

PNNL-30441

# Guidance for Monitoring Passive Groundwater Remedies Over Extended Time Scales

September 2020

Brad G. Fritz\* Michael J. Truex\* Vicky L. Freedman\* Christopher Bagwell\* Richard J. Cameron\* Jonathan Counts\* Louis E. Martino\*\* Kurt C. Picel\*\* John Quinn\*\* Eugene Y. Yan\*\*

\*Pacific Northwest National Laboratory \*\*Argonne National Laboratory



Prepared for the U.S. Department of Energy under Contract DE-AC05-76RL01830

#### DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes **any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.** 

#### PACIFIC NORTHWEST NATIONAL LABORATORY operated by BATTELLE for the UNITED STATES DEPARTMENT OF ENERGY under Contract DE-AC05-76RL01830

#### Printed in the United States of America

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831-0062; ph: (865) 576-8401 fax: (865) 576-5728 email: <u>reports@adonis.osti.gov</u>

Available to the public from the National Technical Information Service 5301 Shawnee Rd., Alexandria, VA 22312 ph: (800) 553-NTIS (6847) email: orders@ntis.gov <<u>https://www.ntis.gov/about</u>> Online ordering: <u>http://www.ntis.gov</u>

# **Guidance for Monitoring Passive Groundwater Remedies Over Extended Time Scales**

September 2020

Brad G. Fritz\* Michael J. Truex\* Vicky L. Freedman\* Christopher Bagwell\* Richard J. Cameron\* Jonathan Counts\* Louis E. Martino\*\* Kurt C. Picel\*\* John Quinn\*\* Eugene Y. Yan\*\*

\*Pacific Northwest National Laboratory \*\*Argonne National Laboratory

Prepared for the U.S. Department of Energy under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory Richland, Washington 99354

# 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. MNA can also be used after active remediation has been completed (e.g., pump-and-treat) as a polishing step to reach ultimate remedial action objectives. However, MNA and existing monitoring guidance primarily target situations where the remedial action objectives are met within a few decades. When timescales for passive remediation extend to many decades, 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 receptors will not be impacted within the remediation timeframe.

ESM applies to slow moving groundwater contaminant plumes and emphasizes monitoring primarily of potential 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 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 change are slower. To this end, a scenario-based strategy is described for different plume and source conditions, defining a controlled zone and receptor zone for all scenarios. The controlled zone is the area where 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 controlled zone, slow plume migration may occur, leading to concentrations which 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 controlled zone and diminish to meet compliance standards within the extended timeframe (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 controlled zone. An ESM approach is thus expected to require less frequent sampling than approaches used for conventional scale remediations.

The guidance provided in this document is intended to 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. 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 controlled zone and to verify that the plume is behaving as predicted, consistent with the conceptual site model. This means that a standard monitoring tool may be implemented in a nontraditional manner to verify performance. 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.

# Acronyms and Abbreviations

AFB	Air Force Base
AFCEE	Air Force Center for Engineering and the Environment
ARAR	applicable or relevant and appropriate requirements
CERCLA	Comprehensive Environmental Resource, Conservation, and Liability Act
COC	contaminant of concern
COPC	contaminants of potential concern
CSIA	compound- specific isotope analysis
CSM	conceptual site model
CSMoS	Center for Subsurface Modeling Support
DENR	U.S. Department of Environment and Natural Resources
DET	diffusive equilibration in thin films
DGT	diffusive gradients in thin films
DoD	U.S. Department of Defense
DOE	U.S. Department of Energy
DQO	data quality objective
DST	Decision Support Tool
EPA	U.S. Environmental Protection Agency
ESM	extended-scale monitoring
ESTCP	Environmental Security Technology Certification Program
FOCS	fiber optic chemical sensors
GIS	Geographic Information Systems
GMS	Groundwater Modeling System
ISM	Integrated system monitoring
ITRC	Interstate Technology & Regulatory Council
LOD	limit of detection
LOQ	limit of quantitation
LTM	long-term monitoring
MAROS	Monitoring and Remediation Optimization System
MNA	Monitored Natural Attenuation
NAPL	non-aqueous phase liquid
NAS	Natural Attenuation Software
NRMRL	National Risk Management Research Laboratory
ORP	oxidation reduction potential
OSWER	Office of Solid Waste and Emergency Response
PFAS	per- and polyfluoroalkyl substances
PFM	passive flux monitor

PIM	polymer inclusion membrane	
POCIS	polar organic chemical integrative sampler	
PTB	permeable treatment barriers	
PVD	passive vapor diffusion	
RAO	referred to as remedial action objectives	
RBDC	risk-based decision criteria	
ROD	Record of Decision	
SADA	Spatial Analysis and Decision Assistance	
SERDP	Strategic Environmental Research and Development Program	
SOMERS	Scientific Opportunities for Monitoring at Environmental Remediation Sites	
SPE	screen printed electrode	
SSRBL	site-specific risk-based levels	
TI	technical impracticability	
TRV	Toxicity Reference Values	
95UCL	95% Upper Confidence Limit	
USGS	U.S. Geological Survey	
VOC	volatile organic compound	
VSP	Visual Sample Plan	

# Contents

Summa	ary			ii
Acrony	ms and	Abbrevia	tions	iii
Conten	ıts			v
1.0	Introdu	ction		1.1
	1.1	Monitor	ed Natural Attenuation in Groundwater in an Extended Scale Context	1.1
2.0	Extend	ed-Scale	Monitoring Considerations	2.1
	2.1	Monitor	ing Objectives	2.2
	2.2	Quantita	tive Conceptual Site Model	2.2
	2.3	Monitor	ing Network	2.3
	2.4	Monitor	ing Frequency	2.3
	2.5	Regulate	bry Considerations	2.3
	2.6	Stakeho	lder Considerations	2.4
3.0	Scenari	ios for Ex	tended-Scale Monitoring	3.1
4.0	Implen	nentation	Approach	4.1
	4.1	Detache	d Plume	4.3
		4.1.1	Phase 1: Initial Monitoring of the Existing Well Network	4.4
		4.1.2	Phase 2: Expanded Well-network Monitoring	4.5
	4.2	Diminis	hing Source and Plume	4.6
		4.2.1	Phase 1: Initial Monitoring of the Existing Well Network	4.7
		4.2.2	Phase 2: Expanded Well-network Monitoring	4.8
	4.3	Non-Co	ntiguous Contaminated Zones	4.8
		4.3.1	Phase 1: Initial Monitoring of the Existing Well Network	4.10
		4.3.2	Phase 2: Expanded Well-network Monitoring	4.11
	4.4	Compos	ite Plume	4.11
		4.4.1	Phase 1: Initial Monitoring of the Existing Well Network	4.13
		4.4.2	Phase 2: Expanded Well-network Monitoring	
	4.5	Additior	nal Considerations and Configurations	4.14
		4.5.1	Long-Term Data Management and Interpretation Considerations	4.15
		4.5.2	Managing Changing Hydraulic Conditions	4.15
		4.5.3	Managing Unexpected Plume Behavior	4.16
		4.5.4	Monitoring Only at Sentinel and/or Diagnostic Locations	4.16
5.0	Sampli	ng Metho	dology	5.1
	5.1	Optimiz	ation of Sample Collection	5.2
		5.1.1	Sentinel Wells	5.2
		5.1.2	Sample Design	5.3
	5.2	Alternat	ive Sampling Options	5.4
		5.2.1	Sampling	5.4

	5.2.2	Surrogate Species	
	5.2.3	Sensors	5.5
	5.2.4	Groundwater Flow Characterization	5.6
	5.2.5	Passive Monitoring	5.7
	5.2.6	Mass Flux and Mass Discharge	5.8
	5.2.7	Geophysical Monitoring	5.9
	5.2.8	Compound Specific Isotope Analysis	5.9
	5.2.9	Gas-phase Sampling	5.10
	5.2.10	Methods Synopsis	5.10
6.0	Conclusion		6.1
7.0	References		
Appendi	ix A – Data Qual	ity Objectives in an Extended Plume Monitoring Scenario	A.1
Appendi	ix B – Software H	Packages	B.1
Appendi	ix C Sentinel Wel	ls	C.1

# Figures

Figure 3.1. Con	ceptual depiction of a detached plume that is translating and diminishing. Over time the plume size and position changes progressively through Conditions 1, 2, 3, and 4 (each condition represents a conceptual change in plume configuration and location over time).	3.2
Figure 3.2. Con	ceptual 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.	3.2
Figure 3.3. Con	ceptual depiction of a noncontiguous contaminated zones that can potentially be managed as a composite "plume" (dotted line).	3.2
Figure 3.4. Con	ceptual depiction of a composite plume/source situation with co-mingled contaminants that can potentially be managed as a composite with respect to protection of the receptor zone.	3.3
Figure 4.1. Con	ceptual well network for extended-scale monitoring of a detached-plume scenario. The site and plume conditions are such that the plume translates along the exposure pathway (e.g., from location 1 to 2 to 3 to 4) but diminishes such that the receptor zone is not affected.	4.4
Figure 4.2. Con	ceptual well network for extended-scale monitoring of a diminishing source and plume scenario. In this scenario, the plume may expand and then decline (e.g., as shown by progression from numbers 1 to 3 for the source and the plume) in response to source flux changes and any previous remediation conditions	4.7
Figure 4.3. Con	ceptual well network for extended-scale monitoring of a noncontiguous contaminated zone scenario. In this scenario, individual contaminated zones are present as identified by previous site efforts and, collectively, these contaminated zones are not expected to expand to reach receptors and will ultimately decline to meet objectives for the controlled zone over time.	4.10

igure 4.4. Conceptual well network for extended-scale monitoring of a composite plume	
scenario. In this scenario, individual plumes (of different contaminants) are	
present as identified by previous site efforts and, collectively, these plumes are	
not expected to expand to reach receptors and will ultimately decline to meet	
objectives for the controlled zone over time4	.13

# Tables

Table 1.1. Monitoring Objectives Identified in MNA Guidance	. 1.2	2

# 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 objectives of the site being monitored and the stage of the remediation process (Bunn et al. 2012). Monitoring issues stem from either failing to meet objectives and data needs or from being overly expensive. 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. Although SOMERS provides a foundation for developing a site monitoring plan centered on the CSM, it does not provide detailed guidance for monitoring throughout the different remediation stages. Here, we expand on some of the SOMERS concepts and present guidance for development of a new sort of monitoring program, 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. MNA is often used after active remediation techniques have been completed (e.g., pump-and-treat). Multiple guidance documents for the design of MNA monitoring programs are available (ITRC 2007, ITRC 2010; Wilson 2012), providing information on spatial and temporal monitoring intensity. 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 controlled zone separate from receptors. Within this zone, natural processes such as biodegradation, dilution, and evaporation impede plume transport (USEPA 1999b). 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 1.1. Information supporting these objectives provides confidence in the natural attenuation process and the ability to maintain protectiveness.

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). 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; Memon 2014). TI waivers may involve the establishment of groundwater management or containment zones, with passive or active measures and actions applied to meet site objectives, based on the ARAR waiver designation. Typically, extended monitoring time periods are needed for TI waiver applications to verify compliance with ARAR waiver designations and to ensure protectiveness.

MNA Objective <sup>1</sup>			
1."Demonstrate that nat occurring according t			
2. "Detect changes in er (e.g., hydrogeologic, microbiological, or oth reduce the efficacy of attenuation processe	geochemical, her changes) that may f any of the natural		
3."Identify any potential transformation produce			
4. "Verify that the plume down gradient, latera	(s) is not expanding (either lly or vertically)"		
5. "Verify no unacceptat receptor"	ole impact to downgradient		
6."Detect new releases environment that cou of the natural attenua	Id impact the effectiveness		
7."Demonstrate the effic that were put in place receptors"	cacy of institutional controls to protect potential		
8. "Verify attainment of r	emediation objectives"		

Table 1.1. Monitoring Objectives Identified in MNA Guidance

<sup>1</sup> Direct quotes from the "Performance Monitoring and Evaluation" subsection within the "Implementation" section of the EPA OSWER Directive 9200.4-17P (USEPA 1999c).

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 a long time period. Passive remedies may also include assuring that the groundwater plume is contained within a particular zone. However, such containment strategies are only recommended when plume movement and contaminant flux is efficiently and persistently slowed by natural conditions (Rügner et al. 2006).

Monitoring intensity and locations 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 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 where the rate of change in plume conditions is slow. For example, the New Jersey Department of Environmental Protection (NJDEP 2012) describes a process for determining the monitoring frequency of sentinel wells as the seepage velocity divided by half the distance between the source and the nearest receptor. 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. Annual sampling is likely cost prohibitive and unnecessary, whereas sampling once every 180 years does not demonstrate protectiveness and meet regulatory 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 about 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, hydrogeologic, geochemical, and contaminant-related conditions as well as large-scale or surface conditions.

The ITRC (2017) document provides guidance and a framework for the use of adaptive site management approaches for complex site conditions. 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 monitoring guidance that complements existing MNA monitoring guidance for long-duration situations (e.g., longer than about 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. The ESM approach is not intended for shorter-duration remediation (e.g., less than 50 years) or groundwater plumes that pose short-term exposure potential.

This document is structured to provide a description of the ESM approach and monitoring tool resources. Section 2 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. These scenarios are then used in Section 4 as generic case studies to describe implementation approaches and demonstrate the type of monitoring strategy appropriate for each of the scenarios described in Section 3. Section 5 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. Appendices contain supplemental information on data quality objectives relevant to ESM (Appendix A), software packages to support ESM, (Appendix B), and the use of sentinel wells for verifying compliance with protection of receptors to support ESM (Appendix C).

# 2.0 Extended-Scale Monitoring Considerations

An ESM approach is not appropriate for most groundwater clean-up sites. Most groundwater contamination sites 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 specific criteria. Site characteristics that can make the ESM approach a possibility include the following:

- 1. a cleanup remedy involving a passive remediation approach (though potentially the ESM approach could be linked to other monitoring applied for active remedies in a subsection of the overall plume);
- 2. a predicted long remediation management duration (more than 50 years);
- 3. 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; and
- 4. 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 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. In subsequent sections, scenarios are introduced and used to illustrate examples of how these considerations are incorporated into an ESM approach.

For plume remediation management that spans more than 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 (Marker 2007; ITRC 2017). The ITRC Remediation Management of Complex Site document (ITRC 2017) discusses this type of site situation and identifies approaches such as management under ARARs or related waivers associated with the site remediation objectives (e.g., TI waiver) and/or using an adaptive site management approach.

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 requires (1) appropriate monitoring objectives, (2) a suitable monitoring network and a monitoring frequency, supported by a quantitative conceptual site model, and (3) regulatory and stakeholder acceptance. These components are described 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, as described by the Remediation Management of Complex Sites document (ITRC 2017), as well as factors unique to large, long-duration plumes where exposure pathways can be effectively controlled throughout the long remediation time period.

For plumes that require long-duration remediation management, the rate of change in plume conditions is 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 stated above in Section 2 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.

This guidance promotes 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 ultimate 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.

## 2.2 Quantitative Conceptual Site Model

A suitable conceptual site model, trend analysis, and/or predictive modeling are important inputs for establishing ESM objectives addressing exposure pathways and plume dynamics. These tools or the information needed to develop them 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 could predict contaminant migration paths and arrival times, which would help inform decisions on sampling location, well placement and sample frequency. It is expected that there will be a high degree of confidence in the CSM before beginning an ESM program. Substantial CSM refinement should <u>not</u> be occurring regularly over the duration of an ESM program. If deviation of plume behavior from the CSM cannot be confidently expected to be minimal or slow over a long plume management duration, then it is probably inappropriate to implement an ESM approach.

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. 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, that is not actually the case. Rather, it is expected that refinement should not be necessary, or should occur infrequently, and that refinement only needs to occur for aspects of the plume that may 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 is migrating at an

acceptable rate. This is to balance the costs associated with CSM refinement, and to prevent the collection of data associated with refining aspects of the CSM that are not relevant to plume confinement.

For the long-duration plumes targeted for ESM, the CSM needs to predict plume migration and identify exposure pathways to quantitatively define plume movement over time and support the monitoring design. 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 which 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 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 frequency, 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 time period of the 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 controlled 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 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.

# 2.5 Regulatory Considerations

As discussed by the ITRC (2017), there are multiple strategies for managing a long-duration plume (e.g., complex site), including the potential use of ARAR waivers. It is important that the regulatory approach to remediation, setting of remediation objectives, and identification of performance metrics be established to evaluate the appropriateness of ESM at a site. However, it may be useful to consider and incorporate concepts of ESM 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 costeffective 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. One way to enlist regulator and stakeholder support is through use of a DQO process when developing the ESM plan (Appendix A).

# 3.0 Scenarios for Extended-Scale Monitoring

Extended-scale plumes are defined as having a long duration of remediation and a large spatial scale (i.e., slow plume migration and long distances, relative to migration rate, to potential receptors). These factors enable selection of a passive remedy for which there is good confidence that protectiveness can be maintained throughout the long remediation 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 later in this document. For each scenario, there is a plume and source condition within a controlled zone where exposure can be controlled 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 controlled zone. For the ESM approach, a primary objective and key element of monitoring is to verify that the plume will not reach the receptor zone.

The scenarios are briefly described below and considered in examples of monitoring approaches later in this document.

- <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 [P&T] 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 controlled area, it can still meet passive remediation objectives with monitoring along a flow path during the remediation period.
- <u>A slowly diminishing primary or secondary source and associated plume</u>. If a primary or secondary source cannot be fully treated/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 non-contiguous 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, 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 changes progressively through Conditions 1, 2, 3, and 4 (each condition represents a conceptual change in plume configuration and location over time).











Figure 3.4. Conceptual depiction of a composite plume/source situation 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. These examples are provided as general overviews that sites can use in developing site-specific CSM and associated remediation scenarios for monitoring.

# 4.0 Implementation Approach

Implementation of ESM needs to reflect the types of plumes and source characteristics that lead to the need for ESM. For any of the scenarios described in Section 3 (Figure 3.1–Figure 3.4), the characteristics listed below are relevant if passive approaches are being applied over extended time (more than 50 years) and physical scales.

- The rate of plume change is slow. 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 eventually becoming stable or diminishing within the controlled 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 controlled zone. Sources may be present over a long time period at or below the threshold for acceptable plume conditions that are protective of receptors and are acceptable within the controlled zone (e.g., evolving toward concentration goals within the controlled 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 decade time scales to verify conditions, with low risk of continuing sources, 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 and some form of a predictive assessment will have been used to support a remedy decision for long-term passive remediation management of the site and the corresponding applicability of ESM. The initial site data establish starting conditions for ESM, including a CSM, plume/source conditions, and plume/source trends over the period of initial data collection. The predictive assessment will include an estimate of plume/source behavior over time that provides a basis of comparison for interpretation of 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 decade) 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 controlled 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 and reaching a receptor and concentrations above the site-specific objectives (compliance limit) for protection of human health and the environment.

The characteristics listed above lead to ESM approaches that can apply decade-scale time frames and be 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. However, building from the common ESM site characteristics discussed above and the scenarios introduced in Section 3, key elements of an ESM approach can be identified. Using this information can help with developing site-specific monitoring designs based on the relevant site-specific data quality objectives (DQOs), monitoring objectives, and site interim and end-state objectives. In particular, these overall characteristics and scenarios can be a starting point for applying a site-specific DQO process to set monitoring objectives and design the monitoring approach. Data quality objectives define a process for identifying the type, quantity, and quality of data needed to evaluate environmental risks and support decision-making (USEPA 1999a). The DQO process is a systematic seven-step iterative planning process for environmental data collection and is described within the ESM context in Appendix A.

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. At this time, 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. Thus, verification of plume behavior is by comparison of monitoring data to trend analysis or numerical modeling prediction intervals for individual wells or groupings of wells. If observations are consistent with the expected range of concentrations that remain protective of receptors (at the time of the monitoring event or in the future), 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 conceptual site model.

Extended-scale monitoring 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 controlled 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 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 the frequency 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.

ESM approaches for the scenarios introduced in Section 3 are described in Sections 4.1-4.5 to provide examples of how relevant monitoring elements can be configured. Site-specific objectives must be determined to drive the development of a unique monitoring plan. For the scenario discussion, the primary objective of the monitoring is to verify that the plume does not affect receptors and progresses toward meeting completion objectives.

## 4.1 Detached Plume

This scenario considers a plume after source treatment or after an active treatment (e.g., after P&T or a focused in-situ treatment) that is translating along a flow path but is diminishing and will not affect receptors (Figure 3.1). This scenario is related to the diminishing plume scenario described in the MNA guidance (USEPA 1999c) except that the translation of the plume along a flow path needs to be considered in the monitoring (and compliance) approach.

Several ESM conditions are relevant to this scenario, including

- slow plume movement such that differences in plume concentration and extent are meaningfully quantifiable over decadal time scales
- use of a phased sampling approach guided by predictive assessment of plume migration
- use of parameters and locations that are diagnostic of plume conditions.

Site-specific monitoring objectives are needed to guide monitoring design. However, some generalized relevant overall objectives are listed below to guide the conceptual monitoring design for this scenario.

- Data that indicate receptors are not affected.
- Data that verify the rate of plume translation and that the plume is not farther downgradient than expected at a given time.
- Data that verify hydraulic conditions and that features that control the translation and diminishing of the plume are within the predicted bounds.
- Data that demonstrate the plume is diminishing as needed to meet remediation objectives.

In summary, the following elements are envisioned as a conceptual approach for a detached-plume scenario. Given the infrequent monitoring approach, constituents for standard groundwater sample analysis of the plume include all the contaminants of concern (COCs) and other groundwater chemistry information needed to assess plume behavior, including MNA-related parameters. Accumulation samplers (e.g., passive samplers) or other alternative approaches can target specific COCs or all COCs, as appropriate.

- 1. Verify the plume migration rate with 3–5 sampling events using the well network that exists at the onset of ESM (i.e., the wells in the plume that were used to support the decision for use of long-term passive remediation) over 15–50 years, with sampling occurring every 5–10 years (depending on expected plume migration rate).
- 2. Verify hydraulic conditions (e.g., hydraulic heads and hydraulic boundary conditions) that drive plume transport in conjunction with sample collection.

- 3. After verifying the plume migration rate, identify diagnostic and sentinel locations for continued monitoring downgradient of the initial plume location, and verify sampling frequency.
- 4. Monitor diagnostic locations every 5–10 years (depending on the expected plume migration rate) using standard sampling and analysis or alternative methods (e.g., passive flux meters [see Section 5]) in downgradient locations.
- 5. 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).

The conceptual design of an ESM approach for the detached-plume scenario is described below and annotated conceptually in Figure 4.1. This conceptual design is primarily for the monitoring elements associated with use of groundwater wells. As needed, based on site-specific conditions, additional monitoring techniques derived from information in Section 5 can be incorporated or substituted in an ESM program (e.g., geophysics).



• Wells initially present prior to long-term remediation decision

- Wells on exposure path transect spaced at expected intervals of plume translation or key diagnostic locations (can be sited/installed after initial monitoring phase) – dashed wells indicate that there may be more than one diagnostic well per monitored detached plume condition
- Sentinel well(s) to demonstrate receptor protection or at another selected compliance location upgradient of the receptor zone (can be sited/installed after initial monitoring phase) – dashed wells indicate that there may be more than one sentinel well
- Figure 4.1. Conceptual well network for extended-scale monitoring of a detached-plume scenario. The site and plume conditions are such that the plume translates along the exposure pathway (e.g., from location 1 to 2 to 3 to 4) but diminishes such that the receptor zone is not affected.

#### 4.1.1 Phase 1: Initial Monitoring of the Existing Well Network

Given the extended time frames associated with an ESM approach, the initial monitoring can use the existing well network to provide "snapshots" (i.e., sampling from the full well network in a single sampling event) of the plume. Based on expected plume behavior, these snapshots occur every 5–10 years, with the results used in later phases. Plume behavior illustrated by these snapshots is then compared to predictions, and the predictions updated as needed (i.e., by comparison of data to trend analysis or numerical modeling prediction intervals for individual wells or groupings of wells). This

monitoring phase requires 3–5 snapshots to verify plume behavior. Eventually, the plume is expected to move beyond the monitoring network (i.e., the initial monitoring wells drop in concentration). 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, but provides a time series of data for the plume to extend monitoring. Analysis for contaminant trends includes analysis of trends for individual wells, well-to-well transect trend analysis, and full plume analysis using mass-based or 95UCL concentration approaches.

#### 4.1.2 Phase 2: Expanded Well-network Monitoring

After the initial monitoring phase, sampling shifts to diagnostic monitoring locations chosen from predictive assessments as modified by 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 (open circles in Figure 4.1) and sentinel wells (gray-filled circle in Figure 4.1). As the plume migrates downgradient of a monitoring well, it is dropped from the well network. The diagnostic locations are based on the expected location of the detached plume over time (for instance, in Zones 2, 3, and 4 shown in Figure 4.1), locations based on key hydraulic features at the site (e.g., locations where dilution is expected to occur), and locations. Note that the number of plume conditions (e.g., Zones 2, 3, and 4 shown in Figure 4.1) are selected based on the rate the plume is expected to migrate and diminish, major hydrologic features, and the overall distance to the receptor zone. This assessment determines the distance between wells as a function of travel time and total distance to the receptors. The distance between wells should also consider that the focus on monitoring frequency targets intervals of at least 5–10 years (when appropriate).

The number of wells needed for each downgradient diagnostic location (e.g., how many wells within Zones 2, 3, and 4 in Figure 4.1) 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. If more data are needed to verify plume movement, then the well network may be suitable to take plume snapshots at each monitoring interval (e.g., every 10 years). The benefits of additional complete plume snapshots as the detached plume migrates are to be considered along with the cost of well network installation and monitoring.

During this phase of monitoring, well monitoring based on passive devices (e.g., passive flux meters) can be deployed in wells expected to start receiving contaminant within a selected monitoring interval to provide an integrated measure of contaminant mass arriving at a monitoring location. This data is 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 are 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). Diagnostic locations can also have water level measurements taken at sampling times to check against expected hydraulic conditions, and fundamental available hydrologic data like precipitation and river stage information compiled, if appropriate, for a given site. Additionally, this phase of monitoring can incorporate alternative monitoring techniques, as described in Section 5.2.

## 4.2 Diminishing Source and Plume

This scenario considers a plume that is persisting due to a continuing primary or secondary source but is, or will be, diminishing over time (Figure 3.2). In this case, the plume dynamics are controlled both by plume transport and the source flux. This scenario is related to the diminishing plume scenario described in shorter-term MNA guidance, except that there may be some permissible plume expansion within the controlled zone before the plume diminishes over long timescales.

Several ESM conditions are relevant to this scenario, including:

- slow plume movement and source flux changes such that differences in plume concentration and extent and source flux are meaningfully quantifiable over decadal time scales
- use of a phased sampling approach guided by predictive assessment results for plume migration
- use of parameters and locations that are diagnostic of plume conditions.

Site-specific monitoring objectives are needed to guide a monitoring design. However, some generalized relevant overall objectives are listed below and are used to guide the conceptual monitoring design for this scenario.

- Data that indicate receptors are not affected.
- Data that verify the rate of plume migration and that the plume is not farther downgradient than expected at a given time.
- Data that verify hydraulic conditions and features that control the migration and diminishing of the plume and source flux are within predicted bounds.
- Data that demonstrate the plume and source flux are diminishing as needed to meet remediation objectives.

In summary, the following elements are envisioned as a conceptual approach for a diminishing source and plume scenario. Given the infrequent monitoring approach, constituents for standard groundwater sample analysis of the plume include all the COCs and other groundwater chemistry information needed to assess plume behavior. Accumulation samplers (e.g., passive samplers) or other alternative approaches can target specific COCs or all COCs, as appropriate.

- 1. Verify plume migration rate with 3–5 events using the well network that exists at the onset of ESM (i.e., the wells in the plume that were used to support the decision for use of long-term passive remediation) over 15–50 years with sampling every 5–10 years (depending on expected plume migration rate).
- 2. Verify the source flux conditions (e.g., measure source flux via concentrations and more direct flux measurements such as passive flux meters) coupled with the plume assessment.
- 3. Verify hydraulic conditions that drive plume transport in conjunction with the plume assessment.
- 4. After verifying the plume migration rate, identify diagnostic and sentinel locations for continued monitoring downgradient of the initial plume location to verify the approximate maximum extent of the plume.
- 5. Monitor initial sampling locations, diagnostic locations, and source flux every 5–10 years (depending on the expected plume migration rate) using standard sampling and analysis and complementary monitoring techniques until the plume begins to recede. At the same time, monitor sentinel locations that demonstrate receptor protection using passive devices, active sampling, or other alternative methods at 10-year intervals (depending on expected plume migration rate).

6. After the plume begins to recede, decrease the monitoring frequency to at most every 10 years and remove non-sentinel wells as they become unnecessary.

The conceptual design of an ESM approach for the diminishing source and plume scenario is described below and annotated conceptually in Figure 4.2. This conceptual design is primarily for the monitoring elements associated with the use of groundwater wells. Based on site-specific conditions, additional elements derived from information in Section 5 can be incorporated or used to replace the following examples (e.g., use of geophysical plume monitoring, CSIA, etc.) if plume characteristics can be assessed with these other types of monitoring.



• Wells initially present prior to long-term remediation decision

- Wells on exposure path transect at diagnostic locations associated with maximum estimated extent of plume (can be sited/installed after initial monitoring phase) – dashed wells indicate that there may be more than one diagnostic well for the maximum plume condition
- Sentinel well(s) to demonstrate receptor protection or at another selected compliance location upgradient of the receptor zone (can be sited/installed after initial monitoring phase) – dashed wells indicate that there may be more than one sentinel well
- Figure 4.2. Conceptual well network for extended-scale monitoring of a diminishing source and plume scenario. In this scenario, the plume may expand and then decline (e.g., as shown by progression from numbers 1 to 3 for the source and the plume) in response to source flux changes and any previous remediation conditions.

#### 4.2.1 Phase 1: Initial Monitoring of the Existing Well Network

Given the extended time frames associated with an ESM approach, the initial monitoring phase can use the existing well network to provide "snapshots" (i.e., sampling from the full well network in a single sampling event) of contaminant concentrations and other indicators expected to be used in later phases. These snapshots occur every 5–10 years depending on the expected rate of plume migration. Over this same time interval, alternative monitoring technologies can be deployed in or just downgradient of the source zone to monitor source flux. Plume and source flux behavior must be verified by comparing against predictions and expected behavior. The predictions can then be updated as needed (i.e., by comparing data to trend analysis or numerical modeling prediction intervals for individual wells or groupings of wells). This monitoring phase requires 3–5 snapshots to verify plume and source behavior as the plume moves and the source flux begins to diminish. Water level information, precipitation data, and other hydraulic boundary condition data important to the site hydraulic conditions can be collected coincident with contaminant data as input to evaluating hydraulic conditions for interpretation of plume transport and source flux 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. Determination of source flux stems from data collected from accumulation devices or calculated from groundwater velocity and concentration data.

#### 4.2.2 Phase 2: Expanded Well-network Monitoring

After the initial monitoring phase, 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 the exposure path transect (open circles in Figure 4.2) and sentinel wells (gray-filled circle in Figure 4.2). 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 (e.g., locations where dilution is expected to occur), 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 Zones 2 and 3, in Figure 4.1) 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 dropped from the network if a smaller set of wells provide 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 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 could be 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. 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). Water level measurements are taken at sampling times to evaluate hydraulic conditions (relative to expected conditions), and fundamental available hydrologic data like precipitation and river stage information can also be compiled, if appropriate.

### 4.3 Non-Contiguous Contaminated Zones

This scenario addresses sites with contamination consisting of noncontiguous contaminated areas within the overall controlled zone (i.e., smaller separate "plumes") that can be collectively managed (Figure 3.3). For instance, a plume or contaminated area with either multiple discrete primary or secondary source areas or areas with different remediation potential may result in noncontiguous contaminated zones. Plume remediation management of these zones as a single unit focuses on the collective behavior relative to protection of receptors and meeting compliance objectives. In this case, typical interpolation of data into a single plume is not appropriate, but other analyses can be applied (e.g., overall mass-based trends or individual well trends).

This scenario considers monitoring for passive remediation implemented under conditions with no continuing source concern. Where there is a continuing source concern for one or more of the individual contaminated zones, the scenario described in Section 4.2 should be consulted.

Several ESM conditions are relevant to this scenario, including

- slow plume movement such that differences in plume concentration and extent are meaningfully quantifiable over decade time scales
- use of a phased approach guided by predictive assessment results for plume migration
- use of parameters and locations that are diagnostic of plume conditions.

Site-specific monitoring objectives are needed to guide a monitoring design. However, some generalized relevant overall objectives are listed below and used to guide the conceptual monitoring design for this scenario.

- Data that indicate receptors are not affected.
- Data that verify the rate of individual contaminated zone migration and that a contaminated zone is not farther downgradient than expected at a given time.
- Data that verify hydraulic conditions and features that control the migration of contaminated zones are within predicted bounds.
- Data that demonstrate the individual contaminated zones are diminishing as needed to meet remediation objectives.

In summary, the following elements are envisioned as a conceptual approach for a noncontiguous contaminated zones plume scenario. Given the infrequent monitoring approach, constituents for standard groundwater sample analysis of the plume includes all COCs and other groundwater chemistry information needed to assess plume behavior. Alternative monitoring approaches can also be implemented to target specific COCs or other plume characteristics.

- 1. Verify the migration rate of individual contaminated zones with 3–5 events using the well network that exists at the onset of ESM (i.e., the wells that were used to support the decision for use of long-term passive remediation) over 15–50 years with sampling every 5–10 years (depending on expected migration rate).
- 2. Verify hydraulic conditions that drive contaminated zone transport.
- 3. After verifying the migration rate of individual contaminated zones, identify any individual contaminated zones that are migrating more than anticipated or that may reach an extent of concern with respect to the receptor zone. Based on this information, select diagnostic and sentinel locations within or downgradient of the initial well network.
- 4. Monitor the diagnostic and sentinel well network every 5–10 years (depending on expected migration rate) using standard sampling and analysis and/or alternative monitoring techniques (Section 5). Monitor 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.
- 5. After the individual contaminated zones of concern begin to recede, decrease the monitoring frequency to at most every 10 years and remove non-sentinel wells as they become isolated from contamination.

The conceptual design of an ESM approach for the noncontiguous contaminated zones scenario is described below and annotated conceptually in Figure 4.3. This conceptual design is primarily for the monitoring elements associated with use of groundwater wells. Based on site-specific conditions, additional elements derived from information in Section 5 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.



• Wells initially present prior to long-term remediation decision

- Wells on exposure path downgradient of individual plumes dashed wells indicate that these wells would only be installed where there is a concern about an individual plume migration (can be sited/installed after initial monitoring phase)
- Sentinel well(s) to demonstrate receptor protection or at another selected compliance location upgradient of the receptor zone (can be sited/installed after initial monitoring phase) – dashed wells indicate that there may be more than one sentinel well
- Figure 4.3. Conceptual well network for extended-scale monitoring of a noncontiguous contaminated zone scenario. In this scenario, individual contaminated zones are present as identified by previous site efforts and, collectively, these contaminated zones are not expected to expand to reach receptors and will ultimately decline to meet objectives for the controlled zone over time.

#### 4.3.1 Phase 1: Initial Monitoring of the Existing Well Network

With the extended time frames associated with an ESM approach, the initial monitoring phase can use the existing well network to provide "snapshots" (i.e., sampling from the full well network in a single sampling event) of contaminant concentrations and other indicators every 5–10 years depending on the expected rate of individual contaminated zone migration. These data are used to compare individual contaminated zone behavior to predictions; subsequent predictions are then updated based on results from monitoring in the initial phase (i.e., by comparison of data to trend analysis or numerical modeling prediction intervals for individual wells or groupings of wells). This monitoring phase requires 3–5 snapshots to verify the behavior of individual contaminated zones. Water level information, precipitation data, and other hydraulic boundary condition data important to the site hydraulic conditions are collected coincident with contaminant data as input to evaluating hydraulic contaminated zone behavior is not as rigorous as shorter-term monitoring for MNA. Rather, the purpose is to provide a timeseries of data to extend the monitoring of migration rate into the first few decades of the long-term passive remediation monitoring. Analysis for contaminant trends involves individual well trend analysis, well-to-well transect trend analysis, and overall mass-based analysis of the composite of the individual contaminated zones.

#### 4.3.2 Phase 2: Expanded Well-network Monitoring

Following the initial phase, monitoring of an expanded well-network occurs. The expanded well network for a noncontiguous contamination scenario has a primary focus on sentinel locations for demonstrating receptor protection and evaluating if there is continued contaminant migration of concern from identified problematic contaminated zones. In this case, diagnostic monitoring locations are identified from predictive assessments as modified by the initial monitoring phase to identify new well locations for use as sentinel wells (gray-filled circle in Figure 4.3) and for a small number of wells along the exposure path transect from problematic contaminated zones, if needed (open circles in Figure 4.3). The diagnostic locations are based on the expected migration of individual problematic contaminated zones, but locations may also need to consider key hydraulic features at the site (e.g., locations where dilution is expected to occur), and locations selected based on their use for verifying compliance with protection of receptors (sentinel wells).

The number of wells necessary for each downgradient diagnostic location depends on the uncertainty of individual contaminated zone migration (e.g., due to heterogeneity). Monitoring during this phase includes the collection of trend data for the identified problematic individual contaminated zones 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 contaminated zones shown to be declining during Phase 1 can be dropped from the network or monitored very infrequently to verify reaching controlled zone objectives. After contamination begins to recede, monitoring intervals can be lengthened 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, well monitoring based on alternative monitoring techniques (e.g., passive flux meters) can also be deployed in the downgradient diagnostic wells to provide an integrated measure of contaminant mass arriving at a monitoring location. These data can be collected along with the standard sampling-based concentration measurement, or independently 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 sampling may be particularly useful at sentinel locations to evaluate if contaminants are present with 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 against expected hydraulic conditions, and fundamental available hydrologic data like precipitation and river stage information are compiled, if appropriate.

## 4.4 Composite Plume

Any of the scenarios described thus far may be co-located with other contaminants that may be of similar or disparate sizes depending on the contaminant transport and source characteristics (Figure 3.4). These multiple plumes can be potentially managed in composite with primary consideration of compliance and 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. In this scenario, the presence of multiple co-mingled plumes may also drive the need for a primary monitoring objective to demonstrate that individual plume/source conditions are within thresholds for reaching concentration objectives assigned within the contaminated area and that comingling of plumes does not negatively impact natural attenuation rates. In this case, the monitoring approach includes support for managing the broader composite plume and support for decisions about individual plumes to make needed adjustments and meet the composite goal.

Several ESM conditions are relevant to this scenario, including

- slow plume movement and source flux changes such that differences in plume concentration and extent and source flux are meaningfully quantifiable over decade time scales
- use of a phased sampling approach guided by predictive assessment results for plume migration
- use of parameters and locations that are diagnostic of plume conditions.

Site-specific monitoring objectives are needed to guide a monitoring design. However, some generalized relevant overall objectives are listed below and are used to guide the conceptual monitoring design for this scenario. For this scenario, these objectives can be applied to the largest, most mobile plume as an overall indicator of behavior with targeted application to individual plumes determined to have the highest potential to be problematic.

- Data that indicate receptors are not affected.
- Data that verify the rate of plume migration and that the plume is not farther downgradient than it is expected to be at a given time.
- 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 assessment.
- Data that demonstrate the plume and source flux are diminishing as needed to meet remediation objectives.

In summary, the following elements are envisioned as a conceptual approach for a composite plume scenario. Given the infrequent monitoring approach, constituents for standard groundwater sample analysis of the plume include all COCs and other groundwater chemistry information needed to assess plume behavior. Alternative monitoring approaches can also be implemented to target specific COCs or other plume characteristics.

- 1. Verify the plume migration rate, focusing on the largest, most mobile plume and targeted verification of other plumes with 3–5 events using the well network that exists at the onset of ESM (i.e., the wells in the plume that were used to support the decision for use of long-term passive remediation). This verification monitoring can occur over a 15–50 year period with sampling every 5–10 years (depending on expected plume migration rate).
- 2. Verify the source flux conditions (e.g., measure source flux via concentrations and more direct flux measurements such as passive flux meters) coupled with the plume assessment. In particular, this monitoring may be needed for source zones determined to have the potential to support a temporarily expanding plume.
- 3. Verify the hydraulic conditions (e.g., hydraulic heads and hydraulic boundary conditions) that drive plume transport in conjunction with plume assessment.
- 4. After verifying the plume migration rate, identify diagnostic and sentinel locations for continued monitoring downgradient of the initial plume location to verify the approximate maximum extent of the largest, most mobile plume and for selected other plumes where continued plume expansion for some time is expected.
- 5. Monitor the well network, diagnostic locations, and source flux every 5–10 years (depending on expected plume migration rate) using standard sampling or alternative methods (e.g., passive flux meters) in downgradient locations until the plumes begins to recede. At the same time, monitor sentinel locations that demonstrate receptor protection using primarily passive devices evaluated at 10-year intervals (depending on expected plume migration rate).

6. After the plumes begin to recede, decrease the monitoring frequency to at most every 10 years and remove wells as they become downgradient of the plume (other than the sentinel location).

A simplified conceptual design of an ESM approach for the composite plume scenario is described below and annotated conceptually in Figure 4.4. This conceptual design is primarily for the monitoring elements associated with use of groundwater wells. Based on site-specific conditions, additional elements derived from information in Section 5 can be incorporated or used to replace the following examples (e.g., use of geophysical plume monitoring, CSIA, etc.) if plume characteristics can be assessed with these other types of monitoring approaches.



• Wells initially present prior to long-term remediation decision

- Wells on exposure path downgradient of individual plumes dashed wells indicate that these wells would only be installed where there is a concern about an individual plume migration (can be sited/installed after initial monitoring phase)
- Sentinel well(s) to demonstrate receptor protection or at another selected compliance location upgradient of the receptor zone (can be sited/installed after initial monitoring phase) – dashed wells indicate that there may be more than one sentinel well
- Figure 4.4. Conceptual well network for extended-scale monitoring of a composite plume scenario. In this scenario, individual plumes (of different contaminants) are present as identified by previous site efforts and, collectively, these plumes are not expected to expand to reach receptors and will ultimately decline to meet objectives for the controlled zone over time.

#### 4.4.1 Phase 1: Initial Monitoring of the Existing Well Network

Given the extended time frames associated with an ESM approach, the initial monitoring phase can use the existing well network to provide "snapshots" of contaminant concentrations and other indicators expected to be used in later phases. In the existing well network, the appropriate locations for monitoring the largest, most mobile plume and any other individual plumes that are expected to expand need to be identified. From this modified well network, snapshots of contaminant concentrations and other indicators are used in later phases every 5–10 years depending on expected rate of migration for the largest, most mobile plume. For this same time interval, source flux just downgradient of the source zone requires monitoring. Plume and source flux behavior are verified by comparison to predictions and field measurement (i.e., by comparison of data to trend analysis or numerical modeling prediction intervals for individual wells or groupings of wells). This monitoring phase requires 3–5 snapshots to verify the behavior of the plumes. Water level information, precipitation data, and other hydraulic boundary condition data important to the site hydraulic conditions are collected coincident with contaminant data for interpretation of plume transport and source flux conditions. Note that the verification of individual

contaminated zone behavior is not as rigorous as for shorter-term MNA, but provides a timeseries of data for the contamination to extend monitoring of the migration rate into the first few decades of the ESM program. Analysis of contaminant trends includes individual well trend analyses, well-to-well transect trend analyses, and overall mass-based analyses of the composite of the individual contaminated zones. Determination of source flux stems from data collected from accumulation devices or calculated from groundwater velocity and concentration data.

#### 4.4.2 Phase 2: Expanded Well-network Monitoring

After the initial monitoring phase, monitoring shifts to an expanded well network. The expanded well network for a composite plume scenario has a primary focus on sentinel locations for demonstrating receptor protection from the largest, most mobile plume and evaluating if there is continued contaminant migration of concern from the largest plume or from identified problematic plumes. In this case, diagnostic monitoring locations are identified from predictive assessments as modified by the initial monitoring phase to identify new well locations for use as sentinel wells (gray-filled circle in Figure 4.4) and for a small number of wells along the exposure path transect from the largest, most mobile plume and problematic individual plumes, if needed (open circles in Figure 4.4). The diagnostic locations are based on the expected migration of the largest, most mobile plume and individual problematic plumes, but locations may also need to consider key hydraulic features at the site (e.g., locations where dilution is expected to occur), and sentinel well locations selected based on their use for verifying compliance with protection of receptors.

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.

### 4.5 Additional Considerations and Configurations

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 discussion of considerations for implementing ESM (Section 4.5.1 and 4.5.2) and an alternative ESM approach that may be appropriate for some sites to evaluate (Section 4.5.3).

#### 4.5.1 Long-Term Data Management and Interpretation Considerations

Extended-scale monitoring as described in this document is for remedies that 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 impact data collection and interpretation:

- 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 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 such as those discussed in the ITRC document Remediation Management of Complex Sites (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.

#### 4.5.2 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 conditions have changed enough that plume behavior could change and be 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.

#### 4.5.3 Managing Unexpected Plume Behavior

As described in Section 2, 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. 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.

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

If there is low risk from a plume, reliable controls for the controlled zone (see Figure 3.1–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 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. This type of well network does not attempt to provide snapshots of the plume (e.g., for plume mapping or comparison to previous plume mapping).

For ESM adoption, decision-makers and stakeholders need to agree that the risk from the plume is managed effectively by the controlled 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 5–10 years so that there are periodic data for plume management. However, the site could select longer monitoring intervals depending on the plume conditions, risk, and administrative situation of the site. As with the monitoring approach described in Sections 4.1 through 4.4, collection of data on site hydraulic conditions is also warranted if hydraulic conditions change (Section 4.5.2).

# 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 periods 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 at a large complex site analyzed for a full suite of constituents could cost \$5,000 (including collection costs, analytical costs, administration and data management). Over 100 years, with an every-five-year sample frequency, the cost for collecting one extra sample from an additional well during each event accumulates to \$100,000.

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 identified four basic data needs for verifying that the extended-scale approach is working and appropriate:

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

There are two fundamental approaches 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 or data that have low cost burden compared to samples collected using traditional fully purged groundwater well sampling methods. To this end, two approaches are presented to support the ESM approach: 1) sample collection optimization; and 2) alternative methods. In Section 5.1 (optimization), ways to reduce the number of samples necessary for collection are discussed; in Section 5.2, less costly alternatives that might be used in lieu of, or in conjunction with, bulk water sample collection/analysis are considered. One important note is that for an ESM program, it is anticipated that the available technologies will change substantially throughout the duration of the monitoring program. Due to the time scales involved, these sections provide ideas and suggestions, not exact methodologies and approaches. More detailed descriptions of the current state-of-the-art for these monitoring approaches can be found in other reference material (Looney et al. 2006; Delepine-Lesoille et al. 2017; Barrias et al. 2016).

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. Monitoring may be applied to (1) track contaminant movement, (2) quantify source flux into the downgradient plume, (3) assess remedy processes and performance, (4) provide information useful to enable prediction of future contaminant movement, or (5) verify subsurface conditions related to remediation or long-term plume behavior. Even within a single, hydraulically connected groundwater zone, there is rarely a homogeneous distribution of groundwater flow. These variations in flow regimes and heterogeneity in physical and chemical processes that affect contaminant and/or remediation processes create challenges for monitoring, especially in translating information from a specific monitoring location to information about the spatial three-
dimensional behavior of the contaminant or remediation process (e.g., fluxes and flux distribution). 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 cost prohibitive, 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.

An ESM program can benefit from a multiple lines-of-evidence approach to guide data collection (Rügner et al. 2006). 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 species may be used in conjunction with active groundwater sampling. Active groundwater sample collection can be deployed infrequently, as long as the sensor does not indicate presence of the plume.

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 controlled 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).

#### 5.1 Optimization of Sample Collection

In an ESM approach, regular plume monitoring is not used for updating plume boundaries, quantifying contaminant mass, or other purposes typical of the characterization phase. The objective of an ESM approach is to monitor for protectiveness and verify expected migration behavior. Development of the ESM implementation approach using a DQO process can help to ensure that the plan is focused and targeted to meet these objectives, and that monitoring is designed accordingly (Appendix A). This could include active sample collection, passive sampling, hydraulic data, analysis for primary COCs or indicator species, down-hole sensors, remote sensing, geophysical monitoring, etc. The nature of an ESM scenario is that the area immediately surrounding the plume does not contain any receptors and is not expected to for an extended period. Therefore, targeted plume monitoring is limited to ensure that the plume behavior is consistent with the CSM, and that the extended time scale approach is appropriate. 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 Sentinel Wells

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. A sentinel well is a monitoring well that is located between the plume source and the receptor. The purpose of the sentinel well is to identify plume migration prior to its arrival at a receptor. At a fundamental level, the use of sentinel wells indicates that what is happening in the plume is of minimum concern; as long as contaminants are not reaching the sentinel wells then the remedy is still protective of human health and the environment.

#### 5.1.2 Sample Design

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), as amended, requires monitoring to ensure that any remedial action is protective of human health, welfare, and the environment. Because ESM presumes that contaminants remain within a defined controlled zone, sampling has a role in substantiating that a remedial action is both protective and functioning as established in legal documents, such as permits, Records of Decision (RODs), etc. Fundamentally, sampling is used to measure progress toward meeting a cleanup objective while providing justification for either a continuation or adaptive change in procedures.

As described in Section 4, 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, monitoring of an expanded well-network could commence. These sample collection timelines and spatial density should be site specific and negotiated. However, it is important that an optimal ESM program only collects enough data to verify that the contaminant remains within the controlled 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, while also introducing a groundwater monitoring methodology to improve existing monitoring plans. The authors use three stand-alone methods: (1) spatial redundancy reduction, (2) well siting for new sampling locations, and (3) sampling frequency determination (Ling et al. 2003). In a specific field application, 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) could be implemented for ESM applications. The characterization and active-remedy performance monitoring phases that occur prior to implementation of ESM may result in redundant wells, but not provide diagnostic and sentinel wells, as described in Section 4. The optimization may be implemented immediately upon adoption of ESM, or after the initial 3 to 5 verification sampling events when the continued monitoring plan is developed.

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 the Department of Energy 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 twodimensional sampling plan. The statistical based approach 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 site managers with 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. 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. There are numerous software packages currently available that can be used to assist with sample plan optimization, and likely many more will be developed over time. The extended spatial and temporal scales encountered with an ESM approach make computer aided design useful. Implementation of computer aided statistical analysis and visualization can assist with achieving regulatory and stake-holder acceptance of an optimized sample collection plan.

#### 5.2 Alternative Sampling Options

When implementing an ESM program, traditional groundwater well sampling with laboratory analysis may be the most appropriate sample collection approach. However, the next generation of monitoring at DOE sites will use an integrated systems-based approach (Bunn et al. 2012; Otero et al. 2009) where monitoring data could support alternative paths to closure by demonstrating system behavior, understanding and documenting trends, and understanding relations between 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), when the end state is long-term maintenance, unique approaches that avoid costly reliance on monitoring concentrations at specific locations should be considered and potentially integrated with the end state for the site. 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 plan development is the sample collection approach for groundwater (USEPA 2005). Reducing the cost of sample collection can lower the overall monitoring costs. Traditionally, groundwater sample collection requires a significant amount of purging prior to sample collection; either multiple well bore volumes, or until parameters stabilize. However, other whole-water collection methods have, in some instances, proven capable of collecting representative samples at a lower cost. For example, one study examined sampling costs and short-term sample variability (that is, variability caused by the sample collection method) for several volatile organic compound (VOC) sampling approaches (McHugh et al. 2015). For the goals of minimizing monitoring costs and sample variability, low-flow small volume purge and passive no-purge collection methods were determined to be acceptable. A dual rate pumping system to purge and equilibrate wells, with potential to substantially decrease labor, sampling time, and wastewater volume has also been recommended (Wang et al. 2019). Careful consideration of the sample collection method can result in cost savings without sacrificing data quality. This is important when collecting samples over many decades; the cost differentials may appear trivial on a per-well basis, but significant cost savings may be realized when implemented over a century of plume monitoring.

#### 5.2.2 Surrogate Species

Surrogate species can be used as an indicator of contaminant presence or migration to provide a cheaper analysis methodology (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 were known to have been disposed of with other conductive compounds, a change in specific conductance of the groundwater may indicate a change in contaminant concentration. Examples of surrogate species use includes conductivity measurements (Galhardi and Bonotto 2016), fecal indicators (Ferguson et al. 2012), or gross radioactivity (Mendoza et al. 2007). It is important to remember that in an ESM application, characterization is not the purpose of monitoring; monitoring is only intended to demonstrate that the contaminant plume is moving at (or slower) than the expected rate. Measurement of concentrations of surrogate species, in some instances, provides an indication of change in the subsurface at a lower cost than achievable by measuring the primary analyte of interest.

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). This approach could have some

drawbacks, such as temporarily changing the hydraulic conditions, accounting for diffusion of the tracer, and regulatory hurdles associated with the introduction of additional chemicals. This method is most useful for initial site characterization; it may not be desirable for long term monitoring.

#### 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, proxies of COCs, 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 currently under development is expected to drive costs down (USEPA 2003). Production of disposable sensors with much lower costs than laboratory testing is also anticipated within the ESM timescale (Hayat and Marty 2014).

All sensors incorporate two essential elements, a receptor which 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 which is placed in the sample or adsorbs contaminant and experiences a resultant change in conductive properties. Electrodes are often formed from polymers which can selectively accumulate analyte, increasing the limit of quantitation (LOQ). Biosensors typically involve an enzyme or biomolecule which reacts with certain COCs, generally pesticides (Andrianova et al. 2016). Some sensors discussed in literature are hybrids, measuring a reaction with biological or chemical elements impregnated into an electrode (Noori et al. 2020).

Ongoing research and development will continue to result in chemical sensors that are robust, reliable, cost-effective, and commonplace over the lifecycle of a century plume (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 quantitate VOCs, heavy metals, pesticides, and radionuclides (Li et al. 2012).

Biosensor technology for monitoring water quality has garnered significant research attention. The most recognizable biosensors are used for monitoring glucose in diabetic patients; however, 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 many enzymes. However, analysis of specific pesticides is often limited as the enzymes have low selectivity among such compounds.

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 VOC's 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.

Current laboratory evaluation of groundwater samples incurs significant costs of transportation and analysis. Given the current pace of sensor development for environmental applications, sensor monitoring may soon be conducted in the field. Over the time frame of a century plume this can result in significant cost savings. Careful consideration must be taken to select the proper sensor type for a given application as selectivity is often limited. Additional considerations must be taken as some sensors only operate within a specific pH range or depth when measuring *in situ* (Cuartero and Crespo 2018).

#### 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 provide an estimate of the groundwater velocity. The fundamental concept for an ESM approach is that the contaminant plume is slow moving; the expectation is that velocity is low enough that it will take many decades to reach a potential receptor. It is expected that before implementation of an ESM program, the hydraulic gradient and flow direction of the site is well characterized and understood. This includes both temporal and spatial variations. Even though the groundwater characteristics should be well understood before beginning ESM, that does not mean that measurement of the hydraulic gradient is not important in an ESM approach. As noted in Section 4, monitoring of groundwater flow conditions is an important aspect of monitoring, and identifying significant changes in hydraulic conditions is important for identifying potential changes to the CSM (Section 4.5).

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 site 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 grouped together for a 2D (map) view of hydraulically connected units.

Water level data collection may benefit from frequent, sensor-based monitoring. This approach can provide important details that are missed by occasional hand measurements. Inspection of water level data from a sensor network may provide insights into the dynamic response of water levels in the aquifer(s) to

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

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 in an ESM program should be weighed against the volume of data generated and stored. As noted in Section 4.5, long-term data management should be considered in the design of an ESM plan. 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 has the potential to be the preferred monitoring technology for ESM programs. Passive sampling refers to a device that accumulates and traps the analyte of interest over time without pumping or purging. 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 polar organic chemical integrative sampler (POCIS), 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 program. Passive samplers can provide a low-cost sample collection approach, and they measure a time-integrated average concentration rather than a point-in-time measurement. Numerous articles have been published in recent years detailing passive sampler performance: the consensus appears to be that, in some instances, passive samplers can replace traditional purge-based sampling and low-flow purge methods without loss of data quality (Vrana et al. 2005; ITRC 2006). It should also be noted that development of passive sampler technology is advancing rapidly because researchers and regulators recognize the potential benefits of passive sampling.

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 traditional pumped samples can take. In addition, passive samplers require less hardware (pumps, hose, purge tanks) and no power, making them cheaper to deploy. A final cost saving consideration for passive samplers is the lack of sample generated waste. Pumped samples from a contaminated groundwater plume can incur significant costs associated with disposal of purge water and other sampling waste; passive sampling can reduce the costs because little to no waste is generated by a passive sampling system (Stroo 2014).

In addition to cost savings, 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; it provides more temporal coverage, can allow for lower detection limits, can reduce uncertainty associated with vertical heterogeneity, and can allow for 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 large heterogeneities, active sampling will provide a sample that is biased towards the portions of the aquifer with higher hydraulic conductivity (which is 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.

Another benefit of passive samplers is that they can 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 10x 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 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, comparing passive sampler data to legacy groundwater data collected with traditional methods, must be performed with care. 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.

Passive sample methodology is still being developed for a wide range of contaminants. Extended longterm passive monitoring (~1 year) is not currently used as biofouling, sampler saturation, and physical degradation can greatly diminish accuracy (Harman et al. 2012). For shorter time frames, 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 developed for organic compounds and has been successfully deployed for VOCs and per- and polyfluoroalkyl substances (PFASs) (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. For these reasons, development of passive sampling technology continues at a rapid pace.

#### 5.2.6 Mass Flux and Mass Discharge

Passive flux monitors (PFMs) are a unique adaptation of passive samplers which provide estimates of contaminant flux and groundwater velocity. PFMs accumulate contaminants over a period of days or

<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>

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 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>TM</sup>, PFMs were developed through funding provided by several government agencies (Campbell et al. 2006). Most devices utilize several alcohols of varying molecular weight and branching as tracer compounds. These tracers elute from the device at rates proportional to the groundwater flux (Darcy's Law). 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.

Passive flux monitors can be deployed for more than two 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 electro-magnetic) used to measure properties of the earth. Geophysical measurement techniques have been applied to groundwater problems for different purposes, including to measure 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). 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 is 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 would need to be

collected using traditional well sampling methodologies: mobilization, well purging with stabilization of parameters, sample collection, and then analysis in a laboratory. This methodology typically combines chromatography with IRMS to measure isotopic ratios of elements in organic compounds ( $^{13}C/^{12}C$ ,  $^{15}N/^{14}N$ ,  $^{37}Cl/^{35}Cl$ ,  $^{2}H/^{1}H$ ). These measurements can be used to infer the extent of transformation and verify contaminant degradation both spatially and temporally. 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).

#### 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 as 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 (PVD) 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.

#### 5.2.10 Methods Synopsis

The various methods presented here represent a current summary of some 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. As has been demonstrated within this document, 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 so that they provide a maximum benefit and minimal costs for ESM.

## 6.0 Conclusion

Passive remediation can be appropriate where natural attenuation processes, together with mechanisms such as institutional controls, can be used to mitigate exposure to contaminated groundwater and achieve remedial action objectives to maintain protectiveness of human health and the environment. Monitored natural attenuation is widely employed as a passive method of remediating contaminated zones, typically applied for plumes expected to reach objectives within less than five decades. Long-duration passive remediation using extended scale monitoring 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. Passive remediation and ESM over long durations is suitable if the plume is expected to stay within a controlled zone where exposure to groundwater can be mitigated and diminishes over time to reach compliance conditions determined for the site. Groundwater plumes may move during this time, but any plume advancement must stabilize or recede within the controlled 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 controlled zone and receptor zone. The approach is rooted in a sound conceptual site model and strong technical basis for the predictive analyses that are used to support an ESM approach. 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 remedial action objectives, 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 remedy to help support the technical defensibility of the predicted plume behavior during the passive 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 controlled 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 the reduced monitoring frequency and the number of well network locations selected for sampling and analysis. Savings may also be realized through the employment of alternative or innovative monitoring techniques such as those described in Section 5. For implementation of ESM, an adaptive monitoring approach that considers updates in 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 intended to enable sites to identify a monitoring approach most appropriate for managing long-duration passive remedies under the circumstances where confidence in plume behavior is high and risk to receptors is low. When timescales for this type of passive remediation extend to many decades, a monitoring strategy tailored to these conditions is needed. ESM provides this type of strategy with a focus on monitoring of exposure pathways 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 and there is substantial evidence that the plume will dissipate before reaching downgradient receptors within a zone where contact with the plume can be controlled to prevent exposure during the remediation time period.

## 7.0 References

Adamson, David, Thomas McHugh, Michal Rysz, Roberto Landazuri, and Charles Newell. 2012. 'Field Investigation of Vapor-Phase-Based Groundwater Monitoring', *Ground Water Monitoring & Remediation*, 32: 59-72.

Ahkola, Heidi, Sirpa Herve, and Juha Knuutinen. 2013. 'Overview of passive Chemcatcher sampling with SPE pretreatment suitable for the analysis of NPEOs and NPs', *Environmental Science and Pollution Research*, 20: 1207-18.

Ahmadi, Seyed Hamid, and Abbas Sedghamiz. 2007. 'Geostatistical Analysis of Spatial and Temporal Variations of Groundwater Level', *Environmental Monitoring and Assessment*, 129: 277-94.

Andrianova, Mariia, S., Oksana V. Gubanova, Natalia V. Komarova, Evgeniy V. Kuznetsov, and Alexander E. Kuznetsov. 2016. 'Development of a Biosensor Based on Phosphotriesterase and n-Channel ISFET for Detection of Pesticides', *Electroanalysis*, 28: 1311-21.

Arduini, Fabiana, Stefano Cinti, Viviana Scognamiglio, Danila Moscone, and Giuseppe Palleschi. 2017. 'How cutting-edge technologies impact the design of electrochemical (bio)sensors for environmental analysis. A review', *Analytica Chimica Acta*, 959: 15-42.

Audí-Miró, Carme, Stefan Cretnik, Clara Torrentó, Mònica Rosell, Orfan Shouakar-Stash, Neus Otero, Jordi Palau, Martin Elsner, and Albert Soler. 2015. 'C, Cl and H compound-specific isotope analysis to assess natural versus Fe(0) barrier-induced degradation of chlorinated ethenes at a contaminated site', *Journal of Hazardous Materials*, 299: 747-54.

Ávila, Cristina, Víctor Matamoros, Carolina Reyes-Contreras, Benjamí Piña, Marta Casado, Luigi Mita, Claudia Rivetti, Carlos Barata, Joan García, and Josep Maria Bayona. 2014. 'Attenuation of emerging organic contaminants in a hybrid constructed wetland system under different hydraulic loading rates and their associated toxicological effects in wastewater', *Science of The Total Environment*, 470-471: 1272-80.

Bakkour, Rani, Jakov Bolotin, Börje Sellergren, and Thomas B. Hofstetter. 2018. 'Molecularly Imprinted Polymers for Compound-Specific Isotope Analysis of Polar Organic Micropollutants in Aquatic Environments', *Analytical Chemistry*, 90: 7292-301.

Balbarini, Nicola, Vinni Rønde, Pradip Maurya, Gianluca Fiandaca, Ingelise Møller, Knud Erik Klint, Anders V. Christiansen, Philip J. Binning, and Poul L. Bjerg. 2018. 'Geophysics-Based Contaminant Mass Discharge Quantification Downgradient of a Landfill and a Former Pharmaceutical Factory', *Water Resources Research*, 54: 5436-56.

Barrias, António, Joan R. Casas, and Sergi Villalba. 2016. 'A Review of Distributed Optical Fiber Sensors for Civil Engineering Applications', *Sensors (Basel, Switzerland)*, 16.

Bondehagen, Diane. 2010. 'Measuring Groundwater and contaminant Flux: passive Flux Meter Field Applications and Issues with Alcohol Degradability', *Air, Soil and Water Research*, 3: ASWR.S4785.

Booij, Kees, and Sunmao Chen. 2018. 'Review of atrazine sampling by polar organic chemical integrative samplers and Chemcatcher', *Environmental Toxicology and Chemistry*, 37: 1786-98.

Bunn Amoret L., Dawn M. Wellman, Rula A. Deeb, Elizabeth L. Hawley, Michael J. Truex, Mark Peterson, Mark D. Freshley, Eric M. Pierce, John McCord, Michael H. Young, Tyler J. Gilmore, Rick Miller, Ann L. Miracle, Dawn Kaback, Carol Eddy-Dilek, Joe Rossabi, M. Hope Lee, Richard P. Bush, Paul Beam, Grover M. Chamberlain, Justin Marble, Latrincy Whitehurst, Kurt D. Gerdes, and Yvette Collazo. 2012. *Scientific Opportunities for Monitoring at Environmental Remediation Sites (SOMERS): Integrated Systems-Based Approaches to Monitoring*. DOE/PNNL-21379. Prepared for Office of Soil and Groundwater Remediation, Office of Environmental Management, U.S. Department of Energy, Washington, D.C., by Pacific Northwest National Laboratory, Richland, WA.

Campbell, Timothy J., Kirk Hatfield, Harald Klammler, Michael D. Annable, and Purna S. C. Rao. 2006. 'Magnitude and Directional Measures of Water and Cr(VI) Fluxes by Passive Flux Meter', *Environmental Science & Technology*, 40: 6392-97.

Cuartero, María, and Gastón A. Crespo. 2018. 'All-solid-state potentiometric sensors: A new wave for in situ aquatic research', *Current Opinion in Electrochemistry*, 10: 98-106.

Delepine-Lesoille, Sylvie, Sylvain Girard, Marcel Landolt, Johan Bertrand, Isabelle Planes, Aziz Boukenter, Emmanuel Marin, Georges Humbert, Stéphanie Leparmentier, Jean-Louis Auguste, and Youcef Ouerdane. 2017. 'France's State of the Art Distributed Optical Fibre Sensors Qualified for the Monitoring of the French Underground Repository for High Level and Intermediate Level Long Lived Radioactive Wastes', *Sensors (Basel, Switzerland)*, 17: 1377.

DENR - North Carolina Department of Environment and Natural Resources, Division of Waste Management, Solid Waste Section. 2008. "Examples of Approved Groundwater Corrective Measures for Solid Waste Management Facilities."

https://files.nc.gov/ncdeq/Waste%20Management/DWM/SW/Field%20Operations/Environmental%20M onitoring/ExamplesGWCorrectiveMeasuresrev6-08.pdf. *Accessed 09/03/2020* 

Elias, Gemma, Sergi Díez, and Clàudia Fontàs. 2019. 'System for mercury preconcentration in natural waters based on a polymer inclusion membrane incorporating an ionic liquid', *Journal of Hazardous Materials*, 371: 316-22.

Elsner, Martin, and Gwenaël Imfeld. 2016. 'Compound-specific isotope analysis (CSIA) of micropollutants in the environment — current developments and future challenges', *Current Opinion in Biotechnology*, 41: 60-72.

Englert, Andreas, Andreas Kemna, Jun-feng Zhu, Jan Vanderborght, Harry Vereecken, and Tian-Chyi J. Yeh. 2016. 'Comparison of smoothness-constrained and geostatistically based cross-borehole electrical resistivity tomography for characterization of solute tracer plumes', *Water Science and Engineering*, 9: 274-86.

Fatin-Rouge, Nicolas, Kevin J. Wilkinson, and Jacques Buffle. 2006. 'Combining Small Angle Neutron Scattering (SANS) and Fluorescence Correlation Spectroscopy (FCS) Measurements To Relate Diffusion in Agarose Gels to Structure', *The Journal of Physical Chemistry B*, 110: 20133-42.

Ferguson, Andrew S., Alice C. Layton, Brian J. Mailloux, Patricia J. Culligan, Daniel E. Williams, Abby E. Smartt, Gary S. Sayler, John Feighery, Larry D. McKay, Peter S. K. Knappett, Ekaterina Alexandrova, Talia Arbit, Michael Emch, Veronica Escamilla, Kazi Matin Ahmed, Md Jahangir Alam, P. Kim Streatfield, Mohammad Yunus, and Alexander van Geen. 2012. 'Comparison of fecal indicators with pathogenic bacteria and rotavirus in groundwater', *Science of The Total Environment*, 431: 314-22.

Fernández de Vera, Natalia, Jean Beaujean, Pierre Jamin, Vivien Hakoun, David Caterina, Ofer Dahan, Marnik Vanclooster, Alain Dassargues, Frédéric Nguyen, and Serge Brouyère. 2017. 'Tracer Experiment in a Brownfield Using Geophysics and a Vadose Zone Monitoring System', *Vadose Zone Journal*, 16: 1-15.

Forsberg, Jerry, Ralf Dahlqvist, Johan Gelting-NystrÖm, and Johan Ingri. 2006. 'Trace Metal Speciation in Brackish Water Using Diffusive Gradients in Thin Films and Ultrafiltration: Comparison of Techniques', *Environmental Science & Technology*, 40: 3901-05.

Galhardi, Juliana Aparecida, and Daniel Marcos Bonotto. 2016. 'Hydrogeochemical features of surface water and groundwater contaminated with acid mine drainage (AMD) in coal mining areas: a case study in southern Brazil', *Environmental Science and Pollution Research*, 23: 18911-27.

Ghasemizadeh, Reza, Ferdinand Hellweger, Christoph Butscher, Ingrid Padilla, Dorothy Vesper, Malcolm Field, and Akram Alshawabkeh. 2012. 'Review: Groundwater flow and transport modeling of karst aquifers, with particular reference to the North Coast Limestone aquifer system of Puerto Rico', *Hydrogeology Journal*, 20: 1441-61.

Hageman, Kimberly J., Christopher H. F. Aebig, Kim Hoang Luong, Sarit L. Kaserzon, Charles S. Wong, Tim Reeks, Michelle Greenwood, Samuel Macaulay, and Christoph D. Matthaei. 2019. 'Current-use pesticides in New Zealand streams: Comparing results from grab samples and three types of passive samplers', *Environmental Pollution*, 254: 112973.

Hans F. Stroo, Hunter R. Anderson, Andrea Leeson. 2014. 'Passive Sampling for Groundwater Monitoring: Technology Status'. Prepared for Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP), Arlington, VA. December, 2014.

Harman, Christopher, Ian John Allan, and Etiënne L. M. Vermeirssen. 2012. 'Calibration and use of the polar organic chemical integrative sampler—a critical review', *Environmental Toxicology and Chemistry*, 31: 2724-38.

Hayat, Akhtar, and Jean Louis Marty. 2014. 'Disposable screen printed electrochemical sensors: tools for environmental monitoring', *Sensors (Basel, Switzerland)*, 14: 10432-53.

Irshad, Muhammad, Naseer Iqbal, Adnan Mujahid, Adeel Afzal, Tajamal Hussain, Ahsan Sharif, Ejaz Ahmad, and Muhammad Makshoof Athar. 2013. 'Molecularly Imprinted Nanomaterials for Sensor Applications', *Nanomaterials (Basel, Switzerland)*, 3: 615-37.

ITRC - Interstate Technology & Regulatory Council. 2006. "State Survey and Responses." https://www.itrcweb.org/Documents/State\_Survey\_and\_Responses.pdf. *Accessed 09/1/2020*.

ITRC - Interstate Technology & Regulatory Council. 2007. "A Decision Flowchart for the Use of Monitored Natural Attenuation and Enhanced Attenuation at Sites with Chlorinated Organic Plumes " https://www.itrcweb.org/Documents/EACODecisionFlowchart\_v1.pdf. *Accessed 09/1/2020*.

ITRC - Interstate Technology & Regulatory Council. 2010. "A Decision Framework for Applying Monitored Natural Attenuation Processes to Metals and Radionuclides in Groundwater." https://www.itrcweb.org/Guidance/GetDocument?documentID=5. *Accessed 09/1/2020*.

ITRC - Interstate Technology & Regulatory Council. 2017. "Remediation Management of Complex Sites." https://rmcs-1.itrcweb.org/. *Accessed 09/1/2020*.

Johnson, Timothy C., Roelof J. Versteeg, Frederick D. Day-Lewis, William Major, and John W. Lane Jr. 2015. 'Time-Lapse Electrical Geophysical Monitoring of Amendment-Based Biostimulation', *Groundwater*, 53: 920-32.

Kaserzon, Sarit L., Soumini Vijayasarathy, Jennifer Bräunig, Linus Mueller, Darryl W. Hawker, Kevin V. Thomas, and Jochen F. Mueller. 2019. 'Calibration and validation of a novel passive sampling device for the time integrative monitoring of per- and polyfluoroalkyl substances (PFASs) and precursors in contaminated groundwater', *Journal of Hazardous Materials*, 366: 423-31.

Klammler, Harald, Kirk Hatfield, Mark A. Newman, Jaehyun Cho, Michael D. Annable, Beth L. Parker, John A. Cherry, and Irina Perminova. 2016. 'A new device for characterizing fracture networks and measuring groundwater and contaminant fluxes in fractured rock aquifers', *Water Resources Research*, 52: 5400-20.

Kos, S. E. "Vadose zone characterization project at the Hanfod Tank Farms: BY Tank Farm report". United States. doi:10.2172/437678. https://www.osti.gov/servlets/purl/437678. Accessed 08/30/2020.

LeBlanc, D. R., S. P. Garabedian, K. M. Hess, L. W. Gelhar, R. D. Quadri, K. G. Stollenwerk, and W. W. Wood. 1991. Large-scale natural gradient tracer test in sand and gravel, Cape Cod, Massachusetts, 1, Experimental design and observed tracer movement, *Water Resouces. Research*, 5: 895-910.

Lemke, Lawrence D., Linda M. Abriola, and John R. Lang. 2004. 'Influence of hydraulic property correlation on predicted dense nonaqueous phase liquid source zone architecture, mass recovery and contaminant flux', *Water Resources Research*, 40.

Li, Meng, Yuan-Ting Li, Da-Wei Li, and Yi-Tao Long. 2012. 'Recent developments and applications of screen-printed electrodes in environmental assays—A review', *Analytica Chimica Acta*, 734: 31-44.

Li, Ming, Honglei Gou, Israa Al-Ogaidi, and Nianqiang Wu. 2013. 'Nanostructured Sensors for Detection of Heavy Metals: A Review', *ACS Sustainable Chemistry & Engineering*, 1: 713-23.

Li, Xin, Siqun Li, Qingyun Liu, and Zhengbo Chen. 2019. 'Electronic-Tongue Colorimetric-Sensor Array for Discrimination and Quantitation of Metal Ions Based on Gold-Nanoparticle Aggregation', *Analytical Chemistry*, 91: 6315-20.

Li, Yuanhai, and Amy Chan Hilton. 2005. 'Reducing Spatial Sampling in Long-Term Groundwater Monitoring Networks Using Ant Colony Optimization', *International Journal of Computational Intelligence Research*, 1: 19-28.

Ling, Meng, Hanadi S. Rifai, and Charles J. Newell. 2005. 'Optimizing groundwater long-term monitoring networks using Delaunay triangulation spatial analysis techniques', *Environmetrics*, 16: 635-57.

Ling, Meng, Hanadi S. Rifai, Charles J. Newell, Julia J. Aziz, and James R. Gonzales. 2003. 'Groundwater monitoring plans at small-scale sites--an innovative spatial and temporal methodology', *Journal of environmental monitoring*, 5: 126-34. Looney, B., M. Heitkamp, Gary Wein, C. Bagwell, K. Vangelas, K. Adams, Tyler Gilmore, Norman Cutshall, David Major, Mike Truex, Todd Wiedemeier, Francis Chapelle, Tom Early, Jody Waugh, David Peterson, Mark Ankeny, and Claire Sink. 2006. 'Characterization and Monitoring of Natural Attenuation of Chlorinated Solvents in Groundwater: A Systems Approach'. (full report, August 10, 2006); Aitken, South Carolina.

Luo, Qiankun, Jianfeng Wu, Yun Yang, Jiazhong Qian, and Jichun Wu. 2016. 'Multi-objective optimization of long-term groundwater monitoring network design using a probabilistic Pareto genetic algorithm under uncertainty', *Journal of Hydrology*, 534: 352-63.

Márquez Molina, J. J., Susana A. Urricariet, Claudia M. Sainato, Beatriz N. Losinno, and Olga S. Heredia. 2015. 'Effects of feedlot manure on soil and groundwater assessed with electrical resistivity tomography', *Environmental Earth Sciences*, 73: 1459-72.

Martin, Holger, Bradley M. Patterson, Greg B. Davis, and Peter Grathwohl. 2003. 'Field Trial of Contaminant Groundwater Monitoring: Comparing Time-Integrating Ceramic Dosimeters and Conventional Water Sampling', *Environmental Science & Technology*, 37: 1360-64.

McHugh, Thomas, Poonam Kulkarni, Lila Beckley, Charles Newell, and Brian Strasters. 2015. 'ESTCP Project ER-201209'. https://www.serdp-estcp.org/content/download/37513/357294/file/ER-201209-TR.pdf. *Accessed 9/3/2020*.

Memon, Bashir A., Kresic N. Mikszewski. 2014. 'Hydrogeological conceptual site models: data analysis and visualization', *Environmental Earth Sciences*, 72: 623-23.

Mendoza, Donaldo P., Bradley G Fritz, Gregory W. Patton, Tyler J. Gilmore, Mary J. Hartman Robert Mackley, Frank A. Spane, Bruce N. Bjornstad, Mark D. Sweeney, Raymond E. Clayton. 2007. Investigation of the Strontium-90 Contaminant Plume along the Shoreline of the Columbia River at the 100-N Area of the Hanford Site. PNNL-16894, Pacific Northwest National Laboratory, Richland, Washington.

Meyerhoff, Steven B., Reed M. Maxwell, André Revil, Jonathan B. Martin, Marios Karaoulis, and Wendy D. Graham. 2014. 'Characterization of groundwater and surface water mixing in a semiconfined karst aquifer using time-lapse electrical resistivity tomography', *Water Resources Research*, 50: 2566-85.

Moretto, Ligia Maria, and Kurt Kalcher. 2014. Environmental Analysis by Electrochemical Sensors and Biosensors: Fundamentals (Springer New York: New York, NY).

Murdock, Chris, Mike Kelly, Ling-Yuan Chang, William Davison, and Hao Zhang. 2001. 'DGT as an in Situ Tool for Measuring Radiocesium in Natural Waters', *Environmental Science & Technology*, 35: 4530-35.

Newell, Charles, David Adamson, Beth L. Parker, Steven W. Chapman, and Tom Sale. 2013. "Determining Source Attenuation History to Support Closure by Natural Attenuation." ESTCP Project ER-201032 https://clu-in.org/download/techfocus/na/NA-ER-201032-FR.pdf. *Accessed 8/30/2020*.

Nicolle, Jérôme, Valérie Desauziers, Pierre Mocho, and Olivier Ramalho. 2009. 'Optimization of FLEC®-SPME for field passive sampling of VOCs emitted from solid building materials', *Talanta*, 80: 730-37.

NJDEP - New Jersey Department of Environmental Protection. 2012. "Monitored Natural Attenuation: Technical Guidance." (full report, edited by Site Remediation Program.) https://cluin.org/download/techfocus/na/mna\_NJ\_guid\_2012.pdf. *Accessed 09/3/2020*.

Noori, Jafar Safaa, John Mortensen, and Alemnew Geto. 'Recent Development on the Electrochemical Detection of Selected Pesticides: A Focused Review.' *Sensors* (Basel, Switzerland), vol. 20, no. 8, MDPI AG, Apr. 2020, p. 2221-, doi:10.3390/s20082221.

Novakowski, Kent, Greg Bickerton, Pat Lapcevic, John Voralek, and Nathalie Ross. 2006. 'Measurements of groundwater velocity in discrete rock fractures', *Journal of Contaminant Hydrology*, 82: 44-60.

NRC - National Research Council. 2013. Alternatives for managing the nation's complex contaminated groundwater sites (National Academies Press). https://doi.org/10.17226/14668. Accessed 08/20/2020.NRC - National Research Council. 2005. Contaminants in the Subsurface: Source Zone Assessment and Remediation (The National Academies Press: Washington, DC). https://doi.org/10.17226/11146. Accessed 09/03/2020.

Otero, Neus, Clara Torrentó, Albert Soler, Anna Menció, and Josep Mas-Pla. 2009. 'Monitoring groundwater nitrate attenuation in a regional system coupling hydrogeology with multi-isotopic methods: The case of Plana de Vic (Osona, Spain)', *Agriculture, Ecosystems & Environment*, 133: 103-13.

Perri, Maria T., Ilaria Barone, Giorgio Cassiani, Rita Deiana, and Andrew Binley. 2020. 'Borehole effect causing artefacts in cross-borehole electrical resistivity tomography: A hydraulic fracturing case study', *Near Surface Geophysics*, 18: 445-62.

Puschenreiter, Markus. 2017. 'William Davison (Ed.): Diffusive gradients in thin-films for environmental measurements', *Analytical and Bioanalytical Chemistry*, 409: 1973-74.

Quesada-González, Daniel, Grace A. Jairo, Robert C. Blake, Diane A. Blake, and Arben Merkoçi. 2018. 'Uranium (VI) detection in groundwater using a gold nanoparticle/paper-based lateral flow device', *Scientific Reports*, 8: 16157.

Quinn, John J., and Robert L. Johnson. 2005. 'Continuous water-level monitoring in the assessment of groundwater remediation and refinement of a conceptual site model', *Remediation Journal*, 15: 49-61.

Rico, Ma Angeles, Mara Olivares-Marín, and Eduardo Pinilla Gil. 2009. 'Modification of carbon screenprinted electrodes by adsorption of chemically synthesized Bi nanoparticles for the voltammetric stripping detection of Zn(II), Cd(II) and Pb(II)', *Talanta*, 80: 631-5.

Robinson, Judy, Timothy Johnson, and Mark Rockhold. 2020. 'Feasibility Assessment of Long-Term Electrical Resistivity Monitoring of a Nitrate Plume', *Groundwater*, 58: 224-37.

Rügner, Hermann, Michael Finkel, Arno Kaschl, and Martin Bittens. 2006. 'Application of monitored natural attenuation in contaminated land management—A review and recommended approach for Europe', *Environmental Science & Policy*, 9: 568-76.

Stefania, Gennaro, Marco Rotiroti, Letizia Fumagalli, Chiara Zanotti, and Tullia Bonomi. 2018. 'Numerical Modeling of Remediation Scenarios of a Groundwater Cr(VI) Plume in an Alpine Valley Aquifer', *Geosciences (Basel)*, 8: 209. Swager, Timothy M., and Katherine A. Mirica. 2019. 'Introduction: Chemical Sensors', *Chemical Reviews*, 119: 1-2.

USDOE. 2001. "A Report to Congress Detailing DOE's Existing and Anticipated Long-Term Stewardship Obligations." http://lts.apps.em.doe.gov/center/. *Accessed 09/3/2020*.

USEPA - United States Environmental Protection Agency. 1999a. "Groundwater Cleanup: Overview of Operating Experience at 28 Sites." EPA 542-R-99-006; September 1999.

USEPA - United States Environmental Protection Agency. 1999b. "Monitored Natural Attenuation of Chlorinated Solvents." EPA/600/F-98/022; May 1999.

USEPA - United States Environmental Protection Agency. 1999c. "Use of Monitored Natural Attenuation at Superund, RCRA Corrective Action, and Underground Storage Tank Sites." EC-G-2002-095; April 1999.

USEPA - United States Environmental Protection Agency. 2003. 'A Review of Emerging Sensor Technologies for Facilitating Long-Term Ground Water Monitoring of Volatile Organic Compounds'. EPA 542-R-03-007. 2003.

USEPA - United States Environmental Protection Agency. 2005. "Roadmap to Long-Term Monitoring Optimization." EPA 542-R-05-003; May 2005.

USEPA - United States Environmental Protection Agency. 2012. "Groundwater Road Map: Restoring Contaminated Groundwater at Superfund Sites." In *The Hazardous waste consultant*, 1. Lakewood: Aspen Publishers, Inc. OSWER 9283.1-34; July 2012.

Verreydt, Goedele, Jan Bronders, Ilse Van Keer, Ludo Diels, and Paul Vanderauwera. 2010. 'Passive Samplers for Monitoring VOCs in Groundwater and the Prospects Related to Mass Flux Measurements', *Groundwater Monitoring & Remediation*, 30: 114-26.

Vrana, Branislav, Ian J. Allan, Richard Greenwood, Graham A. Mills, Ewa Dominiak, Katarina Svensson, Jesper Knutsson, and Gregory Morrison. 2005. 'Passive sampling techniques for monitoring pollutants in water', *TrAC Trends in Analytical Chemistry*, 24: 845-68.

Vystavna, Yuliya, Frédéric Huneau, Mikael Motelica-Heino, Philippe Le Coustumer, Yuri Vergeles, and Felix Stolberg. 2012. 'Monitoring and flux determination of trace metals in rivers of the Seversky Donets basin (Ukraine) using DGT passive samplers', *Environmental Earth Sciences*, 65: 1715-25.

Wang, Xu-dong, and Otto S. Wolfbeis. 2016. 'Fiber-Optic Chemical Sensors and Biosensors (2013–2015)', *Analytical Chemistry*, 88: 203-27.

Wang, Yidong, Deyi Hou, Shengqi Qi, David O'Connor, and Jian Luo. 2019. 'High stress low-flow (HSLF) sampling: A newly proposed groundwater purge and sampling approach', *Science of The Total Environment*, 664: 127-32.

WDNR - Wisconsin Department of Natural Resources. 2014. "Guidance On Natural Attenuation For Petroleum Releases." RR-614; January 2014.

Willner, Marjorie R., and Peter J. Vikesland. 2018. 'Nanomaterial enabled sensors for environmental contaminants', *Journal of nanobiotechnology*, 16: 95-95.

Wilson, John T. 2012. "Approach for Evaluating the Progress of Natural Attenuation in Groundwater." In, 84. https://semspub.epa.gov/src/document/HQ/175789. *Accessed 09/03/2020*.

Yin, Ming-jie, Bobo Gu, Quan-Fu An, Chengbin Yang, Yong Liang Guan, and Ken-Tye Yong. 2018. 'Recent development of fiber-optic chemical sensors and biosensors: Mechanisms, materials, micro/nano-fabrications and applications', *Coordination Chemistry Reviews*, 376: 348-92.

## Appendix A

## Data Quality Objectives in an Extended Plume Monitoring Scenario

Data quality objectives (DQOs) define a process for identifying the type, quantity, and quality of data needed to evaluate environmental risks and support decision-making. A monitoring strategy for verifying the maintenance of remedial actions for contaminated groundwater for ESM program can be designed by following a DQO process (EPA 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 should represent to satisfy this purpose, and specifies the performance requirements for the quality of information to be obtained from the data (EPA 2000).

Data quality objectives are to be specific, measurable, achievable, relevant, and time-bound, following the 'SMART' protocol (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 contain the COC within the controlled 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 functional objective is cost effectiveness; data must broadly quantify plume movement, but additional monitoring of detailed plume dynamics may generate significant expense for little additional information.

Physical and geochemical heterogeneities and contaminant subsurface behavior often present the largest sources of uncertainty at hazardous waste sites. Thus, the SMART protocol typically focuses on defining absolute and functional objectives based on the current understanding of the conceptual site model (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.

For each of the plume scenarios depicted in Section 3 (Figure 3.1–Figure 3.4), a set of unique functional objectives must be articulated. A detached source and plume require monitoring which advances progressively in both space and time to match the COC migration. A diminishing source may employ advancing, followed by retreating well monitoring to verify plume migration and abatement as predicted by the CSM. Both composite and non-contiguous plumes require tailored functional objectives to adequately monitor the primary COC plume(s) and the variability of contaminant migration caused by heterogeneities and changing (i.e. seasonal) hydraulic conditions. While these different ESM scenarios require some unique functional objectives, they all share optimization of cost as a functional objective.

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 Monitored Natural Attenuation (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, often uncertainties related to the physical and geochemical subsurface, hydrologic conditions, plume dynamics and other sources of uncertainty. 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.

An ESM program presents challenges that differ from traditional monitoring efforts for which guidance has been developed and experience gained. 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 seven DQO steps.

#### A.1 Step 1. State the Problem.

The main outputs of Step 1 of the DQO process is a description of the problem to be addressed though data collection and a CSM, formation of a planning team, and identification of relevant resources. Under an ESM program, the problem statement should explicitly address the scale and time issues confronting the monitoring strategy design. With respect to the scale of groundwater plumes and distances to boundaries and receptors, the problem statement should acknowledge the vast complexity of the potentially affected subsurface, the number of characterization boreholes and monitoring wells, and the large number of samples required to fully characterize the subsurface. The problem statement should also characterize the general plume scenario (detached, diminishing, etc.). Such acknowledgment early on can identify the needs for a more focused ESM investigation.

The CSM should proceed from a basic characterization of expected plume transport. Under ESM, the CSM should also address processes that will occur over decades, including contaminant degradation rate (the main concern of MNA), 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 should be addressed. Seasonal and decadal variations in groundwater conditions should be characterized and anticipate the possible effects of climate change, land and surface water use, and receptor types, locations and numbers. Importantly, potential changes in regulations and action levels should be considered, particularly as they may determine contaminants of interest and their acceptable concentration limits.

## A.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 controlled zone. In all cases of decision identification, a series of alternative actions should be proposed which 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 technical impracticability (TI) waiver might be sought in some instances.

Step 2 should consider 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 timescale, 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. For example, if alternative water uses such as irrigation are available actions, the data needs for such uses need to be identified.

### A.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 modelling 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 modelled value required to make an informed decision on alternative actions. The action level basis is likely to be based on COC 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, however, routine measurements (every 5-10 years) provide continual reassurance that no alternative action is required.

The primary goal of ESM is to verify that the contaminant remains within the containment zone. In century scale plumes, groundwater conditions may change due to climate change or changes in land or water use. Since ESM is executed over decades, the requirements for record keeping and databases may also evolve over time. Challenges of laboratory support continuity and comparability should be considered. 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 should be periodically re-evaluated as new technologies develop.

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

The outputs of Step 4 are definitions of the scope of the investigation, including the geographical limits of the investigation, subsurface strata, and contaminants of interest, including degradation products. This step also sets the sampling time intervals and specifies the initial monitoring network. For active remediation, geographical areas may be divided into populations and subpopulations. As ESM is only prescribed for areas far from receptors, such detailed analysis is unnecessary. ESM geographical boundaries are easily defined: the controlled zone extends from the source plume to the nearest downgradient receptor, at which point the receptor zone begins. The slow movement of contaminant and spatial separation from receptors provide reduced risk and added time for decisions.

As shown in Figures 3.1–3.4 in Section 3, 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 well away from receptors.

Sampling designs should consider how the boundaries and scope of monitoring and compliance might change over several decades. Future receptor conditions might change over time 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 should also be considered. Compliance requirements of the various alternatives, including a TI waiver, may also affect sampling designs if it becomes evident that cleanup to higher uses will not be practicably achievable.

#### A.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 active remediation may be recommended. The 'if statement' may be based on a statistical parameter (mean, median, etc.) which properly characterizes the COC. The concentration at which action is prescribed should surpass the limit of detection 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 COC to cease monitoring is also desirable.

In Step 5, the means by which measurement data will be applied to make decisions is identified. The specific statistical tests that might be applied and their required inputs should be identified early in the planning to ensure that the correct measurements are made. Mean concentration is likely to be the parameter of choice for diminishing plumes, as these should not have a sharp concentration gradient. A unique sampling strategy may be recommended for non-contiguous 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, the 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 could 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.

#### A.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 which 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 controlled 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 and 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 controlled zone. Only a radical deviance in measured concentration from predicted CSM

values would warrant action. In this case, the associated sampling or measurement error is likely well below the threshold for causing a decision error. Non-contiguous and composite plumes are nonhomogeneous and have more error associated with sampling. However, due to the long distances between plume and receptor, the gray area is still large enough to allay concerns of a decision error. If an order of magnitude difference is observed between measured and CSM values, and the measured values are above the LOQ, then an action level may be reached. However, normal measurement error is not likely to contribute significantly in this situation.

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 should not be cause for alarm, due to the associated measurement errors. Concentrations near the LOQ would be 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 both LOQ and LOD.

As part of the procedure for adopting an ESM approach, concentration values should not greatly differ between measurements and the CSM predictive analyses. If measured concentration of COC is significantly higher than predicted, the CSM may be updated accordingly. Only massive deviation should result in action, wherein use of the ESM approach may be reconsidered. 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.

### A.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 is generally judgmental, as it subjectively targets anticipated contaminant locations as modelled by the CSM. Over time the number of sampling wells may diminish, as statistical methods can be used to locate redundant wells. This is especially true for detached plumes, where contaminant 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 not necessary or 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. As stated in A.6, accuracy of measurements is not the primary concern of ESM sampling. The objective is simply to verify that 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.

With respect to the temporal challenges related to ESM of groundwater plumes, Step 7 should employ an informed and flexible strategy to allow updates to sampling designs over time as site knowledge is gained, groundwater assumptions are confirmed or denied, and technologies or regulatory constraints change. Such an approach may rely on multiple lines of evidence and predictive analyses. Planners should periodically review action alternatives and associated action levels to bring into focus leading alternatives at the earliest possible time so that sampling designs can be appropriately focused. Factors that could affect groundwater conditions and receptor populations over decades, such as climate change, changes in

land and water use, and receptor populations, should be examined and monitored for their effects on possible alternatives actions. Identifying these future changes up front and developing potential operational changes with respect to them, will engage regulators and stakeholders in the process of identifying an ESM approach.

#### A.8 References

Bunn AL, DM Wellman, RA Deeb, EL Hawley, MJ Truex, M Peterson, MD Freshley, EM Pierce, J McCord, MH Young, TJ Gilmore, R Miller, AL Miracle, D Kaback, C Eddy-Dilek, J Rossabi, MH Lee, RP Bush, P Beam, GM Chamberlain, J Marble, L Whitehurst, KD Gerdes, and Y Collazo. 2012. *Scientific Opportunities for Monitoring at Environmental Remediation Sites (SOMERS): Integrated Systems-Based Approaches to Monitoring*. DOE/PNNL-21379. Prepared for Office of Soil and Groundwater Remediation, Office of Environmental Management, U.S. Department of Energy, Washington, D.C., by Pacific Northwest National Laboratory, Richland, WA.

Doran, G. T. (1981). There's a S.M.A.R.T. way to write management's goals and objectives. Management Review. 70 (11): 35–36.

EPA (U.S. Environmental Protection Agency) 2000. *Data Quality Objectives Process for Hazardous Waste Site Investigations (QA/G-4HW)*, Final, EPA/600/R-00/007 January 2000.

ITRC (Interstate Technology & Regulatory Council). 2011. *Project Risk Management for Site Remediation*. RRM-1. Washington, D.C.: Interstate Technology & Regulatory Council, Remediation Risk Management Team. <u>www.itrcweb.org</u>.

NRC (National Research Council) 2005. *Contaminants in the Subsurface: Source Zone Assessment and Remediation*, National Academies Press, Washington, D.C.

CERCLA. United States. 1980. Comprehensive Environmental Response, Compensation, and Liability Act of 1980. Pub 1. 96-510, approved December 11, 1980. 42 U.S.C. § 9601 et seq.

## 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 two-dimensional 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 website 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 stats package provides an assessment of sampling frequency, the number and location of well locations needed, and the probabilistic determination of exceeding threshold concentrations at well locations. Based on statistical confidence to determine the number of samples and frequency; the software may not be well suited to limited data-based plume projections. The beta version software package is currently downloadable free of charge.

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

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 environment site cleanup. DSTs often support multiple functions, such as data acquisition, spatial data management, modeling, and cost estimating. The Federal Remediation Technologies Roundtable matrix 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 Center for Engineering and the Environment (AFCEE) in accordance with the AFCEE Long-Term Monitoring Optimization guide. 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. 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 ProUCL Software

ProUCL is a comprehensive free statistical software package with statistical methods and graphical tools to address many environmental sampling and statistical issues. 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.6 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.7** 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 (NAPL) dissolution, and biodegradation. NAS

determines redox zonation, and estimates and applies varied biodegradation rates from one redox zone to the next.

#### B.8 Mass Flux Toolkit

The Mass Flux Toolkit, developed for the Department of Defense ESTCP 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; and
- a module that provides a review of theory and methods of estimating mass flux.

#### B.9 3DVA

*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 identifies 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 offers 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.

## **Appendix C 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 contaminants of concern. Sentinel wells also provide evidence that the expected plume movement is not radically different than predicted by the CSM. 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 which proceeds from the absolute objective of restricting contaminant movement to the controlled 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.

In 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 supply wells in a period of 2-5 years. For ESM settings, the target area may be defined based on containment boundaries. As the purpose of sentinel wells is solely to verify receptor protection, they should be spaced far downgradient while still allowing sufficient time for action in the unlikely event of elevated contaminant level detection. 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 CMS projections.

#### C.1 References

AMEC E&I PC, 2019, Sentinel Monitoring Well Installation Work Plan Well B Location, Former Unisys Facility, Lake Success, New York, Site No. 130045 Operable Unit 2, Bayside NY. March 2019.

Byrnes, M.E. 2008. "FEASIBILITY STUDY REPORT FOR THE 200-ZP-1 GROUNDWATER OPERABLE UNIT." (DOE/RL – 2007-28). United States

NJDEP - New Jersey Department of Environmental Protection. 2012. "Monitored Natural Attenuation: Technical Guidance." In, edited by Site Remediation Program. https://cluin.org/download/techfocus/na/mna\_NJ\_guid\_2012.pdf. *Accessed 09/03/2020*.

## Pacific Northwest National Laboratory

902 Battelle Boulevard P.O. Box 999 Richland, WA 99354 1-888-375-PNNL (7665)

www.pnnl.gov