# Innovative Strategy for Long Term Monitoring of Metal and Radionuclide Plumes – 14380

Carol Eddy-Dilek, Savannah River National Laboratory Margaret R. Millings, Savannah River National Laboratory Brian B. Looney, Savannah River National Laboratory Miles E. Denham, Savannah River National Laboratory

## **ABSTRACT**

Many government and private industry sites that were once contaminated with radioactive and chemical wastes cannot be cleaned up enough to permit unrestricted human access. The sites will require long term management, in some cases indefinitely, leaving site owners with the challenge of protecting human health and environmental quality at these "legacy" sites. Long-term monitoring of groundwater contamination is one of the largest projected costs in the life cycle of environmental management at the Savannah River Site, the larger DOE complex, and many large federal and private sites. There is a need to optimize the performance and manage the cost of long term surveillance and monitoring at their sites.

Currently, researchers at the Savannah River National Laboratory are initiating a pilot field test using alternative protocols for long term monitoring of metals and radionuclides. A key component of the approach is that monitoring efforts are focused on measurement of low cost metrics related to hydrologic and chemical conditions that control contaminant migration. The strategy combines careful monitoring of hydrologic boundary conditions with measurement of master variables such as chemical surrogates along with a smaller number of standard well analyses. In plumes contaminated with metals, master variables control the chemistry of the groundwater system, and include redox variables (ORP, DO, chemicals), pH, specific conductivity, biological community (breakdown/decay products), and temperature. Significant changes in these variables will result in conditions whereby the plume may not be stable and therefore can be used to predict possible plume migration. Conversely, concentration measurements for all types of contaminants in groundwater are a lagging indicator plume movement - major changes contaminant concentrations indicate that contamination has migrated. An approach based on measurement of master variables and explicit monitoring of hydrologic boundary conditions combined with traditional metrics should lead to improved monitoring while simultaneously reducing costs. This paradigm is being tested at the SRS F-Area where an innovative passive remedial system is being monitored and evaluated over the long term prior to traditional regulatory closure. Contaminants being addressed at this site are uranium, strontium-90, iodine-129, and tritium.

We believe that the proposed strategies will be more effective in early identification of potential risks; these strategies will also be cost effective because controlling variables are relatively simple to measure. These variables also directly reflect the evolution of the plume through time, so that the monitoring strategy can be modified as the plume 'ages'. This transformational

long-term monitoring paradigm will generate large cost savings to DOE, other federal agencies and industry and will provide improved performance and leading indicators of environmental management performance.

## INTRODUCTION

Plumes of contaminated groundwater beneath sites within the DOE complex will require monitoring for tens of years beyond the final cleanup to ensure that the system is behaving as predicted, and the residual level of risk is acceptable. The National Academy of Sciences projects that the total cost to DOE for these activities will be in excess of \$2 billion (NAS, 2003). Much of the cost is associated with frequent analysis of contaminants in groundwater samples from a large number of monitoring wells. We propose that opportunities exist to simultaneously improve the performance of our monitoring systems and lower costs by developing a refined monitoring approach that adds the low cost measurement of leading indicators (boundary conditions and geochemical conditions) while reducing the number and frequency of traditional contaminant measurements in wells.

The fundamental processes of groundwater flow and contaminant migration are generally well understood for most common contaminants. There are a variety of existing techniques and approaches that have been developed and validated to monitor the behavior of contaminants. Because of the historic regulatory framework, current approaches for long term monitoring (LTM) typically are based on analysis of samples collected from wells that are analyzed in the laboratory using standard EPA methods. Most of the existing sites within DOE are regulated under this paradigm.

Over the last three decades, the Department of Energy Environmental Management (EM) program has funded multiple applied technology development programs focused on improving baseline approaches to groundwater characterization and monitoring. Advances made through these programs include development and application of statistical and scientific tools to optimize monitoring networks, sampling frequency and data interpretation. In addition, through the Integrated Demonstration Program and the Focus Area Programs, EM has invested extensively in the development of both in-situ and field-based measurement of contaminants. When used appropriately, the field-based measurements can be used efficiently to supplement and/or replace more traditional well and analytical lab-based approaches. The technical improvements achieved through these programs created regulatory support for the use of direct push systems for environmental characterization and remedial optimization within the DOE system. A perceived advantage of innovative approaches is that they have the potential to provide easily interpretable information at a reasonable cost that may also be of a higher quality than the information garnered from monitoring well results. Use of these systems may have improved the quality of monitoring especially during the early characterization and remedial monitoring activities at many waste sites, but have not decreased the cost of long term monitoring at legacy sites.

To address the need for economical and effective monitoring systems, SRS has initiated a pilot field test to demonstrate and evaluate LTM field sensors at the F-Area Field Research Site as part of the Attenuation-Based Remedies for the Subsurface Applied Field Research Initiative funded by the DOE Office of Soil and Groundwater Remediation. The demonstration is focused on evaluation of monitoring tools that monitor the geochemical properties that control

contaminant fate and transport, facilitate evaluation on the field-scale, and are inexpensive and easy to use.

## **METHODS**

The overarching goals of the field study at SRS to test the efficacy of LTM sensors, and to work concurrently with the local agencies to obtain regulatory acceptance for the approach. At all metal and radionuclide contaminated sites, aqueous reactions are important because they can influence contaminant migration and immobilization through adsorption, dissolution/precipitation, microbial reactions, and abiotic organic reactions. Understanding these reactions is important in developing the conceptual model for the contaminant plume, and in defining the processes that exert the most control on contaminant migration and immobilization. Long term monitoring at these sites needs to include an evaluation of the effectiveness of treatments and the sustainability of immobilized contaminants after the remedial goals have been achieved. The evaluation of "master variables" such as pH, oxidation-reduction potential (ORP), dissolved oxygen (DO), specific conductivity may be used to assess changes, either natural or man-made, in the plume structure and the stability of immobilized contaminants.

The commercial sensor packages proposed for use in this study will provide inexpensive "master variable" data for the F-Area Field Research Site. With a wireless telecommunications system, the sensors can collect measurements and send the data to an onsite database where users can evaluate the data in real time. The F-Area Field Research Site provides the opportunity to assess the sensors and wireless transmittal system at an active remediation site (modified wall and gate system with injection of alkaline solution) as well as within a wetland downgradient of the remediation system.

Description of the F-Area Hazardous Waste Management Facility

The F-Area Hazardous Waste Management Facility consists of three unlined, earthen surface impoundments referred to as seepage basins. From 1955 through 1988, the F-Area seepage basins (FASB) received approximately 1.8 billion gallons (7.1 billion liters) of low-level waste solutions originating from the processing of uranium slugs and irradiated fuel in the F-Area Separations Facility (Figure 1). The effluents were acidic (wastewater with nitric acid) and low activity waste solutions containing a wide variety of radionuclides and dissolved metals (Killian et al., 1987; Cummins et al., 1991). Waste solutions were transported approximately 3,000 feet from each processing area through underground vitrified clay pipes to the basins. After entering the basin, the wastewater was allowed to evaporate and to seep into the underlying soil. The purpose of the basins was to take advantage of the interaction with the basin soils to minimize the migration of contaminants to exposure points. Though the seepage basins essentially functioned as designed, the acidic nature of the basin influent caused mobilization of some metals and radionuclides resulting in groundwater contaminant plumes.

Historically, some 70 environmental investigations have been conducted in the vicinity of the basins since the 1960's (WSRC, 2000a). Monitoring of the groundwater collected from wells at the basins began in the late-1950s and has continued since that time. Over the years, various types and numbers of wells, seepline monitoring points, and surface water locations have been utilized for assessing impacts and remedial efforts associated with the FASB. Numerous studies and reports are available documenting the studies (e.g., Reichert and Fenimore, 1962;

Fenimore and Horton, 1972; Horton and Carothers, 1974; Kantelo, 1987; Killian et al., 1987; Looney et al., 1988; Haselow et al., 1990; Dixon and Rogers, 1994; Dixon, 1996; Dixon et al., 1997; Koch and Dixon, 1998; Friday, 1997; Friday, 2001; Friday et al., 2001; SRNS, 2012; Amidon and Millings, 2013; Millings and Amidon, 2013).

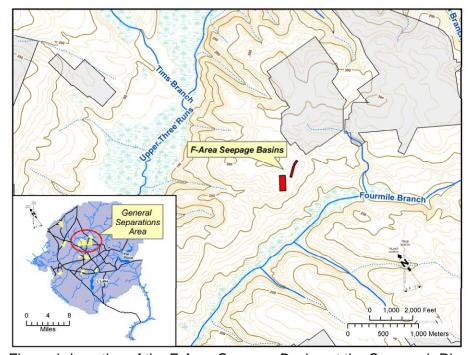


Figure 1. Location of the F-Area Seepage Basins at the Savannah River Site

Operational History of the F-Area Seepage Basins (FASB)

The FASB began operating in 1955 and received processed liquid effluent from the Separations Facilities until 1988. In 1986, the determination was made that the basins should be regulated under the Resource Conservation and Recovery Act (RCRA) as hazardous waste disposal facilities, and closure plans were initiated. The basins were closed by dewatering, physically and chemically stabilizing the remaining sludge, and covering them with a protective multilayer system to reduce rainwater infiltration. The basin closures were completed in 1991. When the FASB were constructed, the conventional belief was that most of the radionuclides would be bound in the soils beneath the basins and would not pollute groundwater. This was true for many radionuclides including plutonium isotopes and cesium-137 (Cs-137), but many such as strontium-90 (Sr-90), uranium isotopes, iodine-129 (I-129), technetium-99 (Tc-99), and tritium migrated to the groundwater. The groundwater remains acidic, with pH as low as 3.2 near the basins and increasing to a pH of approximately 5 downgradient. The Atlantic Coastal Plain aquifer sediments that underlie the F Area have been bathed with acidic solutions for about 40 years, and changes to their mineralogy and texture from the acidic groundwater are currently under study.

In 1997, SRS designed and installed a pump-treat-and-re-inject system with a water treatment unit designed to trap the untreatable tritium in a continuous loop by extracting groundwater from downgradient, removing contaminants other than tritium from the water, and re-injecting the

treated water upgradient of the seepage basins. The treatment system consisted of precipitation/flocculation, reverse osmosis, and ion exchange. The pump-and-treat system operated as designed, but had two significant drawbacks. It was very expensive to operate and generated large amounts of radioactive solid waste. Hence, SRS sought another more efficient way to treat the groundwater contaminant plume. Operation of the water treatment unit began in 1999 (WSRC, 2000b) and were suspended in 2003 (WSRC, 2005).

In 2004, the pump-and-treat system was replaced by a hybrid funnel-and-gate system that was installed about 300 meters from the stream (WSRC, 2005; SRNS, 2012). The purpose of the funnel-and-gate is to slow migration of contaminated groundwater and to funnel it through in situ treatment zones at the gates. Extensive geologic characterization showed that much of the plume migrated along "troughs" at the top of the clay layer that confines the lower aquifer. The walls (or engineered subsurface barriers) were installed across these features to slow contaminant migration and force it through the gates. The treatment zones at the gates attenuate migration of uranium, Sr-90, and I-129 by sorption or precipitation. Tritium migration is slowed by the walls and additional decrease in tritium concentrations is achieved when the stratified plume mixes with less contaminated groundwater as it migrates up through the gates.

Treatment zones for uranium and Sr-90 at the gates are maintained by neutralizing acidity of the groundwater and mineral surfaces with injections of an alkaline solution. This causes sorption of the contaminants and precipitation of uranium phases. Periodic injections are performed with the frequency at each gate dictated by sentry monitoring wells located downgradient.

Monitoring of the performance of the funnel-and-gate with base injection over the past seven years indicates that it has functioned as planned. Analysis of subsurface cores collected downgradient of the middle gate shows that an elevated pH treatment zone has been established. Monitoring of groundwater indicates that tritium flux has been reduced to target levels and regulatory limits on concentrations of Sr-90 and uranium have been achieved downgradient of the treatment system.

In 2009, a pilot study was initiated to evaluate the removal of I-129 by the injection of particles of solid silver chloride (SRNS, 2012). Contaminant I-129 and natural I-127 react with the silver chloride to form insoluble silver iodide, removing I-129 from the groundwater. In 2011, a modification to the RCRA permit was approved to deploy silver chloride technology at the middle gate as part of the corrective action. The treatment zone was from the top of the water table down to the tan clay confining zone (25 to 50 feet below ground surface). Injection was performed starting at the bottom of the aquifer and proceeded upward pumping a specific volume of amendment into each zone at 2.5 foot intervals. Evaluation of the performance of the silver chloride treatment zones continues. Figure 2 provides 2011 plume maps for Sr-90 and U-238.

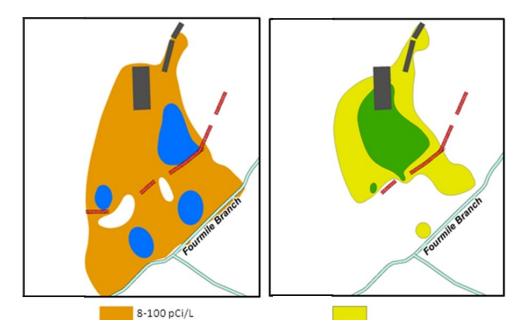


Figure 2. Distribution Map for Sr-90 and Uranium in 2011. Black rectangles show the outline of the seepage basins and red lines show the funnel and gate system. Left – area in orange shows distribution of Sr-90 between 8-100 pCi/l. Right – area in yellow and green shows distribution of U-238 greater than 100 pCi/l.

## Selection of Monitoring Locations

Several criteria were developed and used to select the location of existing monitoring wells to be used in the pilot study. These criteria include the following: screen installed in the transmissive zone within the plume; well screen length of 10 feet or less; at least one sentry well installed within the influence of the current groundwater action used for determining injection of alkaline solution; at least one well down gradient of the current groundwater action, within the plume, and in/near the wetland; and sufficient monitoring history.

Three wells were selected for the initial study (Figure 3). All locations are listed in the RCRA permit as plume assessment wells and are routinely sampled. One well, FSB-131D, is a sentry well just downgradient of a gate (opening) in the subsurface walls. FSB-131D is used to determine when another alkaline injection is needed in the gates. The second well, FSP-12A, is located further downgradient from the gate on the northern edge of the wetland. The third location, FPZ-6, is located within the wetland at the edge of the plume before it discharges into Fourmile Branch. Figure 3 shows the locations of the wells selected for this pilot test. The wells are located within 650 ft. (200 m) of each other and are all downgradient of the middle gate.

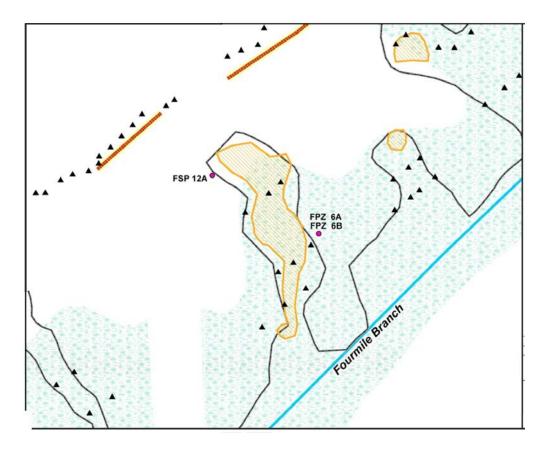


Figure 3. Location of monitoring wells selected for deployment of LTM Sensors

## Selection of Long Term Monitoring Sensors

The sensors for the pilot demonstration will be selected based on the following minimum requirements.

- Ability to measure pH, ORP, DO (optical), temperature, specific conductivity, and water level (pressure transducer) within a monitoring well;
- Stable sensors with little need for recalibration (i.e., only once or twice a year calibration)
- External barometric pressure sensor;
- Ability to fit into a 2 inch monitoring well;
- Sensors located within 1 to 1.5 ft. of each other on the instrument;
- Cables from the instrument to the surface for deployment, communication of data and power;
- Well cap or seal that incorporates connections for the instrument cable, communication of data and power;
- Data logging and wireless transmittal (compatible with Verizon cellular network);
- Low power consumption (able to be powered by battery and solar powered system); and
- Software for real-time viewing, data downloading and managing.

Once installed, the following criteria were developed to provide the metrics for evaluating the performance of LTM instruments and data loggers with wireless transmittal system. The specific objectives of this study include evaluating the following:

- The stability of the sensors over the long term;
- The use of the instruments for decision making as part of groundwater actions; and
- The ease of use and practicality of the system (instruments and wireless system) as a whole for long term monitoring.

Field activities will be initiated in January 2014 after field permits are acquired and commercial sensors/communication packages are procured.

## **CONCLUSIONS**

This purpose of this initial pilot effort at SRS is to document that sensors can provide reliable information on master variable chemistry within the contaminant plume at F-area. These master variable parameters are critical to predict plume instability and deviations from predicted plume behavior at sites. These results from the pilot study will be incorporated into a revised conceptual site model for F-area that incorporates explicit description and monitoring of hydrologic boundary conditions and geochemical master variables to support the design of better long term monitoring approach. The results of the pilot demonstration can be evaluated against the current baseline monitoring results to determine the efficacy of the system.

The results from this effort supplemented by future planned studies at F-area should be applicable to a large number of sites within the DOE complex where corrosive groundwater plumes are contaminated with metals and/or radionuclides. Similar plumes are common outside of the DOE complex and include metal fabrication shops and mining sites. These sites often share similar basic components including a source zone (often in the vadose zone), a contaminated groundwater plume (may be stratified and/or occur in multiple aquifers), treatment zone(s), and possibly discharge zone(s). At this time, field evaluation of a long term monitoring strategy based on measurement of boundary controlling variables would be most appropriate for monitoring of these corrosive groundwater plume contaminated in part because a wide variety of tools and sensors are available to easily measure the variables that control migration for these types of contaminants.

The proposed strategy should be more effective in early identification of potential risks at metal and radionuclide contaminated sites; while simultaneously reducing costs when compared to traditional approaches. A key component for successful integration of this alternative strategy is to obtain early regulatory input and support for the approach. If successful, this transformational long-term monitoring paradigm should generate significant cost savings to DOE, other federal agencies and industry and will provide improved performance and leading indicators of environmental management performance.

## **REFERENCES**

- 1. Amidon, M. B. and Millings, M. R., 2013. Fourmile Branch Seepline Assessment at the F- and H-Area Seepage Basins, Savannah River Site (U), SRNL-RP-2013-00362, Savannah River Nuclear Solutions, Aiken, SC, May 2013.
- 2. Cummins, C. L., Hetrick, C. S. and Martin, D. K., 1991. *Radioactive Releases at the Savannah River Site, 1954-1989*, WSRC-RP-91-684, Westinghouse Savannah River Company, Aiken, SC, February 1991.
- 3. Dixon, K. L. and Rogers, V. A. 1994. Semi-Annual Sampling of Fourmile Branch and Its Seeplines in the F and H Areas of SRS (U), WSRC-TR-93-293, Westinghouse Savannah River Company, Aiken, SC, April 1994.
- 4. Dixon, K. L., 1996. *Monitoring of Water Levels in the Wetlands of Fourmile Branch near F- and H-Areas of SRS*, WSRC-TR-96-0289, Westinghouse Savannah River Company, Aiken, SC, 1996.
- Dixon, K. L., Rogers, V. A., Conner, S. P., Cummings, C. L., Gladden, J. B., and Weber, J. M., 1997. Geochemical and Physical Properties of Wetland Soils at the Savannah River Site, WSRC-TR-96-0115, Westinghouse Savannah River Company, Aiken, SC, May 1997.
- Fenimore, J. W. and Horton, J. H., 1972. Operating History and Environmental Effects of Seepage Basins in chemical Separations Areas of the Savannah River Plant, DPST-72-548, E. I. du Pont de Nemours & Co, Savannah River Laboratory, Aiken, SC, 1972.
- 7. Friday, G. P., 1997. Environmental Summary of the F- and H-Area Seepage Basins Groundwater Remediation Project, Savannah River Site, WSRC-TR-97-0130, Westinghouse Savannah River Company, Aiken, SC, 1997.
- 8. Friday, G. P., 2001. Chemical Properties of Pore Water and Sediment at Three Wetland Sites Near the F- and H-Area Seepage Basins, Savannah River Site, WSRC-TR-2001-00241, Westinghouse Savannah River Company, Aiken, SC, May 2001.
- 9. Friday, G. P., Dunn, D. L., and Halverson, N.V., 2001. Summary of Environmental Investigations in the Vicinity of the F- and H-Area Seepage Basins, Savannah River Site, WSRC-TR-2001-00548, Westinghouse Savannah River Company, Aiken, SC, December 2001.
- Haselow, J. S., Harris, M., Looney, B. B., Halverson, N. V. and Gladden, J. B., 1990.
  Analysis of Soil and Water at the Four Mile Creek Seepline near the F&H Areas of SRS (U), WSRC-RP-90-0591, Westinghouse Savannah River Company, Aiken, SC, June 1990.

- 11. Horton, J. H. and Carothers, G. A., 1974. *Nitrate in the Separations Area Seepage Basins*, DPST-74-293, E. I. du Pont de Nemours & Co, Savannah River Laboratory, Aiken, SC, March 1974.
- 12. Kantelo, M. V., 1987. Summary of I-129 Measurements in Ground and Surface Waters, DPST-87-820, E. I. du Pont de Nemours & Co, Savannah River Laboratory, Aiken, SC, November 1987.
- 13. Killian, T. H., Kolb, N. L., Corbo, P., and Marine, I. W., 1987a. *Environmental Information Document F-Area Seepage Basins*, DPST-85-704, E. I. du Pont de Nemours & Co, Savannah River Laboratory, Aiken, SC, March 1987.
- 14. Koch, J. W. and Dixon, K. L., 1998. Comprehensive Sampling of Fourmile Branch and Its
- 15. Seeplines in the F and H Areas of SRS: June 1996, and March 1997 (U), WSRC-TR-98-
- 16. 00287, Westinghouse Savannah River Company, Aiken, SC, August 1998.
- 17. Looney, B. B., Cantrell, J. E., and Cook, J. R., 1988. Sampling and Analysis of Surface Water in the Vicinity of the F- and H-Area Seepage Basins, DPST-88-229, E. I. du Pont de Nemours & Co, Savannah River Laboratory, Aiken, SC, January 1988.
- 18. Millings, M. R. and Amidon, M. B., 2013. Fourmile Branch Tree Kill Assessment at the F-and H-Area Hazardous Waste Management Facilities, SRNL-TR-2013-00074, Savannah River Nuclear Solutions, Aiken, SC, May 2013.
- National Academy of Sciences. 2003. Long-Term Stewardship of DOE Legacy Waste Sites: A Status Report, Committee on Long-term Institutional Management of DOE Legacy Waste Sites: Phase 2, National Research Council, 73 pages.
- 20. Reichert, S. O. and Fenimore, J. W., 1962. *Lithology and Hydrology of Radioactive Waste Disposal Sites at the Savannah River Plant*, DPSPU-62-30-21B, E. I. du Pont de Nemours & Co, Savannah River Plant, Aiken, SC, October 1962.
- 21. SRNS, 2012. Annual Corrective Action Report for the F-Area Hazardous Waste Management Facility, the H-Area Hazardous Waste Management Facility, and the Mixed Waste Management Facility (U), SRNS-RP-2012-00045, Savannah River Nuclear Solutions, LLC, Aiken, SC, April 2012.
- 22. W. Stumm and J. J. Morgan: Aquatic Chemistry An Introduction Emphasizing Chemical Equilibria in Natural Waters. New York, Wiley-Interscience, 1970, 583 pages.
- 23. WSRC, 2000a. Monitoring Plan for the Wetlands Downgradient from the F- and H-Area Seepage Basins, Savannah River Site, WSRC-TR-99-00146, Revision 1, Westinghouse Savannah River Company, Aiken, SC, 2000.

- 24. WSRC, 2000b. *F-Area Hazardous Waste Management Facility Corrective Action Report (U): First and Second Quarter 2000,* WSRC-TR-2000-00243, Westinghouse Savannah River Company, Aiken, SC, 2000.
- 25. WSRC, 2005. Annual Corrective Action Report for the F-Area Hazardous Waste Management (HWMF), the H-Area HWMF, and the Mixed Waste Management Facility, WSRC-RP-2005-4011, Westinghouse Savannah River Co.

WM2014 Conference, March 2 – 6, 2014, Phoenix, Arizona, USA