appeared to be biased because the water in the unscreened interval of the well was not representative of the water in the screened interval. Head space sampling for vapors may be representative for locations where the water elevation in the well and screened interval are close together.

## 5.3 Methods Synopsis

The various methods presented here represent a current summary of potential alternative monitoring technologies but are not indicative of the technological advances that may occur over the time frame of an ESM application. Hence, this review is intended to provide a starting point for identifying monitoring alternatives to traditional groundwater sampling. When monitoring is conducted over many decades, small cost savings on a per-sample or per-year basis can result in large cost savings over the duration of the monitoring period. Therefore, careful, adaptive planning is needed to select sampling techniques and technologies that provide a maximum benefit and minimal cost for ESM.

# 6.0 Conclusion

Passive remediation can be appropriate where (1) natural attenuation processes (and institutional controls) can be used to mitigate exposure to contaminated groundwater and (2) RAOs to maintain protectiveness of human health and the environment can be achieved. MNA is widely employed as a passive method of remediating contaminated zones, typically for plumes expected to reach objectives within less than 5 decades. Long-duration passive remediation using ESM can be a desirable option for large, complex sites with slow-moving plumes where active remediation is neither cost nor time effective and passive remediation can meet objectives but will require many decades.

ESM is a suitable approach that can support long-term remediation objectives when a plume is predictable and will remain within a containment zone, is expected to diminish over time, and will meet the compliance conditions determined for the site. Groundwater plumes may move during this time, but any plume advancement must stabilize or recede within the containment zone prior to reaching the receptor zone. In applying the ESM approach described in this document, it is important to consider the remediation decision and implementation process for contaminated sites. For CERCLA, selection of a long-duration passive remedy can be part of a standard remedial investigation/feasibility study process. Selection depends on demonstrating the reliability of plume behavior predictions to support the long-duration remedy and to select the boundaries of the containment zone and receptor zone.

The ESM approach is predicated on a sound CSM and predictive analyses that verify contaminant movement. Historical monitoring showing slow plume movement may also be an important factor supporting confidence in predictions of future plume behavior. Selection of a long-duration passive remedy could occur as part of remedy implementation, adaptive site management, or optimization. For instance, if active remediation is applied to diminish a plume to the point where passive remediation can meet ultimate RAOs, a long duration of passive remediation may still be required. Selection of long-duration passive remediation as a step after active remediation enables the use of data and performance analyses from the active remediation phase. In each situation, there will be some upfront effort within the CERCLA process to develop a suitable justification for selecting passive remediation.

The ESM approach builds from this information and applies monitoring that is consistent with the expected slow plume movement within the containment zone that is implicit in selection of the passive remedy. Thus, remediation planning during remedy selection for the passive remedy includes the evaluation of ESM elements as discussed in this document to ensure that the implementation will meet expectations of decision-makers, regulators, and stakeholders. When selected as part of a long-duration passive remedy, ESM can provide cost savings without compromising receptor safety relative to applying monitoring approaches designed for faster-moving plumes and shorter remediation durations. Cost savings are gained through reduced monitoring frequency and selecting optimized monitoring locations for sampling and analysis. Savings may also be realized through the employment of alternative or innovative monitoring technology over the duration of the remedy may provide additional efficiencies and cost savings as the capabilities of these techniques evolve. Statistical methods can also be employed to aid in the design and optimization of well networks and sampling strategy to best meet the requirements of the ESM scenarios described in this document. These methods can be valuable in translating the conceptual ESM approaches in this document to site-specific designs.

The ESM approach and example scenarios presented in this document are appropriate for sites where confidence in plume behavior is high and risk to receptors is low. When time scales for this type of

passive remediation extend to many decades, the ESM approach can be applied, focusing on exposure pathway monitoring to verify protectiveness, with a lower intensity of monitoring applied to confirm plume behavior with respect to meeting ultimate remediation objectives. This approach is suitable when plume movement is slow, risk of exposure is limited, and there is substantial evidence that the plume will dissipate before reaching downgradient receptors within the remediation period.

# 7.0 Quality Assurance

This work was performed in accordance with the Pacific Northwest National Laboratory Nuclear Quality Assurance Program (NQAP). The NQAP complies with DOE Order 414.1D, *Quality Assurance*. The NQAP uses NQA-1-2012, *Quality Assurance Requirements for Nuclear Facility Application*, as its consensus standard and NQA-1-2012, Subpart 4.2.1, as the basis for its graded approach to quality.

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# Appendix A

# Hypothetical Candidate Sites for ESM

Three hypothetical candidate sites for extended-scale monitoring (ESM) are presented to provide examples of ESM as concepts are described in this document. The three long-term monitored natural attenuation (MNA) scenarios are intended to highlight the evidence needed for ESM consideration and to illustrate potential monitoring approaches and potential challenges that may be encountered during ESM execution.

# A.1 Arsenic-Contaminated Site

This scenario describes application of ESM as a remedial option for groundwater at a long-term arseniccontaminated site resulting from solid waste disposal (Figure A.1, Table A.1). Unlined landfills containing arsenic were excavated to a depth of 5 m, removing the primary source of arsenic to groundwater; however, residual arsenic remains within the soil profile above the groundwater table, located at a depth of 15 m. Natural attenuation of arsenic occurs primarily by sorption and precipitation, which are also influenced by arsenic biotransformation, dilution, and dispersion. Partitioning into the solid phase is also strongly influenced by redox conditions because the solubility of arsenic-containing solids and the extent to which arsenic is adsorbed depend on its oxidation state. Arsenic plumes can be sequestered under oxidizing conditions with iron oxides or under reducing conditions as sulfides.

Multiple lines of evidence have demonstrated the attenuation capacity of the vadose zone and groundwater, including aqueous geochemical and redox conditions, solid phase characterization to provide quantitative information on arsenic association with solid phases, microbiological analysis, and data modeling. Groundwater monitoring data by Mann–Kendall trend for groundwater monitoring wells shows the plume is stable and neither expanding nor shrinking.

The site remedial investigation confirmed that the aquifer is composed of interbedded sand, limestone, and dolomite and that groundwater flow is downgradient, generally at right angles to equipotentials represented on the potentiometric surface (see Figure A.1). Hydraulic conductivity of the sand is on the order of  $10^{-7}$  to  $10^{-5}$  m/s and the hydraulic conductivity of the limestone and dolomite range from  $10^{-9}$  to  $10^{-6}$  m/s.

Elevated concentrations above the drinking water standard (10 ppb) are currently measured near the source at 12 to 20 ppb. However, modeling based on the CSM predicts that arsenic concentrations will remain above the drinking water standard for 150 years within an area 2 km downgradient from the current plume footprint. Arsenic concentrations are expected to diminish to concentrations below 10 ppb by the time the leading edge of the plume reaches the potential receptor location at 345 years.

Assuming no sequestration, the contaminated plume would have travelled a distance of 1 km in 20 years, but the current plume has only travelled 200 m from its source within that period. Future land use is industrial, so groundwater in this area is not used for drinking water supply. Site access is controlled through institutional controls. A river is located 5 km downstream from the site, which is the only potential downstream receptor zone. The slow rate of plume movement and low risk of exposure to downstream receptors provides strong evidence that natural attenuation processes will bring arsenic to cleanup goal concentrations through the application of the ESM approach.

Information Type	Description
Plume scenario	Groundwater plume with continuing (and diminishing) source
Hydrogeology	• Aquifer is composed of interbedded sand, limestone, and dolomite as determined by core from monitoring wells. Some uncertainty exists with respect to the influence of fractures in the limestone and dolomite.
Hydrogeologic characterization basis for ESM	<ul> <li>Flow direction downgradient from the main source area determined based on water level measurements</li> <li>Contaminant migration pathways based on point measurements at wells and groundwater modeling</li> <li>Hydrologic boundaries based on measured water levels and seasonal river stage</li> </ul>
Estimated travel time to downstream receptor	• Groundwater modeling estimates travel time to river at 345 years
Arsenic characterization basis for ESM	<ul> <li>Arsenic mass remaining in the vadose zone estimated based on cores; 3D distribution in vadose zone based on modeling</li> <li>Arsenic plume delineated using measured concentrations from existing monitoring well network collected over 20 years</li> <li>Hydrogeologic controls on groundwater and contaminant flow and rates of groundwater and contaminant flow</li> <li>Batch tests conducted to identify adsorption mechanisms</li> <li>Arsenic attenuation mechanisms determined by identifying the chemical forms of arsenic soils (e.g., X-ray diffraction, scanning electron microscopy / energy dispersive X-ray spectroscopy)</li> <li>Sequential batch leaching tests conducted to characterize arsenic readily solubilized from arsenic bound in minerals</li> <li>Arsenic sorption identified to iron hydroxide minerals and organic matter; formation of sulfide minerals</li> </ul>
Modeling	<ul> <li>Sequestered arsenic is relatively stable at the site via adsorption to iron oxyhydroxides</li> <li>Estimated potential exposure concentrations</li> </ul>
	<ul> <li>Estimated attenuation rates using actual data for calibration</li> <li>Evaluated effectiveness of dissolved oxygen to confirm redox conditions</li> <li>Identified attenuation predictions to be used to compare with actual data</li> </ul>
Predictive analyses	<ul> <li>Reactive transport model was calibrated and used to evaluate in situ leaching rates relative to aquifer adsorption and attenuation</li> <li>Arsenic stability was evaluated under both oxidizing and reducing conditions</li> </ul>
Flux to groundwater	• Flux to groundwater estimated at $(5 \text{ mg/m}^2/\text{yr})$ based on estimates of residual waste
Plume velocity	• ~10 m/yr
Uncertainty assessment	<ul> <li>Uncertainty explored with groundwater modeling with respect to (1) source loading, (2) historical process water volumes, (3) aquifer attenuation capacity, and (4) hydraulic conductivity estimates yielding estimated travel times to receptor zone that varied from 250 to 415 years</li> </ul>
Well locations	• Sentinel well locations based on predicted plume velocity and location of receptor zone (see Figure A.1)
Stakeholder and regulator engagement	<ul> <li>Provided objective information to assist in understanding the problem and remedy alternatives and solicited feedback</li> <li>Placed final decision with regulators and public based on measured data, analysis, and modeling results</li> <li>More frequent monitoring requested in initial phase, to become less frequent as measurements concur with predictive analyses</li> </ul>

#### Table A.1. ESM Approach for Arsenic

Information Type	Description
Initial monitoring	<ul> <li>First 5 years, annual sampling from groundwater and sentinel wells</li> <li>Monitor dissolved oxygen to confirm oxidizing conditions</li> <li>Monitor dissolved phase arsenic concentrations</li> <li>Monitor water levels to confirm no changes in hydraulic conditions</li> <li>Next 10 years, bi-annual sampling</li> <li>Subsequent sampling established with regulators and stakeholders</li> </ul>
5-year review	<ul> <li>First 5-year review supported by annual sampling at all wells within network</li> <li>Understand the attenuation mechanisms so that the risk for contaminant mobilization or remobilization can be anticipated, incorporated into the long-term monitoring plan, and addressed in a manner that ensures protectiveness of human health and the environment</li> <li>Requirements for subsequent reviews to be determined as part of ongoing discussions with regulators and stakeholders</li> </ul>
Requirements	<ul> <li>Plume stability needs to be consistently demonstrated by decreasing concentrations at all wells and with static or contracting plume boundaries</li> <li>If concentrations increase, then more frequent sampling will be required, the need for additional characterization data evaluated with subsequent updates to the CSM and numerical model, and the applicability of ESM re-evaluated</li> </ul>
Technology integration	• Low flow sampling to be tested during first 5 years for concentration representativeness for both dissolved oxygen and arsenic



Figure A.1. Conceptual depiction of the arsenic contaminated site.

## A.2 TPH-Contaminated Site

This scenario describes application of ESM as a remedial option for total petroleum hydrocarbon (TPH) contaminated groundwater site (Figure A.2, Table A.2). Access to the site is controlled, with no residents or public access allowed. The site contains multiple industrial areas spread out over many square miles. At one such industrial area, day tanks were used to house fuel (heating oil #2) at intermittently used

ancillary locations. These day tanks were refilled as needed though underground piping. At one such location, in the 1960s, the underground piping developed a leak. Eventually, discrepancies in the volumes between the larger supply tanks and the day use tanks were noted and the leak was identified. An estimated 60,000 gallons of fuel leaked into the vadose zone over a 5-year period. The piping was excavated and the leak fixed, but no additional remediation was performed. The result was a TPH source in the vadose zone that eventually reached the water table 45 m below grade. The contaminated groundwater plume may have gone undetected except a monitoring well intended for hydraulic gradient measurements (associated with a distant remedial action) was drilled downgradient of the spill site. The smell indicated petroleum hydrocarbons and reducing conditions. Follow-up water analysis confirmed the leaking pipe and repair as the likely source.

A remedial investigation/feasibility study was initiated following the discovery of TPH plume. Due to the thickness of the vadose zone, only three characterization wells were installed: one 100 m downgradient and two located 150 m downgradient. Because of other monitoring in the area, the hydraulic gradient was well characterized, allowing for a high degree of confidence in the placement of monitoring wells near the plume centerline. TPH measurements made in sediments collected during drilling indicated that the TPH was limited to the top meter of the water table. Groundwater samples collected from the three monitoring wells indicated an average water concentration of 600 mg/L 100 m downgradient of the spill and 3 mg/L 150 m downgradient of the spill. Dissolved oxygen was very low (less than 0.5 mg/L) in all three monitoring wells. Depth discrete water samples collected during drilling at the two downgradient wells indicated that dissolved iron and manganese concentrations were elevated near the top of the water table relative to samples collected 3 m below the top of the water table. Similarly, nitrate concentrations at the top of the water table were undetected (less than 1 mg/L), but close to 10 mg/L 3 m below the top of the water table. Sediment samples collected during drilling were also analyzed for the presence of TPHdegrading microorganisms. These tests confirmed the presence of TPH-degrading microorganisms, and additional sediment (collected during drilling) was used in slurry reactor tests to estimate the degradation rate. The degradation rate, the conceptual site model, and measured concentrations were used to develop a numerical model of the site.

A weight of evidence approach led to a conceptual model consistent with a diminishing source scenario. Microbial activity results in TPH degradation, as evidenced by the low dissolved oxygen and nitrate and the elevated iron and manganese (which are used as electron donors after oxygen and nitrate have been consumed). The numerical modeling indicated that the plume will recede gradually over 100 to 150 years. The long duration is primarily driven by the depth of the vadose zone as the source will continue to feed the groundwater plume for a substantial amount of time.

This site would normally be a good candidate for source term removal and MNA of the groundwater plume. However, the depth of the vadose zone makes excavation/removal an expensive solution to implement. Due to the arid environment and sandy lithology (which results in moisture content on the order of 2%), bioventing was considered to have only a marginal chance of success. Irrigation of the vadose zone to enhance bioventing was not desirable as it could result in gradient changes impacting other nearby remediation activities.

An ESM approach is a potentially viable solution for treatment of this TPH contaminant plume. After characterization, it is understood to be slow moving with an active degradation mechanism. The nearest receptor is a publicly accessible river 2 km downgradient, and Monte Carlo numerical simulations indicated that there is a near-zero probability of contaminants from this plume reaching the river. Access control and other administrative controls are expected to remain in-place for the lifespan of this contaminant plume. While detailed planning is necessary to establish the framework for an ESM

approach, the installation of a sentinel well and continued monitoring at existing monitoring wells could be sufficient for long-term monitoring.





Information Type	Description
Plume scenario	Groundwater plume with continuing (and diminishing) source
Hydrogeology	• Aquifer is characterized and understood. Characterization largely associated with other near-by remediation efforts.
Hydrogeologic characterization basis for ESM	<ul> <li>Flow direction downgradient from the main source area determined based on water level measurements</li> <li>Contaminant migration pathways based on point measurements at wells and groundwater modeling</li> </ul>
Estimated travel time to downstream receptor	Groundwater modeling estimates plume never reaches river
TPH characterization basis for ESM	<ul> <li>TPH mass remaining in the vadose zone estimated based on fuel inventory logs and modeling</li> <li>TPH plume delineated using measured concentrations from existing monitoring well network</li> <li>Hydrogeologic controls on groundwater and contaminant flow and rates of groundwater and contaminant flow</li> <li>Batch tests conducted to identify attenuation/degradation mechanisms</li> </ul>
Modeling	<ul> <li>Estimated potential exposure concentrations</li> <li>Estimated attenuation rates using actual data for calibration</li> <li>Identified attenuation predictions to be used to compare with actual data</li> </ul>
Predictive analyses	<ul><li>Transport model was calibrated to this data</li><li>Sensitivity analysis done to evaluate confidence in predictions</li></ul>
Flux to groundwater	• Flux to groundwater estimated based on literature values and soil properties
Plume velocity	• ~1 m/yr
Uncertainty assessment	Uncertainty explored with groundwater modeling
Well locations	• Sentinel well locations based on predicted plume velocity and location of receptor zone

Table A.2.	ESM	Approach	for TPH
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Information Type	Description
Stakeholder and regulator engagement	<ul> <li>Provided objective information to assist in understanding the problem and remedy alternatives and solicited feedback</li> <li>Placed final decision with regulators and public based on measured data, analysis, and modeling results</li> <li>More frequent monitoring requested in initial phase, to become less frequent as measurements concur with predictive analyses</li> </ul>
Initial monitoring	<ul> <li>First 5 years, annual sampling from groundwater and sentinel wells</li> <li>Monitor dissolved oxygen to confirm oxidizing conditions</li> <li>Monitor TPH concentrations</li> <li>Monitor water levels to confirm no changes in hydraulic conditions</li> <li>Next 10 years, bi-annual sampling</li> <li>Subsequent sampling established with regulators and stakeholders</li> </ul>
5-year review	<ul> <li>First 5-year review supported by annual sampling at all wells within network</li> <li>Requirements for subsequent reviews to be determined as part on ongoing discussions with regulators and stakeholders</li> </ul>
Requirements	<ul> <li>Plume stability needs to be consistently demonstrated</li> <li>Concentrations may increase without triggering the need for more frequent sampling</li> <li>Updates to the CSM and numerical model, and the applicability of ESM, may be re-evaluated</li> </ul>
Technology integration	• Passive sampling is an established approach for organic compounds

# A.3 Mixed Radionuclide-Contaminated Site

This scenario describes application of ESM as a remedial option for a landfill at a government testing facility containing tritium, uranium, and other mixed wastes due to activities related to explosive testing (Figure A.3, Table A.3). Solid wastes from these tests were placed in unlined landfills with an approximate depth of 10 m. Discharges to the landfills were terminated after 30 years of operation. Soil and groundwater contamination includes tritium, strontium-90 (Sr-90), uranium (U), trichloroethene (TCE), and 1,3,5-hexahydro-1,3,5-trinitrotriazine (RDX). Continuing sources were eliminated when contaminated soils were removed to a depth of ~5 m and their surfaces capped. Contaminants of concern have been measured under the trenches at concentrations greater than, or close to, maximum contaminant levels (MCLs) and other threshold concentrations. RDX is already below the MCL beneath the trenches.

Multiple groundwater aquifers exist beneath the site. The upper aquifer consists of interbedded sand and silty clay with clay lenses. The aquifer is shallow and thin, with a depth to water of ~10 m and an average saturated thickness of approximately 5 m. The aquifer is approximately 200 m wide and has no history of use due to its low yield and the availability of other nearby water sources. Sandstone exists beneath a clay aquitard that serves as an impermeable boundary to the upper aquifer, preventing contaminant migration to the lower aquifers. The sandstone has been interpreted as a layered aquifer system with groundwater occurring in discrete horizons with occasional vertical connection. Groundwater movement is interpreted to be variable with both primary granular flow and secondary flow along fractures.

Neighboring areas around the trenches includes two municipal landfill sites. Historically, these land uses have included excavation, burial of municipal waste, and leachate extraction, which could have an effect on the site hydrological regime. The area is located on the southern edge of a catchment that flows into a stream located at a distance of approximately 5 km from the site. Groundwater flows average 10 m/yr. The stream flows to the east, eventually reaching a bay located 75 km from the site. The largest near-term risk is associated with mobile contaminants (e.g., tritium) reaching the stream. Intense, episodic rainfall

events have the potential to increase the hydraulic gradient and accelerate contaminant transport to the stream for contamination that is already located downstream of the capped landfill.

Column leach tests were performed on several clay samples to identify a range of representative distribution coefficients (K<sub>d</sub>) for uranium, RDX, TCE, and Sr-90 transport, with average K<sub>d</sub> values reported here. Results indicated that tritium moves unretarded, TCE moves with a low retardation (K<sub>d</sub> of 0.3 mL/g), RDX moves more slowly (K<sub>d</sub> of 1.5 mL/g), and U and Sr-90 have the highest distribution coefficients at 5.0 and 25 mL/g, respectively. Distribution coefficients were used to support solute transport modeling, with attenuation simulated as an equilibrium partitioning process between the aqueous phase and aquifer materials. Hydraulic properties were obtained from sediment samples.

Simulations predicted that (undecayed) tritium is the first contaminant to reach the stream within 50 years, so radioactive decay has an impact on significantly reducing tritium flux to the stream (i.e., four half-lives). TCE reaches the river in 65 years assuming only aqueous advection at concentrations below the MCL, but a low concentration of TCE reaches the river sooner due to volatilization and much faster gas phase diffusion in the vadose zone than repartitioning into the aquifer downgradient. RDX reaches the river in 85 years at concentrations below the MCL, assuming no degradation. U reaches the river in 260 years at concentrations below the MCL. Sr-90 is highly retarded, reaching the river in 1,260 years, but given the 29.1 year half-life, Sr-90 will have decayed to nearly all Yttrium-90 (Y-90) with a half-life of 64 hours, then to stable Zirconium-90 (Zr-90) within 300 years (i.e., 10 half-lives).

To further assess risk associated with contaminant arrivals at the stream, an analytical solution accounting for dilution and volatilization was used assuming that the current plumes would immediately discharge through the stream banks. After mixing, predicted peak stream concentrations indicated that tritium, TCE, and uranium would dilute significantly below MCLs established for aquatic and ecological receptors. With the potential for multiple episodic events to accelerate contaminant transport to the stream, the stakeholder community requested repetitive stream sampling. Because frequent sampling to accommodate episodic events was logistically challenging, a passive sampler was identified as an appropriate technology for monitoring contaminant concentrations in the stream.

Although the aquifer is generally an oxidative environment, under reducing conditions, the TCE could undergo reductive dichlorination, producing dichloroethylene (DCE) and vinyl chloride (VC) daughter products. Since the aquifer is shallow and consists of sand and silt, the aquifer is likely to sustain aerobic conditions. Although anaerobic conditions could exist within the clay lenses, transport through these clay lenses would be limited. If diagnostic wells detect one of these degradation products, compound specific isotope analysis (CSIA) can trace the reactive chlorine atoms by measuring the <sup>37</sup>Cl/<sup>35</sup>Cl isotopic ratio. This method can provide spatial and temporal information to verify the extent of TCE degradation within the upper aquifer and inform long-term remedial planning.

Given that transport and mixing calculations identified minimal risk for exceeding MCLs and the subsequent minimal risk of exposure, the framework for an ESM remedy can be established. Modeling predictions, in conjunction with monitoring for the most mobile contaminants (tritium and TCE), provided the technical basis for selecting an ESM remedy, but at later times, uranium represents the highest risk and will be used to manage the remedy.



Figure A.3. Conceptual depiction of the mixed waste (composite) contaminated site.

Information Type	Description
Plume scenario	Composite groundwater plumes with co-mingled contaminants
Hydrogeology	• Shallow sand and silty-clay aquifer underlain by an aquitard and sandstone
Hydrogeologic characterization basis for ESM	<ul> <li>Flow direction downgradient from the main source area determined based on water level measurements</li> <li>Contaminant migration pathways based on point measurements at wells and groundwater modeling</li> </ul>
Estimated travel time to downstream receptor	• Groundwater modeling estimates travel time to river at 50 years for tritium, 65 years for TCE (assuming aqueous advection), 85 years for RDX (assuming no degradation), 260 years for uranium, and 1,260 years for strontium-90 (where it will be nearly all decayed to stable Zr-90)
Characterization basis for ESM	<ul><li>Trenches capped so no continuing sources are anticipated from the vadose zone</li><li>Column tests conducted to identify distribution coefficients</li></ul>
Modeling	• Transport predictions for all three contaminants are anticipated to decrease below MCLs within 105 years
Predictive analyses	<ul> <li>Transport model calibrated to concentration data</li> <li>Several samples used in column leach tests to identify potential range of transport behavior that was simulated in the modeling</li> </ul>
Flux to groundwater	• No continuing source assumed given excavation depth and capping of the trenches
Plume velocity	<ul> <li>Tritium flows with groundwater and has the highest velocity of 10 m/yr, which will be used to manage the composite plume at early times</li> <li>Uranium velocity is estimated at 0.1 m/yr and will be used to manage plume movement at later times</li> </ul>

Table A.3.	. ESM Approac	h for Mixed	Waste Co	mposite Plumes
	11			1

Information Type	Description
Uncertainty assessment	<ul> <li>Uncertainty explored with representative distribution coefficients in the groundwater modeling</li> <li>Nearby landfills can potentially impact future flow regime</li> </ul>
Well locations	• Sentinel well region based on tritium predicted plume velocity, location of receptor zone, and municipal landfill locations
Stakeholder and regulator engagement	• Web portal established to communicate technical information in story map format, allowing for stakeholders to submit concerns electronically between formal meetings and reviews
Initial monitoring	<ul> <li>First 5 years, annual sampling from existing groundwater wells and new sentinel wells to establish groundwater concentration trends and monitor hydrologic boundary influences from municipal landfills</li> <li>Next 10 years, bi-annual sampling if landfill activity has stabilized</li> <li>Subsequent sampling established with regulators and stakeholders</li> </ul>
5-year review	<ul> <li>First 5-year review supported by annual sampling at all wells within network</li> <li>Requirements for subsequent reviews to be determined as part on ongoing discussions with regulators and stakeholders</li> </ul>
Requirements	<ul> <li>Tritium concentrations will be used as an indicator of plume stability, with concentrations in sentinel wells triggering the need for more frequent sampling and potential exit from ESM</li> <li>If TCE degradation products are detected, then additional characterization data from CSIA will be used to determine the extent of transformation, and the applicability of ESM re-evaluated</li> </ul>
Technology integration	<ul> <li>Standard groundwater sampling planned as tritium is used to manage the composite plume</li> <li>If TCE degradation products are detected, CSIA will be included in the standard groundwater sampling</li> </ul>

# Appendix B

# **Software Packages**

This appendix contains a summary of software packages that may be useful for implementation or review of extended-scale monitoring plans.

# B.1 DOE Visual Sample Plan (VSP) Software

The Visual Sample Plan (VSP) software assists in the development of cost-effective, statistically defensible sampling plans, and is applicable to any 2D sampling plan. VSP calculates the number of samples under various scenarios, includes cost considerations, and provides random or gridded sampling locations for overlay onto a site map. The VSP website (<u>https://www.pnnl.gov/projects/visual-sample-plan</u>) also provides training information and links to other sites that provide software for use in contaminated site cleanup. Design and analytics foci include environmental monitoring and stewardship, and long-term legacy and groundwater monitoring. The statistics package provides an assessment of sampling frequency, the number and location of well locations. Based on statistical confidence to determine the number of samples and frequency, the software may not be well suited to limited databased plume projections.

## B.2 Federal Remediation Technologies Roundtable Decision Support Tools Matrix

Decision support tools (DSTs) are interactive software tools used by decision-makers to help answer questions, solve problems, and support or refute conclusions. They can be incorporated into a structured decision-making process for environmental site cleanup. DSTs often support multiple functions, such as data acquisition, spatial data management, modeling, and cost estimating. The Federal Remediation Technologies Roundtable matrix (<u>https://frtr.gov/decisionsupport/</u>) is a table that provides general information about each DST, such as the types of files that may be imported to, or exported from, the DST, the characteristics of applicable sites (contaminants and media) and the functions it performs. All DSTs that were evaluated are free to the public.

## **B.3 Monitoring and Remediation Optimization System**

The Monitoring and Remediation Optimization System (MAROS) software has been developed by Groundwater Services Inc. and the University of Houston for the Air Force Civil Engineering Center. The software provides site managers with a strategy for formulating appropriate long-term groundwater monitoring programs that can be implemented at lower costs. MAROS is a decision support tool based on statistical methods applied to site-specific data that accounts for relevant current and historical site data as well as hydrogeologic factors (e.g., seepage velocity) and the location of potential receptors (e.g., wells, discharge points, or property boundaries). Based on this site-specific information, the software suggests an optimization plan for the current monitoring system in order to efficiently achieve the termination of the monitoring program.

Plume-level analysis calculates total contaminant mass remaining in a plume relative to total area captured by sampling wells. Analysis can tolerate concentration uncertainty in the generation of spatial distribution maps, though its intended purpose is to highlight appropriate frequency of sampling or well coverage to improve confidence.

The features available in the MAROS software are designed to optimize a site-specific monitoring program that is currently tracking the occurrence of contaminant migration in groundwater. As stated above, MAROS is a decision support tool based on statistical methods applied to site-specific data that account for hydrogeologic conditions, groundwater plume stability, and available monitoring data. This process focuses on analyzing relevant current and historical site data and optimizing the current monitoring system in order to efficiently achieve the termination of the monitoring program. For example, plumes that appear to be decreasing in extent, based on adequate monitoring data over a several year period, can be analyzed statistically to determine the strength and reliability of the trend. If it can be demonstrated statistically through plume analyses (i.e., Mann-Kendall trend analysis and/or linear regression trend analysis or moment analysis) and/or external plume information (modeling or empirical) that the plume is shrinking with a high degree of confidence, then future monitoring may be suspended. MAROS has the option to either use simple rules based on trend analysis results and site information or more rigorous statistical methods to determine the minimum number of wells and the minimum sampling frequency and well density required for future compliance monitoring at the site.

# B.4 Sustainable Management Approaches and Revitalization Tools - electronic

Sustainable Management Approaches and Revitalization Tools – electronic (SMARTe) is a Web-based information source and decision support tool. The purpose of SMARTe is to aid stakeholders in identifying, applying, and integrating tools and technologies to facilitate the revitalization of potentially contaminated sites in the United States. SMARTe is intended to be a web-based system that can be updated as new tools, technologies, and approaches become available for revitalization.

# B.5 U.S. EPA completion of Groundwater Remedial Action Statistical Tool (e.g., attainment guidance)

This is a simple spreadsheet tool that performs trend analysis and other useful tasks (https://www.epa.gov/superfund/completing-groundwater-response).

## **B.6 ProUCL Software**

ProUCL is a comprehensive, free, statistical software package with statistical methods and graphical tools to address many environmental sampling and statistical issues. U.S. Environmental Protection Agency (EPA) regions, states, contractors, and other stakeholders use ProUCL to establish background levels, determine outliers in data sets, and compare background and site sample data sets for site evaluation and risk assessment.

# **B.7** Spatial Analysis and Decision Assistance

Spatial Analysis and Decision Assistance (SADA) is a free software package from the University of Tennessee that integrates modules for visualizing contaminant concentrations, geospatial analysis, statistical analysis, human health risk assessment, cost/benefit analysis, sampling design, and decision analysis. SADA can be used to address site-specific concerns when characterizing a contaminated site, assessing risk, determining the location of future samples, and designing remedial action.

## **B.8 Natural Attenuation Software**

Natural Attenuation Software (NAS) is a screening tool to estimate remediation time frames for monitored natural attenuation (MNA) to reduce groundwater contaminant concentrations to regulatory limits, and to assist in decision-making on the level of source zone treatment in conjunction with MNA using site-specific remediation objectives. NAS is designed for application to groundwater systems consisting of porous, relatively homogeneous, saturated media such as sands and gravels, and assumes that groundwater flow is uniform and unidirectional. NAS consists of a combination of analytical and numerical solute transport models. Some natural attenuation processes that NAS models include are advection, dispersion, sorption, non-aqueous phase liquid dissolution, and biodegradation. NAS determines redox zonation, and estimates and applies varied biodegradation rates from one redox zone to the next.

## B.9 Mass Flux Toolkit

The Mass Flux Toolkit, developed for the U.S. Department of Defense Environmental Security Technology Certification Program, is an easy-to-use software tool that enables users to learn about different mass flux approaches, calculate mass flux from transect data, and apply mass flux values to managing groundwater plumes. The Toolkit presents the user with three main options:

- A module to calculate the total mass flux across one or more transects of a plume, calculate the uncertainty in the calculation, and plot mass flux vs. distance to show the effect of remediation/impact of natural attenuation processes.
- A module allowing users to perform critical dilution calculations for plumes approaching production wells or streams. An additional feature calculates the capture zone of the supply well and compares it to the transect used to calculate the mass flux, directing the user to alter the transect dimensions if the transect does not encompass the capture zone.
- A module that provides a review of theory and methods of estimating mass flux.

# **B.10 Earth Volumetric Studio**

Earth Volumetric Studio unites advanced volumetric gridding, geostatistical analysis, and 4D visualization tools. Studio can be used to analyze all types of analytical and geophysical data in any environment (e.g., soil, groundwater, surface water, air, noise, resistivity, etc.). Earth Volumetric Studio's integrated geostatistics provides quantitative evaluation of the quality of the data and site models and identify locations that require additional data collection.

Features include borehole and sample posting; parameter estimation using 2D and 3D kriging algorithms with best fit variograms; exploding geologic layers; finite-difference and finite-element modeling grid generation; advanced gridding; comprehensive Python scripting of virtually all functions; high level animation support; interactive 3D fence diagrams; multiple analyte data analysis; and integrated volumetric and mass calculation for soil and groundwater contamination. Integrated geostatistics offer quantitative appraisal of the quality of site assessments and identification of optimal new sample locations at sites that require additional investigation. It includes features for remediation but is strongly geared toward the mining industry.

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