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**Miles E. Denham, Mark B. Amidon,
Haruko M. Wainwright, Baptiste
Dafflon, Jonathan Ajo-Franklin & Carol
A. Eddy-Dilek**

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Improving Long-term Monitoring of Contaminated Groundwater at Sites where Attenuation-based Remedies are Deployed

Miles E. Denham¹ · Mark B. Amidon² · Haruko M. Wainwright³ · Baptiste Dafflon³ · Jonathan Ajo-Franklin^{3,4} · Carol A. Eddy-Dilek²

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Abstract

This study presents an effective approach to tackle the challenge of long-term monitoring of contaminated groundwater sites where remediation leaves residual contamination in the subsurface. Traditional long-term monitoring of contaminated groundwater sites focuses on measuring contaminant concentrations and is applicable to sites where contaminant mass is removed or degraded to a level below the regulatory standard. The traditional approach is less effective at sites where risk from metals or radionuclides continues to exist in the subsurface after remedial goals are achieved. We propose a long-term monitoring strategy for this type of waste site that focuses on measuring the hydrological and geochemical parameters that control attenuation or remobilization of contaminants while de-emphasizing contaminant-concentration measurements. We demonstrate how this approach would be more effective than traditional long-term monitoring, using a site in South Carolina, USA, where groundwater is contaminated by several radionuclides. A comprehensive enhanced attenuation remedy has been implemented at the site to minimize discharge of contamination to surface water. The immobilization of contaminants occurs in three locations by manipulation of hydrological and geochemical parameters, as well as by natural attenuation processes. Deployment of our proposed long-term monitoring strategy will combine subsurface and surface measurements using spectroscopic tools, geophysical tools, and sensors to monitor the parameters controlling contaminant attenuation. The advantage of this approach is that it will detect the potential for contaminant remobilization from engineered and natural attenuation zones, allowing potential adverse changes to be mitigated before contaminant attenuation is reversed.

Keywords Groundwater · Long-term monitoring · Radionuclide contamination · Remediation

Introduction

Post-closure long-term monitoring is required at waste sites where residual contamination is left in the subsurface to inform site owners and regulators of any unexpected contaminant behavior that could be a potential threat to human health and the environment. Sites with residual contamination are those where contaminant source zones have been contained but not eliminated, as well as those in which

remediation of contaminated groundwater is designed to immobilize contaminants in the subsurface, rather than remove them. These include many types of sites, such as landfills, coal- and metal-mining sites, industrial sites, and locations of accidental spills of toxic substances. The objective of long-term monitoring at these sites is to ensure that risk to humans and the environment from residual contaminants remains low long after operational and remedial activities have ceased.

Here we focus on an approach to improve long-term monitoring at sites where contaminants remain in the subsurface after remediation of contaminated groundwater. Regulatory agencies have become more accepting of groundwater-remediation strategies that rely on immobilizing, or attenuating, contaminants in the subsurface, referred to here as attenuation-based remedies (USEPA 1999, 2007a, 2015; IAEA 2004, 2006; ITRC 2010; NRC 2013). Formal guidance has been issued by federal and state agencies in the United States for use of monitored natural

✉ Miles E. Denham
mdenham@panoramic.consulting

¹ Panoramic Environmental Consulting, LLC, Aiken, SC, USA

² Savannah River National Laboratory, Aiken, SC, USA

³ Lawrence Berkeley National Laboratory, Berkeley, CA, USA

⁴ Rice University, Houston, TX, USA

attenuation (MNA) to remediate metal- and radionuclide-contaminated groundwater (USEPA 2007a, 2015; ITRC 2010). MNA is an accepted remedy in Europe and elsewhere for contamination by organic compounds, but attenuation-based remedies are less prevalent for metals and radionuclides (Rügner et al. 2006; Usher et al. 2008; Declercq et al. 2012; Majone et al. 2015). There were 16 years between the time the United States Environmental Protection Agency (USEPA) issued a formal directive on MNA for organic compounds and the issuance of a similar directive for metals and radionuclides. In the interim, extensive research was done to demonstrate that MNA was a safe and effective remediation strategy for metals and radionuclides under the right circumstances. The abundance of research in other countries on natural and engineered attenuation of metals and radionuclides (e.g., Blowes et al. 2000; Lee and Hartwig 2005; LaPointe et al. 2005; Fytas 2010; Krishna et al. 2010; Vázquez et al. 2011; Jurkovič et al. 2019; Wang et al. 2019; Sakala et al. 2020) suggests that these will become accepted remedies in other countries as well, increasing the need for efficient long-term monitoring.

Attenuation-based remedies for metals and radionuclides in groundwater have become common in the United States because they are effective and efficient at sites where contaminant removal is impractical. In many cases, natural processes, such as precipitation, sorption, and dilution, limit the migration of contaminants sufficiently to minimize any hazard. In other cases, subsurface zones are engineered to produce conditions conducive to contaminant attenuation (Evanko and Dzombak 1997; Hashim et al. 2011; Obiri-Nyarko et al. 2014). Long-term monitoring is particularly important where attenuation-based remedies are deployed to ensure that attenuation capacity remains high enough to affect the entire mass of contamination and ensure that conditions do not change in a way that promotes remobilization of contaminants.

The time span of long-term monitoring depends, in part, on how long contaminants will persist. Long-term monitoring may be required for only years to decades for organic contaminants because the attenuation of these contaminants generally results in their transformation or degradation to less-harmful chemicals. Long-term monitoring at these sites is done until the risk posed by the residual mass of contaminants is acceptable. Thus, for organic contaminants, there is a finite time period for long-term monitoring based on degradation rate and mass of contaminants. In contrast, toxic metals and long-lived radionuclides will persist for long time periods in attenuation zones, if hydrologic and geochemical conditions continue to limit their migration. Thus, the period required for long-term monitoring is indefinite and can span decades to centuries, depending on the toxicity of the contaminants,

their concentrations, and their proximity to potential receptors.

The original definitions of long-term monitoring included the objective of evaluating the effectiveness of remedial activities in addition to ensuring that future risk at a site remains acceptable. Within the framework of this definition, long-term monitoring is the last stage of a continuously evolving program and sampling network that primarily measures contaminant concentrations at point locations (e.g., monitoring wells or springs). For the long-term monitoring stage, statistical methods and numerical modeling are used to optimize the preexisting network of sampling points and sampling frequency to maintain collection of key information while reducing the costs (Reed et al. 2000, 2001; Reed and Minsker 2004; USEPA 2004, 2005a; Harre et al. 2009; Hunter et al. 2011). This approach is appropriate for sites at which contaminant mass is removed from the subsurface by extraction or in situ degradation because the objective of long-term monitoring remains similar to that of remedy-effectiveness monitoring, ensuring that remedial processes are sustained until the remaining contaminant mass is no longer a risk.

Such a traditional approach to long-term monitoring is less appropriate for attenuation-based remedies of metal and radionuclide contaminants. First, the objective of long-term monitoring of attenuated metals and radionuclides should be different than the objective of remedy-effectiveness monitoring. These contaminants will remain in the subsurface in perpetuity, and the objective of long-term monitoring should be to ensure that the contaminants stay attenuated. Measuring contaminant concentrations can only indicate when attenuated contaminants are remobilized. In other words, measurements of contaminant concentrations downgradient from an attenuation zone are lagging indicators. It is preferable to measure leading indicators that warn of changing conditions that could potentially remobilize attenuated contaminants before they are affected. Second, for sites that require long-term monitoring for decades to centuries, the cumulative cost of obtaining samples and analyzing them for contaminant concentrations becomes prohibitive (NRC 1999, 2013). Given these reasons and the proliferation of attenuation-based remedies for metals and radionuclides, alternative approaches to long-term monitoring should be considered.

In this paper, we present an improved approach to long-term monitoring at sites where attenuation-based remediation of metal and radionuclide contamination has been deployed. The approach de-emphasizes measurement of contaminant concentrations in favor of measuring the variables that control attenuation of the contaminants. While previous guidance on monitoring of attenuation-based remedies recommends measuring controlling variables, these measurements have always been secondary to

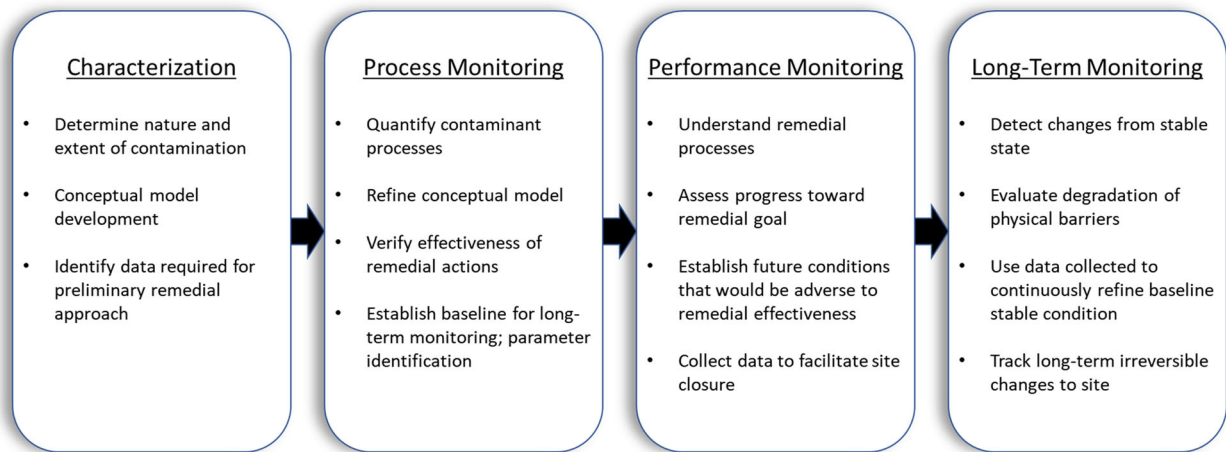


Fig. 1 Phases of monitoring a waste site (modified from Bunn et al. 2012)

measurements of contaminant concentrations. We show that putting primary focus on measuring controlling variables is a more effective and efficient approach to long-term monitoring at these sites. We then present an example of how improved long-term monitoring would be implemented at the F-area Seepage Basins on the US Department of Energy's Savannah River Site using a structured approach and new-generation tools. Recently, a multiyear project began at this site to assess the improved long-term monitoring approach contemporaneous with the current more traditional monitoring program. We present preliminary data here, yet because of the long-term nature of the project it will be many years before there is definitive data demonstrating the effectiveness of this new approach. Nevertheless, we believe that it is important to present this now for consideration by waste-site owners, regulatory agencies, and stakeholders because acceptance of new remediation and monitoring strategies is, by necessity, a slow and careful process.

Framework for a New Approach to Long-term Monitoring

The framework for the new long-term monitoring approach proposed here is built upon USEPA (1999, 2007a, 2015) and Bunn et al. (2012). The USEPA documents provide guidance on the use of MNA, including the monitoring objectives necessary to demonstrate that residual contamination is not a risk. The overall monitoring objective is summarized by the statement in USEPA (2015):

“Ultimately, monitoring programs should be designed to demonstrate continued stability of the plume over time and to identify changes in groundwater chemistry

that may lead to decreases in rates or capacity of the aquifer to attenuate the contaminant of concern or changes that may lead to re-mobilization of attenuated compounds.”

Bunn et al. (2012) provide a systematic approach to monitoring a contaminated site throughout the remediation lifecycle. They defined monitoring in four phases, shown in Fig. 1, proceeding in the sequence “characterization monitoring → process monitoring → performance monitoring → long-term monitoring.” In the first three monitoring phases, plume stability is established, and understanding of the processes controlling contaminant attenuation is developed. In the long-term monitoring phase, contaminant concentrations and controlling variables are measured to warn of remobilization of contaminants. Bunn et al. (2012) suggested that long-term monitoring networks should be passive, robust, low maintenance, low cost, and able to use leading indicators.

The primary difference between the proposed long-term monitoring approach and more traditional approaches is the way in which potential receptors are protected from contaminants. Traditional long-term monitoring protects receptors by emphasizing the monitoring of pathways by which contaminants reach receptors and detecting the presence of contaminants in those pathways. The emphasis of the proposed approach is on protecting receptors by protecting the stability of attenuated contaminants. Guarding the pathways to receptors is still a part of the proposed long-term monitoring strategy, but more as a “defense in depth” against contaminants reaching receptors. The basis for this is that if contaminants are prevented from being remobilized, the need to guard the pathways to receptors is less urgent. The operational result is a difference in what to monitor, where to monitor, and the methods for monitoring.

Table 1 Parameters important for assessing hydrologic, morphologic, and geochemical stability of a waste site

Parameter	Definition	Potential influence
Hydrologic parameters		
Infiltration	Flux of water migrating into the subsurface from rainfall/snowfall	Can increase flux of water to the water table, affecting groundwater flow, diluting, and/or pushing contaminant plumes downward
Evapotranspiration	Flux of water lost from the subsurface by evaporation and uptake by plant roots	Subtracts water from infiltration and potentially the top of the water-table aquifer; affects groundwater flow
Hydraulic head	Elevation of the top of the water column in a well, screened in an aquifer	Means for determining groundwater-flow direction and velocity
Morphologic characteristics		
Topography	Depiction of surface features	Controls surface-water drainage; influences infiltration and groundwater flow
Vegetation	Type and density of plants	Influences evapotranspiration; mode of degradation of surface barriers to infiltration; can indicate changing groundwater conditions
Chemical parameters		
pH	Negative log of hydrogen-ion activity; measures acidity of groundwater	Important control on precipitation and adsorption of most inorganic contaminants
Oxidation-reduction potential	General measure of potential for electrons to transfer between dissolved ions and between ions and minerals	Important control on precipitation and adsorption of contaminants with multiple valence states

Monitoring Controlling Variables

The parameters measured in the proposed new long-term monitoring strategy affect attenuation of contaminants and provide information necessary to keep the monitoring network relevant over long time periods. These parameters, or controlling variables, reflect the physical forces that drive contaminant movement and the chemical forces that control contaminant attenuation. Table 1 defines important hydrologic, morphologic, and geochemical controlling variables and their influence on contaminant migration and attenuation. An assumption for beginning long-term monitoring is that the site is hydrologically, morphologically, and geochemically stable, and contaminant behavior is well understood following the first three phases of monitoring. Parameters can vary spatially and temporally at stable sites, but their variations are understood and consistent with maintaining attenuation of contaminants. Interpretation of long-term monitoring data consists of recognizing abnormal spatiotemporal trends in controlling variables that may affect contaminant behavior or the efficacy of the monitoring network. Action levels will be established for parameters that strongly influence contaminant attenuation. These will be specified in a long-term monitoring plan that will also describe the response to adverse trends and the measurement of an action level for each pertinent parameter.

Measuring such physical and chemical parameters that indicate change to a system has multiple advantages over measuring contaminant concentrations at specific locations. First and foremost, they are “leading” indicators of potential unexpected contaminant behavior that promote proactive decisions that can prevent remobilization of attenuated contaminants. Second, most of them are easily and inexpensively measured by robust in situ sensors that transmit data wirelessly to a central location (Schmidt et al. 2018).

Monitoring Hydrologic Stability

The purpose of monitoring hydrologic stability is to detect events or conditions outside the norm of the known stable state and identify whether they will potentially affect contaminant attenuation or the relevance of elements of the monitoring network. Water is the physical force that drives contaminant migration by leaching contaminants from near-surface sources, vadose-zone sources, or locations where contaminants are attenuated in the saturated zone. Therefore, flux of water passing through contaminant sources at the surface or deeper in the vadose zone must be monitored. Furthermore, as long-term monitoring begins at many sites, contaminants in the saturated zone will still be migrating into zones where they will be immobilized. A change in groundwater-flow direction can alter the path of the

contamination plume, resulting in contaminants bypassing the attenuation zone. Similarly, a change in groundwater-flow direction can render monitoring locations irrelevant because the groundwater they monitor no longer passes through an attenuation zone. Infiltration, evapotranspiration, and hydraulic head are key parameters for monitoring long-term hydraulic stability.

Infiltration is a measure of the flux of water entering subsurface soils, and the balance of infiltration and evapotranspiration determines the flux of water through the vadose zone into the saturated zone. This recharge drives groundwater flow and can dilute the top of a contaminant plume in a water-table aquifer and push it deeper into the aquifer (Weaver and Wilson 2000). Temporally averaged regional or site-wide values of infiltration are normally used for groundwater modeling. Yet, some sites may require more frequent or localized measurement of infiltration, such as the sites that have a significant mass of contaminant at the surface or deeper in the vadose zone. If these contaminant sources are not covered by impermeable barriers, then flux of water through the source is an important parameter for understanding the rate of contaminant leaching from the source. If sources are protected by physical barriers to water, measuring infiltration into, and through, the barrier, is important for understanding barrier degradation.

Evapotranspiration is a measure of water removed from infiltration by evaporation or uptake by plant roots. It is important because of its role in controlling water flux through the vadose zone. Evapotranspiration increases significantly where there is dense vegetation, and its effect may vary across a waste site, depending on the vegetation density. In arid regions, evapotranspiration may equal infiltration for most of the year and severely limit the flux of water into the vadose zone. Furthermore, in arid regions where the water table is near the surface, such as near-discharge points, removal of water by evapotranspiration can result in precipitation of contaminant-bearing evaporite minerals (Looney et al. 2014; Dam et al. 2015). Dissolution of these minerals occurs when infiltration exceeds evapotranspiration releasing the contaminants to groundwater or surface water.

Hydraulic head is the elevation to which water rises in a well that is screened within an aquifer. It is the most important parameter in long-term monitoring of hydrologic stability because the potentiometric surface delineated by interpolation between numerous hydraulic head measurements is how groundwater-flow velocity and direction are determined. Groundwater flows from a higher to a lower hydraulic head, and flow velocity depends on the gradient between hydraulic head measurements. Measurement of hydraulic head in wells screened at different depths allows determination of vertical groundwater flow. Changes in

groundwater-flow directions with time will be reflected by the potentiometric surfaces periodically constructed from hydraulic head measurements. Thus, it is important to long-term monitoring to collect hydraulic head measurements on a regular schedule and on a fine-enough spatial scale to be able to determine any significant changes to groundwater-flow direction near contaminant-attenuation zones.

There are other parameters that are easy to measure that influence hydrologic stability. Infiltration and evapotranspiration depend on precipitation (rainfall and snowfall), relative humidity, and temperature. These vary on time-scales ranging from hourly to yearly, yet the importance to long-term monitoring is when systematic changes occur over long periods that may indicate irreversible changes to climate.

Monitoring Geomorphic Stability

The important geomorphic features for long-term monitoring of a waste site are topography and the density and type of vegetation. Changes in these characteristics can affect both the hydrological and geochemical stability of a waste site, and therefore are important for long-term monitoring.

Topography encompasses the structural features at the surface, including surface elevations, drainage patterns, stream courses, and architecture of groundwater-discharge areas such as wetlands. Changes to these features can have profound effects on groundwater flow and can also result in geochemical changes to sediments where contaminants have been naturally attenuated. For example, changes to topography can remobilize contaminants attenuated in naturally reduced zones (Janot et al. 2015) by exposing them to rapid oxidation. Erosion can also release contaminants from anoxic wetland soils by exposing them to oxygen. Long-term monitoring should measure changes to topography at different spatial and temporal scales. There is the measure of large features such as drainage patterns that change slowly, barring intervention from man or catastrophic events like extreme storms, floods, or seismic activity. Yet, on covers protecting surface-contaminant sources, topographic changes at the centimeter scale can be important indications of cover degradation. Fine-scale topographic measurements can detect subsidence of the surface that indicates degradation of the underlying layers of the cover, as well as detecting animal burrows and fissures that can be pathways for increased infiltration. These small-scale changes can occur rapidly relative to changes in the large-scale features.

The nature and density of vegetation affects evapotranspiration and can also affect contaminant behavior by the uptake of contaminants and replenishing organic matter that adsorbs contaminants in sediments. Natural vegetative cover changes slowly, usually in response to topographic

Table 2 List of common metal and radionuclide contaminants in groundwater and whether their behavior is sensitive to pH and ORP (from Denham and Vangelas 2008)

Contaminant	pH	ORP
Tritium	No	No
Nitrate	No	Yes
Chromium (VI)	Yes	Yes
Nickel	Yes	Yes ^a
Copper	Yes	Yes
Arsenic	Yes	Yes
Selenium	Yes	Yes
Strontium-90	Yes	No
Technetium-99	No	Yes
Cadmium	Yes	Yes ^a
Iodine-129	Yes	Yes
Cesium-137	Yes	No
Mercury	Yes	Yes
Lead	Yes	Yes ^a
Radium isotopes	Yes	No
Uranium isotopes	Yes	Yes
Neptunium-237	Yes	Yes
Plutonium isotopes	Yes	Yes
Americium-241	Yes	No

^aOnly by sulfide mineralization

changes, unless human intervention by removal of vegetation or introduction of invasive species occurs. In contrast, deep-rooted vegetation can become established on caps and covers of contaminant sources relatively rapidly and contributes to degradation of these structures. Therefore, caps and covers over surface sources should be surveyed for vegetation more frequently than the overall site.

Monitoring Geochemical Stability

Quantifying changes in parameters that most influence chemical and biological processes that attenuate contaminants is a critical function of long-term monitoring. A wealth of literature is available that discusses the behavior of metals and radionuclides in natural waters (e.g., Stumm and Morgan 1996; Drever 1997; USEPA 2007a). Basic discussions of the behavior of specific metal and radionuclide contaminants in groundwater are presented in Evanko and Dzombak (1997), IAEA (2006), and USEPA (2007b, c).

In summary, pH and oxidation-reduction potential (ORP) are of primary importance in controlling the behavior of metals and radionuclides in soils and groundwater. Acidity of groundwater, measured as pH (negative log of hydrogen-ion activity), is a fundamental control on metal and radionuclide attenuation. It controls surface charge on most

minerals, and hence, adsorption of ions to mineral surfaces (Stumm and Morgan 1996). Likewise, pH influences aqueous speciation of most metals and radionuclides, which, in turn, influences their adsorption and precipitation (USEPA 2007a; Dafflon et al. 2013). The redox state of an aquifer system, measured in groundwater as ORP, also influences aqueous speciation and solubility of contaminants that can exist in multiple oxidation states. Under sulfate-reducing conditions, even metals that are not normally sensitive to ORP, such as lead, cadmium, and zinc, can be strongly attenuated by precipitation of sulfide minerals (USEPA 2007a). Measured ORPs are not a direct indication of the redox state of any contaminant, but changes in such measurements with time do generally indicate changes to the system that may be important to the stability of an attenuated contaminant. Table 2 lists common metal and radionuclide contaminants and whether their behavior in groundwater is sensitive to pH and ORP.

At some sites, parameters other than ORP and pH may be important indicators of system changes that can lead to contaminant remobilization. For example, carbonate alkalinity or dissolved carbon dioxide coupled with pH is a critical parameter for mobilization of uranium (Langmuir 1978; Hsi and Langmuir 1985; Waite et al. 1994) and other metals readily complexed by carbonate ions (USEPA 2007b, c). Ionic strength is also an important influence on adsorption of many metals and radionuclides, and increases in ionic strength could portend desorption of these contaminants. The conceptual site model must dictate the important chemical parameters to measure for each site, or even for individual areas within a site.

Monitoring Vulnerabilities

Monitoring locations are defined by the objective of the new long-term monitoring approach, guarding the stability of residual contaminants. Thus, monitoring focuses on locations where contaminants are attenuated, referred to here as vulnerable zones, to detect changes in conditions that could potentially remobilize contaminants. Vulnerable zones can be at the surface, in the vadose zone, or in the saturated zone. Vulnerable zones at the surface should be monitored for infiltration through the zones or barriers covering the zones. If barriers to infiltration are in place, then monitoring should include methods to assess their degradation. Monitoring a vulnerable vadose zone should consist of measuring changes in water flux that could increase mobilization of contaminants. In the saturated zone, monitoring should be done upgradient of vulnerable zones for adverse changes in hydrologic and chemical conditions that could mobilize attenuated contaminants. Conditions that reverse attenuation of contaminants in the saturated zone can originate from within the waste site or from outside the

site boundaries because waste sites are rarely hydrologically isolated. Therefore, events that occur beyond the waste-site boundaries, such as clearcutting timber or dewatering of a construction site, that may not be known by waste-site managers, can affect groundwater-flow direction at the waste site. Likewise, altered groundwater chemical conditions caused by off-site events or practices that are unknown to site managers can migrate onto a waste site and affect vulnerable zones. An extra layer of protection is gained by monitoring the perimeter of the site to provide early warning of adverse conditions originating from off-site events.

Wetlands that have received groundwater contaminated with metals and radionuclides present a unique long-term monitoring challenge because wetlands are a hydrologically and geochemically dynamic environment. Wetlands become a vulnerable zone because natural processes result in attenuation of metals and radionuclides in wetland soil (Gambrell 1994; Du Laing et al. 2009; Frohne et al. 2011). Yet, attenuation can also be reversed by natural conditions, releasing contaminants to surface water. The storage and periodic release of contaminants from wetlands means that long after remedial goals have been met, contaminants may continue to be released from wetland soils to surface water. The challenge to long-term monitoring of wetlands is to detect spatiotemporal changes in wetland conditions, both natural and man-made, that can potentially cause release of contaminants to exceed remedial goals. This requires monitoring a large heavily vegetated area for physical and chemical conditions that change naturally over various timescales.

Monitoring Methods and Technologies

Bunn et al. (2012) suggest that the extended time span requires different qualities for long-term monitoring than the first three stages of site monitoring where toxic metals or radionuclides remain in the subsurface. The list of long-term monitoring qualities includes that it should be predominantly passive, robust, low maintenance, low cost, and measure parameters that predict potential threats to remobilization of contaminants. This guides the selection of monitoring methods and tools used to measure parameters important to insuring the stability of attenuated contaminants.

In-well in situ sensors

In recent years, an increasing number of configurable multiparameter sensor platforms equipped with wireless data-transmission technology have become commercially available for the long term in-well measuring of water-quality parameters such as pH, ORP, dissolved oxygen, temperature, and specific conductance, as well as water

levels. These sensor packages continue to improve as more sophisticated sensors, such as optical sensors for nitrate and organic matter (Pellerin et al. 2012), are developed. Downhole multiparameter probes were not particularly advantageous for long-term monitoring of groundwater, until the advent of wireless technology, because they required either a person present to record the measurement or download dataloggers that stored measurements. Now, systems are available that continuously and autonomously measure parameters and upload measurements wirelessly to cloud storage so that the data are available any time to designated people via web-based services. Diagnostics are also available so that faulty sensors can be identified and replaced, minimizing gaps in time-series data. The above developments enable the deployment and use of wireless sensor networks involving scores of sensor platforms across a waste site to characterize spatially heterogeneous properties (e.g., Kerkez et al. 2012).

There are multiple factors that determine which sensors are suitable for a particular site and condition. Danielson (2020) evaluated commercially available point source in situ single- and multiparameter sensor platforms for deployment in wells at the US Department of Energy's Savannah River Site. A semiquantitative optimization function was used that rated sensor packages by parameters measured, diameter, the required calibration frequency, data logging/wireless communication platform, detection sensitivity, and price. The rating system was optimized for long-term monitoring needs at a specific site and could easily be tailored to the needs of other sites.

Distributed fiber-optic sensors

Significant advances have been made in the past two decades in use of optical fibers for measuring environmentally relevant parameters, including temperature (Selker et al. 2006; Suárez et al. 2011), strain (Schenato 2017), soil moisture (Sayde et al. 2010), acoustic waves (Bao and Chen 2012; Cox et al. 2012), gamma radiation (Gaebler 1984), and limited chemical parameters (e.g., Potyrailo and Hieftje 1998). For distributed sensing approaches, a pulsed laser source at one end of the fiber interrogates the state of the fiber at all locations through measurement of back-scattered light, yielding property measurements along the entire length at a fine lateral resolution, often at up to submeter resolution depending on the technique. Coherent optical time or frequency-domain reflectometry methods are typically utilized to measure localized differences in optical scattering (Rayleigh, Brillouin, or Raman) along fibers caused by changes in the environment (e.g., Hartog 2017). Secondary codeployed cables may be used to actively probe the area around the cable with perturbations measured using fiber-optic methods; an example is active heat-pulse-

distributed temperature sensing, which can be utilized for soil moisture quantification (Sayde et al. 2010). Fiber-optic measurement approaches can function effectively over a broad range of temperatures since the cables contain no electronics and can be packaged to withstand harsh conditions in either near-surface or borehole environments. Significantly, distributed fiber-optic sensing (DFOS) systems only require power and environmental control at the location of the interrogator unit (IU); since a single IU can conduct measurements of up to 50 km of fiber depending on measurement approach, DFOS methods can replace massive arrays of point sensors and provide for large-scale site measurements.

To date, distributed temperature and acoustic sensing have found a wide variety of applications in monitoring infrastructure, including leak detection in buried pipelines (Frings 2011), the structural health of buildings (Lopez-Higuera et al. 2011), and road conditions in tunnels (Krohn and Nicholls 2009). Distributed fiber-optic systems have also been deployed for deep-borehole (Daley et al. 2013) and integrated monitoring of shallow arctic test sites (e.g., Ajo-Franklin et al. 2017).

Distributed fiber-optic sensors have yet to be used for long-term monitoring of waste sites, but they have enormous potential use for passive monitoring. Moisture flux in the vadose zone is a key parameter controlling contaminant attenuation in the vadose zone (Truex et al. 2013), and measuring changes in moisture content with depth over time in the vadose zone can be done passively with distributed fiber-optic sensors, as well as measuring infiltration rates. Strain sensors can be used to monitor degradation of physical barriers installed to contain contaminants. Seismic measurements, acquired using distributed acoustic sensing, could be used to monitor the impacts of strong ground motion from natural seismicity (e.g., Lindsey et al. 2017) on disposal sites in tectonically active regions. Gamma-radiation sensors can be used to monitor temporal changes in radionuclide distributions in dynamic environments, such as wetlands, streams, and estuaries. They could also be installed on caps over uranium-tailing piles or NORM-disposal sites for spatiotemporal monitoring of radon emanation. Sensors that measure pH or other chemical parameters could be deployed in boreholes for depth-discrete monitoring or placed along groundwater-discharge zones such as wetlands and streams. During long-term monitoring, it is not known where or when a contaminant-controlling variable will change, and point sensors can miss the change because they are not in the right location. The spatially integrative property of distributed fiber-optic sensors and substantial linear extent makes them valuable for monitoring controlling variables over time along continuous profiles. Likewise, 2D networks of fiber-optic cables can be installed to provide higher-density measurements over the areas of interest.

Autonomous geophysical monitoring

Geophysical methods are spatially integrative, some allowing imaging of properties in large volumes of the subsurface over time. They have been increasingly used in environmental studies to characterize the subsurface in a noninvasive manner (e.g., Binley et al. 2015). Geophysical methods can image subsurface structure and physical properties (e.g., Wainwright et al. 2016), contaminant plumes (e.g., Johnson et al. 2010, 2012; Dafflon et al. 2013; Liao et al. 2018), and hydro-biogeochemical properties that are important for long-term monitoring (e.g., Johnson et al. 2010, 2012; Dafflon et al. 2011; Wainwright et al. 2014). High-performance computing capabilities allow high-resolution imaging (submeter) in a large spatial extent (up to several kilometers).

Autonomous electrical resistivity and phase tomography (ERT) is a geophysical method that is particularly sensitive to the spatiotemporal distribution of hydrological and geochemical properties relevant for short- to long-term monitoring, including soil-water content and fluid ionic strength. ERT provides spatiotemporally resolved information using an array of electrodes installed at the surface or in wellbores to measure the subsurface electrical resistance. The data are computationally reduced to three-dimensional images, or four-dimensional if resistance is measured as time lapses. ERT has been used to monitor degradation of low-permeability caps (Genelle et al. 2012; Sirieix et al. 2015), measure hydrologic recharge (Gasperikova et al. 2013), and soil moisture (Uhlemann et al. 2017) at field scales, and track the movement of fluids with contrasting specific conductance, such as contaminant plumes or reagent injections (Johnson et al. 2015; Dafflon et al. 2013). This approach can bridge the gap in sparse well-bore locations, by providing high-resolution and spatially extensive information in a minimally invasive manner. While electrodes are generally installed at the ground surface or buried using trenching or horizontal drilling technology, they can also be deployed in wellbores to enhance vertical resolution in strongly stratified plumes and related heterogeneity (Dafflon et al. 2013). The autonomous ERT system is robust and can be left in place for years with minimal maintenance while collecting data. Most of the cost of ERT is in the installation of the electrodes and cables, which can be combined with deployment of fiber-optic sensing methods. Once those are in place, measurements are inexpensive with most of the cost going to data analysis.

Likewise, seismic methods can be automated to allow autonomous active-source monitoring; to date, deployment of such systems has been more limited due to the complexity of active-source construction and automation, but they have recently been deployed for permafrost (Ajo-Franklin et al. 2017) and deep-borehole monitoring (Dou

et al. 2017). In this case, their application to contaminant-site monitoring would be to probe perturbations in seismic measurables that could be inverted for elastic moduli and other mechanical properties, particularly at depth where ERT measurements might prove more difficult to obtain.

Unmanned aerial vehicle (UAV)-based surface mapping

UAVs are promising new tools for aerially mapping features and parameters of interest to long-term monitoring of waste sites. A number of review articles have covered the rapid development of various aspects of this technology (Whitehead and Hugenholtz 2014; Whitehead et al. 2014; Pádua et al. 2017; Aasen et al. 2018; Manfreda et al. 2018; Singh and Frazier 2018; Ren et al. 2019; Tmušić et al. 2020). While these articles mostly highlight UAV uses in ecological and agricultural sciences, many of the advances are relevant to the proposed new approach to long-term monitoring. The advantages are that they can survey large areas of terrain at high resolution (up to cm scale) with an array of sensors to gather data, including photogrammetry, topography, fluvial morphology, gamma spectroscopy, surficial soil moisture, magnetic field anomalies, surface temperature, and health and type of vegetation. The key to UAV use in long-term monitoring is detection of changes in features or parameters between surveys. Therefore, accurate georeferencing and high-quality data collection and processing are critical, as discussed in the review papers cited above.

Periodic surveys by UAVs can be used in long-term monitoring to detect changes in surface characteristics that are important to contaminant attenuation and cannot be measured at high spatial resolutions by walk-over surveys or satellite platforms. For example, changes to topography and vegetative cover over time can have significant effects on infiltration rate (Christensen et al. 2018) and groundwater flow and contaminant transport, as well as indicate degradation of covers and caps installed over contaminant sources, or changes in surface-water-drainage paths and accumulation zones. Thermal maps can indicate where springs and other groundwater discharges are located, and track changes in the morphology of stream beds.

In addition, UAV capabilities have been coupled with radiation detectors for mapping gamma-radiation sources on the surface (e.g., Vetter et al. 2019). Machine-learning methods have been used to reconstruct complex environments (e.g., topography and buildings) fusing them with radiological information in three dimensions (Haefner et al. 2015; Barnowski et al. 2015). This so-called Scene-Data Fusion capability enables the effective and accurate detection and mapping of radiological and nuclear materials and its visualization in indoor and outdoor domains. Hand-portable and unmanned aerial system platforms have been

deployed effectively in the contaminated area in the Fukushima Prefecture and in several locations in the United States (Pavlovsky et al. 2018). Further, periodic gamma-radiation surveys can indicate shifts in the distribution of contaminated windblown dust near uranium-mining and milling sites, as well as changes in the distribution of gamma-emitting radionuclides in soils of wetlands and estuaries.

Data analytics

The new long-term monitoring strategy integrates data analytics, predictive modeling, and machine learning to develop an optimal initial program and provide the basis for the long-term monitoring program to evolve as needed. These tools allow systemic assessment of the status of contaminant attenuation at the site through understanding of the complex relationships between variables and threats to contaminant attenuation. In addition, the integration of these tools into long-term monitoring promotes flexibility in the program by warning when a part of the network is functioning improperly or becoming less relevant and predicting where new monitoring locations should be established.

Data analytics has multiple uses in the new long-term monitoring approach. It allows decisions to be made in designing groundwater-monitoring networks when multiple diverse objectives must be considered (Kollat et al. 2011; Reed and Kollat 2013; Luo et al. 2016), ascertains complex correlations between variables and contaminant concentrations (Schmidt et al. 2018), and optimizes selection of variables to observe and at which sampling frequency (Schmidt et al. 2018). Data analytics will also be important to identifying action values for the rate of trends in critical variables and absolute values that present potential threats to contaminant attenuation.

A variety of machine-learning methods are available to integrate the disparate forms of data and assist decision-making in the new long-term monitoring strategy. Data from well-bore sensors, distributed fiber-optic sensors, UAV surveys, contaminant concentrations, and groundwater-flow directions must be integrated into actionable intelligence. Multiview machine learning can extract critical information from these data sets (e.g., Sun 2013) and integrate it to enable decisions on mitigation of threats to attenuated contaminants or the need for network maintenance. Importantly, machine learning can identify abnormal data and continually adapt the definition of abnormal over time (Liu et al. 2020). In addition, supervised learning can evaluate the accuracy of estimating contaminant concentrations based on in situ-measurable parameters (Schmidt et al. 2018), as well as the effectiveness of a monitoring configuration to capture contaminant-concentration distributions (Sun et al. 2020). The

extracted information can support key decisions such as site-closure strategies and well/sensor placement.

Predictive modeling

Predictive contaminant transport modeling has long been used in all stages of groundwater monitoring (e.g., Mangold and Tsang 1991; Loaiciga et al. 1992; Reed et al. 2000), and it will be an integral aspect of the new long-term monitoring strategy. Contaminant transport modeling has been improved dramatically in recent years, thanks to high-performance computing (e.g., Bea et al. 2013; Wainwright et al. 2019). Transport modeling will also benefit from the increasing amount of observations that will improve their parameterization, validation, and/or calibration. Predictive modeling, validated and verified by existing monitoring data, will be used to calculate the spatial and temporal distribution of key properties and fluxes, as well as to refine the deployment and frequency of data collection of the downhole and surface-water sensor network. Stress-testing the monitoring design will be done by simulating potentially adverse events, such as chemical spills or changes to water balance, to be certain that the monitoring system provides sufficient warning of possible threats to attenuated contaminants. Climate-change effects on contaminant attenuation will also be simulated to build flexibility into the monitoring program (Libera et al. 2019), and provide input into programmatic projections of long-term monitoring maintenance needs and costs.

Case Study: F-area Seepage Basins—Savannah River Site

Site Background

The F-area Seepage Basins at the United States Department of Energy Savannah River Site in South Carolina is used here as an example of how the proposed approach to long-term monitoring can be implemented. It was chosen for evaluation of long-term monitoring strategies and tools because it is a mature well-characterized site with 30 years of monitoring data and in the latter stages of remediation. The site has complex soil and groundwater contamination with multiple contaminants having disparate behavior. It has faced the same basic challenges of many other sites where groundwater is contaminated by metals and radionuclides. The groundwater contamination is widespread and deep (20 m below the surface source); thus, excavation would have created enormous quantities of solid-radioactive waste. A pump-and-treat system operated briefly, but ultimately proved ineffective, and more innovative solutions were sought. Since 2005, a comprehensive attenuation-

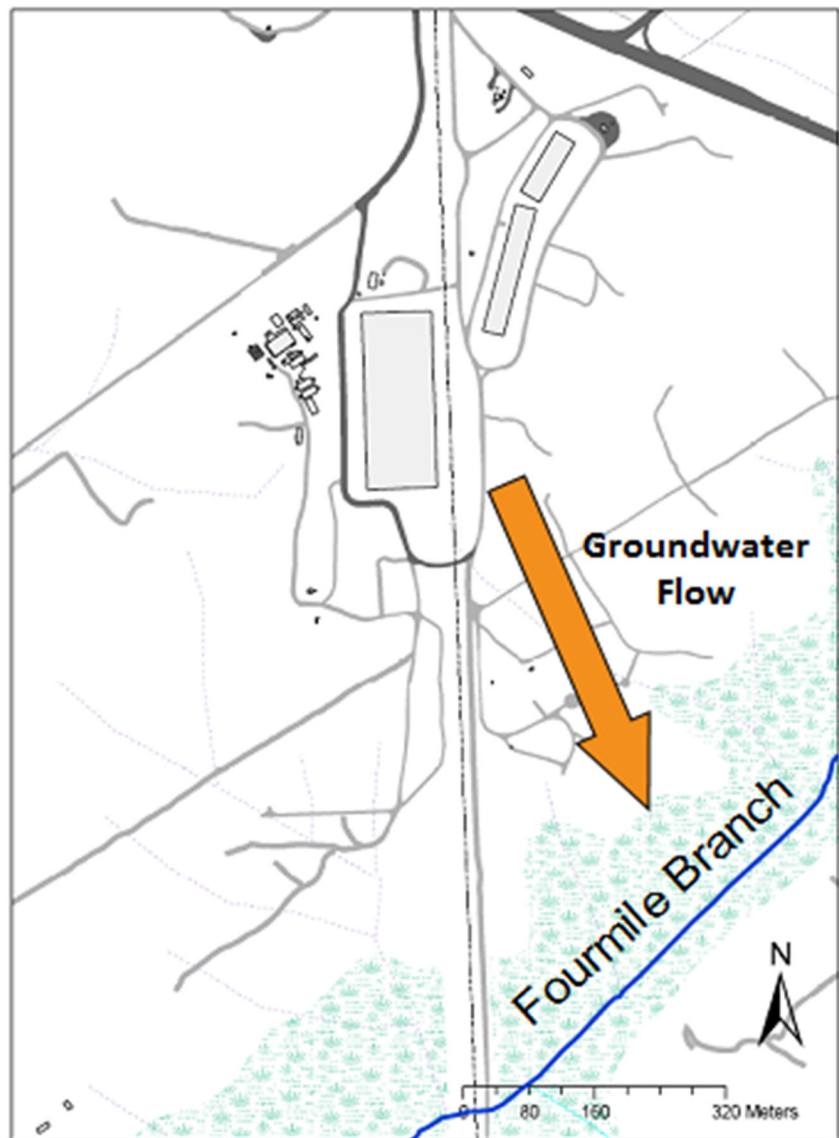
based remedy has been employed that will leave contaminants beneath a capped source, in an engineered attenuation zone, and attenuated in wetland soils. Hence, a robust long-term monitoring program will be important to achieving closure of the F-area Seepage Basins. The new long-term monitoring strategy presented in this paper has not been proposed formally, but has been discussed with state and federal regulators who are open to the possibility of using this strategy in some form, if it proves to be effective. The USDOE has funded a multiyear project (Advanced Long-term Monitoring Systems) to test the new long-term monitoring strategy contemporaneous with traditional monitoring of contaminant concentrations.

The F-area Seepage Basins consisted of three man-made unlined ponds into which low-level radioactive liquid waste was disposed (Killian et al. 1987). Disposal began in 1955 and ended in 1988, with ~7 billion liters disposed during this time. The waste was acidic with sodium and nitrate as the dominant constituents and contained various radionuclides associated with plutonium processing. The mobile radionuclides, tritium, uranium, iodine-129 (I-129), and strontium-90 (Sr-90), migrated through the vadose zone, contaminating groundwater in the saturated zone at concentrations of environmental concern. The resulting plume contaminates groundwater beneath ~1 square kilometer of the surface and discharges into wetlands and a local stream called Fourmile Branch. The map in Fig. 2 shows the location of the three basins relative to the wetlands and Fourmile Branch, with an arrow showing the general direction of groundwater flow in the upper aquifer.

The contamination plume occupies only a portion of the vertical extent of the upper-saturated aquifer zone—~3 m of a total thickness of 10 m. Recharge downgradient of the basins and a downward hydraulic gradient cause the contamination to migrate downward from the basins toward a discontinuous clay layer at the bottom of the aquifer. Two lower aquifers are also contaminated, but hydrogeological factors make the risk to human health and the environment posed by contamination in these aquifers substantially less than the risk posed by contamination in the water-table aquifer. Thus, remediation has focused on the uppermost aquifer, with the first objective being to minimize discharge of contaminants to surface water followed by reducing concentrations in upgradient groundwater to the maximum concentration levels allowable.

Remediation of the F-area Seepage Basins began with installation of a low-permeability cap in 1990 on chemically stabilized contaminated soils at the bottoms of the basins, and evolved to a comprehensive attenuation-based remedy. Installation of a subsurface barrier system that funnels contaminated groundwater into gaps in the barrier, into which alkaline fluids are periodically injected, creates in situ-treatment zones for Sr-90 and uranium. The injections

Fig. 2 Map of F-area Seepage Basins (gray rectangles), wetlands (green patterned area), and Fourmile Branch



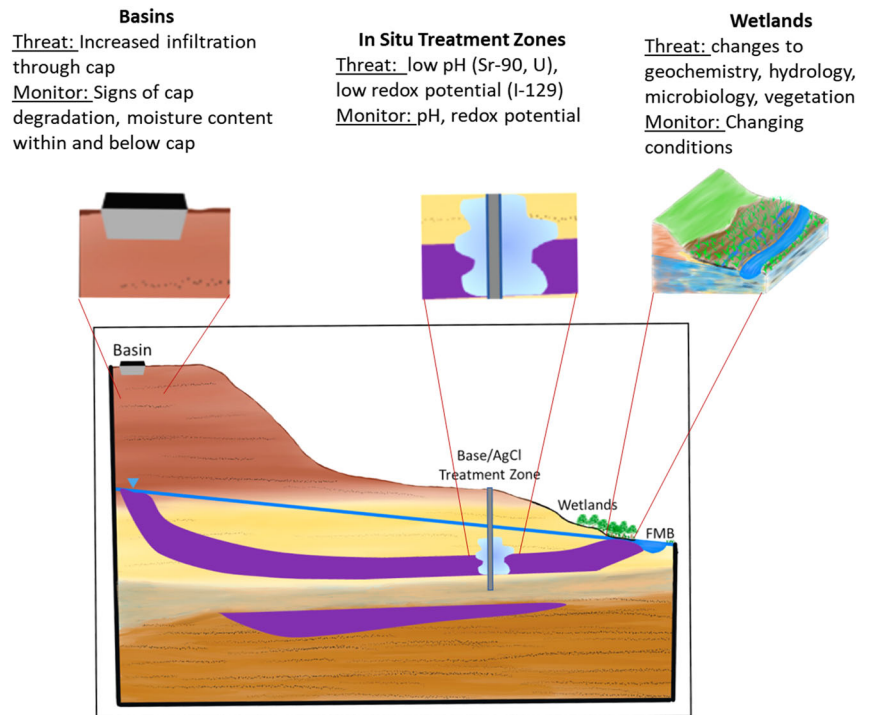
are intended to keep pH of groundwater downgradient of the treatment zones >5.5 . The subsurface barriers were placed across “troughs” in the top of the local confining zone that were preferential flow paths for contaminant migration to the wetlands and Fourmile Branch. This effectively blocked tritium migration, facilitating attainment of the remedial goal of a 70% reduction in tritium flux to Fourmile Branch. The elevated pH in the treatment zones within the gates causes attenuation of uranium and Sr-90 by enhanced adsorption to mineral surfaces. I-129 is treated by injection of silver chloride particles upgradient of the base-injection zone at the center gate. The silver chloride particles react with natural iodine and I-129 to form sparingly soluble silver iodide, causing partitioning of I-129 from groundwater to solid silver iodide.

Remediation of F-area Seepage Basins groundwater is also affected by natural attenuation of contaminants in the

organic-rich soils of the wetlands associated with Fourmile Branch. Uranium is attenuated by binding with organic matter and plant roots as U(VI), with some fraction attenuated by reduction to U(IV) (Li et al. 2014, 2015). I-129 is also primarily attenuated by binding with organic matter (Xu et al. 2011). Less is known about Sr-90 attenuation, though based on its known behavior elsewhere, Sr-90 is likely bound to the relatively abundant clay-size particles in wetland soils. The controlling variables for attenuation of uranium, Sr-90, and I-129 in the wetlands are not fully understood and are the subject of ongoing research.

Currently, monitoring at the F-area Seepage Basins is focused on remediation performance. Substantial progress has been made toward remedial goals, and development of a long-term monitoring strategy is underway. As stated earlier, the traditional approach would be to reduce the number of monitoring points by eliminating those that provide redundant

Fig. 3 Summary of long-term monitoring of vulnerable zones at the F-area Seepage Basins. Purple represents the contamination plume in the water-table aquifer and the next lower aquifer



or irrelevant data, but most of the monitoring data would still consist of contaminant concentrations. There are 93 monitoring wells, 16 wetland groundwater locations, and 6 surface-water stations in the current monitoring plan. Traditional optimization of the monitoring network by reducing the number of monitoring locations and frequency of sampling would reduce costs. Nevertheless, while reduction in long-term monitoring cost is a goal, the more important objective is to be sure that funding allocated for long-term monitoring is spent wisely and efficiently. The long-term monitoring strategy proposed here would achieve both goals by reducing sampling and analytical costs, and measuring leading indicators that warn of potential threats to attenuated contaminants in time to implement mitigation actions.

Vulnerable Zones

The current remediation of the F-area Seepage Basins relies on attenuation of contaminants in basin soils beneath impermeable caps, in the treatment zones in the gaps in the subsurface barrier, and in the wetlands. A summary of the vulnerable zones, the threats to attenuated contaminants, and parameters to be monitored for each zone is shown in Fig. 3.

Basin soils and vadose zone

The bottoms of the basins were not excavated prior to capping and a significant mass of contaminants remains in the basin's

soil (Corbo et al. 1985). In addition, contaminants remain in the vadose zone, either adsorbed to mineral surfaces or in dissolved pore water held in place by capillary pressure. The attenuation of these contaminants depends on the integrity of the low-permeability caps preventing infiltration of water through these sources. The two measures of this threat are evidence of cap degradation and moisture increases within the cap and upper vadose zone.

Evidence of cap degradation will be detectable from near-surface measurements made with distributed fiber-optic sensors and multisensor UAV-based surveys. Erosion, animal burrows, plant roots, and damage from trespassers can lead to pathways for water to breach the protective clay layer of the cap. Damage can also come from natural settling and seismic activity that fractures the clay layer. Currently, subsidence and surface disturbances of the basin caps are monitored once a year by walk-over assessments and surveys of subsidence markers. UAVs equipped with photogrammetry and Lidar sensors will be used to make high-resolution topographic maps and identify any erosion, deep-rooting vegetation, burrows, ant mounds, or other damage to the surface of the caps. Overlays of georeferenced images from subsequent flights will identify areas of subsidence. The periodic flights will initially be done annually to compare with the manual surveys of the caps. Over time, the frequency of flights may be varied, corresponding to the rate of change in cap conditions. Distributed fiber-optic strain sensors will be installed over the surface of the cap to detect subsidence in the interim between flights.

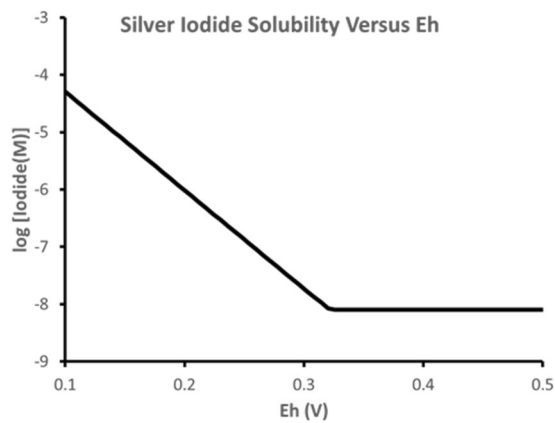


Fig. 4 Solubility of silver iodide as a function of Eh (ORP normalized to the $\text{H}_{2(\text{g})}:\text{H}^{+}$ couple), calculated with The Geochemist's Workbench® (Bethke et al. 2020), pH = 5

Monitoring moisture content in and below the impermeable clay layer of the basin caps is a direct measurement of cap degradation. This can be done with ERT by installing an array of electrodes on the cap surface and along the sides of the caps. If a moisture increase is detected, the vadose-zone thickness of ~20 m allows sufficient time for cap repair before contaminants mobilized from the upper vadose zone become a threat to the saturated zone. This is preferable to waiting until increases in contaminant concentrations are detected in monitoring wells downgradient of the basins. Nevertheless, monitoring wells will be maintained adjacent to downgradient edges of the basins that will be sampled periodically and instrumented with sensor packages measuring pH, specific conductance, ORP, and water level.

Currently, the low-permeability caps and vadose zone beneath are in a steady-state condition with minimal drainage, and a transition to long-term monitoring of this zone of vulnerability can begin. Modeling and experiments to evaluate the effectiveness of ERT for cap monitoring are underway at the site. Additionally, testing the effectiveness of UAV-deployed imagery of the cap surfaces is in the planning stages.

In situ-treatment zones and groundwater

Three contaminants of interest are attenuated by the remedial actions within the treatment zones between segments of the subsurface barrier. Sr-90 and uranium are attenuated by enhanced adsorption caused by increasing the pH of the acidic plume with periodic alkaline-fluid injections. I-129 is attenuated by precipitation of silver iodide on silver chloride particles. Maintaining attenuation of these contaminants depends on preventing specific chemical changes from occurring within this zone of vulnerability. If pH returns to pretreatment acidic levels, then Sr-90 and uranium will be

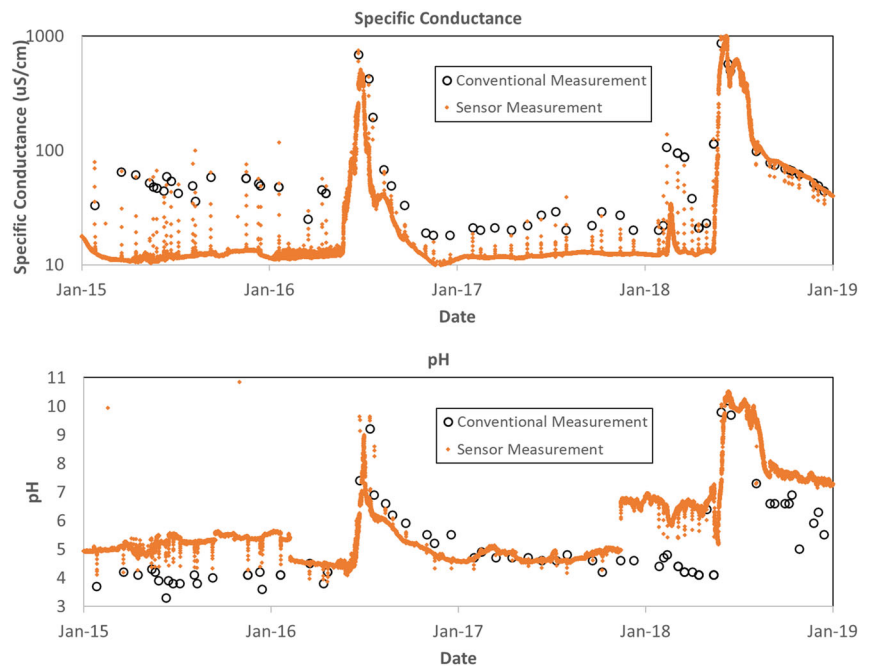
remobilized. Changes in redox potential will not remobilize Sr-90 and uranium, but solubility calculations indicate that decreasing redox potential will cause dissolution of silver iodide and remobilization of I-129 (Fig. 4).

Natural aquifer conditions are protective of the attenuated contaminants in the treatment zones. ORPs in groundwater in water-table aquifers at the Savannah River Site are oxidizing and close to saturation with dissolved oxygen (Strom and Kaback 1992). The median pH of uncontaminated groundwater at the F-area Seepage Basins site is 6.0. As remediation proceeds, the pH of groundwater entering the treatment zones will approach 6.0 when all acidic groundwater has flushed through the portion of the system upgradient of the subsurface barrier. Once this occurs, there are no natural mechanisms that will change pH and ORP in the subsurface-treatment zones in a way that would remobilize contaminants. Only artificial influences, such as a chemical spill, can cause conditions that threaten contaminant attenuation in the treatment zones. Therefore, long-term monitoring of the in situ-treatment zones will focus on monitoring ORP and pH of groundwater entering this zone of vulnerability. Sensor platforms measuring these parameters, specific conductance, and water level will be deployed in wells upgradient of and within the in situ-treatment zones. Existing monitoring wells downgradient of the in situ-treatment zones will remain in place for periodic sampling and measurement of contaminant concentrations.

An initial test deployment of sensor packages in three wells at the F-area Seepage Basins site was conducted from 2015 until 2019 to assess their ability to provide inexpensive long-term data on attenuation-controlling variables. The sensors collected measurements, and data were sent to an off-site database, via a wireless telecommunication system, and users were able to evaluate the data in real time. Figure 5 compares data acquired by a sensor platform to measurements made during routine monitoring at the sentry well for an in situ-treatment zone. During the sensor trial period, there were 43,000 measurements recorded by the sensors and 87 samples collected and analyzed for contaminants. The sensors effectively recorded the changes in pH and specific conductance induced by base-injection events, and the subsequent influx of acidic groundwater into the treatment zone. The pH measurements from late 2017 to 2019 indicate some issues with the pH sensor, possibly compromise of the electrolyte solution within the sensor or calibration issues. Newer pH sensors under development (Khan et al. 2017; Lu et al. 2019) should have fewer problems with maintenance and calibration than the galvanic cell electrode used in the sensor platforms initially deployed at the F-area Seepage Basins.

The sensor measurement of specific conductance and pH also shows the effect of purging the wells prior to sampling. For each sampling event, the sensor measurements are

Fig. 5 Time-series comparison of specific conductance and pH measurements by a sensor package (lines with no symbols) compared to measurements made during sampling of a well in an in situ-treatment zone (symbols)



consistent with measurements made by the sampling crew, but the sensors record increasing specific conductance and decreasing pH during well purging. This likely reflects heterogeneity in hydraulic conductivity across the length of the well screen. When the well is purged and sampled, a higher proportion of groundwater reaching the well is from zones of the highest hydraulic conductivity. In the in situ-treatment zone, these preferential flow paths are likely to contain more highly contaminated groundwater. Thus, as purging proceeds, specific conductance increases and pH decreases. The sensor measurements between sampling periods resemble no purge or passive sampling methods (e.g., ITRC 2007). As with other no purge or passive sampling, vertical placement of the sensors within a well screen is important. Vertical flow within wellbores should also be considered when installing sensor platforms in wells (McMillan et al. 2014). In locations with substantial vertical heterogeneity, the long-term monitoring may benefit from deployment of sensors at multiple depths, or from depth-resolved geophysical methods such as ERT or fiber-optic sensing.

Values of ORP and pH that are potential threats to contaminant attenuation, action values, will be determined from experimental results, groundwater modeling, and existing monitoring data. An example of the usefulness of existing monitoring data is presented in Fig. 6. It shows monitoring data for pH and U-238 concentrations from 2005 to 2015 from the sentry well in a treatment zone used to indicate when injections of alkaline fluids are needed. The monitoring data suggest that the pH-action value for uranium is between 4.3 and 5.3. This is consistent with

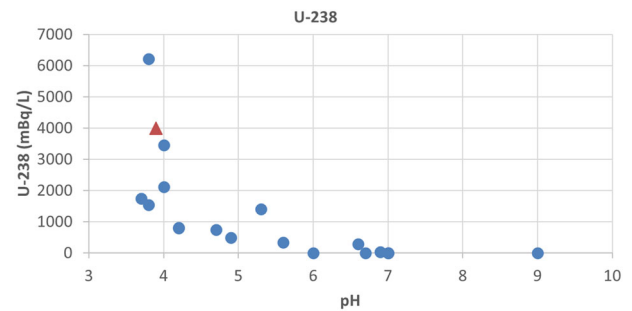
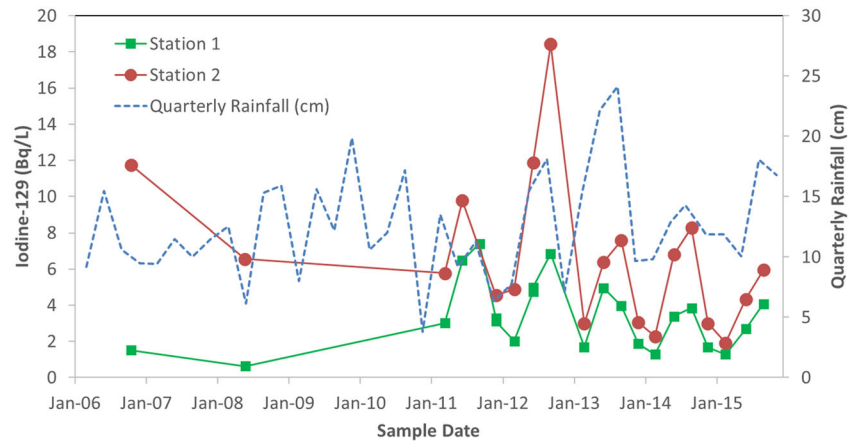


Fig. 6 U-238 concentration (mBq/L) versus pH (blue circles) in groundwater sampled from a well within one of the in situ-treatment zones. The red triangle is the median value of U-238 concentrations and pH in groundwater entering the treatment zone

adsorption experiments using cored aquifer solids from the F-area Seepage Basins site reported in Dong et al. (2012). In their experiments, the adsorption edge for uranium was between pH values of 4 and 5.3, with >70% of uranium adsorbed at pH > 5. The monitoring data do not provide a clear indication of a range of action values for Sr-90 and I-129, so these values will be determined experimentally.

Groundwater modeling, data analytics, and machine learning will be used to refine criteria for decisions on mitigation actions. For example, a single exceedance of an action value will not initiate a mitigation action because of sensor imprecision and natural variation in controlling variables. Data analytics and machine learning will discern patterns in parameter variation, recognize abnormal patterns, and inform decisions on mitigation actions. In addition to aiding the optimization of the initial sensor locations, groundwater modeling will be used to examine various

Fig. 7 Variation in I-129 concentration at two wetland surface-water stations (symbols) compared with quarterly rainfall (dashed blue line)



scenarios of contaminant remobilization to design a suite of responses to abnormal and potentially threatening parameter variations (Wainwright et al. 2019).

Wetlands

Contaminants have interacted with organic matter and clays in wetland soils associated with the F-area Seepage Basins since the contaminants initially reached the wetlands, at least 20 years prior to capping of the basins. The mass of contaminants in the wetlands and the controls on the mechanisms of attenuation and release are poorly understood and are currently the focus of ongoing studies. For example, monitoring data show seasonal effects on attenuation of I-129 in wetland soils with concentrations in surface water varying with quarterly rainfall (Fig. 7). Ongoing studies are focused on determining whether this is predominantly a hydrodynamic or a biogeochemical process. This is important to long-term monitoring because it will determine the parameters to be measured and the range of values that are acceptable. This is just one example of the dynamic processes in the wetlands that must be monitored.

Long-term monitoring of the wetlands will be done with a combination of UAV-deployed imagery and sensors on the surface or in the shallow subsurface. UAVs will be deployed periodically to survey changes in topography, vegetation, the locations of groundwater seeps, the course of Fourmile Branch, and the distribution of gamma-emitting radionuclides in wetland soils. Distributed fiber-optic sensors can be used to measure pH (Shao et al. 2013; Lu et al. 2019), flow rates in the area of rapid fluid movement (using heat pulse or thermal tracer methods, e.g., Somogyvári, Bayer 2017), dissolved gas concentrations, temperature (Selker et al. 2006), and potentially other parameters that indicate changing patterns of groundwater discharges along stretches of wetland soils and Fourmile Branch.

There will be a network of monitoring wells instrumented with sensor platforms to measure pH, ORP, and

water level upgradient and within the wetlands. The existing surface-water-monitoring locations will also be monitored for the same parameters using sensors. Nevertheless, samples from the surface-water-monitoring stations will continue to be collected and analyzed for contaminant concentrations, until attenuation mechanisms for Sr-90, uranium, and I-129 are better understood. The integration of these monitoring tools will provide information on systemic changes to the wetlands across all pertinent time frames. Long-term monitoring in the wetlands highlights the benefit of its systemic view because contaminant measurements alone cannot provide insight into the dynamic processes affecting contaminant attenuation.

Implementing the New Long-term Monitoring Approach

The new long-term monitoring approach will be implemented in phases. Sensors will be deployed, and baseline surveillance by UAV imagery will initially be done contemporaneously with the current monitoring of contaminant concentrations. ERT or other geophysical techniques will also be field-tested during this time. When all interested parties are comfortable with these alternative methods, select monitoring wells will be removed from scheduled contaminant monitoring and another period of evaluating the new approach will begin. Assuming that the new approach is assessed as valid, this process will continue until 70–80% of the contaminant-monitoring wells are removed. During these implementation phases, the frequency of well sampling will also be reduced as appropriate. Data analytics will be used to decide the optimum frequency of contaminant monitoring in the remaining wells (Schmidt et al. 2018).

Location, type of sensor platform, and nature of installation will be determined based on function. The function will be defined by the zones shown in Fig. 8. The perimeter, shown as the purple zone, will have an array of sensor

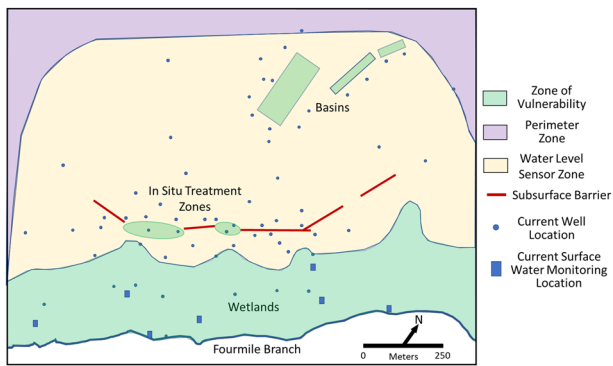


Fig. 8 Zones for long-term monitoring at the F-area Seepage Basins and the current locations of monitoring wells and surface-water-sampling locations

platforms to detect the effects of off-site events that could influence conditions at the waste site. The sensor platforms will include probes for measuring water level, pH, ORP, and specific conductance. They can be installed in wells pushed into the subsurface by direct push technology as exposed screen installations (USEPA 2005b) with no infrastructure other than the well screen and casing. If samples are ever needed, a pump can be lowered into the well to the correct depth. The vulnerable zones are shown in green. The same type of sensor platforms used in the perimeter zone will be used at the vulnerable zones, except that they will be installed in monitoring wells constructed according to the specifications in the South Carolina Department of Health and Environmental Control Regulation 61-71 (SCDHEC 2016). Sensor platforms deployed in existing monitoring wells will, by definition, adhere to this regulation. Those installed in new locations will adhere to the regulation in case the location needs to be converted to a standard monitoring well in the future. Sensor platforms will be installed upgradient and within the in situ-treatment zones and the wetlands. They will be installed at the downgradient edges of the basins. Sensor platforms installed in the yellow zone will be used solely to monitor water levels, so that high-precision water-table maps can be made. These can be installed in exposed screen wells placed by direct push technology. The locations of each type of sensor and the frequency of measurement will be determined by groundwater modeling and data analytics.

Conclusion

The proposed new strategy for long-term monitoring of waste sites at which attenuation-based remedies have been used to treat groundwater contaminated with metals and/or radionuclides will provide early warning of systemic changes that may remobilize attenuated contaminants.

Attenuation-based strategies leave contaminants in the subsurface by design, and thus will require monitoring for long periods of time after site closure to ensure that contaminants remain in place. Traditional long-term monitoring, with emphasis on measurement of contaminant concentrations, is inefficient at sites where attenuation-based remedies have been used. It is more efficient to monitor changes to the system that threaten to remobilize attenuated contaminants. This will lead to more proactive responses in the event such changes occur. Furthermore, the methods used in the new strategy are less costly than traditional long-term monitoring strategies. This is important given the long monitoring periods that will be required for sites where attenuation-based remedies are used for treatment of metal- and radionuclide-contaminated groundwater.

The long-term monitoring strategy proposed here emphasizes monitoring of the physical and chemical processes responsible for contaminant attenuation. In groundwater, these are the direction and rate of the flow of groundwater, as well as the chemical parameters controlling contaminant behavior. These can be monitored with sensor platforms deployed in monitoring wells and equipped with wireless data-transmission technology. For low-permeability caps over contaminant sources, evidence of cap degradation can be detected using imagery from UAVs. Additionally, geophysical methods, including ERT and fiber-optic methods, can be used to measure moisture increases within the caps or in the upper vadose zone. Wetland and surface-water monitoring can be done using a combination of sensor technology and imagery from UAV flights.

Measuring contaminant concentrations at specific locations will remain a part of the new strategy, but the number of locations and frequency of sampling will be significantly reduced. This will be accomplished by phasing in the new strategy in a way that meets regulator and stakeholder needs for demonstrating the efficacy of the new strategy. Part of the design of the new strategy will be establishing thresholds of change in the indicator parameters that will trigger sampling and analysis of groundwater for contaminant concentrations. This will be done using historical monitoring data and data collected during the phase-in period to determine natural variation in parameters and experimental results to determine action values of the chemical parameters.

The new long-term monitoring approach will allow conditions that threaten to remobilize attenuated contaminants to be mitigated before remobilization occurs. In contrast, traditional long-term monitoring, relying on contaminant-concentration measurements, can only alert that remobilization has occurred.

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Compliance with Ethical Standards

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