Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Disclaimer:

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U. S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:

1) warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
2) representation that such use or results of such use would not infringe privately owned rights; or
3) endorsement or recommendation of any specifically identified commercial product, process, or service.

Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

We put science to work.™

Savannah River National Laboratory ™

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

A U.S. DEPARTMENT OF ENERGY NATIONAL LABORATORY • SAVANNAH RIVER SITE • AIKEN, SC

A New Paradigm for Long Term Monitoring at the F-Area Seepage basins, Savannah River Site

Miles E. Denham, Carol A. Eddy-Dilek, Haruko M. Wainwright, Jeffrey Thibault, and Kevin Boerstler

January 2019

SRNL-STI-2019-00019

SRNL.DOE.GOV

DISCLAIMER

Printed in the United States of America

Prepared for
U.S. Department of Energy

SRNL-STI-

Keywords: *Long Term Monitoring*

Retention: *Permanent*

A New Paradigm for Long Term Monitoring at the F-Area Seepage basins, Savannah River Site

Miles E. Denham, Carol A. Eddy-Dilek, Haruko M. Wainwright, Jeffrey Thibault, and Kevin Boerstler

January 2019

Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.

Savannah River National Laboratory™

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

PREFACE OR ACKNOWLEDGEMENTS

The authors acknowledge the U.S. Department of Energy Office of Environmental Management for funding the Soil and Water Assistance Team (SWAT) that compiled this report and Savannah River Nuclear Solutions, LLC, Area Completion Projects for facilitating the preparation of this report through their personnel and logistical support.

EXECUTIVE SUMMARY

A Soil and Water Assistance (SWAT) team of experts was assembled to evaluate the application of a new approach to long-term monitoring of a waste unit, contaminated with metals and radionuclides, located on the U.S. Department of Energy's (DOE) Savannah River Site. The site formally known as the F-Area Hazardous Waste Management Facility is referred to here by the more descriptive and widely used F-Area Seepage Basins.

Low level radioactive waste solutions were disposed in 3 unlined basins, known as the F-Area Seepage Basins from 1955 until 1988. The solutions were acidic with a high nitrate content and mobile constituents, such as tritium, nitrate, uranium, strontium-90, iodine-129, and technetium-99, passed through the soils at the bottoms of the basins, through the vadose zone, and into the saturated zone. The result is a large volume of contaminated groundwater that discharges into the local stream, Four Mile Branch, and the wetlands associated with this stream. Placement of a low permeability cap over the basins was completed in 1991 to minimize infiltration through basin soils and the vadose zone. A pump-and-treat system was installed in 1997 to address contamination of groundwater and minimize discharge to the surface waters and has since been replaced by attenuation-based remedies. The attenuation-based remedies use subsurface barriers that were installed across preferential flow paths in the upper-most aquifer, creating a funnel-and-gate system where in situ treatment of contaminants occurs within the gates.

As the F-Area Seepage Basins enters the latter stages of remediation, DOE and Savannah River Nuclear Solutions, LLC are formulating plans for long-term monitoring of the site. In situ treatment leaves contaminants in place in the subsurface in addition to contaminants attenuated in the basin soils and the soils of the wetlands. A comprehensive long-term monitoring program must monitor the locations where contaminants remain attenuated to be certain they are not remobilized. Traditional approaches to long-term monitoring rely heavily on analysis of contaminant concentrations in groundwater at many locations and are not efficient at monitoring sites where attenuation-based remedies for metals and radionuclides have been used.

The SWAT proposed using an approach to long-term monitoring developed by the Savannah River National Laboratory with contributions from Lawrence Berkeley National Laboratory. The new approach focuses primarily on monitoring systemic changes in groundwater flow and chemistry that could potentially remobilize attenuated contaminants rather than focusing on increases in contaminant concentrations after they have been remobilized. The new approach is more efficient and promotes proactive decisions if site conditions change in a way that increases risk of reversal of contaminant attenuation.

In the new approach, zones of vulnerability are defined that delineate where monitoring should be concentrated. Threat conditions are determined for each zone of vulnerability and these establish the hydrological and geochemical parameters that control the behavior of attenuated contaminants. The zones of vulnerability at the F-Area Seepage Basins are the locations where contaminants remain attenuated – basin soils beneath the caps, the gates where in situ treatment has occurred, and the wetlands. The threat condition to the basin soils is increased infiltration through the caps and long-term monitoring should focus on any indication that the caps may be breached. The threat conditions within the gates are a decrease in pH and/or redox potential. The threat conditions in the wetlands are more complex because contaminants are attenuated near the surface and near-surface conditions within wetlands are dynamic.

The SWAT proposed the use of a suite of recently developed tools combined with sensors in groundwater wells that measure pH, redox potential, specific conductance, and water levels to implement the new long-term monitoring approach at the F-Area Seepage Basins. In addition, the plan calls for analysis of contaminant concentrations in samples from a few strategically located monitoring wells and surface water

stations. The plan proposed by the SWAT calls for a gradual phased transition to the new long-term monitoring approach.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1.0 Introduction

This document presents the recommendations of a Technical Assistance Team that was tasked with developing an innovative long-term monitoring strategy and applying it to a contaminated groundwater unit on the Savannah River Site. The Technical Assistance program is funded by the Department of Energy Office of Environmental Management (DOE-EM) through their Technology Development program to help DOE sites with difficult remediation problems. Typically, the Technical Assistance process involves a small team of selected subject matter experts visiting the site to rapidly assesses and recommend solutions to difficult contaminated soil and groundwater problems. The teams are technical, not programmatic, and findings are non-binding. DOE has deployed over fifty similar technical assistance teams since 2000 and has found that the right mix of technical expertise with a fresh approach has been beneficial to sites struggling with solutions to environmental problems.

A technical assistance team visited the Savannah River Site June 17-19, 2018 to assist Savannah River Nuclear Solutions, LLC, Area Completion Projects with developing an innovative long-term monitoring program for the F-Area Hazardous Waste Management Facility groundwater. The F-Area Hazardous Waste Management Facility is referred to hereafter in this report by the older more descriptive name – the F-Area Seepage Basins. The technical assistance team consisted of experts in geology, geochemistry, data analytics, and predictive modeling. All have had experience working on groundwater problems associated with the F-Area Seepage Basins.

This report compiles the work completed by the Technical Assistance team to apply a new paradigm for long-term monitoring to the F-Area Seepage Basins. The new paradigm has been developed over several years by the Savannah River National Laboratory. Additionally, the new approach to long-term monitoring uses tools and modeling developed by Lawrence Berkeley National Laboratory. The two laboratories have been working together for the past 5 years on data mining and predictive modeling of the F-Area Seepage Basin system. Remediation of contaminated groundwater has been ongoing at the F-Area Seepage Basins since 1997 and the current attenuation-based remedy has been in place since 2005. Multiple regulatory milestones have been completed with additional milestones scheduled for completion within the next 12 years. The attenuation-based remedies will leave metal and radionuclide contamination in a nonbioavailable state within the subsurface and long-term monitoring at this site is thus an important facet of site management.

The current monitoring program is based on collection and analysis of samples of water from more than 100 stations that include groundwater monitoring wells, surface water stations in the wetlands, and surface water stations in the local stream. Traditional long-term monitoring strategies call for optimizing this network to eliminate redundancy, but still rely exclusively on obtaining and analyzing samples for contaminant concentrations. This will be very expensive over the long time period that the F-Area Seepage Basins site will require monitoring. Furthermore, this type of monitoring results in reactive decision making when contaminant concentrations increase at a location. The new paradigm for long-term monitoring promotes proactive decision making by providing data that signals if conditions at the site have changed in a way that would cause attenuated contaminants to become remobilized. The F-Area Seepage Basins site is an excellent facility for application of this new paradigm because it is approaching the latter stages of active remediation and has an extensive history of monitoring data on which to base a new strategy for long-term monitoring.

The main body of the Technical Assistance report consists of summaries of the new paradigm for long-term monitoring and the F-Area Seepage Basins site, followed by the SWAT proposed plan for applying the new paradigm to the site. More detailed discussion of each of the summary sections is in a series of appendices at the end of the report.

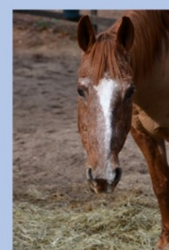
2.0 Background Information

2.1 The New Paradigm

The proposed new strategy for long-term monitoring of contaminated sites de-emphasizes point measurements of contaminant concentrations in favor of measuring parameters that indicate systemic changes to the system that are likely to affect contaminant mobility. Contaminants are left in the subsurface in an attenuated state at sites where monitored natural attenuation (MNA) and/or enhanced attenuation (EA), collectively referred to as attenuation-based remedies, have been deployed. Organic contaminants may be left to degrade by natural or enhanced processes. Metals and radionuclides are left in a relatively immobile state either strongly adsorbed to mineral surfaces or precipitated as minerals. Successful attenuation-based remedies for metals and radionuclides rely on the persistence of the physical and chemical conditions that promote attenuation of the contaminants. These conditions include rate and direction of groundwater flow, pH, oxidation-reduction potential, total dissolved solids, and in some cases the continued presence or absence of specific chemical species. The objective of the new long-term monitoring strategy is to detect changes to the "boundary conditions", the physical factors that control groundwater flow, and/or changes to "master variables" the chemical conditions that influence contaminant mobility that might reverse the mechanisms responsible for contaminant attenuation.

New Paradigm vs. Traditional Long-Term Monitoring

Traditional = Monitoring Location of Horse



New Paradigm = Monitoring Security of Barn Door

The old idiom that it is too late to shut the barn door after the horse has escaped the barn illustrates an advantage of the new long-term monitoring paradigm over traditional long-term monitoring. The traditional approach is analogous to monitoring the location of the horse (contaminant concentrations in groundwater). The new paradigm is like monitoring that the barn door is securely locked (conditions in the zone where a contaminant is attenuated), so the horse cannot escape the barn.

There are two advantages of the new paradigm for long-term monitoring over the traditional strategy of collecting and analyzing water samples from point locations (e.g., monitoring wells, surface water stations, etc.). The first is that the traditional strategy only detects a problem once contaminants have been remobilized from their attenuated state. This results in reactive decisions and by the time contaminants have remobilized, restoring the system to compliance may be difficult. The object of the new paradigm is to be able to detect changes to the system that could remobilize contaminants before the contaminants are affected. This will lead to proactive decisions and more efficient management of the problem.

The second advantage of the new paradigm is efficiency and cost. Obtaining a sample at the F-Area Seepage Basins and having it analyzed for contaminants costs approximately $3000. This is with SRS sampling personnel and supplies available. Additional costs are incurred at the many DOE and commercial sites that have no permanent sampling infrastructure. If long-term monitoring must be done for 50-100 or more years, the life-cycle costs become enormous. Many of the tools used in the new paradigm enable monitoring data collection with minimal man-power and results can be transmitted wirelessly to scientists and engineers for evaluation. Additionally, the spatially integrative tools used to collect data over wide areas rather than single points, provides more information with higher efficiency.

Over and above the efficiency of the tools used for monitoring, additional efficiency is achieved in the new paradigm by focusing on the specific locations where contaminants are attenuated. These specific locations are referred to here as zones of vulnerability. The site as whole is monitored for changing conditions, but detailed attention is placed on monitoring around the zones of vulnerability for threat conditions, conditions that could remobilize contaminants.

Predictive modeling and data analytics will be used in the new paradigm to optimize monitoring and establish "trigger levels" for measurements that when exceeded would indicate that additional analysis is required. A predictive model for the F-Area Seepage Basins system has been developed and used to simulate various future scenarios that may challenge a long-term monitoring network. Data analytics was used to establish correlations of easily measured parameters to contaminant concentrations. This allows estimations of contaminants concentrations from sensors deployed in monitoring wells. In addition, data analytics will help in establishing the threat conditions that would remobilize contaminants from zones of vulnerability During long-term monitoring, regular use of predictive modeling and data analytics will provide information to allow monitoring optimization.

Appendix A contains a more detailed discussion of the new monitoring paradigm. Appendix B presents the use of predictive models and data analytics in the new long-term monitoring paradigm. Appendix C presents a discussion of monitoring tools to be used in the new long-term monitoring paradigm.

2.2 Site Conceptual Model

An accurate conceptual site model is the basis for applying the new long-term monitoring plan. The F-Area Seepage Basins consisted of three unlined ponds into which low level radioactive liquid waste was disposed. Disposal began in 1955 and ended in 1988, with approximately 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. Mobile radionuclides migrated through the vadose zone (approximately 20 meters thick), contaminating groundwater in the saturated zone at concentrations of environmental concern. The resulting contamination plume has an aerial extent of approximately 1 square kilometer and discharges into wetlands and a local stream called Fourmile Branch. The map in Figure 1 shows the location of the three basins relative to the wetlands and Fourmile Branch, with an arrow showing the general direction of groundwater flow.

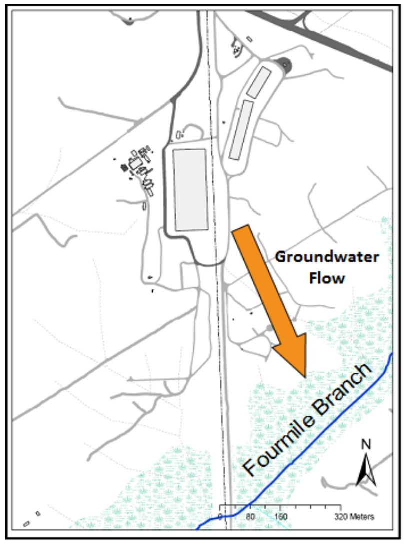


Figure 1: Map of F-Area Seepage Basins, wetlands (green patterned area), and Fourmile Branch.

Contaminated groundwater has penetrated the top three aquifers of the hydrostratigraphic column with the most severe contamination present in the water table aquifer. This aquifer is separated from the next aquifer by a leaky aquitard known as the Tan Clay Confining Zone. Groundwater in the top two aquifers flows toward and drains into Fourmile Branch, whereas groundwater in the deepest affected aquifer flows toward Upper Three Runs, to the north of the seepage basins. The groundwater contamination plume is stratified and, over most of its extent, flows along to top of the Tan Clay, drawn down by recharge between the basins and the wetlands and the downward gradient through the Tan Clay. Preferential flow paths are created by depressions in the top of the Tan Clay and these “troughs” contain the most contaminated portions of the plume.

The history of the F-Area Seepage Basins is depicted in the timeline in Figure 2. Disposal of waste into the basins began in 1955 and ended in 1988. Closure and installation of a low permeability cap over the basins was completed in 1991. Unlined drainage ditches surround the capped basins to collect and divert runoff from the cap to an outfall. The cap minimized infiltration through the source, allowing concentrations of radionuclides to begin decreasing in the vadose zone and ultimately in the saturated zone. The rate of drainage of the vadose zone decreased significantly between 6 and 8 years after closure of the basins, as drainage neared completion (Tokunaga et al., 2012). This approximately coincides with the start-up in 1997 of a pump-and-treat system that extracted groundwater from downgradient, removed contaminants other than tritium, and re-injected the treated water upgradient of the basins. The pump-and-treat system was replaced in 2004 with the current remediation, a funnel-and-gate with periodic base injection in the gates and beneath the wetlands.

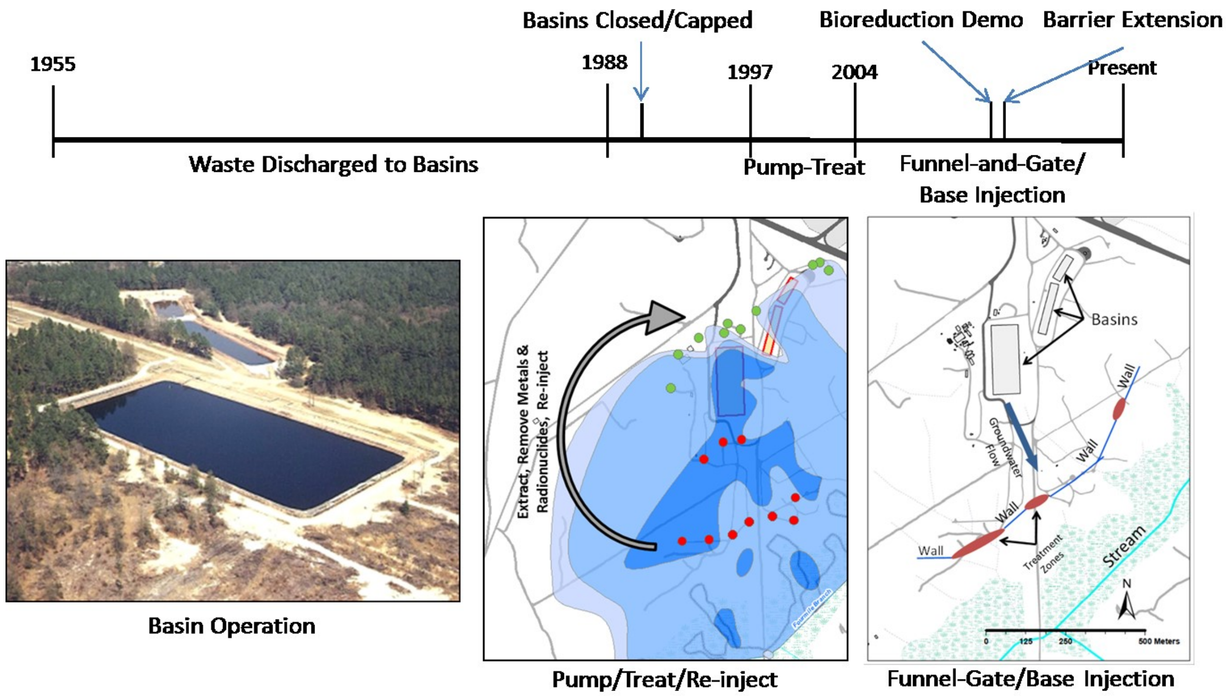


Figure 2: Time line of major events in the history of the F-Area Seepage Basins.

The funnel-and-gate consists of a subsurface barrier that extends from near ground surface to the Tan Clay. The subsurface barrier was placed across "troughs" in the top of the Tan Clay that were preferential flow paths for contaminant migration to the wetlands and Fourmile Branch. Gaps in the subsurface barrier were left across the topographic highs of the Tan Clay and groundwater is forced by the barriers through these gaps, or gates, where in situ treatment of contamination occurs. The treatment zones have an elevated pH compared to the contaminated groundwater, causing uranium and Sr-90 to adsorb to mineral surfaces within these zones. The treatment zones are created by periodic injection of alkaline (base) fluids. Just upgradient of the base injection zones at the center gate, I-129 is treated by injection of silver chloride particles. The particles react with natural iodide and I-129 that exists as iodide to form sparingly soluble silver iodide, removing I-129 from the groundwater.

Remediation of F-Area Seepage Basins groundwater also relies on natural attenuation of contaminants in the organic-rich soils of the wetlands associated with Fourmile Branch. Uranium and iodine, both natural I-127 and the contaminant I-129, are known to bind strongly to natural organic matter. This has been proven for I-129 in the Fourmile Branch Wetlands. Sr-90 is more likely bound to the relatively abundant clay-size particles in wetland soils. Wetland soils are the last opportunity for attenuation of contaminants before groundwater passes into the surface water of the wetlands and Fourmile Branch.

Surface water is the target of these major regulatory milestones (SCDHEC, 2017):

- Before October 31, 2012 reduce the mass flux (Curies/year) of tritium discharging from the F-Area plume to Fourmile Branch by 70%
- Before October 31, 2017 reduce the concentration of the remaining Appendix IVB-A constituents in Fourmile Branch (except tritium and I-129) to levels that that are less than groundwater protection standards as measured at Surface Water Sampling Stations FMC-002F and FMA-7U
- Before October 31, 2025 reduce the concentration of I-129 in Fourmile Branch to levels that are below groundwater protection standards

- Before July 31, 2020 reduce the discharge from the F-Area plume of all Appendix IVB-A constituents in the surface water at the seepline to concentrations that are less than the groundwater protection standards (except tritium and I-129)

Before October 30, 2030 reduce the discharge from the F-Area plume of I-129 in the surface water at the seepline to concentrations that are less than the groundwater protection standard as measured at Wetland Seepline Surface Water Sampling Locations FAS-91, FAS-92, FAS-93, FAS-96, and FAS-103.

The first two regulatory milestones have been achieved and the rate of concentration decrease suggest the others could be met as well (Denham and Amidon, 2016).

A more detailed discussion of the conceptual site model for the F-Area Seepage Basins is presented in Appendix D.

2.3 Zones of Vulnerability

Zones of vulnerability within the F-Area Seepage Basins groundwater contamination system are those locations at which residual contamination is expected to exist in an attenuated form for long periods of time. The attenuation-based remedies currently active at the F-Area Seepage Basins rely on physical and chemical conditions remaining conducive to contaminant attenuation within these locations for long periods of time. Hence, the proposed long-term monitoring plan focuses on the vicinity of the zones of vulnerability. The water inlet side of the zones of vulnerability is particularly important because changes to water flow and/or water chemistry on the inlet side signal future changes within the zones of vulnerability.

Three zones of vulnerability can be defined based on the conceptual model for the F-Area Seepage Basins: 1) The soils directly beneath the former seepage basins and the underlying vadose zone, 2) the gates where in situ treatments enhance attenuation of contaminants, and 3) the wetlands where contaminants are attenuated by primarily natural processes. Table 1 summarizes the zones of vulnerability.

Table 1: Summary of zones of vulnerability.

Zone of Vulnerability	**Vulnerable Contaminants**	**Threat Conditions**	**Long-Term Monitoring Focus**
Basin soils & vadose zone	All	Infiltration through cap	Cap integrity, moisture content
Treatment zones in gates	Uranium, Sr-90, I-129	Low pH (Sr-90, uranium) and reducing conditions (I-129)	pH, redox conditions, groundwater flow rate
Wetlands	Uranium, Sr-90, I-129	Low pH, significant change in wetland morphology, vegetation, etc., loss of organic matter	pH, redox conditions, physical configuration (topography, boundaries, course of Fourmile Branch, frequency of intense rain events)

3.0 Specific Long-Term Monitoring Plan for the F-Area Seepage Basins

The F-Area Seepage Basins specific long-term monitoring plan will incorporate traditional sampling and analysis of groundwater, sensors for important parameters, and relatively new spatially integrative methods for detecting systemic changes in the F-Area Seepage Basins system. The plan will be phased in during a transition period. The goal will be to have a monitoring system that will focus on leading indicators of system change with a minimum of sampling and analysis of contaminants. The zones of vulnerability where contaminants are stored in the primary and secondary sources will be monitored closely to detect any changes in indicator parameters that signal potential mobilization of contaminants from the vulnerable zones. The monitoring network will use two strategies – point measurements and spatially integrative measures.

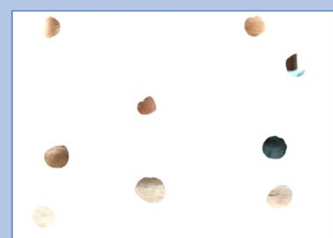
3.1 Point Measurements

Monitoring of groundwater and surface water will provide the primary basis for long-term monitoring of the F-Area Seepage Basins site. The difference in the new paradigm is that the approach will target changes in water parameters that signal potential mobilization of contaminants from the vulnerable zones where the primary and secondary contaminant sources occur. This will be accomplished with a nuanced approached using predominantly monitoring points at which sensors will be deployed to measure water levels and master variables. Far fewer samples will be routinely obtained from monitoring wells for contaminant analysis. The relatively few traditional monitoring wells that will be used will be located to allow evaluation of contaminant mobilization from the vulnerable zones in the event changes in boundary conditions and/or master variables warrant such evaluation.

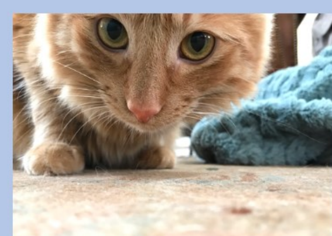
Figure 3 shows an example of a possible network for monitoring groundwater and surface water in the wetlands. The green squares are locations of monitoring wells constructed so that sampling can continue to meet RCRA Permit requirements as necessary while transitioning the site to a long-term monitoring program. All monitoring wells specified in the current RCRA Permit will be operable at the beginning of the transition period. Those shown in Figure 3 are in locations of existing monitoring wells and will remain after transition is complete. The monitoring wells in the long-term network may have to be reconstructed to better capture the vertical extent of the contaminant plume and to accommodate sensor packages to measure water level, pH, specific conductance, and oxidation-reduction potential. These monitoring wells are located primarily on the downgradient side of the basins and in the gates of the funnel-and-gate system to detect any contaminant mobilization from the basin soils and the treatment zones in the gates. The final locations, and hence the

The Big Picture

Point Source Measurements



Spatially Integrative Measurements



Point source measurements, such as information from individual monitoring wells or core samples, provide tiny glimpses of a system. Any larger picture must be inferred from prior knowledge of the system. Spatially integrative measurements, such as satellite and UAV imaging, geophysics, and distributed fiber optic sensors provide 2-D, 3-D, or even 4-D (if done over time) pictures of large portions of a system. The trade-off is that more detailed information, molecular level if needed, from a small sample can be obtained from point source measurements, whereas less detailed information over a very large sample can be obtained with spatially integrative measurements. The latter is typically more suitable for long-term monitoring number, of these wells will be determined from monitoring data collected before and during the transition period.

The blue squares are surface water sampling stations and are located where current stations exist. They will allow for sampling of surface water and will not be configured with sensor packages. If other methods of measuring master variables such as distributed fiber optic sensors are not sufficient, then sensor packages can also be deployed at these locations. The purpose of these stations is to detect contaminants released from wetland soils.

The pink circles are background sentry locations where sensor packages are deployed capable of measuring water level, pH, specific conductance, and oxidation-reduction potential. The 40 years of monitoring data that exist indicate that the only sources of acid within the site are the basins themselves and drainage from these is minimal. Likewise, there is no plausible geochemical mechanism for the aquifer to transition from oxidizing to reducing conditions without an influence from outside the site. There was slag put in the basins to induce reducing conditions in the basin soils, but drainage from these soils is unlikely to maintain reduction capacity because of the thickness of the oxygen-rich vadose zone. Thus, the purpose of the background sentry locations is to detect the influx of any acidic or reducing groundwater from outside the site. The water level sensors provide additional control points for constructing potentiometric surfaces of the aquifer.

The yellow circles will be locations at which only sensors to measure water levels are deployed. These will provide additional control for constructing potentiometric surfaces of the aquifer.

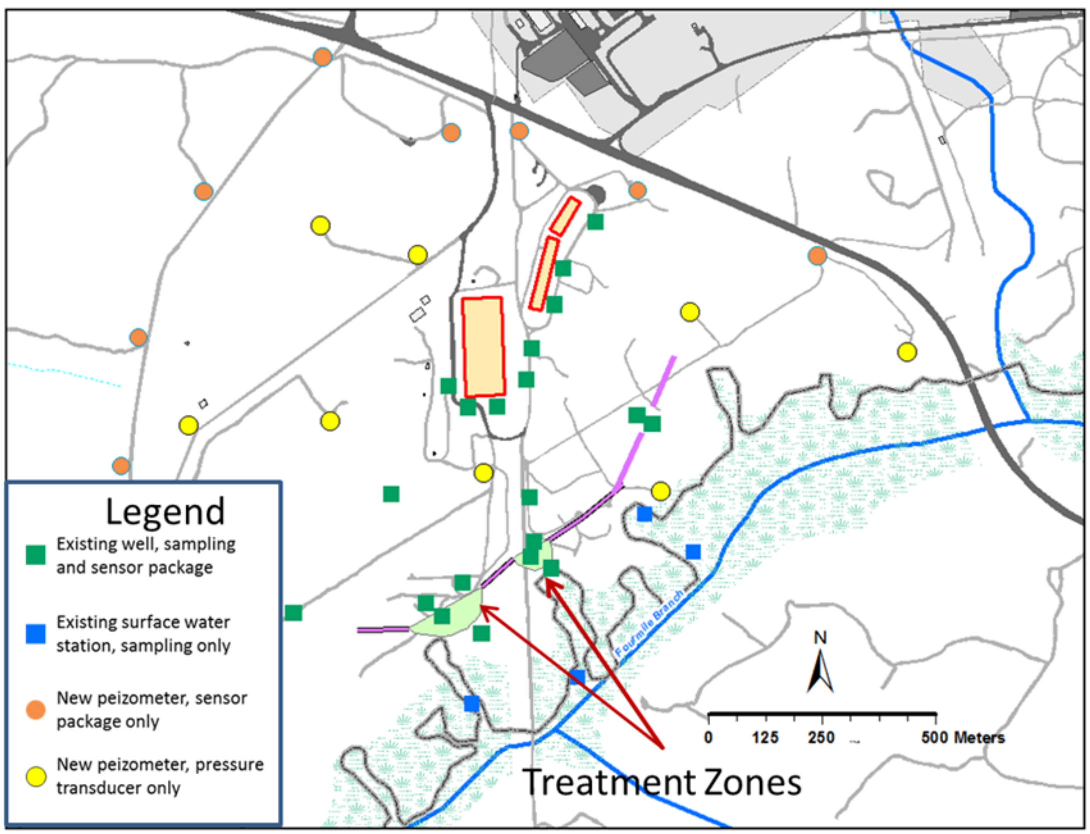


Figure 3: Map of a potential network of single point measurement locales.

Certain trends in parameters values or specific trigger levels will prompt actions to be taken. For example, a decrease in pH over several months or a short period with a pH<5 at a well would trigger sampling and measurement of pH at that well to determine if the sensor is functioning properly. If it is, then samples will be obtained for analysis of contaminants. Similarly, if groundwater levels change by a predetermined amount in a portion of the site, then a site visit will be made to assess the cause. The nature of the trends and the specific trigger levels will be determined during the transition period based on data analytics, geochemical factors, and predictive modeling.

It is important to note that in an analytical chemistry setting pH and redox probes require frequent calibration, but in a long-term monitoring setting calibration may be less important. The goal of monitoring redox potential and pH in a long-term monitoring program is to detect trends with time and large changes in these parameters, rather than absolute values. A multi-year study was conducted by SRNL at the F-Area Seepage Basins site in which sensor packages were deployed in three monitoring wells – one near the middle gate and two near the wetlands (Amidon and Millings, 2015). The study found that the pH probes failed after several months. The redox probes were reliable for longer.

Some of the newer fiber optic probes may be more robust. Their primary mode of failure is that the reactive gel coating the fibers is exhausted within a year or two. However, it does not seem like a large developmental step to produce fiber optic sensors that last much longer. It would require development of longer lasting indicators or ways to defeat the aging problem. For example, a sensor might consist of several bundles of fibers, one with the reactive gel exposed and others in which the reactive gel is coated with materials that degrade at different rates. Sometime before the originally uncoated fibers fail, the protective coating on another bundle would be degraded sufficiently to expose pristine reactive gel.

3.2 Spatially Integrative Strategy

Spatially integrative tools measure over large portions of a site, whether it be along a line (distributed fiber optic sensors), over a planar surface (UAV or satellite imaging), or through a large volume of sediment (geophysical methods). These types of tools are ideal and efficient for detecting systemic changes in the low permeability cap over the basins and within the wetlands and stream area.

3.2.1 Cap Assessment

The purpose of the current cap and drainage system assessment is to detect any changes that signal cap disturbance that could result in potential failure including subsidence, animal burrows, ponding of water, etc. The new long-term monitoring strategy will accomplish this goal using multiple imaging techniques of the cap and drainage system surface obtained from UAV flights and ongoing government satellite imaging programs. A single UAV flight over the cap and drainage system can provide multiple types of imaging. High resolution photogrammetry can detect disturbances at the surface of the cap, as well as water ponding. Lawrence Berkeley National Laboratory has developed integrated above-and-below ground monitoring technologies to evaluate the cap integrity. UAV imaging (spectral and LiDAR) provides the surface elevation at a centi-meter resolution which enables tracking of surface flow paths as well as evapotranspiration (Christiansen et al., 2018). Combined with the isotope analysis, it can identify the flow accumulation, fast flow paths and potential leaks. Some consideration might also be given to whether there is enough radon or radioactive xenon generation from contaminants in basin soils to be detected by gamma imaging if they emanated from fractures in the clay layer of the cap. Likewise, spectral imaging may detect non-radioactive gas emanating from materials unique to the basin contents.

An initial UAV overflight would be done before the transition period between traditional monitoring and the new long-term monitoring approach to collect baseline data and to compare with current methods of cap and drainage system assessment. Figure 4 shows example patterns of UAV flights over the two basin caps. During the transition period, UAV overflights would be done each year initially and could become less frequent with time as a technical baseline is established. The results of each overflight would be compared to previous results to detect any changes. Satellite multi-spectral imagery will be analyzed periodically as well.

Figure 4: Example of UAV overflight patterns.

The new long-term monitoring approach would add moisture measurement in the vadose zone as an indicator of cap effectiveness. Geophysical methods such as electrical resistance tomography (ERT) can detect moisture increases, indicative of degradation, within or beneath low permeability covers (Genelle et al., 2012; Sirieix et al., 2016; Tran et al., 2017). ERT electrodes could be permanently installed on the surface of the cap. They would need to be in contact with, but not penetrate, the top surface of the clay layer. These combined with electrodes installed in an angle boring beneath the cap could allow frequent visualization of soil moisture content in the vadose zone over long periods of time. Likewise, numerous methods have been employed to measure moisture changes in the vadose zone that would indicate increased infiltration through the cover (Vereecken et al., 2008). Older methods such as running a neutron logging tool down a permanent angle boring beneath the basins could also be used. However, deploying distributed fiber optic moisture sensors in angle bore holes beneath the basins would be much less labor intensive for long-term monitoring.

3.2.2 Long-Term Monitoring of Fourmile Branch and Wetlands

The spatially integrative tools used to monitor Fourmile Branch and the wetlands are various UAV mounted sensing methods, distributed fiber optic sensors, and multi-spectral satellite imagery. The purpose will be to detect changes in topography, vegetation, location of springs (groundwater cropping out at the surface), distribution of gamma emitting contaminants, pore water pH, and the course of Fourmile Branch.

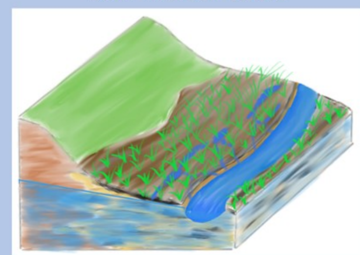
Topography is important because it determines drainage patterns and erosion that can create new springs. Additionally, it can identify low points where contaminant-bearing particles are likely to accumulate, as well as track changes in the course of Fourmile Branch. As the course of Fourmile Branch changes over time, the boundary conditions controlling groundwater flow change.

Similarly, changes in vegetation density, area, and species diversity are indicators of large-scale changes in the boundary conditions of the site. Furthermore, vegetation reflectance measured by multi-spectral satellite imagery has been used to detect nitrogen uptake by vegetation (Guo et al. (2017). Nitrate concentration in F-Area groundwater is a primary contributor to the specific conductance, a surrogate measure for the contaminant plume. Thus, changes in nitrogen uptake by vegetation, as measured by satellite imagery, may be a good integrated measure of plume movement through the wetlands.

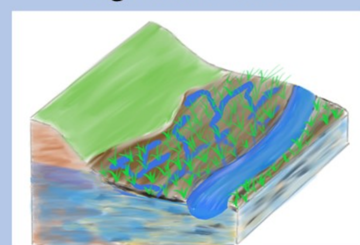
Understanding the distribution of radionuclides in the surface sediments of the wetland and changes of the distribution with time are important aspects of the long-term monitoring of the wetland. New high-resolution gamma detectors may be able to distinguish radionuclides such as I-129 and Tc-99 that have “weak” gamma emissions. They can also detect uranium isotopes and decay products. Identification of small “hot-spots” containing these contaminants during baseline data collection for long-term monitoring may provide opportunities for small-scale excavations that would significantly decrease the risk associated with contaminants in the wetlands. It is also important to know if, when, and how the distribution of radionuclides in wetland soils changes.

Dynamic Conditions in Wetlands

Low Water Table



High Water Table



One of the characteristics of the wetlands that distinguish them from other zones of vulnerability are the dynamic conditions. Vertical fluctuations in the water table cause lateral changes in the wetlands configuration (shown above) that can affect where contaminants are located and how they are attenuated. Seasonal changes in rainfall and temperature cause variations in vegetation, microbial activity, and dilution of near surface water. Longer-term changes in wetlands occur because of erosion and the changing course of the stream.

Before or during the transition to long-term monitoring the available satellite data will be obtained for the baseline satellite imagery. Additional baseline data will be obtained by UAV outfitted with LiDAR capability and the appropriate detectors for photogrammetry, gamma detection, and thermal imaging. LiDAR will provide topography data and potentially soil parameters such as organic content. Gamma imaging will indicate the baseline distribution of gamma emitting contaminants. Photogrammetry and thermal imaging will locate springs. The known locations of springs where existing sampling stations are will provide good verification of this method of spring location. As the transition proceeds these same data will be collected periodically with frequency decreasing at an appropriate rate as time passes.

The topographic data, locations of springs, and distribution of gamma emitters collected as baseline data will guide the placement of distributed fiber optic sensors, if preliminary studies indicate they have value for the long-term monitoring program. Groundwater springs or seeps in the wetlands tend to be linear features as illustrated by the photograph of a seepline in the Fourmile Branch wetlands shown in Figure 5. The sampling stations at these seeps allow collection of water at a single point. Distributed

Figure 5: Photograph of a groundwater seep in the wetlands along Fourmile Branch.

fiber optic sensors would allow collection of data along the length of groundwater seeps. In addition, distributed thermal sensors would indicate exactly where groundwater was cropping out into the seeps. This would provide information on locating sampling stations to obtain the most reliable samples. Gamma sensing fiber optic cables would be placed across both seeps and soil hotspots highlighted by UAV gamma imaging. It will be important to know that concentrations of gamma emitters are not increasing at the seeps and to know that hot spots remain static.

3.2.3 Implementation of Long-Term Monitoring

It is recommended that implementation of the long-term monitoring program at the F-Area Seepage Basins Site be done in three phases. In the first phase, baseline data will be collected, and validation of the new approach will occur. The second phase will be the transition from the traditional monitoring program to the new approach. The third phase will be the final configuration of the long-term monitoring network. The duration of these phases will depend on assessment of the data collected during each phase.

Phase I – Baseline Data Collection and Approach Validation
Existing groundwater chemistry data, well locations, and well screen configurations will be evaluated to determine number, optimum location, and optimum vertical screen placement for monitoring wells to be used in the long-term monitoring program. This evaluation will include groundwater modeling of various long-term scenarios such as climate change and cap failure. The wells should be installed with sensor packages in them and then monitoring data should be collected at a frequency and for a period determined by data analytics of historical data. Another consideration in determining the length of the baseline monitoring is the length of time required to evaluate the sensor performance. The baseline data together with historical data will be used to set the action criteria for trends and maximum/minimum values of water levels and master variables.

During Phase I, baseline data from UAV overflights of the cap/drain system and the wetland/stream system will be collected. Multiple overflights should be done and compared for consistency. The first overflight of the cap/drain system should be done within a timeframe that the assumption can be made with certainty that the cap is not leaking. It would be prudent to follow the first UAV overflight of the wetland/stream system with a round of soil and water sampling in the wetlands based on the results of the overflight. Hot

spots and all seeps should be sampled, but sampling might also include low topographic areas that tend to collect fine mineral and organic particles that may be hot spots unidentified by gamma imaging or potential future hot spots. Historical multi-spectral satellite data will be evaluated to determine the most useful satellite datasets for long-term monitoring of the site and how often satellite data should be evaluated.
Once UAV overflights of the wetland/stream system are done and seeps and hot spots have been mapped, distributed fiber optic sensors can be installed at these locations as deemed appropriate. Then baseline data for these sensors should be collected.

Tools for measuring moisture in the vadose zone will be deployed early in the Phase I to allow sufficient baseline data to be collected.

Phase II – Transition to Long-Term Monitoring

The transition of the site from traditional long-term monitoring to the new approach will occur by gradually decreasing the traditional monitoring at a pace determined by evaluation of the data, but also that meets the needs of regulators and stakeholders. For example, a set of wells will be selected for the initial phase out based on historical data. These will be wells that do not monitor a vulnerable zone. The selected wells will be removed from service on a schedule that is based on the information they provide about the plume and the time trends of contaminants. The number and/or frequency of sampling of wells that monitor vulnerable zones may also be reduced as appropriate during Phase II.

Data from the spatially integrative tools will be evaluated early in Phase II to determine the frequency at which data should be collected or analyzed. The goal should be to reduce this frequency during Phase II to that which will be operable in Phase III.

Phase III – Out-Year Long-Term Monitoring

Phase III is the final phase of long-term monitoring. The goal entering Phase III should be to have the long-term monitoring program optimized to a final state. However, this state must remain flexible to accommodate changes in boundary conditions, master variables, and status of vulnerable zones brought about by climate change or other events. For example, if the plume shifts further westward, additional monitoring may be needed on the west side of the site while monitoring stations may be eliminated on the east side. The length of Phase III will be determined by the data and agreement with regulators and stakeholders.

4.0 Appendix A: Description of New LTM Approach

Original definitions of long-term monitoring included the objective of evaluating the effectiveness of remedial activities in addition to ensuring future risk at a site remained acceptable (Reed et al., 2000; Reed et al., 2001; Reed and Minsker, 2004; USEPA, 2004; USEPA, 2005; Harre et al., 2009; Hunter et al., 2011). Within the framework of this definition long-term monitoring was the last stage of a continuously evolving monitoring program that primarily measured contaminant concentrations at point locations (e.g., monitoring wells or springs). Such measurements are expensive and most efforts at improving long-term monitoring have been focused on optimizing the pre-existing monitoring network by using statistical methods and numerical modeling to reduce redundancy in measurements. Additional advances have been made in field measurements of contaminants (e.g., Ho et al., 2005) that reduce costs of long-term monitoring. Nevertheless, long-term monitoring still relies almost exclusively on measuring contaminant concentrations in groundwater at individual points. With increasing use of in situ attenuation-based remedies, particularly for metals and radionuclides, that rely on leaving contaminants in the subsurface (USEPA, 2007; ITRC, 2010), even optimized networks of contaminant measurements become quite expensive over the life-cycle of a waste site.

Furthermore, long-term monitoring networks that rely primarily on contaminant measurements at specific points only alert an environmental manager that a problem has occurred, rather than warning of a potential problem. Once contaminant concentrations have increased to a level of concern at sentry wells, the problem is often more difficult to address. It would be valuable to incorporate indicators into long-term monitoring that signal when changes occur to system parameters that control contaminant behavior and might cause destabilization and mobilization of attenuated contaminants (Bunn et al., 2012).

A different view of long-term monitoring was taken by Bunn et al. (2012) allowing for development of a more effective and efficient approach. They stated that the overall objective of long-term monitoring is:
"…to confirm or assess contaminant stability, remedy stability, and site maintenance over the long term after long-term remedial actions have been completed."

Severing the tie between "remedy effectiveness monitoring" and "long-term monitoring" opens the possibility of a new paradigm for long-term monitoring. Long-term monitoring can become a discrete monitoring stage rather than an incremental evolution of previous monitoring at a site. Long-term monitoring can then emphasize detecting systemic changes that are likely to destabilize contaminants attenuated at the primary and secondary sources within the system. In doing so, the role of concentration measurements at specific points can be substantially reduced and the emphasis can be placed on monitoring leading indicators of systemic change. In cases where attenuation-based remedies have been used, long-term monitoring can be focused on locations where contaminants are attenuated, here termed "zones of vulnerability". Attenuated contaminants are subject to remobilization when systemic changes influence conditions in zones of vulnerability. The difference between traditional long-term monitoring and the proposed new approach is summarized in Figure 6.

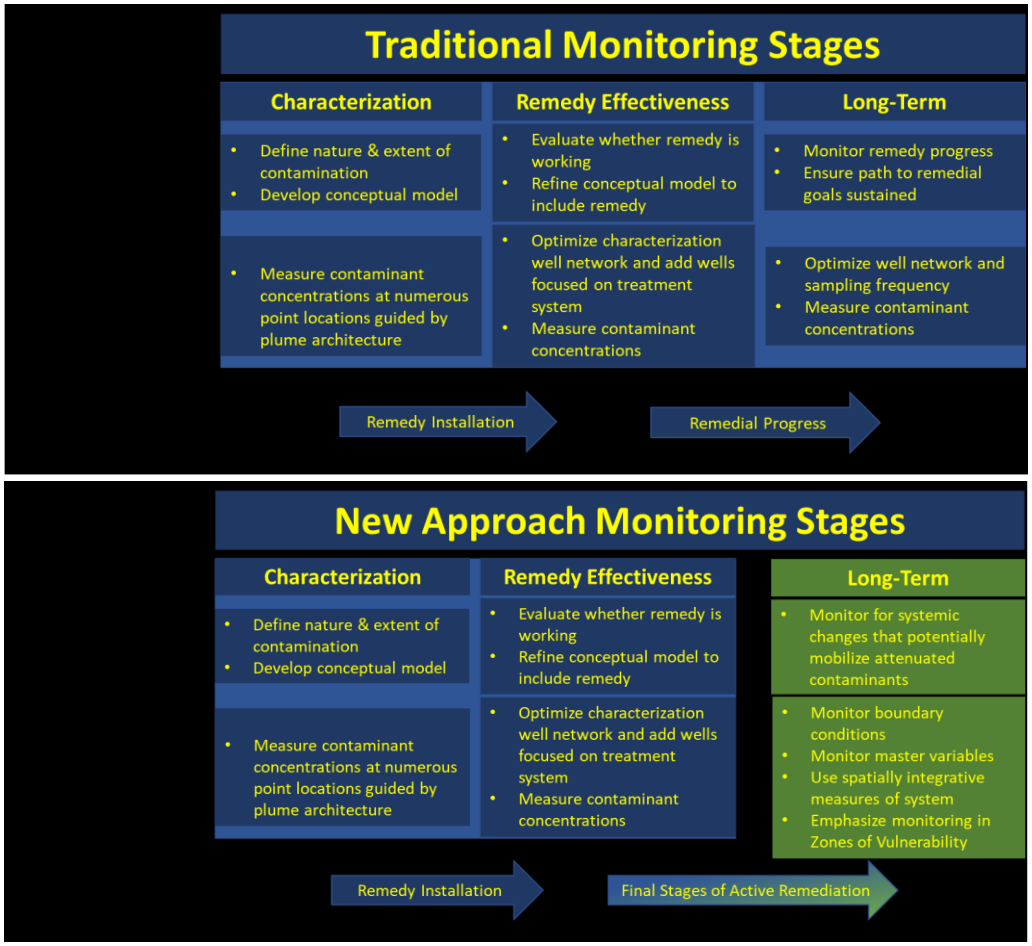


Figure 6: Comparison of traditional long-term monitoring to the proposed new approach.

4.1 A New LTM Paradigm

The object of long-term monitoring is to both verify the behavior of a site through time, based on the conceptual model of the site, and to alert environmental managers of any significant deviation from that expected behavior. For long term monitoring, significant deviation usually means a behavior which results in an unacceptable change in the value of a target/regulated parameter or contaminant of concern. A key assumption of long-term monitoring is that the plume system is at some stable condition following mitigation of the source. Specifically, the assumption is that the plume is shrinking at a steady rate, contaminant concentrations are decreasing at a steady rate, or remedial objectives have been met and contaminant concentrations remain below maximum concentration levels (MCLs). So, the objective of long-term monitoring can be restated as monitoring to be sure the stable system remains unperturbed.

When a mature plume deviates from a stable condition it is because there has been a change in the physical or chemical forces that control contaminant movement. There are cases of contaminants emerging from unknown sources causing deviations in contaminant versus time trends, and this is one reason to maintain some point source monitoring of contaminant concentrations. Nevertheless, at sites with well documented history of disposal and extensive characterization, monitoring focus is on detecting some deviation in the physical and chemical processes controlling contaminant movement.

The physical process controlling contaminant movement is the flow of water. This includes infiltration passing through a near surface source zone, water movement through the vadose zone, and groundwater movement in the saturated zone. The primary components of this water balance are influx and efflux of water into and out of the site – typical boundary conditions in groundwater modeling. Secondary effects that do not change the overall water balance can also influence contaminant behavior. For example, turning off a pump-treat-reinject system may maintain the water balance, but alter the migration of contaminants. Likewise, localized changes in hydraulic conductivity from remediation activities may alter the migration of contaminants.

Local or regional changes to groundwater flow can lead to variations in the attenuation of contaminants associated with in situ treatment zones. Consider flow of groundwater through a treatment zone in which the release of stabilized contaminants is solubility controlled. An increase in groundwater flow rate would increase the flux of contaminants to the boundary of the waste site, but not the concentrations. In contrast, if the release of contaminants is kinetically controlled, an increase in flow rate would decrease the contaminant concentrations at monitoring points, but not necessarily the contaminant flux to the site boundary.

Of equal importance to long-term monitoring are changes in groundwater flow that shift the position of the plume without changing attenuation of the contaminants. As plume flow lines shift, concentrations of contaminants may increase or decrease at specific monitoring locations. It is important to understand whether the variations in flow direction are oscillatory, the plume shifting back and forth at some regular frequency or are long-term, the result of some singular event near the site. Examples of singular events that can cause long-term changes in flow directions are clear cutting of timber, installation of production or injection wells, paving of large areas, or dewatering of construction sites. If changes to flow direction are long-term, then monitoring locations may have to be changed accordingly.

Chemical forces are those parameters that most influence chemical and biological processes that attenuate contaminants. For metal and radionuclide contaminants, pH and oxidation-reduction potential are of primary importance and have often been referred to as “master variables”. Charge on most mineral surfaces is dependent on pH, and hence, adsorption of contaminants is sensitive to pH. Likewise, pH influences aqueous speciation of most metals and radionuclides which, in turn, influences their adsorption and precipitation. The redox state of an aquifer system is also an important control on aqueous speciation of contaminants that can exist in multiple oxidation states in groundwater. There can be profound differences in solubility and adsorption between oxidation states for metals or radionuclides such as uranium and I-129. Under sulfate reducing conditions, even metals that are not redox sensitive, such as lead, cadmium, and zinc can be strongly attenuated by precipitation of sulfide minerals. Measured oxidation-reduction potentials 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.

At some sites, parameters other than oxidation-reduction potential and pH may be important indicators of system changes that could lead to contaminant mobilization. For example, alkalinity or dissolved CO_2 coupled with pH is a critical parameter for mobilization of uranium and other metals readily complexed by carbonate. Ionic strength is an important influence on adsorption of many metals and radionuclides and increases in ionic strength could portend desorption of these contaminants. Hence, the conceptual site model for each site dictates the important chemical parameters to measure.

Measuring 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 on mitigating contamination mobilization caused by a systemic change. Second, most are easily and inexpensively measured by robust in situ sensors that transmit data wirelessly to a central location. Finally, rainfall, evapotranspiration, and stream gages integrate information over large areas so that a single measurement provides systemic information.

We propose a long-term monitoring strategy for sites with contamination left in the subsurface that de-emphasizes numerous measurements of contaminant concentrations at specific points in favor of measuring the parameters that indicate systemic changes that could lead to contaminant mobilization from zones of vulnerability. Contaminant concentrations would still be monitored at wells and surface water locations, but at fewer locations and less frequently. When parameters measuring physical and chemical stability of the system vary beyond established threshold or "trigger" values, it would trigger a campaign of measuring pertinent contaminant concentrations.

Implementation of the new long-term monitoring strategy will generally proceed as shown in Figure 7, though variations may be made to accommodate specific sites. The first step is to identify zones of vulnerability based on the conceptual site model. Identifying "threat conditions", changes in conditions that could remobilize attenuated contaminants, is the next step. This is done using knowledge of site-specific behavior of the contaminants, attenuation mechanisms, and the nature of the zone of vulnerability. The threat conditions may be different for each contaminant and for different zones of vulnerability. Trigger values for the threat conditions are defined based on the geochemical behavior of the contaminants and the rate of remobilization compared to groundwater flow. In addition to or as an alternative to trigger values, it may be useful to establish an acceptable slope and duration of a trend in a threat condition with time. Predictive modeling is particularly useful for establishing trigger values and acceptable trends. Selecting appropriate monitoring tools, the next step, is done with the objective of obtaining the maximum useful information with minimal sample collection and analysis. This includes tailoring tools to the nature of the vulnerability. For example, spatially integrative tools are very efficient ways to obtain monitoring data but are not feasible for assessing all threat conditions or for certain zones of vulnerability. Once the monitoring tools are selected, the optimum monitoring network can be defined based on the zones of vulnerability, geochemical behavior of the contaminants, groundwater flow, and an assessment of potential off-site influences (e.g., construction sites, other waste sites, well fields, etc.). This is best done with the aid of predictive modeling that can simulate different configurations of the monitoring network, as well as scenarios for off-site influences. Finally, a long-term monitoring plan can be developed and implemented. The long-term monitoring plan should specify actions to be taken if trigger values are exceeded or trends in threat conditions are unacceptable. The plan should also describe how the transition from the current monitoring program to the long-term monitoring program will occur. This should be done in a phased approach with careful evaluation of each phase after it has been in place for a specified time.

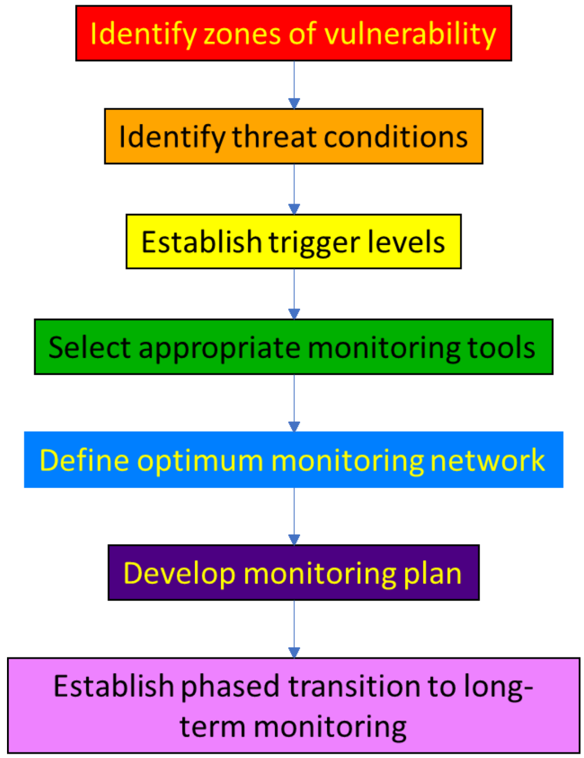


Figure 7: The general steps in developing a long-term monitoring program using the proposed approach.

5.0 Appendix B: Predictive Modeling and Data Analytics

5.1 Predictive Modeling

Predicting the fate and transport of contaminants under various conditions is crucial to the proposed new paradigm for long-term monitoring. The modeling tool used thus far is the DOE-EM developed Advanced Simulation Capability for Environmental Management (ASCEM). ASCEM software is an open source, modular computing framework that incorporates new advances and tools for predicting contaminant fate and transport in natural and engineered systems. ASCEM has been transformative in modeling reactive transport over the past five years. Before ASCEM, the complex geochemical reactions, such as pH dependency of uranium sorption kinetics, were only considered in a simplified domain (Bea et al., 2013). Now ASCEM can solve this system in 3 dimensions (3D) with more than one million grid cells. In addition, the robust flow solver allows us to include complex geological contrasts and artificial structures such as low-permeability barriers. We can now simulate a realistic domain and reactions in 3D and implement various long-term scenarios to be a virtual test bed for the F-Area Seepage Basins system (Wainwright et al., 2016). The virtual test bed is important for long-term monitoring because it allows us to optimize the monitoring strategy and network for potential future conditions such as increased annual rainfall, significant perturbance to groundwater flow brought about by an off-site activity, or a breached cap.

For example, Libera et al. (2018) identified and quantified the impact of precipitation shift and extreme events on the residual contaminants and plume; particularly in the vadose zone. According to the National Climate Assessment (science2017.globalchange.gov), the area of South Carolina where the Savannah River Site is located is expected to have increased precipitation by 10-20% and more frequent extreme precipitation in the future. Libera et al. (2018) found that the increased precipitation could mobilize the residual contaminants in the vadose zone and increase concentrations in the saturated zone. Furthermore, the responses at the monitoring wells would be delayed by years to a decade depending on the well locations, which could be confusing for the monitoring data analysis. Their simulations also showed that there is a trigger level of precipitation above which the concentrations are more influenced by the increased precipitation.

When the cap integrity is reasonably maintained, it is considered that the residual contaminants are mobilized mainly by the water table changes (Libera et al., 2018). This is because the groundwater divide is approximately 1500-meter upgradient (Bea et al., 2013). The increased infiltration over this large recharge area could affect the groundwater table below the basins. Continuous monitoring of the groundwater table is critical for detecting changes in the residual source contributions, in addition to the plume mobility and direction. In parallel, Libera et al. (2018) showed the importance of cap integrity not only to reduce the impact but also to reduce the uncertainty associated with precipitation events. The wells near the source zones are important for detecting the changes in the residual contaminants (Wan et al., 2013; Libera et al., 2018).

Bea et al. (2013) performed uncertainty quantification (UQ) analyses of modeling of contaminant migration near the F-Area Seepage Basins to find that that the uranium concentrations is most sensitive to the pH of the waste solution, discharge rates, and the reactive surface area available for adsorption. Constraining these parameters through the data-model integration would improve the accuracy of the model prediction. At the same time, these parameters are either initial conditions or material properties that do not change over time. As a key finding, their UQ analysis also indicates that this model (and parameters) sensitivity evolves in space and time. In the trailing edge of the plume, for example, the infiltration and groundwater recharge become increasing important.

The virtual testbed (i.e., A 3D flow and reactive transport model) has provided a mechanistic understanding of the correlations between *in situ* variables and contaminant concentrations. In addition, the virtual testbed has proved to be useful to project the correlations into the future, and to investigate the effectiveness of the proposed monitoring strategy. The uncertainty quantification has been used to investigate the impact of the uncertainties and variability in hydrological and geochemical parameters.

In the future, the virtual testbed will be used to explore the impact of climate change and other hydrological shifts on monitoring strategies, as well as to develop a better strategy for optimal spatial-temporal placements of the monitoring well locations. The UQ simulations will be used to estimate the life-cycle cost of monitoring and other key metrics (e.g., how many wells are enough, and how long we need monitoring).

5.2 Data Analytics

Data mining of the historical groundwater monitoring datasets from the F-Area Seepage Basins has shown excellent correlations between in situ measurable variables (e.g., pH, and nitrate) and contaminant concentrations, including tritium and uranium. Note that nitrate can be measured in situ at this site, since it dominates total dissolved solids, and hence determines specific conductance. Such strong correlations suggest the feasibility of inferring contaminant concentrations based on the *in-situ* sensors, by describing the contaminant concentration as a function of the in situ measurable parameters. There is some uncertainty in the correlations, suggesting the importance of quantifying the uncertainty at each location, as well as the quantifying critical points for different variables at which contaminant concentrations begin to deviate from the correlation.

In the historical datasets, the time series of U-238 and H-3 concentrations are correlated to the *in situ* measurable specific conductance (SC) and H^+ activity at each well (Figure 8). Such correlations have been reported in laboratory experiments and modeling studies (e.g., Bea et al., 2013; Dong et al., 2012). Specific conductance is equivalent to nitrate concentrations, since nitrate dominates the total dissolved solids (TDS) at this site. These correlations are associated with the fact that U-238 and H-3 were discharged together into the F-Area basins with nitric acid, since nuclear fuel (mainly consisting of U-238) is processed in nitric acid during reprocessing. In addition, pH is the key control on U-238 concentrations and U-238 is mobile in acidic conditions of F-Area Seepage Basins groundwater.

These correlations are consistent across the site (Figure 9). The Pearson correlation coefficients between the SC and U-238 are positive up to 0.96 with an average of 0.55, with the exception of low correlations at a few wells in the fringe of the plume (see Figure 2a). The correlation between the H^+ activity and U-238 is also positive up to 0.91 with an average of 0.58 (see Figure 9b). The results for H-3 are similar with positive correlations for both the SC (maximum: 0.98, average: 0.73) and the H^+ activity (maximum: 0.93, average: 0.51). The statistically insignificant correlations and outliers are found to be due to low contaminant concentrations and the location of some of the wells at the edge or out of the plume. The pH gradient at the edges of the plume is where U-238 is removed from groundwater by adsorption (naturally attenuated), thus negating the correlation with SC and introducing large uncertainty in the correlation with pH.

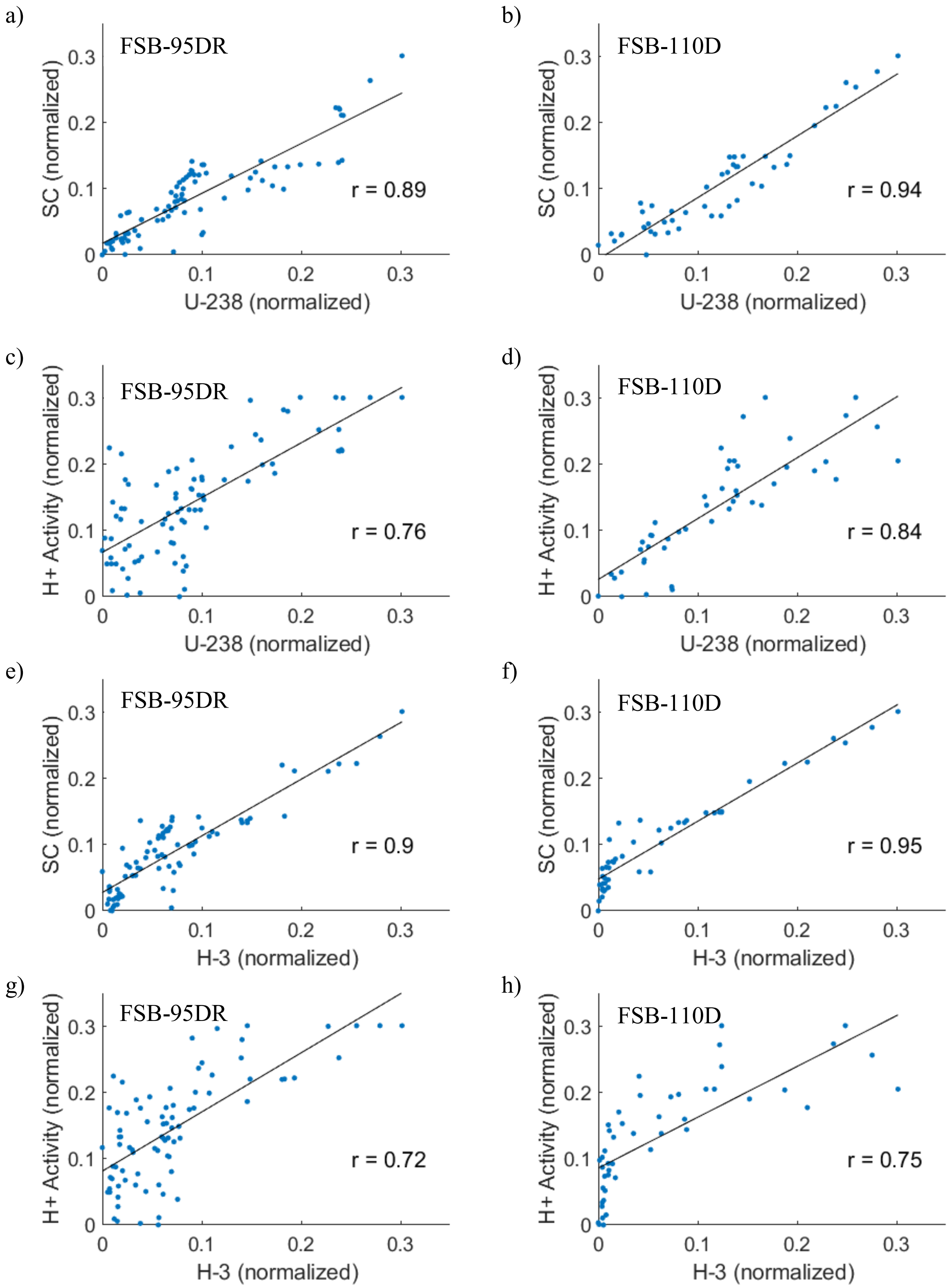


Figure 8: a) Correlation plots for the entire time series with first order fitted trend lines for a) the SC and c) H^+ vs. U-238 at well FSB-95DR and well FSB-110D (b) and d), respectively). e) – h) The same plots with H-3 as the contaminant.

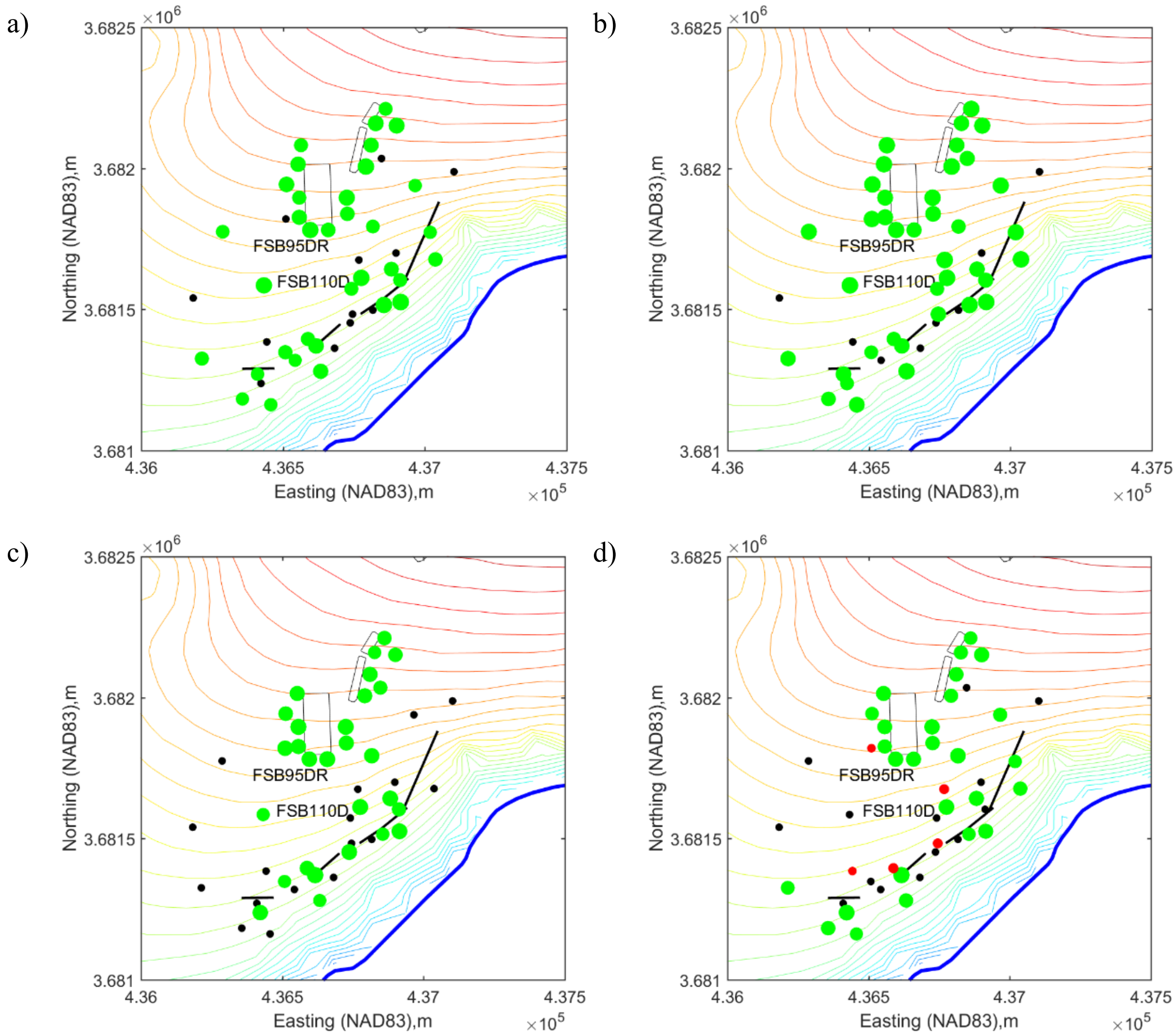
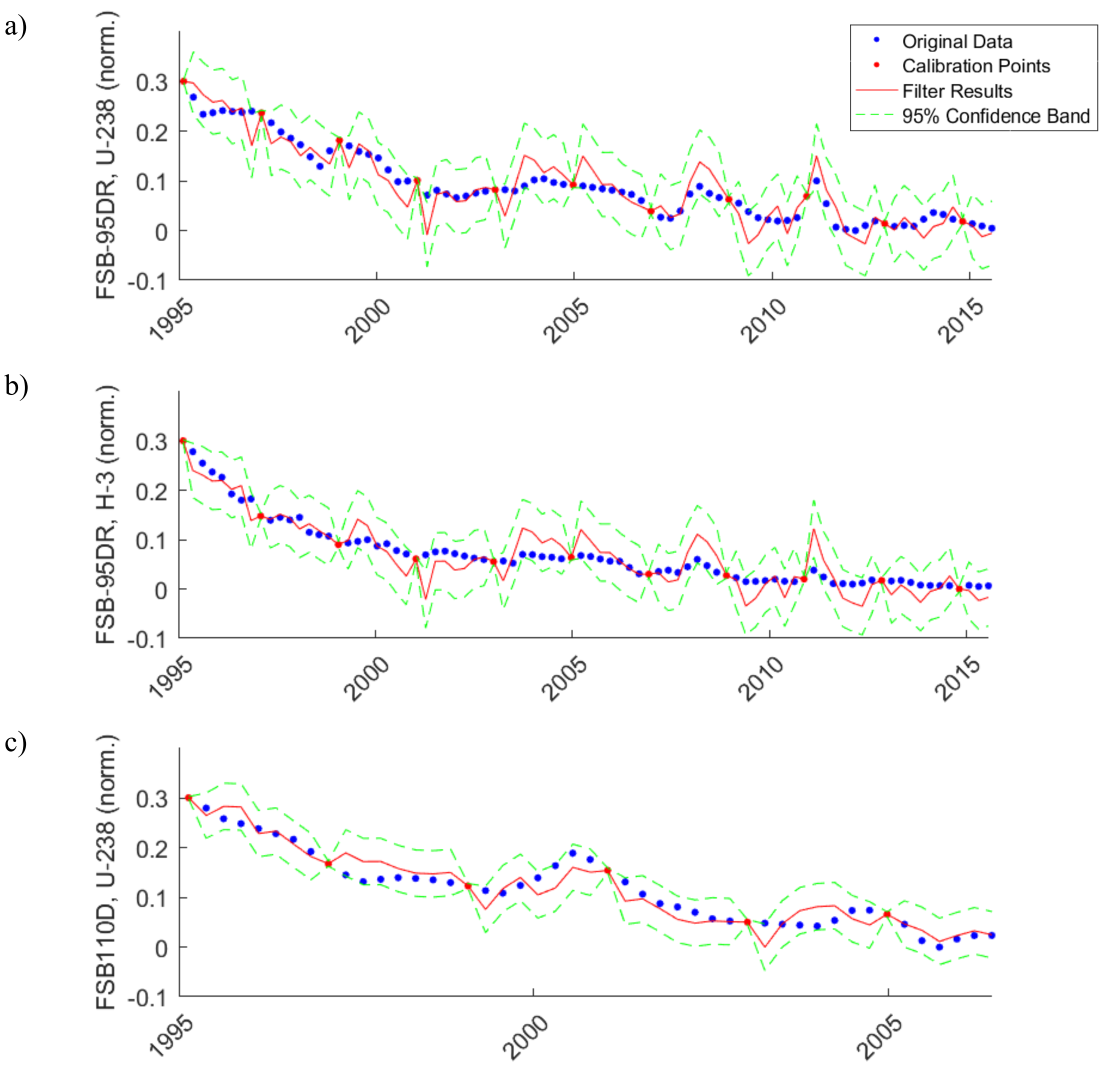


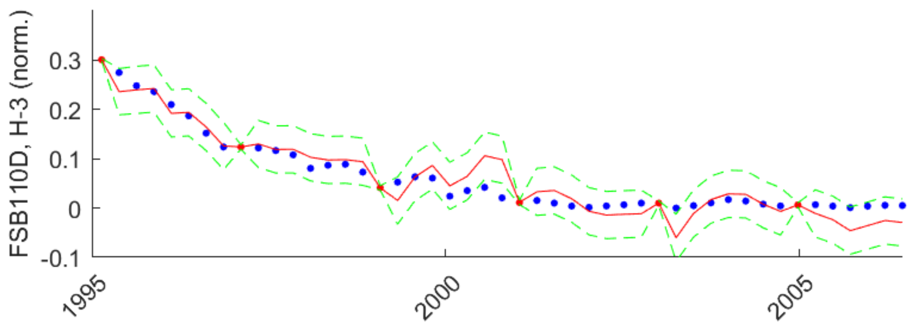
Figure 9: Bubble plots of the Pearson correlation coefficients for a) SC and U-238, b) H+ and U-238, c) SC and H-3, and d) H+ and H-3. All the concentrations are log-scaled. Positive correlations are shown in green, while negative ones in red. A black dot marks a well with an insignificant p-value (> 0.05). The size of a bubble represents the absolute value of the coefficient. All wells shown here are fully screening the upper aquifer.

To achieve more accurate estimation of the contaminant concentrations, the future work focuses on implementing the automated estimation method based on the Kalman filtering approach. The Kalman filter was originally developed to control spacecraft or robots by tracking (i.e., estimating) their trajectory and movement based on indirect data or noisy signals. For groundwater monitoring, the Kalman filter enables us to continuously estimate contaminant concentrations based on *in situ* measured data. It also provides a systematic approach to update the correlation parameters real-time (which leads to more accurate estimation), as well as to quantify the uncertainty of the estimates, given noise and measurement errors. The approach will be demonstrated using the in situ sensors currently deployed at the F-Area. In addition, other machine learning approaches such as artificial neural network can be tested and compared.

Schmidt et al. (2017) has developed the Kalman filter-based method to estimate contaminant concentrations continuously in real-time based on *in situ* measurable groundwater quality parameters. The Kalman filter effectively couples data-driven concentration-decay models with the correlations between the contaminant concentrations and *in situ* measurable parameters. The method was demonstrated using the historical datasets at the SRS F-Area Seepage Basins site. Results show that, even with groundwater sampling every two years, we still obtain reasonable results with most of the predicted values lying within the bounds of the 95% confidence interval for both U-238 and H-3 (Figure 10). The proposed method is expected to reduce the groundwater sampling frequency, while still reliably monitoring the evolution of the plume continuously in real-time. It also indicates its potential as part of an early warning system in the case of plume-remobilization.



d)



Time [y]

Figure 10: Kalman filter results: (a) U-238 concentrations at well FSB-95DR, (b) H-3 concentrations at well FSB-95DR, (c) U-238 concentrations at well FSB-110DR and (d) H-3 concentrations at well FSB-110DR. In the plots, the red lines are the estimated mean concentrations from the Kalman filter, the green lines are the confidence intervals, the red circles are the direct measurements of contaminant concentrations used for calibration, and the blue circles are the measured concentrations not used for estimation, but used for validation. All predictions are based on continuous measurements (1 per 90 days) of SC and pH and occasional direct samples (every 8 time steps or 720 days).

6.0 Appendix C: Tools to Achieve Maximum Monitoring Efficiency

To achieve cost-effective monitoring, Eddy-Dilek et al. (2014) have developed an innovative long-term monitoring strategy that focuses on measuring the key variables that control contaminant plume mobility and their spatial and temporal distribution (e.g., pH, redox potential, electrical conductivity, and groundwater level). The main advantage is that many of these variables can be measured using in situ autonomous sensors that allow frequent measurement of parameters and wireless transmission of the data to a long-term monitoring database. Three solar powered sensor packages have been deployed in contaminated groundwater associated with the F-Area Seepage Basins for 3 years (Amidon and Millings, 2015). The packages measure pH, redox potential, specific conductance, temperature, and pressure (a measure of water table elevation). Data is regularly transferred to a cloud server and is available to those with restricted access. The pH sensor has had issues operating for periods of more than several weeks without maintenance, but new pH sensors that may be more stable are becoming available. The other sensors operate for long periods without maintenance.

Methods of data analytics enable us to determine the most important variables and the values that trigger additional monitoring in space and time. The strategy of emphasizing leading indicators of plume change reduces point measurement of contaminants, thereby reducing costs, but more importantly facilitates proactive rather than reactive response to the changes. Coupled with sparse groundwater sampling, the data analytics methods – data mining and machine learning – allow us to estimate contaminant concentrations and detect which changes of the plume mobility are significant.

Our proposed new strategy also takes advantage of state-of-art spatially integrating techniques – such as fiber optics sensing, geophysics, and unmanned aerial vehicles (UAVs) – for mapping heterogeneity in plumes and other key environmental variables. The fiber optics technology uses optical fibers for measuring environmentally relevant parameters including temperature (Suarez et.al. 2011; Briggs et al., 2016a), strain, soil moisture, acoustic waves (Bao & Chen, 2012, Cox et.al. 2012), gamma radiation (Gaebler, 1983), and some chemical signatures (e.g. Potyrailo and Hieftje, 1998). Each pulse of light samples the state of the fiber at all locations, yielding property measurements along the entire length at a fine lateral resolution (~ 0.25 - 1m). In contrast to autonomous point sensors, the fiber optics technology can acquire the real-time high-frequency datasets combining large extent and fine space/time sampling.

Geophysical methods – including electrical resistivity, seismic, and radar – have been increasingly used to characterize the subsurface in a non-invasive manner (e.g., Binley et al., 2015). They can image subsurface contaminant plumes (e.g., Johnson et al., 2010, 2012; Dafflon et al., 2012), as well as map flow and biogeochemical properties that are important for predictive modeling and understanding (e.g., Johnson et al., 2010; Dafflon et al., 2011; Johnson et al., 2012; Wainwright et al., 2014). In particular, autonomous electrical resistivity and phase tomography (ERT) monitoring has the potential to achieve rapid and automated detection and identification of contaminant plumes, as well as water infiltration within the vadose zone. This approach can bridge the gap in sparse wellbore locations, by providing high-resolution and spatially extensive information in a minimally invasive manner (e.g., Johnson et al., 2015).

The UAV technologies are rapidly expanding into the areas of environmental remediation and monitoring. The high-resolution surface elevation from LiDAR or PhoDAR, for example, enables us to map surface runoff patterns and surface subsidence in the capping system (Christensen et al., 2018). Thermal cameras are increasingly used to map the locations of groundwater seep zones and river-groundwater interactions (Briggs et al, 2016b). In addition, the coupled spectral and structural information from the UAV images can map the heterogeneity of plant species, photosynthetic activities, as well as evapotranspiration -- key components in the water budget and groundwater recharge. In parallel, the UAV-based gamma-ray detection or imaging technologies have been rapidly developed over the past seven years, enabling the reconstruction and fusion of gamma-ray activities within the environment in 3D (Haefner et al., 2015; Barnowski et al., 2015). Integrating these data layers from UAV images enables us to gain an understanding of radioactive plume heterogeneity and migration over large areas.

7.0 Appendix D: Conceptual Model for F-Area Seepage Basins

7.1 General Physical, Hydrogeological, and Geochemical Setting

The F-Area Seepage Basins consisted of three unlined ponds into which low level radioactive liquid waste was disposed. Disposal began in 1955 and ended in 1988, with approximately 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. Mobile radionuclides migrated through the vadose zone (approximately 20 meters thick), contaminating groundwater in the saturated zone at concentrations of environmental concern. The resulting contamination plume has an areal extent of approximately 1 square kilometer and discharges into wetlands and a local stream called Fourmile Branch. The map in Figure 11 shows the location of the three basins relative to the wetlands and Fourmile Branch, with an arrow showing the general direction of groundwater flow.

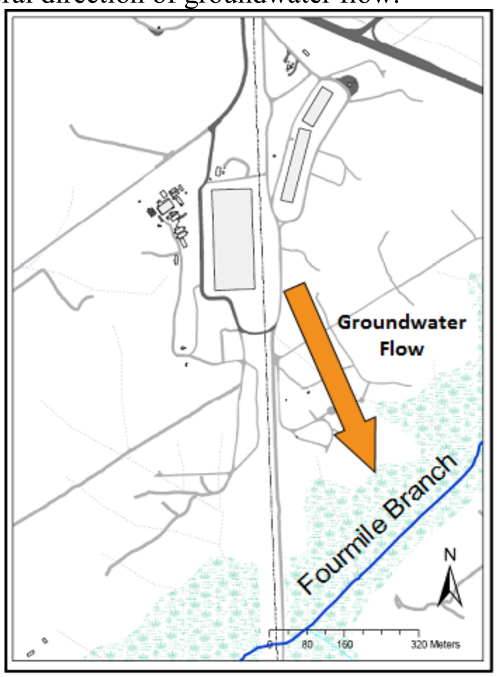


Figure 11: Map of F-Area Seepage Basins, wetlands (green patterned area), and Fourmile Branch.

The site is underlain by unconsolidated to consolidated, primarily Eocene, sands and clays. The lithostratigraphic and hydrostratigraphic columns are shown in Figure 12, with the yellow shaded portions indicating the section of interest. The most widespread and concentrated groundwater contamination occurs in the unconfined Upper Aquifer Zone (UAZ) of the Upper Three Runs Aquifer (UTRA). There is a downward groundwater gradient through the Tan Clay Confining Zone (TCCZ) that drove some contamination into the Lower Aquifer Zone (LAZ) of the UTRA. There is also a smaller mass of contamination that passed through the Gordon Confining Unit into the Gordon Aquifer. Horizontal groundwater flow in the UAZ and the LAZ is toward Fourmile Branch, whereas groundwater flow in the Gordon Aquifer is northward toward Upper Three Runs, the stream into which it discharges.

Groundwater monitoring has been more focused on the UAZ than the other two aquifers because of the extent of contamination and the rapid travel time of contaminated groundwater from beneath the basins to discharge point in the wetlands or Fourmile Branch. Discussion of long-term monitoring of groundwater in this document also focuses more on the UAZ and it is anticipated that long-term monitoring of groundwater in the lower aquifers would be similar, but less extensive than in the UAZ.

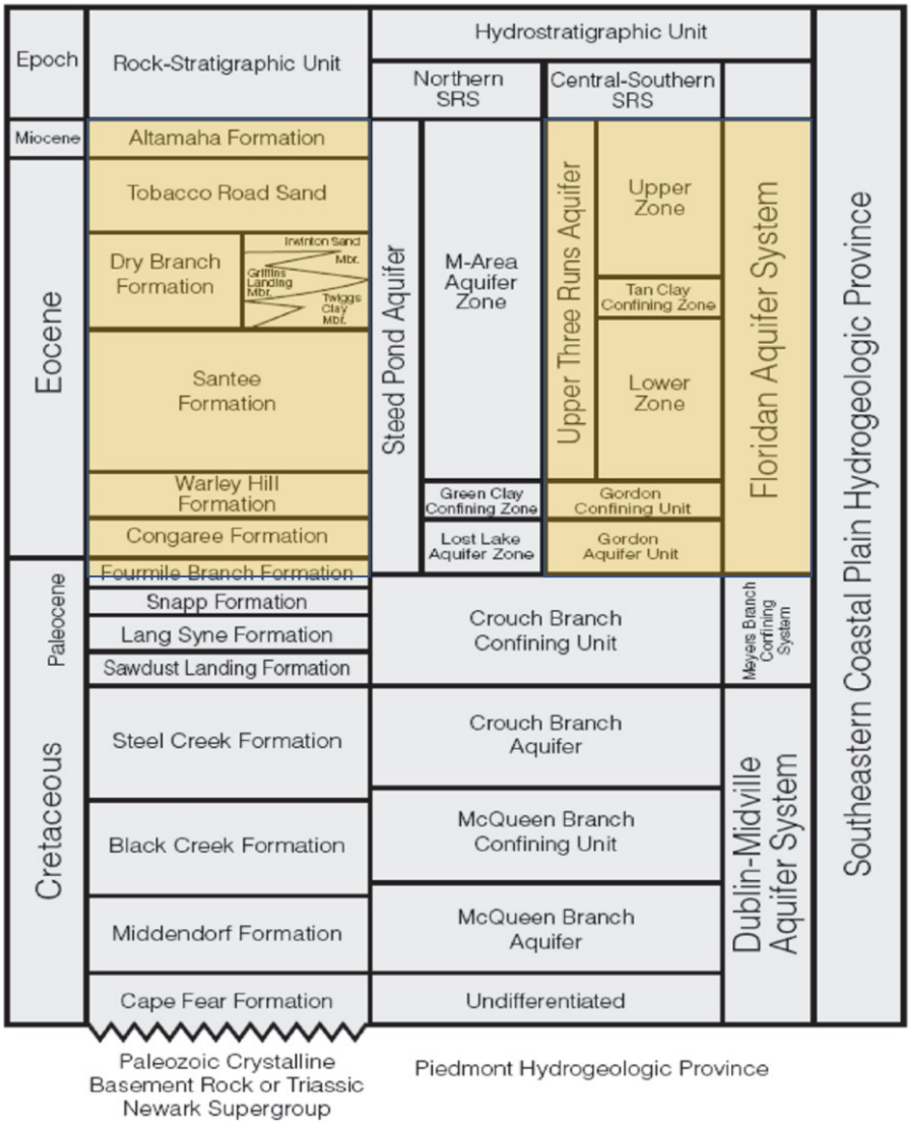


Figure 12: Lithostratigraphic and hydrostratigraphic columns with the interval of interest highlighted in orange.

The contamination plume occupies only a portion of the vertical extent of the UAZ – approximately 3 meters of a total saturated thickness of 10 meters. During the period of active basin use, the plume was likely more extensive vertically within the UAZ than it is now. Recharge downgradient of the basins and a downward hydraulic gradient caused the contamination to migrate downward as it moved horizontally. As a result, over much of the area between the basins and Fourmile Branch the plume moves along the top of the TCCZ.

Interpretation of concentration data is complicated by the fact that monitoring well screens do not all penetrate the same vertical portion of the plume and highlights the necessity of understanding the vertical distribution of contamination.

Vertical position of well screens relative to the plume and varying water levels are significant issues when evaluating time trends for contaminants, particularly in a stratified plume. Figure 13 depicts a stratified plume with monitoring well screens positioned at different elevations relative to the plume. In the upper block, the water table is higher than in the lower block. As the water table elevation decreases to that in the lower block, the portions of screens C and D that are in the saturated zone decrease. This can result in an apparent increasing trend in concentration because the contamination intersected by the screen is diluted less by relatively clean water above the stratified contamination. In contrast, the concentration trends in samples from well screens A and B that are more vertically in line with the plume are likely to be less affected by the decrease in water table elevation. It is also possible for plumes to shift vertically relative to well screens, yielding concentration versus time trends that are apparent, but not real.

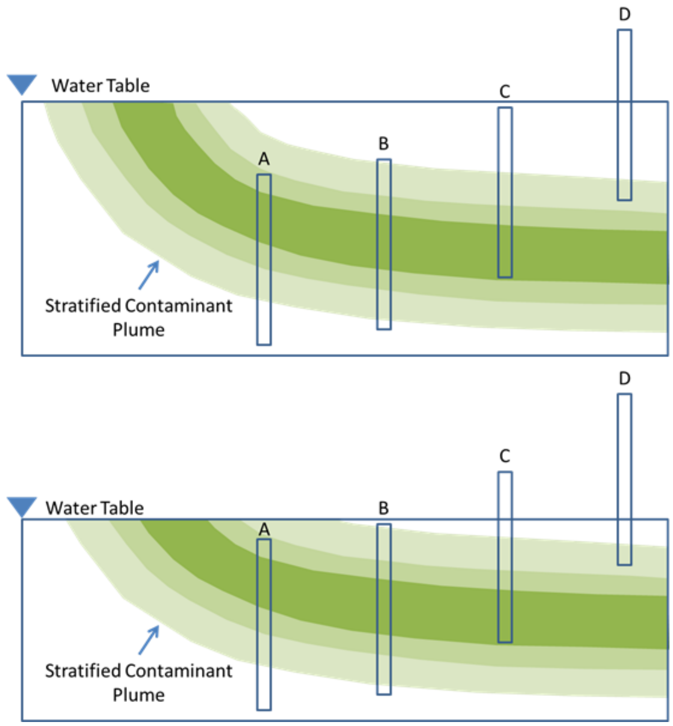


Figure 13: Diagram demonstrating how well screen location and water table elevation changes can cause apparent trends in contaminant concentration.

7.2 Remediation History

The history of the F-Area Seepage Basins is depicted in the timeline in Figure 14. Disposal of waste into the basins began in 1955 and ended in 1988. During basin operation, the concentration of radionuclides entering the basins varied considerably, but these variations were dampened by mixing in the basins (Millings et al., 2012) and by processes that occurred during migration through the vadose zone. Closure and installation of a low permeability cap over the basins was completed in 1991. Prior to cap installation, the basin bottoms were filled with limestone and slag to neutralize acidity and provide some chemical reduction capacity in the basin sediments. The low permeability portion of the cap is compacted kaolinite. On top of that is a drainage layer topped by filter cloth and a vegetated soil layer. Unlined drainage ditches surround the capped basins to collect and divert runoff from the cap to an outfall.

The cap minimized infiltration through the source, allowing concentrations of radionuclides to begin decreasing in the vadose zone and ultimately in the saturated zone. The rate of drainage of the vadose zone decreased significantly between 6 and 8 years after closure of the basins, as drainage neared completion (Tokunaga et al., 2012). This approximately coincides with the start-up in 1997 of a pump-and-treat system that extracted groundwater from downgradient, removed most of the radionuclides except tritium, and re-injected the treated water upgradient of the basins. The pump-and-treat system was replaced in 2004 with the current remediation, a funnel-and-gate with base injection in the gates.

The funnel-and-gate consists of a subsurface barrier that extends from near ground surface to the Tan Clay. The subsurface barrier was placed across “troughs” in the top of the Tan Clay that were preferential flow paths for contaminant migration to the wetlands and Fourmile Branch. Gaps in the subsurface barrier were left across the topographic highs of the Tan Clay and groundwater is forced by the barriers through these gaps, or gates, where in situ treatment of contamination occurs. The treatment zones have an elevated pH compared to the contaminated groundwater, achieved by periodic injections of an alkaline solution. This causes attenuation of uranium and Sr-90 by adsorption to mineral surfaces within these zones. Just upgradient of the base injection zones, I-129 is treated by injection of silver chloride particles. The particles react with natural iodide and I-129 that exists as iodide to form sparingly soluble silver iodide, removing I-129 from the groundwater.

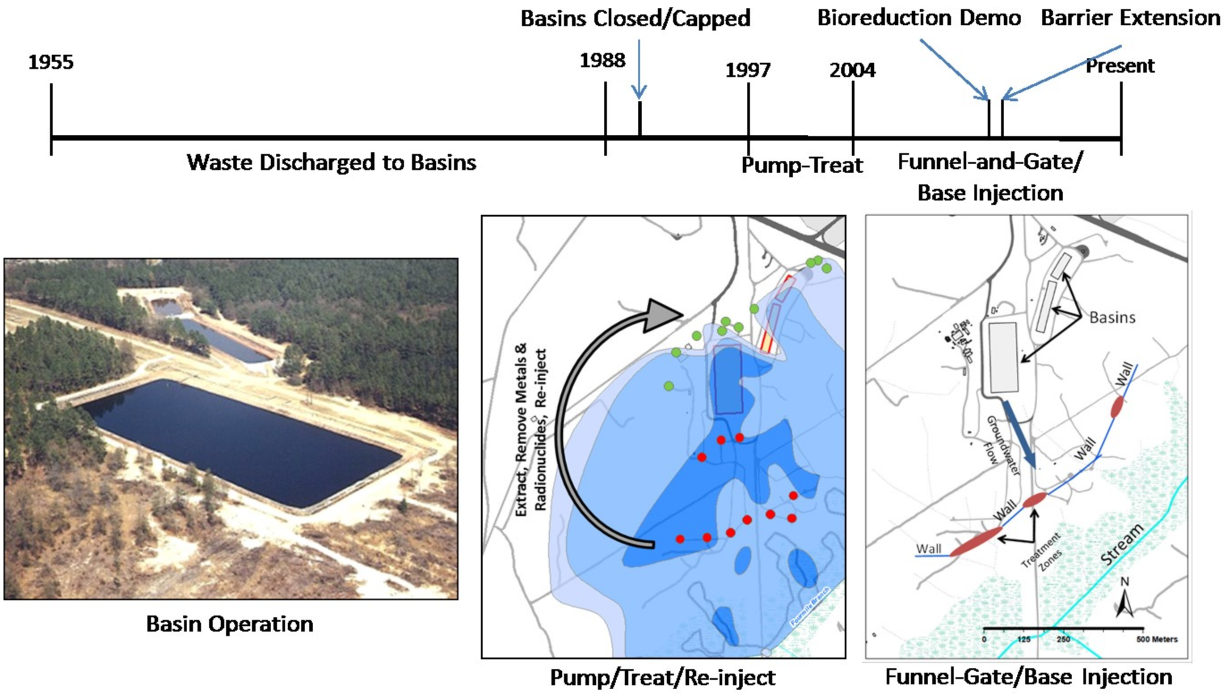


Figure 14: Time line of major events in the history of the F-Area Seepage Basins.

Contaminated groundwater associated with the F-Area Seepage Basins, and of interest here, is in the uppermost aquifer and can be divided into the following three segments (Figure 15).

1. The source basins and underlying vadose zone make up the first segment. Flux of contaminants from basin soils into the vadose zone was minimized by basin closure and capping. Relatively mobile contaminants reached the saturated zone before basin closure and are the current targets of remediation. Cores of the basin soils obtained before closure showed that there was still a significant mass of these contaminants – excluding tritium – and most of the released mass of less mobile contaminants in the soils 0-2 meters below the basin bottoms (Corbo et al., 1985).

2. The saturated zone underlying the vadose zone and stretching 350 to 600 meters downgradient is the primary plume zone. This zone is composed of relatively permeable sands to clayey sands with very low concentrations of natural organic matter. The primary reactive minerals are kaolinite and goethite. Currently, the geochemical conditions of the primary plume zone are oxic throughout and

acidic, with pH as low as 3.2, upgradient of the base injection treatment zone and mildly acidic (pH.4.5) to alkaline in the base injection treatment zone.

3. The third segment is the wetlands, where the plume intersects the topographic surface. Within this segment subsurface sediments are similar to the primary plume zone, but sediments within 1-2 meters of the surface contain high concentrations of natural organic matter. The wetlands segment is highly dynamic because of fluctuations in the elevation of the water table, seasonal variations, and rainfall events. The primary influences on groundwater flow are local recharge and the receiving stream, Fourmile Branch. However, perturbations in groundwater flow within the waste site have been caused by installation of the low permeability cover on the basins, the pump-and-treat system, and the installation of the subsurface barriers.

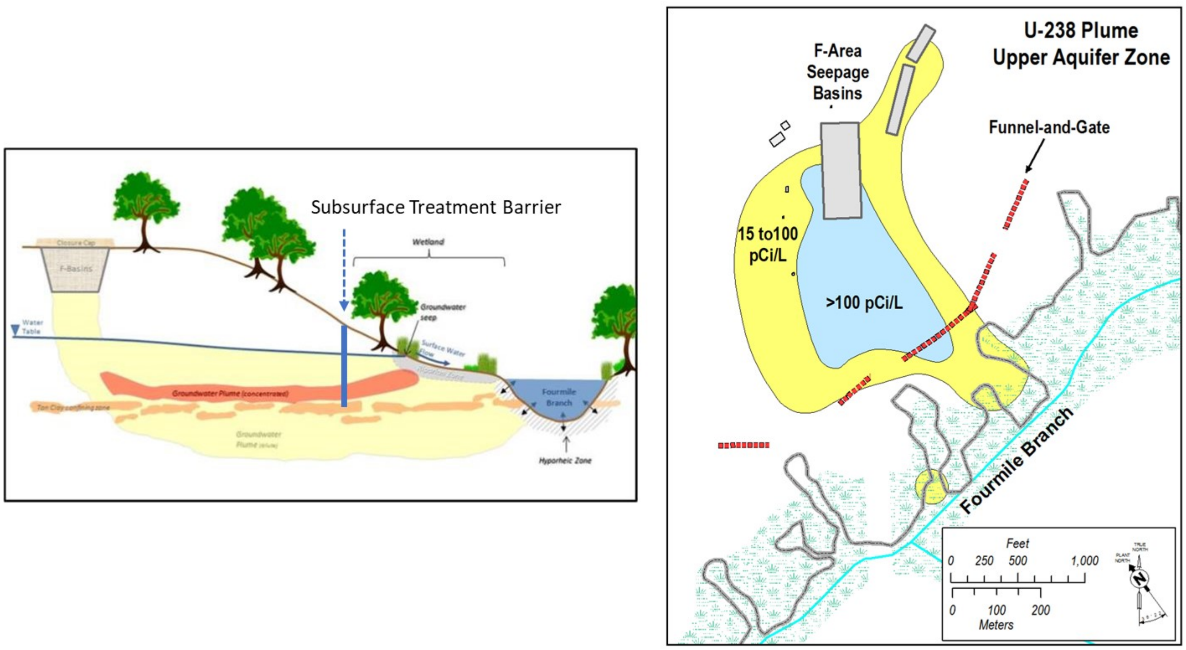


Figure 15: Cross-section and plan view of the contaminant plume and the different segments.

Potentiometric surface maps of the water table aquifer from various stages throughout the history of the basins in Figure 16 illustrate changes in groundwater flow directions induced by various remedial actions at the site. During active disposal of liquid waste there was mounding of the water table beneath the basins, resulting in flow of contamination away from the basins in three directions. Once the basins were closed and capped, the water table and groundwater flow directions returned to near the natural gradient. The slope of the water table increased when the pump-and-treat system began operating, but general flow directions remained unchanged. Finally, elimination of the pump-and-treat system and installation of the funnel-and-gate significantly altered the flow regime, causing groundwater flow upgradient of the subsurface barriers to shift toward the west. This westward shift is corroborated by contaminant distribution maps.

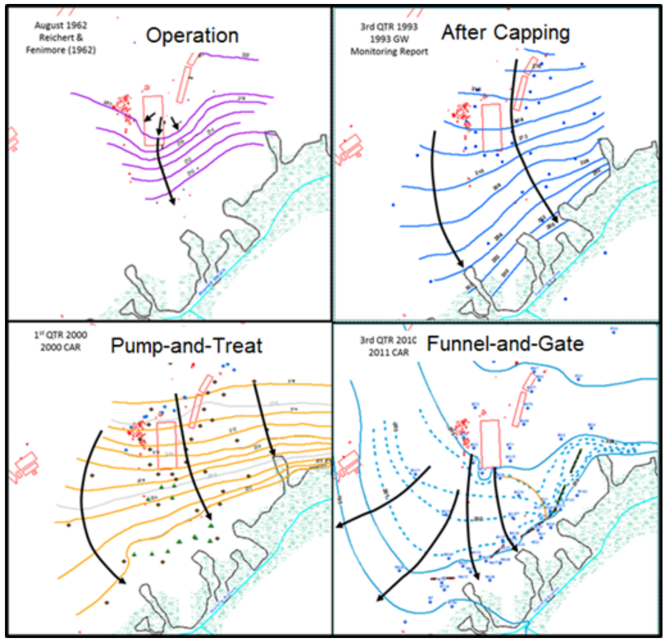


Figure 16: Changes in potentiometric surface of water table aquifer and groundwater flow directions during different stages in the history of the F-Area Seepage Basins.

Shifting of the plume to the west in response to installation of subsurface barriers caused concentrations of contaminants to decrease at a faster rate in some wells on the eastern side of the plume. The change in the water table following barrier installation is captured in the water elevation measurements from wells FSB-78 and FSB-120D shown in Figure 17A. Prior to 2007 the water table elevations at wells FSB-78 and FSB-120D were very similar. Three years after installation of the original subsurface barriers, in 2004, the water table elevations began to diverge, with the relative elevation at FSB-78 becoming increasingly higher than at FSB-120D, indicating development of a stronger westward component to the hydraulic gradient. Figure 17B shows that tritium concentration in samples from well FSB-78 began to decrease as the plume shifted westward.

A more localized shift in groundwater flow lines was caused by the extension of the funnel-and-gate to the east in 2011. This induced further westward shift of the eastern edge of the plume. Figure 18A shows the concentrations versus time trend for samples from well D, located near the intersection of the original funnel-and-gate and the extension. Well D is also located near the eastern edge of the contaminant plume. Tritium concentrations at well D were decreasing at a relatively constant slope until 2011. After the subsurface barrier extension was completed, the tritium concentrations decreased at a much faster rate until they reached background concentrations. The reason for the rapid decrease in tritium concentrations is that well D was near the edge of the plume and the subsurface barrier extension forced groundwater that had been moving southeastward to move southwestward. The change in plume flow lines moved the edge of the plume from east of well D to west of well D, so that well D now samples relatively clean water. The cross-section of the water table along A-B-C-D (Figure 18B) shows the hydraulic gradient dipping from well C toward well D prior to the barrier extension (2004 and 2010) and the dip reversing after the barrier was extended (2013 and 2016).

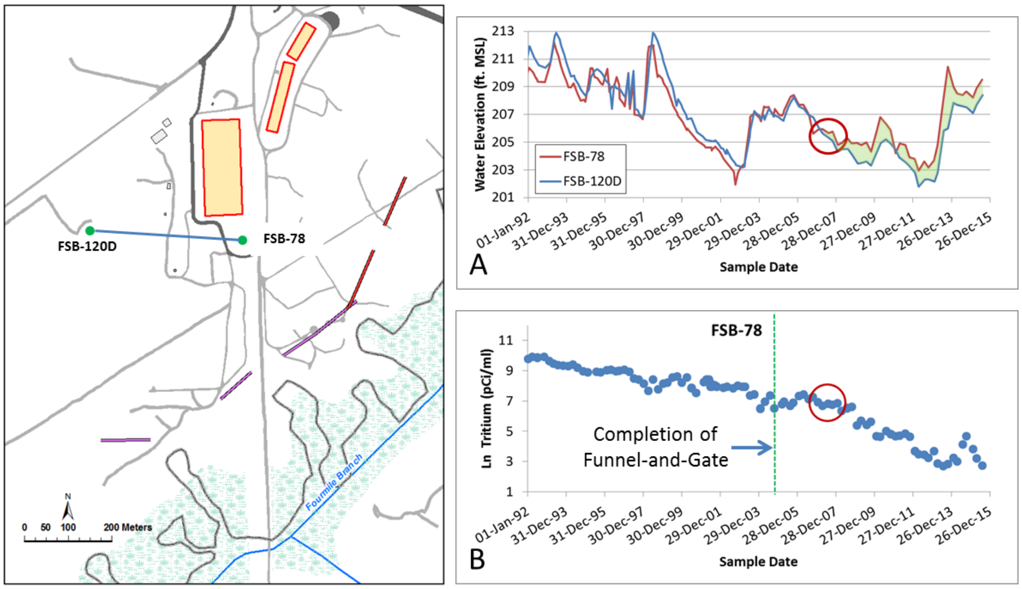


Figure 17: A) Comparison of the water table elevations in wells FSB-78 and FSB-120D, green shaded area shows consistently higher water table in well FSB-78; B) Effect of the westward shifting plume on tritium concentrations in samples from well FSB-78.

These examples illustrate the effect of changing groundwater flow on contaminant concentrations at specific monitoring locations in a controlled and well understood situation. During long-term monitoring of a site, unknown activities may occur outside the boundaries of the site that affect the flow of groundwater within the site. Monitoring groundwater elevations at the periphery of the site will provide early warning of changing groundwater flow, so that effects on the contamination plume can be predicted.

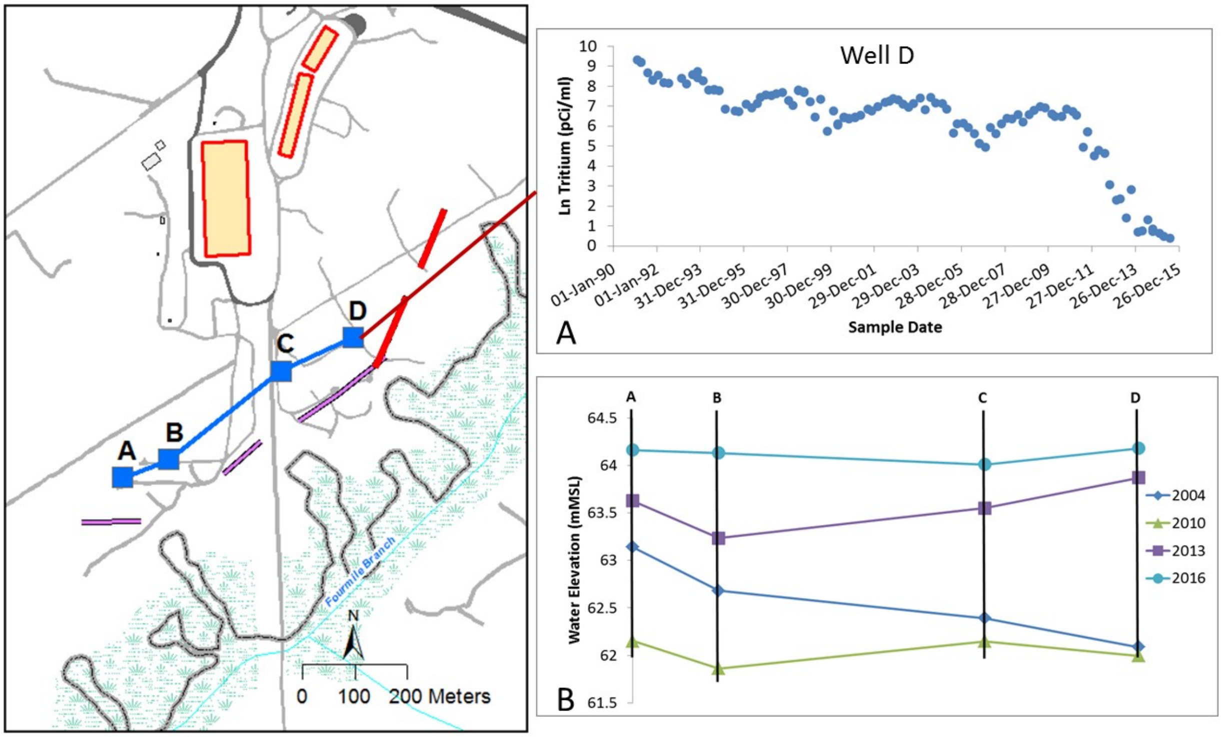


Figure 18: A) Effect of installation of subsurface barrier extension on tritium concentrations in samples from well D; B) Cross-sections of water table from wells A-D in 2004, 2010, 2013, and 2016.

The shifts in groundwater flow caused by the installation of the subsurface barrier also caused shifts in the locations of springs in the wetlands, where groundwater intersects the ground surface. The wetland springs were mapped, and a new sampling location was installed in 2015 to supplement the existing 4 locations.

7.2.1 *Groundwater Modeling*

There have been many studies of groundwater associated with the F-Area Seepage Basins using flow and reactive/non-reactive transport simulations to predict the future plume behaviors of several key contaminant species, particularly tritium and uranium (e.g., Bea et al., 2013; Wainwright et al., 2016; Arora et al., 2018; Libera et al, 2018). These studies were part of cooperative research between Lawrence Berkeley National Laboratory and Savannah River National Laboratory, working in conjunction with Area Completions Projects of Savannah River Nuclear Solutions. Detailed investigations on uranium geochemistry have enabled us to simulate the pH dependent behaviors of the uranium plume, which is expected to persist at the site for a long time (Bea et al., 2013; Arora et al., 2018). In addition, detailed data analysis and data-driven models have been developed for predicting contaminant concentrations at the monitoring wells, including non-reactive species such as nitrate and tritium (Wan et al., 2013; Denham and Amidon, 2016; Schmidt et al., 2018).

Since the seepage basins have been capped, the main body of plumes has exited the area for all the contaminant species, including tritium and uranium. All the wells across the site are currently at the trailing edge of the plumes. However, residual contaminants in the vadose zone, as well as clay-rich low-permeability layers (Tan Clay) have contributed to the persistence of the plumes (Wan et al., 2013). Some contaminant concentrations remain above the maximum concentration level (MCL). Still, all the studies have concluded that the contaminant concentrations will continue to decrease mainly by dispersion and mixing with clean groundwater from the upgradient. The consistent concentration decrease has been confirmed by the long history of groundwater monitoring data collection (Wan et al., 2013; Denham and Amidon, 2016; Schmidt et al., 2018).

For the uranium plume, pH rebound/neutralization through groundwater mixing has been considered to be a primary mechanism to retard plume mobility and attenuate uranium through sorption. It was recognized that low pH would persist for long periods without some remedial action, so the funnel-and-gate system with base injection was installed to neutralize pH and enhance sorption of uranium. Using the model simulations, Bea et al. (2013) corroborated these assumptions and showed that mineral dissolution and precipitation combined with adsorption reactions on clay minerals could buffer pH at the site for long periods of time. Nonetheless, the uranium aqueous concentrations upgradient of the base injection treatment zones are also expected to continue to decrease at the site.

7.3 Status of Remaining Contaminants of Interest

In addition to the changes in contaminant concentration caused by the subsurface barrier installation, concentrations of contaminants have generally been decreasing with time at key points of compliance – groundwater near the basin and surface water in the wetlands and Fourmile Branch. The four contaminants that remain a concern are tritium, I-129, uranium, and Sr-90. Denham and Amidon (2016) investigated the effective decay of concentrations of these contaminants in F-Area Seepage Basin groundwater. They found that decreases in tritium concentration with time were consistent with a first-order decay model, but that effective half-lives varied among monitoring wells because of the injection of tritium upgradient of the basins during pump-and-treat and because of water table variations relative to vertical placement of well screens. The time trends of other contaminants were complicated by pH variations, as well as by variations in the elevation of the water table. A summary of the geochemical behavior of each contaminant and the observations made by Denham and Amidon (2016) are presented in the sections below.

7.3.1 Tritium

Tritium concentrations in groundwater throughout the plume have been decreasing with time, generally following first-order decay. This indicates that the trailing edge of the plume is currently passing through the system. Tritium exists predominantly in water molecules in the plume and does not react chemically. However, diffusion of tritium into low permeability zones during plume migration can lengthen the trailing edge of the plume as tritium diffuses out of these zones during passage of the trailing edge. Injection of tritium upgradient of the basins during the pump-and-treat phase also significantly affected the rate at which tritium concentrations decrease in groundwater. The effect is more prominent in monitoring wells closer to the series of injection wells. Figure 19 shows the natural logarithm of the tritium concentration versus time at two wells at the downgradient edges of Basin 3. The elevation of the water table with time are also on the graphs. There are two distinct periods of decreasing tritium concentration, highlighted by different colors. The rate of tritium concentration decrease is greater in the earlier periods than in the later periods as indicated by the different slopes. The change in decay rates occurs approximately 2-3 years following the initiation of tritiated water injection upgradient. Effects of water table elevation changes are observed in well FSB-93D (Figure 19B) beginning in 2010. From 2010 until 2012 the water table elevation decreases more rapidly than it had been, reaching a low between 2011 and 2012. During this time tritium concentration increases. As the water table rises again, tritium concentrations decrease. These effects are not prominent in well FSB-95DR (Figure 19A). The difference between the wells most likely reflects the different vertical placement of the well screens relative to the vertical extent of the tritium plume.

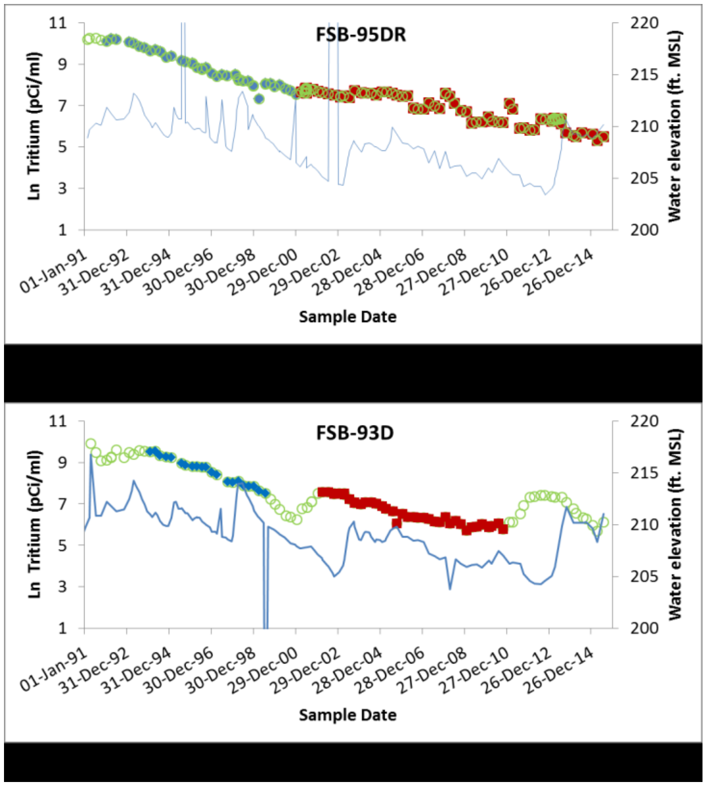


Figure 19: Ln (Tritium) versus time graphs for wells FSB-95DR (A) and FSB-93D (B); all data (green circles), first linear trend (blue diamonds), second linear trend (red squares), water elevation (blue line).

Trends in tritium concentration are also decreasing in surface water of the wetlands and Fourmile Branch. In the wetlands there are seasonal effects in which tritium concentrations generally decrease during rainy seasons and increase during dry seasons, reflecting dilution of the tritium concentrations by rainfall.

7.3.2 Iodine-129

The chemical behavior of I-129 is complicated in groundwater and surface water associated with the F-Area Seepage Basins. I-129 exists in multiple species having disparate behavior. In the acidic groundwater near the basins I-129 is present predominantly as the iodide (I^-) species and occurs predominantly as iodate (IO_3^-) in neutral pH groundwater downgradient of the base injection system (Kaplan et al., 2011). Both species sorb more strongly to F-Area aquifer sediments at lower pH values, but the sorption of iodate is significantly stronger than that of iodide at pH values less than 7 (Emerson et al. 2014). Zhang et al. (2011) found in column studies that iodine is bound strongly by the organic-rich surface sediments of the F-Area wetlands. Xu et al. (2011) confirmed that I-129 in the F-Area sediments is strongly bound to organic matter and showed that much of the I-129 is bound to “water extractable colloids”. This means that under conditions in which the colloids are released, erosion or chemical conditions that favor colloid dispersal, organically-bound I-129 may be released to surface water (Xu et al., 2011). Likewise, if redox conditions change significantly, I-129 may be released from the organic matter in a soluble form.

Silver chloride particles are injected just upgradient of the gates to remove I-129 from groundwater by causing it to coprecipitate with natural I-127 as silver iodide. Silver iodide has a very low solubility and will limit I-129 to very low concentrations under normal aquifer conditions. However, if conditions were to change to highly alkaline (pH>9) or become reducing enough to cause the reduction of silver ions to metallic silver, then I-129 would be released by dissolution of the silver iodide.

Concentration versus time trends for I-129 vary spatially and are complicated by variation in pH and water table elevations. In general, monitoring wells near the basins have stable concentrations of I-129. This may be because pH has increased with time in groundwater beneath the basins causing some iodide to desorb (Denham and Vangelas, 2008; Kaplan et al., 2011). I-129 concentrations in most wells downgradient of the funnel-and-gate are decreasing with time. The concentrations of I-129 in surface water from the four wetland sampling stations are all above the maximum concentration level (MCL) of 1 pCi/L, but concentrations have been trending downward at three of the four stations (Figure 20). I-129 concentrations in surface water of the wetlands do vary seasonally, with higher concentrations occurring during rainy seasons. This is opposite of the pattern of tritium concentrations and is consistent with the idea posited by Xu et al. (2011) that I-129 may be released to surface water as organically bound colloids during periods of high seepage in the wetlands.

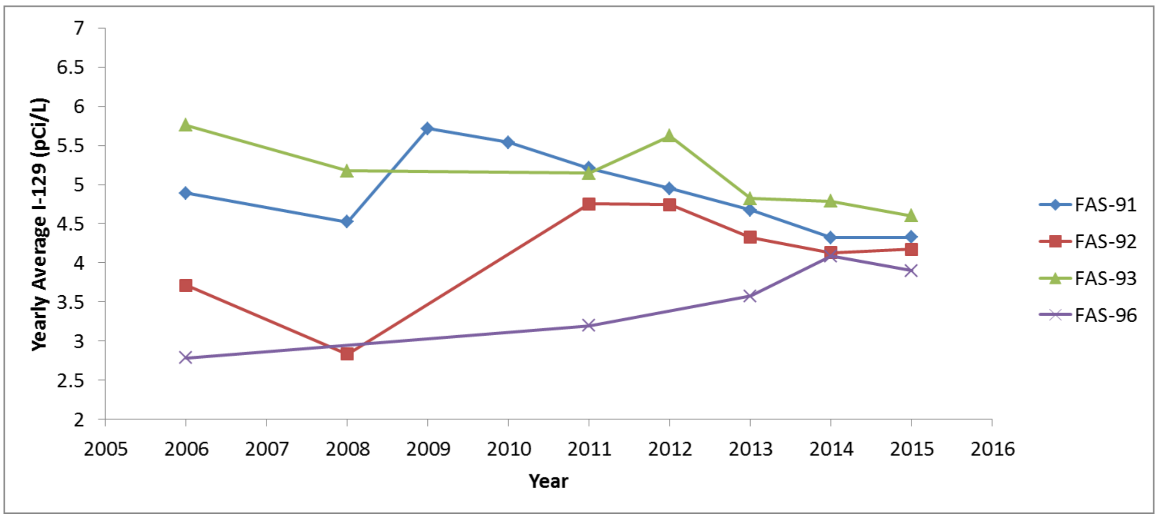


Figure 20: Yearly average ^{129}I concentrations versus time for wetland surface water stations.

7.3.3 Strontium-90

Sr-90 behavior in groundwater is controlled primarily by pH (Chen and Hayes, 1999; Small et al., 1999; Wallace et al., 2012). It sorbs strongly to SRS sediments at neutral pH and the strength of sorption decreases as pH decreases. Thus, Sr-90 is mobile in the acidic portions of the F-Area contamination plume and is sorbed in the zones where base is injected to raise pH. Oxidation-reduction potential only affects the behavior of Sr-90 in F-Area groundwater if it becomes reducing enough to dissolve iron oxyhydroxides that might be important Sr-90 sorbents. Sr-90 is not known to have a strong relationship with organic matter. Hence, in the wetland, clays and oxyhydroxides probably serve as the primary sorbents for Sr-90.

The trends in concentration versus time for Sr-90 at wells near the basins are mixed – decreasing trends at several wells and stable or increasing trends at a few wells. There is some evidence that water table variations and pH changes complicate trends in wells in which Sr-90 concentrations are not decreasing with time. Trends in Sr-90 concentration at wells between the funnel-and-gate and the wetlands are decreasing with time, indicating that the base injection system is effectively attenuating Sr-90. The time trends in Sr-90 concentrations are stable in surface water from two of the wetland sampling stations, but the concentration values are below the MCL (Figure 21). At the other two surface water sampling stations, Sr-90 concentrations have been decreasing with time and are very near the MCL.

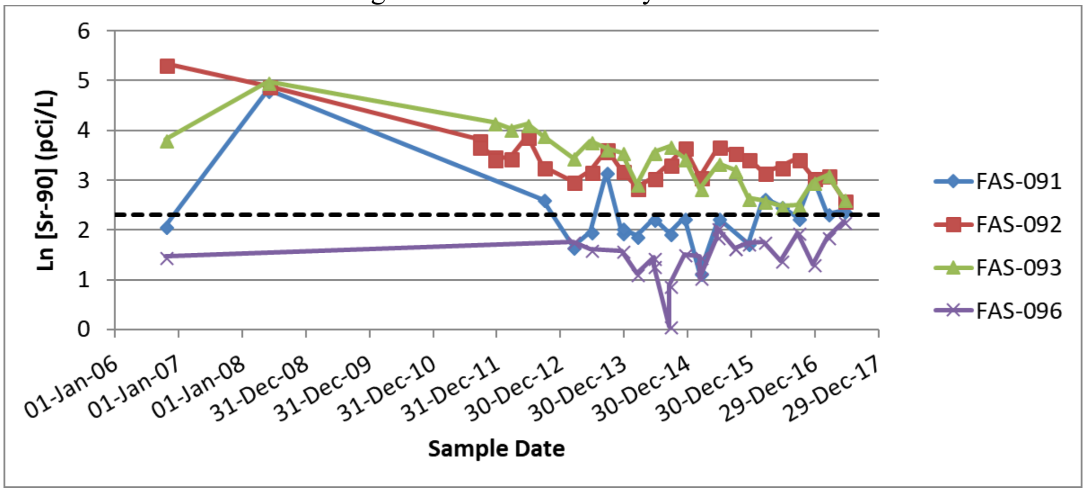


Figure 21: Ln (Sr-90) versus time trends for F-Area wetland surface water sampling stations; dashed line is the MCL.

7.3.4 Uranium

Uranium geochemical behavior is complicated. It occurs in the environment in two predominant oxidation states, U(VI) and U(IV) and numerous aqueous species, depending on conditions. In the oxidized conditions throughout most of the F-Area contamination plume, dissolved uranium is in species consisting of U(VI) as the uranyl ion UO_2^{+2} either alone or in aqueous hydroxyl or carbonate species. Uranyl species are mobile in SRS sediments up to pH values of approximately 4.5. At higher pH values uranium is attenuated by strong sorption to SRS sediments. However, if sufficient dissolved carbonate is present, mobile uranyl carbonate species can form at pH values of 5 and higher. Nevertheless, uranium may also be attenuated by precipitation of uranyl silicate minerals as pH is increased to values higher than approximately 5. The mobilizing effects of carbonate complexes at high pH values would be less if uranium existed in a mineral form rather than as sorbed uranium. Under reducing conditions U(VI) converts to U(IV) that forms relatively low solubility oxides. The only place in the F-Area system where this might occur is in the wetlands.

Trends of U-238 concentration versus time vary at monitoring wells near the basin. Several wells have decreasing trends, while others have stable or increasing trends. The stable or increasing trends may be complicated by variations in water table elevation and pH. Uranium concentrations have been decreasing with time at most wells between the funnel-and-gate and wetlands. At three of the four wetland surface water sampling stations, uranium concentrations have been either stable or decreasing with time, but the concentrations are very near the MCL (Figure 22). The concentration of uranium at the one station that has had an increasing trend is well below the MCL.

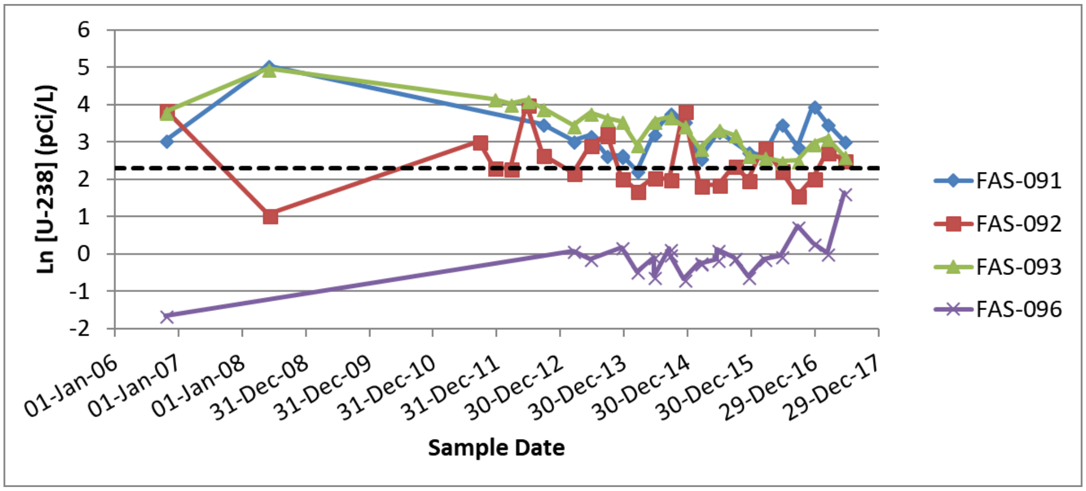


Figure 22: Ln (U-238) versus time trends for F-Area wetland surface water sampling stations; dashed line is the MCL.

The trends in contaminant concentration versus time indicate that the primary source is no longer contributing to the contamination plume and the trailing edge of the plume is passing through the enhanced attenuation treatment system. This is consistent with the calculations of Tokunaga et al. (2012) and numerical modeling results of Wainwright et al. (2016). Perturbation of groundwater flow was introduced by the installation of the funnel-and-gate system. In the near future, groundwater flow will equilibrate with the presence of the subsurface barrier and the contamination plume will reach the mature status at which the validation phase of a long-term monitoring program can begin.

8.0 Appendix E: Zones of Vulnerability

Zones of vulnerability within the F-Area Seepage Basins groundwater contamination system are those locations at which residual contamination is expected to exist in an attenuated form for long periods of time. The attenuation-based remedies currently active at the F-Area Seepage Basins rely on physical and chemical conditions remaining conducive to contaminant attenuation within these locations for long periods of time. Hence, the proposed long-term monitoring plan focuses on the zones of vulnerability. The water inlet side of the zones of vulnerability is particularly important because changes to water flow and/or water chemistry on the inlet side signal future changes within the zones of vulnerability.

Three zones of vulnerability can be defined based on the conceptual model for the F-Area Seepage Basins: 1) The soils directly beneath the former seepage basins and the underlying vadose zone, 2) the gates where in situ treatments enhance attenuation of contaminants, and 3) the wetlands where contaminants are attenuated by primarily natural processes.

8.1 Seepage Basin Caps

A large mass of contaminants remains attenuated in the soils directly beneath the former seepage basins (Corbo et al. 1985). This includes both contaminants that are mobile enough to have contaminated the saturated zone and contaminants that are only slightly mobile. The limestone and slag added to the basin bottoms during closure were meant to promote chemical conditions that would minimize migration of most contaminants. The low permeability clay cap covering the basin was meant to minimize infiltration of water into the contaminated soils that could move the contaminants toward the saturated zone.

The primary long-term vulnerability is degradation of the low permeability cap. An increase in infiltration through the cap would provide the driving force to remobilize residual uranium, Sr-90, I-129, Tc-99 and other relatively mobile contaminants from the basin soils and the vadose zone. Over time various mechanisms can lead to cap degradation. Subsidence can cause cap fracturing as materials beneath the cap compact or degrade. Bioturbation by burrowing animals and penetrating plant roots can breach the cap. Singular events such as earthquakes or damage caused by intruders can also degrade cap performance. Therefore, monitoring and maintaining cap integrity indefinitely is of primary importance. The post-closure plan for the basins requires subsidence monitoring and yearly inspection of the caps. These are currently done by physical survey of subsidence monitors and walk-over inspections for burrows and other intrusions. The drainage system around the caps is also currently inspected yearly for any evidence of performance degradation.

Detecting subsidence and disturbances at the surface of the cap is important for preventive maintenance, but measurement of changes in moisture content of basin soils and the underlying vadose zone is the only direct measure of cap performance. If moisture content in these locations increases from a baseline state during long-term monitoring it is an indication that a potential driving force exists for transporting contaminants to the saturated zone.

8.2 Funnel-and-gate Treatment Zones

The purpose of the treatment zones in the gates of the funnel-and-gate system is to enhance attenuation of Sr-90, uranium, and I-129 within and downgradient of these zones. Enhanced attenuation of Sr-90 and uranium is achieved by neutralizing the acidic pH of the contaminated groundwater causing increased adsorption of both contaminants and potentially precipitation of uranium. Attenuation of I-129 is enhanced by causing it to coprecipitate with natural iodine as silver iodide.

If chemical conditions change, the attenuated contaminants are vulnerable to re-mobilization. The most likely condition that would cause remobilization of Sr-90 and uranium would be a return to a groundwater pH value below 5 (Denham, 2017). This will happen if the base injection program is terminated before upgradient pH values exceed 5. It could also happen if the cap over the basin breached, allowing transfer of sufficient acidity from the vadose zone into the saturated zone to cause decreasing pH at the gates. The only other way this could occur would be a large acid spill upgradient from the basins. Acidic conditions would not remobilize I-129. A scenario that would remobilize I-129 is the advent of reducing conditions that would cause reductive dissolution of the AgI (Ag^+ reduced to Ag metal). This is only likely to occur in the event of a large spill or subsurface release of material containing organic carbon.

A change in the rate of groundwater flow is of less concern but could cause changes in contaminant behavior within the gates. For example, if uranium is precipitated within the treatment zone, the maximum concentration of uranium in the future, when the system is at a natural pH value, will be the solubility of the controlling uranium-bearing phase. If groundwater contact time with the treatment zone is fast relative to the dissolution rate of the controlling phase, then uranium concentrations will be less than the solubility and a function of the solubility rate and the groundwater flow rate. In this case, if groundwater flow rates were to decrease in the future, then uranium concentration in groundwater would increase. Therefore, long-term monitoring of groundwater near the gates should focus on changes to pH, redox conditions, and groundwater flow rate.

8.3 The Wetlands

Attenuation of contaminants in the wetlands is the result of natural processes and campaigns of base injection in groundwater beneath the wetlands. Contaminants have interacted with organic matter and clays in wetland soils since the contaminants initially reached the wetlands, long before any remediation activities. The base injection campaigns beneath the wetlands enhanced attenuation of Sr-90 and uranium, and likely released some I-129 (Denham, ????), in deep wetland soils. Nevertheless, the processes of natural attenuation and release of contaminants have been dominant and will continue to control the behavior of contaminants in the wetlands. The mass of contaminants in the wetlands and the controls on mechanisms of attenuation and release are poorly understood and continue to be investigated.

The wetland vulnerability zone is unlike the other two because of the wetland's dynamism. There are short-term dynamic processes dominated by intense rain storms that cause erosion of the wetland surface soils and change their chemistry. An example of the effects of these short-term processes was detailed by Batson et al. (1996) at another waste site on SRS. They found that particulate-bound uranium was released from flood plain sediments to a stream at much higher masses during intense rainstorms than at baseflow conditions.

Longer term seasonal processes that include extended periods of wet and dry weather and shedding of leaves by vegetation also affect the physical and chemical processes attenuating and releasing contaminants. Denham and Amidon (2016) found that uranium and I-129 concentrations in wetland surface water increased during seasons of increased rainfall. The seasonal shedding of leaves renews the organic layer responsible for significant attenuation of contaminants. Likewise, seasonal temperature changes affect rates of microbially processes that may influence contaminant attenuation.

There are longer-term processes such as the climatic effects of sustained droughts and periods of sustained heavier rainfall. These result in fluctuations in the water table that can have profound effects on the configuration of the wetlands and the chemistry/microbiology of the associated soils and porewaters. The fact that the wetlands result from the water table intersecting surface topography means that the extent of water saturated soil migrates upslope as the water table rises and reverses as the water table drops (Figure 23). The saturated-unsaturated cycles likely affect redox and microbial processes that strongly influence contaminant mobility. Also important is that problematic soil contamination may be present in locations of the wetlands where there are no current groundwater seeps because seeps shift location in response to changes in the water table and surface topography.

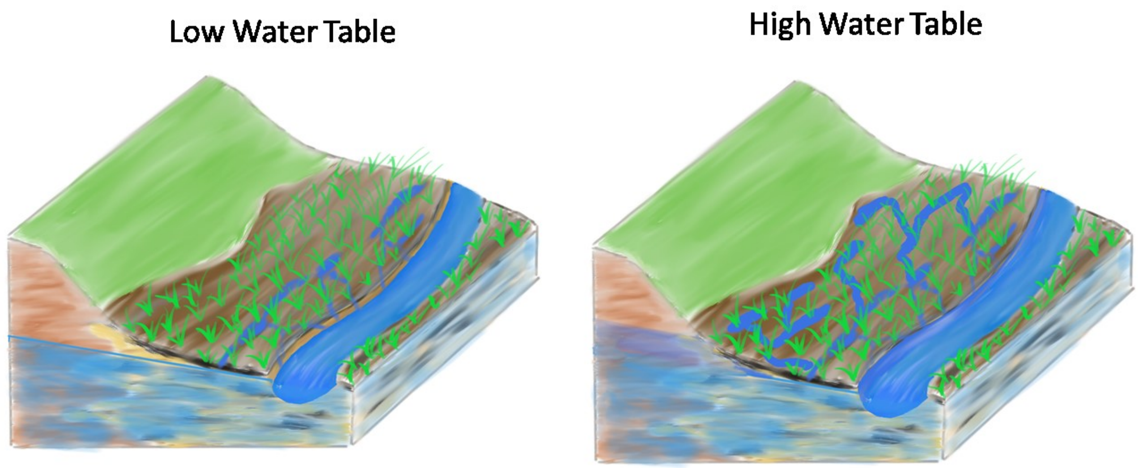


Figure 23: Wetland dynamics controlled by water table fluctuations.

The long-term monitoring program must also consider slowly progressing processes such as the changing course of Fourmile Branch and large-scale changes to surface topography. All streams naturally change course with time. Construction of beaver dams and man-made infrastructure can accelerate the course changes. With changes to the course of a stream come changes to the configuration of wetlands associated with the stream. Natural and man-made processes over time also change large-scale surface topography upslope of the wetlands. Changes to the topography affect surface drainage and groundwater flow patterns, that in turn alter attenuation processes in the wetlands.

Table 2 summarizes the zones of vulnerability. The contaminants vulnerable to remobilization in each zone of vulnerability are shown in the second column. The third column, “Threat Conditions” summarizes the conditions within each zone that would potentially remobilize contaminants. The fourth column summarizes the factors that long-term monitoring should focus on relative to each zone of vulnerability.

Table 2: Summary of the zones of vulnerability and the recommended focus of long-term monitoring for each zone.

Zone of Vulnerability	Vulnerable Contaminants	Threat Conditions	Long-Term Monitoring Focus
Basin soils & vadose zone	All	Infiltration through cap	Cap integrity, Moisture content
Treatment zones in gates	Uranium, Sr-90, I-129	Low pH (Sr-90, uranium) and reducing conditions (I-129)	pH, redox conditions, groundwater flow rate
Wetlands	Uranium, Sr-90, I-129	Low pH, significant change in wetland morphology, vegetation, etc., loss of organic matter	pH, redox conditions, physical configuration (topography, boundaries, course of Fourmile Branch, frequency of intense rain events)

9.0 References

Amidon, M.B. and M.R. Millings. 2015. Deployment of Long-Term Monitoring Sensors at the F-Area Field Research Site Savannah River Site (U). August 2015, SRNL-RP-2015-00520, Savannah River Site, Savannah River Nuclear Solutions LLC, Aiken, SC

Arora, B., J. A. Davis, N. F. Spycher, Wenming Dong, and H. M. Wainwright. 2018. Comparison of electrostatic and non-electrostatic models for U(VI) sorption on contaminated sediments and the impact on reactive transport simulation, *Groundwater*, DOI:10.1111/gwat.12551.

Bao, X. and L. Chen. 2012. Recent Progress in Distributed Fiber Optic Sensors, *Sensors,* 12, pp. 8601-8639.

Barnowski, R., Haefner, A., Mihailescu, L., & Vetter, K. 2015. Scene data fusion: Real-time standoff volumetric gamma-ray imaging. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 800, 65-69.

Batson, V. L., P. M. Bertsch, and B. E. Herbert. 1996. Transport of Anthropogenic Uranium from Sediments to Surface Waters During Episodic Storm Events. *J. Environ. Qual.* 25:1129-1137. doi:10.2134/jeq1996.00472425002500050028x

Bea, S. A., Wainwright, H., Spycher, N., Faybishenko, B., Hubbard, S. S., & Denham, M. E. 2013. Identifying key controls on the behavior of an acidic-U (VI) plume in the Savannah River Site using reactive transport modeling. *Journal of Contaminant hydrology*, 151, 34-54.

Binley, A., S. S. Hubbard, J. A. Huisman, A. Revil, D. A. Robinson, K. Singha, and L. D. Slater. 2015. The emergence of hydrogeophysics for improved understanding of subsurface processes over multiple scales, *Water Resour. Res.*, 51, 3837–3866, doi:10.1002/2015WR017016.

Briggs, M. A., S. F. Buckley, A. C. Bagtzoglou, D. D. Werkema, and J. W. Lane. 2016a. Actively heated highresolution fiber-optic-distributed temperature sensing to quantify streambed flow dynamics in zones of strong groundwater upwelling, Water Resour. Res., 52, 5179–5194, doi:10.1002/2015WR018219. https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1002/2015WR018219

Briggs, M.A., D.K. Hare, D.F. Boutt, G. Davenport, and J.W. Lane. 2016b. Thermal infrared video details multiscale groundwater discharge to surface water through macropores and peat pipes. *Hydrological Processes*, 30, 2510-2511.

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, H Lee, RP Bush, P Beam , GM Chamberlain, KD Gerdes, and Y Collazo. 2012. "Scientific Opportunities for Monitoring of Environmental Remediation Sites - (SOMERS)." In Annual Waste Management Symposium (WM2012): Improving the Future in Waste Management, February 26 - March 1, 2012, Phoenix, Arizona, p. Paper No. 12224. WM Symposia, Phoenix, AZ.

Chen, C-C. and K.F. Hayes. 1999. X-ray absorption spectroscopy investigation of aqueous Co(II) and Sr(II) sorption at clay-water interfaces. *Geochimica et Cosmochimica Acta*, 63, 3205-3215.

John N. Christensen, J.N., B. Dafflon, A.E. Shiel, T.K. Tokunaga, J. Wan, B. Faybishenko, W. Dong, K.H. Williams, C. Hobson, S.T. Brown, S.S. Hubbard. 2018. Using strontium isotopes to evaluate the spatial variation of groundwater recharge. *Science of The Total Environment*, 637–638, 672-685. https://doi.org/10.1016/j.scitotenv.2018.05.019.

Corbo, P., M.V Kantelo, C.B. Fliermans. 1985. Analytical results, database management and quality assurance for analyses of soil cores from the F- and H-Area seepage basins. DPST-85-921. Du Pont de Nemours (E.I.) and Co., Aiken, SC (United States).

Cox, B., Wills, P., Kiyaschenko, D., Mestayer, J., Lopez, J., Bourne, S., Lupton, R. Solano, G., Henderson, N., Hill, D., and J. Roy. 2012. Distributed Acoustic Sensing for Geophysical Measurement, Monitoring, and Verification, *CSEG Recorder*, Feb. 2012, pp. 7-13.

Dafflon, B., Irving, J., & Barrash, W. 2011. Inversion of multiple intersecting high-resolution crosshole GPR profiles for hydrological characterization at the Boise Hydrogeophysical Research Site. *Journal of Applied Geophysics*, 73(4), 305-314.

Dafflon, B., Wu, Y., Hubbard, S. S., Birkholzer, J. T., Daley, T. M., Pugh, J. D., ... & Trautz, R. C. 2012. Monitoring CO2 intrusion and associated geochemical transformations in a shallow groundwater system using complex electrical methods. *Environmental science & technology*, 47(1), 314-321.

Denham, M. 2017. Observations on Acidic Rebound Following Base Injection at the F-Area Central Gate. SRNL-L3200-2017-00090. Savannah River National Laboratory, Aiken, SC.

Denham, M.E. and M.B. Amidon. 2016. Analysis of Concentration Versus Time Trends for Select Contaminants in Groundwater and Wetland Surface Water Associated with the F-Area and H-Area Seepage Basins. SRNL-STI-2016-00558, Savannah River National Laboratory, Aiken, SC.Denham, M. and K.M. Vangelas. 2008. Biogeochemical gradients as a framework for understanding waste-site evolution. *Remediation Journal*. 19, 5-17. https://doi.org/10.1002/rem.20188

Dong, W., T.K. Tokunaga, J.A. Davis, and J. Wan. 2012. Uranium(VI) adsorption and surface complexation modeling onto background sediments from the F-Area Savannah River Site. *Environmental Science & Technology*, 46, 1565-1571.

Eddy-Dilek, C.; Millings, M. R.; Looney, B. B.; and Denham, M. E. Innovative Strategy for Long Term Monitoring of Metal and Radionuclide Plumes. 2014. Savannah River Site (SRS), Aiken, SC (United States); Retrieved from https://www.osti.gov/scitech/biblio/1122792.

Emerson, H.P., C. Xu, Y.F. Ho, S. Zhang, K.A. Schwehr, M.Lilley, D.I. Kaplan, P.H. Santschi, and B.A. Powell. 2014. Geochemical controls on iodine uptake and transport in Savannah River Site subsurface soils. *Applied Geochemistry*, 45, 105-113.

Gaebler, W. 1983. "Characteristics of Fiber Optic Radiation Detectors", *SPIE Vo. 403: Optical Fibers in Broadband Networks, Instrumentation and Urban and Industrial Environments*, pp. 142-145.

Genelle, F., C. Sirieix, J. Riss, and V. Naudet. 2012. Monitoring landfill cover by electrical resistivity tomography on an experimental site. *Engineering Geology*, 145-146, 18-29.

Guo, B. B., Y.J. Zhu, W. Feng, L. He, Y.P. Wu, Y. Zhou, X. Ren, Y. Ma. 2018. Remotely Estimating Aerial N Uptake in Winter Wheat Using Red-Edge Area Index From Multi-Angular Hyperspectral Data. *Frontiers in plant science*, *9*, 675. doi:10.3389/fpls.2018.00675

Haefner, A., Gunter, D., Barnowski, R., & Vetter, K. 2015. A Filtered Back-Projection Algorithm for 4π Compton Camera Data. *IEEE Transactions on Nuclear Science*, 62(4), 1911-1917.

Harre, K., Chaundry, T., Greenwald, R., Weiwei, J., Davis, C., Zavislak, M., and Minsker, B. 2009. Adaptive long-term monitoring at environmental restoration sites. ESTCP Project ER-0629 Final Report. U.S. Department of Defense, Environmental Security Technology Certification Program.

Ho, C.K., Robinson, A., Miller, D.R., and Davis, M.J. 2005. Overview of sensors and needs for environmental monitoring. *Sensors* 5: 4-37.

Hunter, P., Cameron, K., and Stewart, R. 2011. Demonstration and validation of GTS long-term monitoring optimization software at military and government sites. ESTCP Project ER-200714.

ITRC (Interstate Technology & Regulatory Council). 2010. A Decision Framework for Applying Monitored Natural Attenuation Processes to Metals and Radionuclides in Groundwater. APMR-1. Washington DC: Interstate Technology & Regulatory Council, Attenuation Processes for Metals and Radionuclides Team. www. itrcweb.org

Johnson, T.C., R.J. Versteeg, A. Ward, F.D. Day-Lewis, and A. Revil. 2010. "Improved hydrogeophysical characterization and monitoring through parallel modeling and inversion of time-domain resistivity andinduced-polarization data." *Geophysics*, 75(4), WA27-WA41. https://doi.org/10.1190/1.3475513

Johnson, T. C., Versteeg, R. J., Rockhold, M., Slater, L. D., Ntarlagiannis, D., Greenwood, W. J., & Zachara, J. 2012. Characterization of a contaminated wellfield using 3D electrical resistivity tomography implemented with geostatistical, discontinuous boundary, and known conductivity constraints. *Geophysics*, 77(6), EN85-EN96.

Johnson, T., Versteeg, R., Thomle, J., Hammond, G., Chen, X., & Zachara, J. 2015. Four‐dimensional electrical conductivity monitoring of stage‐driven river water intrusion: Accounting for water table effects using a transient mesh boundary and conditional inversion constraints. *Water Resources Research*, 51(8), 6177-6196.

Kaplan, D.I., K.A. Roberts, K.A. Schwehr, M.S. Lilley, R. Brinkmeyer, M.E. Denham, D. DiPrete, H.-P. Li, B.A. Powell, C. Xu, C.M. Yeager, S.J. Zhang, P.H. Santschi. 2011. Evaluation of a radioiodine plume increasing in concentration at the Savannah River Site, *Environmental Science & Technology*, 45, 489-495.

Libera, A.; de Barros, F.; Faybishenko, B.; Eddy-Dilek, C.; Denham, M.; Lipnikov, K.; Moulton, J.D., Wainwright, H. 2018. Climatic controls on sustainable remediation of the F-Area Savannah River Site, submitted to Groundwater.

Millings, M.R., B.B. Looney, and M.E. Denham. 2012. Geochemical Modeling of F Area Seepage Basin Composition and Variability. SRNL-STI-2012-00269. Savannah River National Laboratory, Aiken, SC.

Potyrailo, R.A., and G.M. Hieftje. 1998. "Advanced strategies for spatially resolved analyte mapping with distributed fiber-optic sensors for environmental and process applications", *SPIE Vol. 3534, Proceedings on the Conference for Environmental and Remediation Technologies*.

Reed, P. and Minsker, B. 2004. Striking the balance: Long-term groundwater monitoring design for conflicting objectives. *Journal of Water Resources Planning and Management* 130: 140-149.

Reed, P., Minsker, B., and Goldberg, D. 2001. A multiobjective approach to cost effective long-term groundwater monitoring using an elitist nondominated sorted genetic algorithm with historical data. *Journal of Hydroinformatics* 3: 71-89.

Reed, P., Minsker, B., and Valocchi, A.J. 2000. Cost effective long-term groundwater monitoring design using a genetic algorithm and global mass interpolation. *Water Resources Research* 36: 3731-3741.

Schmidt, F., Wainwright, H. M., Faybishenko, B., Denham, M., & Eddy-Dilek, C. 2018. In Situ Monitoring of Groundwater Contamination Using the Kalman Filter. In press *Environmental Science & Technology.*

SCDHEC. 2017. *South Carolina Department of Health and Environmental Control Hazardous and Mixed Waste Permit, Permit Number SC1 898 008 989*, 2014 RCRA Permit Renewal for the Savannah River Site, issued on February 11, 2014, modified on August 17, 2017 and modification effective on September 2, 2017, Module IV – Groundwater Requirements, Section B, F-Area Hazardous Waste Management Facility, South Carolina Department of Health and Environmental Control, Office of Environmental Quality Control, Bureau of Land and Waste Management, Columbia, SC

Sirieix, C., F. Genelle, C.Barral, N. Touze-Foltz, J. Riss, and B. Bégassat. 2015. Characterizing the aging of a geosynthetic clay liner through electrical resistivity. *Canadian Geotechnical Journal*, 52, 1-8.

Small, T.D., L.A. Warren, E.E. Roden, and F.G. Ferris. 1999. Sorption of strontium by bacteria, Fe(III) oxide, and bacteria-Fe(III) oxide composites. *Environmental Science & Technology*, 33, 4465-4470.

Suarez, F, Hausner, M.B., Dozier, J., Selker, J.S., and S.W. Tyler. 2011. "Heat Transfer in the Environmeny : Development and Use of Fiber-Optic Distributed Temperature Sensing", in *Developments in Heat Transfer*, Chapter 31.

Tokunaga, T., J. Wan, and M. Denham. 2012. Estimates of Vadose Zone Drainage from a Capped Seepage Basin, F-Area, Savannah River Site. *Vadose Zone Journal*. 11. 10.2136/vzj2011.0131

Tran, A. P., Dafflon, B., Hubbard, S. S., Kowalsky, M. B., Long, P., Tokunaga, T. K., & Williams, K. H. 2016. Quantifying shallow subsurface water and heat dynamics using coupled hydrological-thermal-geophysical inversion. *Hydrology and Earth System Sciences*, 20(9), 3477-3491.

USEPA. 2004. Demonstration of two long-term groundwater monitoring optimization approaches. United States Environmental Protection Agency: EPA-542-R-04-001b.

USEPA. 2005. Roadmap to long-term monitoring optimization. United States Environmental Protection Agency: EPA-542-R-05-003.

USEPA. 2007. Monitored natural attenuation of inorganic contaminants in ground water: Volume 1 – Technical Basis. Edited by Ford, R.G., Wilkin, R.T., and Puls, R.W. United States Environmental Protection Agency: EPA/600/R-07/139.

Vereecken, H., J.A. Huisman, H. Bogena, J. Vanderborght, J.A. Vrugt, and J.W. Hopmans. 2008. On the value of soil moisture measurements in vadose zone hydrology: A review. *Water Resources Research*, 44, W00D06, doi:10.1029/2008WR006829

Wainwright, H. M., J. Chen, D. S. Sassen, and S. S. Hubbard. 2014. Bayesian hierarchical approach and geophysical data sets for estimation of reactive facies over plume scales, *Water Resour. Res.*, 50, 4564–4584, doi:10.1002/2013WR013842.

Wainwright, H.M., B. Faybishenko, S. Molins, J.A. Davis, B. Arora, G. Pau, J. Johnson, G. Flach, M. Denham and C. Eddy-Dilek, J.D. Moulton, K. Lipnikov, C. Gable, T. Miller and M. Freshley. 2016. Effective Long-term Monitoring Strategies by Integrating Reactive Transport Models with In situ Geochemical Measurements, Waste Management 2016, March 6 – 10, 2016, Phoenix, Arizona, USA.

Wallace, S.H., J.S. Small, A.J. Fuller, and I.T. Burke. 2012. Effect of groundwater pH and ionic strength on strontium sorption in aquifer sediments: Implications for 90Sr mobility at contaminated nuclear sites. *Applied Geochemistry*, 27, pp. 1482-1491. DOI: 10.1016/j.apgeochem.2012.04.007

Wan, J., Tokunaga, T. K., Dong, W., Denham, M. E., and Hubbard, S. S. 2012. Persistent Source Influences on the Trailing Edge of a Groundwater Plume, and Natural Attenuation Timeframes: The F-Area Savannah River Site. *Environmental Science & Technology*. 5735.

Xu, C., S. Zhang, Y-F. Ho, E.J. Miller, K.A. Roberts, H-P. Li, K.A. Schwehr, S. Otosaka, D.I. Kaplan, R. Brinkmeyer, C.M. Yeager, and P.H. Santschi. 2011. Is Soil natural organic matter a sink or source for mobile radioiodine (^{129}I) at the Savannah River Site?. Geochimica et Cosmochimica Acta, 75, 5716.