

**Shifting the Paradigm for Long Term Monitoring at Legacy Sites to Improve Performance while Reducing Costs – 13422**

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**ABSTRACT**

A major issue facing many government and private industry sites that were previously contaminated with radioactive and chemical wastes is that often the sites cannot be cleaned up enough to permit unrestricted human access. These sites will require long-term management, in some cases indefinitely, leaving site owners with the challenge of protecting human health and environmental quality in a cost effective manner. 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 (SRS), the larger DOE complex, and many large federal and private sites.

Currently, most monitoring strategies are focused on laboratory measurements of contaminants measured in groundwater samples collected from wells. This approach is expensive, and provides limited and lagging information about the effectiveness of cleanup activities and the behavior of the residual contamination. Over the last twenty years, DOE and other federal agencies have made significant investments in the development of various types of sensors and strategies that would allow for remote analysis of contaminants in groundwater, but these approaches do not promise significant reductions in risk or cost.

Scientists at SRS have developed a new paradigm to simultaneously improve the performance of long term monitoring systems while lowering the overall cost of monitoring. This alternative approach incorporates traditional point measurements of contaminant concentration with measurements of controlling variables including boundary conditions, master variables, and traditional plume/contaminant variables.

Boundary conditions are the overall driving forces that control plume movement and therefore provide leading indication to changes in plume stability. These variables include metrics associated with meteorology, hydrology, hydrogeology, and land use. Master variables are the key variables that control the chemistry of the groundwater system, and include redox variables (ORP, DO, chemicals), pH, specific conductivity, biological community (breakdown/decay products), and temperature. A robust suite of relatively inexpensive tools is commercially available to measure these variables. Traditional plume/contaminant variables are various

measures of contaminant concentration including traditional analysis of chemicals in groundwater samples.

An innovative long term monitoring strategy has been developed for acidic or caustic groundwater plumes contaminated with metals and/or radionuclides. Not only should the proposed strategy be more effective at early identification of potential risks, this strategy should be significantly more cost effective because measurement of controlling boundary conditions and master variables is relatively simple. 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 significant 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 there are significant opportunities 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.

### **Recent Advances in Technologies and Strategies for Long Term Monitoring**

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 groundwater monitoring 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 approaches. 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 at many waste sites, but have not significantly decreased the cost of long term monitoring at legacy sites.

### **Evolution of Contaminant Plumes through Space and Time**

As a contaminant plume evolves over time, it is important to recognize that specific monitoring strategies are needed to address relevant remedial and monitoring objectives at each stage (initial characterization, remedial design and optimization, and long term monitoring) such that an efficient monitoring approach will evolve through the remedial history of the plume (Figure 1). This is especially relevant in the transition from remediation monitoring to long term monitoring.

The initial stages of characterization and monitoring are typically focused on delineation of the nature and extent of both source zone and dilute phase contamination to support initial remedial decision-making. Source zone contamination is typically present at high concentrations, and the geochemistry of the groundwater is significantly perturbed. Initially, field investigations should take advantage of less expensive, less invasive and integrative measurements such as surface geophysics, soil gas, advanced borehole logging in existing wells, and field-based contamination measurements as appropriate to quickly delineate the rough extent of the location of the source zone and dilute plume. The results from these activities can be synthesized with existing data to develop the initial conceptual model of the site that can be used to guide subsurface investigations. Subsequent field investigations should focus on resolving key technical uncertainties using more expensive and invasive methods, emphasizing collection of depth-discrete geologic, hydrogeologic, and chemical information.

The purpose of the next phase of monitoring is to collect information to support remedial design and optimization. Typically, source zone material is removed and/or aggressively treated or stabilized, and moderate to high concentrations of contaminants are found in the aqueous phase. During this monitoring phase, field-screening methods are particularly useful to determine the zone of capture and to optimize remedial design to reduce treatment volumes. In appropriate geologic environments, direct push technologies can now be used to make densely spaced

depth-discrete measurements or to install temporary monitoring points at critical locations. These temporary points can be used immediately in interim action strategies to reduce contamination and long-term costs. They can also be used as monitoring wells for later additional remedial actions.

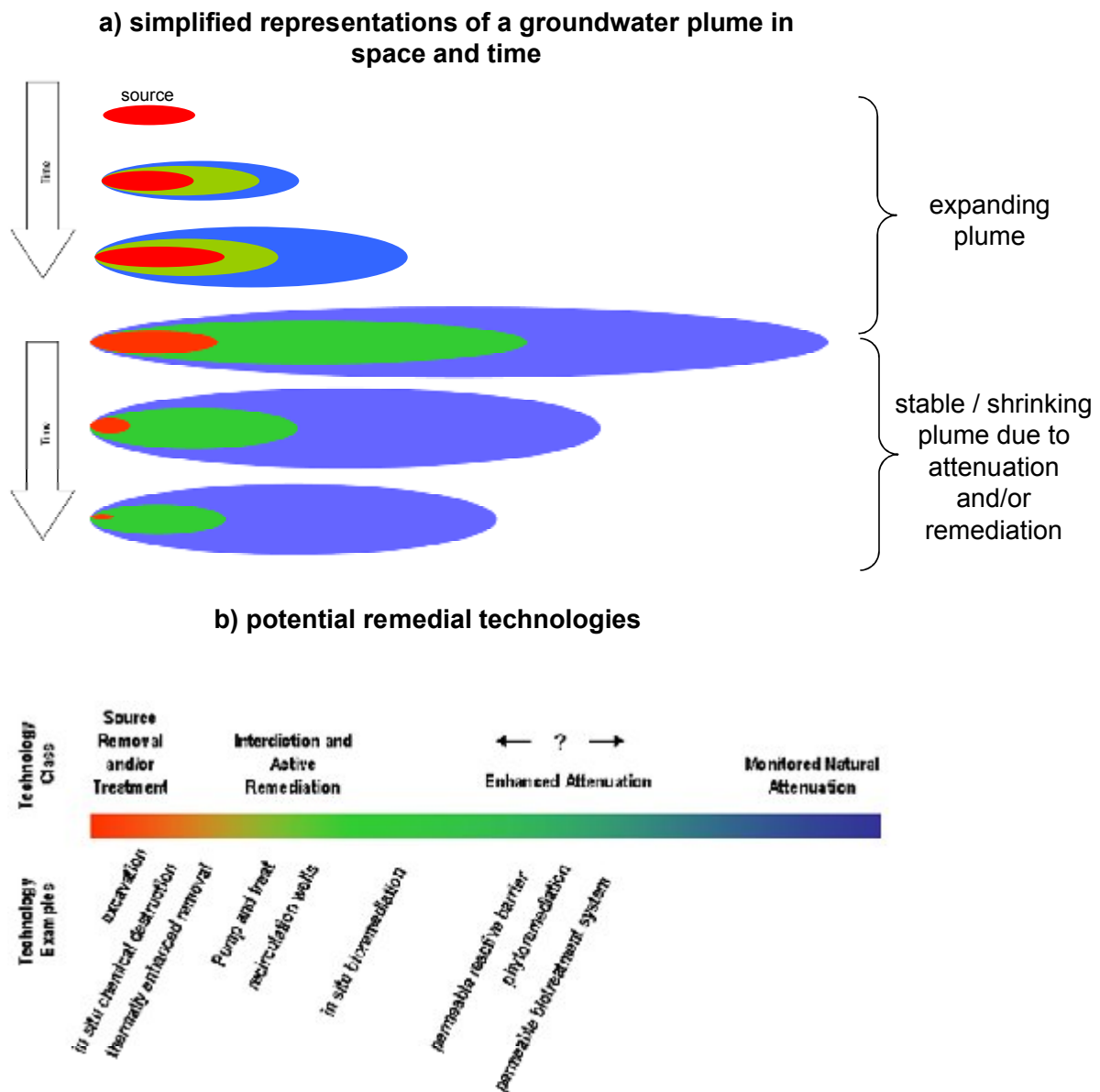


Figure 1. Image showing the lifecycle of a contaminant plume and a continuum of possible remedial technologies matched to different target zone. Characterization and monitoring systems should be optimized to support remedial objectives of each remedial phase.

The next phase is to monitor and ensure the effectiveness of the cleanup strategy, ultimately over

decades, in most cases. The nature and extent of contamination is presumably well understood so that focus of monitoring is to identify deviations from predicted behavior. This is to ensure that the contamination is abating or remaining stable and not changing or moving in an unacceptable way. In this phase of monitoring, traditional approaches using groundwater wells are typically not cost efficient or technically effective, as contaminant transfer is controlled by diffusion or other mass transfer limited processes. In addition, monitoring systems must be rugged enough to withstand long periods of remote deployment in harsh environments, robust enough to perform reliably, and inexpensive enough to be deployed at multiple locations. In this stage of monitoring, sensors should be selected that are simple and often measure global environmental parameters or surrogate parameters contribute to or predominately control the fate and transport of the targeted, but more difficult to measure contaminants of concern. It should be recognized that some traditional well measurements will be required to satisfy state and federal regulatory agreements but could be supplemented with other measurements to provide a more robust monitoring system at a lower cost.

## **DISCUSSION**

To meet the obligation to monitor an estimated 100 sites within the DOE complex that cannot be cleaned up enough to permit unrestricted human access and therefore will require long-term management, we propose that DOE should pursue an innovative strategy focused on monitoring the controlling variables that facilitate contaminant migration at legacy waste sites that are the leading indicators for changes in the stability of the plume. These variables also directly reflect the evolution of the plume through time so that the monitoring strategy can be modified (stepped down) as the plume ‘ages’. These controlling variables include boundary conditions, master variables, and traditional plume/contaminant variables.

### **Boundary Conditions – Driving Forces**

Boundary conditions are the overall driving forces that control groundwater and plume movement and include metrics associated with meteorology, hydrology, hydrogeology and land use. In most situations, since monitoring may be required for decades or centuries, changes in boundary conditions can change the site conceptual model and impact monitoring of nature and extent of contamination. They are the leading indicator parameters of change in a contaminant plume at a site. Several examples include

- Changes in precipitation may increase or decrease groundwater velocity and/or direction, increase contaminant infiltration and could compromise caps.
- New and existing municipal and agricultural wells or changes in the operation of those wells can cause changes in groundwater velocity and direction leading to high variability in monitored parameters.

- New infrastructure and construction can change infiltration rates, and industry discharge outfalls can impact groundwater flow dynamics.

Changes in the boundary conditions can change the groundwater flow dynamics and impact the overall monitoring program. Over time, monitoring locations may no longer be in the correct locations and/or create variability in measurements and false or non-representative trends.

Robust site conceptual models should include scenarios for changes in boundary conditions or be revised to include new boundary conditions. Much of the boundary condition data can be easily obtained and updated with cooperative agreements between stakeholders.

### **Master Variables**

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 capture/alarm any significant deviation from that expected behavior. For long term monitoring, significant can be defined as a behavior which results in an unacceptable change in value of a target or regulated parameter or contaminant of concern. Sensors or measurement systems for long term monitoring should ideally be capable of achieving the two objectives. The enabling attributes of a long term measurement system might be long-held or permanent calibration (for accuracy and precision within the required measurement range), sufficient sensitivity to detect a significant change, capability of acquiring data that sufficiently represents the chemical (both in space and time), physical, and or biological state of the site, and reasonable cost.

The concept of master variables is borrowed from the traditional aqueous chemistry literature that uses a small set of easily measured parameters to nearly comprehensively quantify an entire chemical system (Stumm and Morgan, 1981). In addition to the conventional parameters (eH and pH), a few additional easily measured parameters can be used to describe the chemical state of the groundwater. These parameters are generally inexpensive to measure and help achieve the goals of monitoring as described above. As determined by ORP measurements, dissolved oxygen, redox pairs, etc., eH will help determine the stability, mobility, or toxicity of a contaminant species whether directly related to the contaminant's chemistry or in relation to organisms or compounds that interact or react with the contaminant. Like redox state, a change in pH may predict the contaminant behavior directly or the likely interactions and fate or transport of the contaminant with respect to organisms or compounds in the subsurface system.

Examples in which a change in a master variable results in a change in a regulated parameter include a decrease in ORP which may increase the aqueous solubility of a metal or a change in pH which may reduce the metabolic activity of bacteria, resulting in less degradation of chlorinated solvent contaminants (both translate to an effective increase in the mobility of the contaminant plumes). A change in pH may directly correspond to changes in concentration of

contaminant compounds like heavy metals or radionuclides in groundwater if the aqueous solubility, sorption, or precipitation of the compound are determined by pH.

There may be several relevant indicators of a master variable parameter like eH. This might include concentrations of species indicating redox states such as dissolved oxygen, nitrate/nitrite, sulfate, methane in addition to the direct measurement of ORP by electrode reactions. It is not uncommon for these measurements to be temporarily conflicting such as high methane concentrations yet dissolved oxygen concentration at half saturation in a ground water sample. The kinetics of chemical and biological reactions and the mix of groundwater from different flow regimes is usually the reason for these deviations from the expectations of equilibrium aqueous chemistry. For example, cis-dichloroethylene can often be found in otherwise aerobic groundwater at sites with contamination in a mix of fine- and coarse-grained material. Although most of the groundwater flow occurs in the aerobic coarse grains, reducing conditions can develop in the fine pores of the less mobile groundwater, removed from the advective flow paths. Reduced byproducts (e.g., cis DCE, methane, etc.) can then diffuse into the advective flow paths. This may result in an apparent contradiction in redox parameters in a groundwater sample. To effectively use redox indicators at a site like this requires an accurate conceptual model of the site including the nuances of mixed contributions of species to the accessible groundwater and historical trends of the relevant parameters. If the historic and current status of the groundwater system is understood, monitoring of changes to a specific leading indicator parameter or suite of parameters should provide the least expensive alternative and earliest alert to unexpected contaminant transport or abatement.

Surrogates or other indicators such as electrical conductivity may also be useful. Electrical conductivity measurements indicate the lumped contribution of ionic species in groundwater and are non-specific measurements that can help indicate concentrations of contaminants or other compounds that affect contaminants. Changes in electrical conductivity can sometimes be directly related to concentrations of dissolved metals or to ionic treatment amendments like sodium persulfate, potassium permanganate, or sodium lactate.

Measurements of biological communities can also be a surrogate or indicator parameter. The types, densities, and activity of various organisms may be very important. Like other parameters, the type, density, and activity of organisms may be different in different flow regimes so a paucity of dehalococoides measured in groundwater samples may be accurate for an advective flow zone but not representative of a fine-grained unit containing residual contamination.

## **Conclusions**

Many sites in the DOE complex have corrosive groundwater plumes 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 conditions and master 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.

We are in the early stages of planning a pilot demonstration a F-Area Seepage Basins at the Savannah River Site where the approach can be evaluated against the current baseline monitoring results to determine both the efficacy of the system. The proposed strategy should be more effective in early identification of potential risks; these strategies will be significantly more cost effective. 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.

### **Acknowledgements**

This work was developed as part of a SRNL working group that supported development the groundwater strategy portion of the Scientific Opportunities for Monitoring at Environmental Remediation Sites (SOMERS): Integrated Systems-Based Approaches to Monitoring prepared for the DOE Office of Environmental Management (Bunn et al, 2012). Significant contributions toward the development of the specific technical strategy were made by B. D. Riha, M. R. Millings, M. E. Denham, and J. Rossabi and their contributions are greatly appreciated by the authors.

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WM2013 Conference, February 24 – 28, 2013, Phoenix, Arizona, USA

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