Adapting Advances in Remediation Science to Long-Term Surveillance

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ABSTRACT

Several facets of groundwater remediation stand to gain from the advances made during recent years in disciplines that contribute to remediation science. Engineered remedies designed to aggressively remove subsurface contamination should benefit from this progress, and more passive cleanup methods and the long-term monitoring of such passive approaches may benefit equally well if not more. The U.S. Department of Energy Office of Legacy Management (LM) has adopted a strategic plan that is designed to take advantage of technological improvements in the monitoring and assessment of both active and passive groundwater remedies. Flexible adaptation of new technologies, as they become available, to long-term surveillance at LM sites is expected to reduce site stewardship costs while ensuring the future protection of human health and the environment. Some of the technologies are expected to come from government initiatives that focus on the needs of subsurface monitoring. Additional progress in monitoring science will likely result from continual improvements in our understanding of contaminant fate-and-transport processes in groundwater and the vadose zone.

INTRODUCTION

Advances in the field of groundwater remediation are sometimes viewed as mostly improvements to engineered systems that are used to aggressively remove subsurface contamination at sites over relatively short time spans of a few to several years. However, the professional literature dealing with remediation science suggests that less aggressive approaches to groundwater cleanup, such as permeable reactive barriers, phytoremediation, and monitored natural attenuation, will benefit equally if not more as a result of such advances. In fact, it is possible that the monitoring of more passive groundwater remedies, rather than improvements in remedy implementation, might gain the most from progress achieved in remediation science. The U.S. Department of Energy (DOE) Office of Legacy Management (LM) has adopted a strategic plan that facilitates the adaptation of new monitoring technologies, as they become available, to long-term surveillance at DOE closure sites.

Multiple programs are under way in various parts of DOE that focus on improving the monitoring of groundwater remedies, especially long-term monitoring that spans decades and possibly hundreds of years. Additional programs of this type are progressing in parallel under the auspices of the U.S. Environmental Protection Agency (EPA), the U.S. Nuclear Regulatory Commission (NRC), and the U.S. Department of Defense (DOD). Not surprisingly, common themes are shared among these initiatives given that many long-term surveillance issues tend to be universal. Proposed products of the shared efforts include systems approaches to monitoring;

paradigm shifts for gauging environmental restoration; incorporation of risk evaluation; optimization of monitoring networks; utilization of remote sensing, geophysical measurements, and surrogate indicators of contamination; development of chemical-specific sensors; and use of autonomous performance monitoring systems. Most of these technologies are still in development or have only recently become the subject of widespread attention for long-term monitoring purposes. Nonetheless, the outlook is positive that ongoing, focused attempts to advance monitoring science will eventually improve the effectiveness and reduce the costs of long-term surveillance.

During the past several years, significant strides have also been made in deciphering the interrelated effects of physical, chemical, and biological phenomena on contamination in both groundwater and the vadose zone. Accordingly, attempts are being made to develop new methods and instruments for efficiently identifying and quantifying these phenomena. Examples of enhanced monitoring technologies of this type include sensors for measuring mass flux, sensors for measuring transient changes in groundwater velocity, molecular-based techniques for identifying contaminant-degrading microbes, and geophysical approaches to delineating areas of changing subsurface geochemistry.

This paper describes the relevance of several monitoring techniques and approaches now being studied by Federal Government agencies to long-term surveillance at LM sites. In addition, current research findings regarding selected subsurface transport phenomena (biogeochemical processes, transient groundwater flow) that have bearing on contaminant fate at LM facilities are examined in some detail along with evolving monitoring technologies designed to identify these phenomena. Further advances in these areas are expected to help shed light on the effectiveness of some groundwater remedies, and the flexible utilization of pertinent research findings to improve long-term monitoring will lead to more cost-effective cleanup at DOE sites.

LEGACY MANAGEMENT GOALS, STRATEGIES, AND CHALLENGES

LM was established in 2003 largely for the purpose of providing long-term surveillance and maintenance of closure facilities that no longer support the DOE’s ongoing missions regarding national security, energy, and science. Weapons production and related activities on behalf of DOE and predecessor agencies during World War II and the Cold War left a legacy of nuclear and non-nuclear wastes, hazardous materials, and environmental contamination at more than 100 sites across the country. During the past 15 years, the DOE Office of Environmental Management (EM) made significant progress in remediating these sites and has now begun to transfer many of them to LM for optimal management of legacy responsibilities. At the closure facilities affected by groundwater contamination, LM is tasked with monitoring the performance of environmental remedies that were initiated by EM with the objective of either limiting the migration of subsurface contaminants or eventually reducing their concentrations to non-threatening levels.

A primary goal set forth in LM’s Strategic Plan is to protect “human health and the environment through effective and efficient long-term surveillance and maintenance.”[1] The long-term commitments required to achieve this goal become clear when considering that many of the inorganic and organic chemical species that contribute to groundwater contamination at DOE facilities [2] have the potential to persist in the subsurface for as long as several tens of years. And given the long-lived nature of some radionuclide contaminants, it is reasonable to assume that surveillance of subsurface conditions will, in some instances, be required for hundreds or even thousands of years. Consequently, one of LM’s major objectives is to “ensure resources and tools are in place to provide continuous improvements in the effectiveness of long-term surveillance and maintenance for current and future generations.”[1] To meet this objective, LM intends to “track and use advances in science and technology to improve sustainability and ensure protection.”[1]

The programmatic effort by DOE-LM to keep up with and apply new technologies is similar to the remedy updates initiative started by U.S. Environmental Protection Agency (EPA) in the 1990s.[3] This initiative acknowledged that conventional forms of aquifer cleanup, such as pump and treat, were sometimes less successful than originally projected and that more realistic approaches to site closure could often be achieved if advances in our understanding of subsurface contaminant transport were taken into account. Such considerations are expected to lead to reductions in the cost of effectively operating, monitoring, and maintaining environmental remedies.[1,3]

Optimal use of new monitoring technologies at DOE sites will likely involve some flexibility on the part of LM. Given the relatively rapid pace at which technological advances are made, it will be important to discern which advances could actually improve data collection, interpretation, and analysis. Deciding when and where to adopt a new technology will depend heavily on specific hydrogeologic conditions at each DOE site and whether the benefits of implementing this technology justify its cost.

The effort that goes into long-term surveillance of an LM site is generally reduced in comparison to the workload previously required for site characterization and remedy selection. However, this does not mean that the long-term monitoring of LM sites will be uniform and simple. The monitoring data collected and appropriate interpretation of these data depend on each site’s subsurface conditions and the current status of local aquifer cleanup. Contaminant types, aquifer media, and background water geochemistry can vary widely between sites [2,4,5], and groundwater remedies are in various stages of implementation when EM sites are transferred to LM. At some sites, the remedies have been operating for more than 10 years, significant amounts of monitoring data record the progress of aquifer cleanup, and contaminant transport in the subsurface appears relatively stable. At many other facilities, remedies are started just a year or two prior to site transfer, and the near-term objective of monitoring is remedy verification. Surveillance requirements at these latter sites will, in many cases, become less stringent with time, and monitoring costs should be correspondingly reduced. Successful transition from remedy verification to aquifer restoration monitoring depends on informed interpretation of collected data, which is enhanced if advances in remediation science, including improvements in our understanding of fate-and-transport processes, are tracked and implemented when justified.

Though much of the subsurface monitoring conducted at DOE closure facilities involves the surveillance of conditions in groundwater, monitoring of the vadose zone above groundwater at some sites may be important for ensuring protection of public health and the environment. Unsaturated soil and rock above the saturated zone may contain residual contamination that can be entrained in recharge water resulting from infiltration of precipitation. Monitoring of the vadose zone might also be useful for detecting unforeseen releases of contaminants from waste containment facilities over the long term. Accordingly, LM will benefit from tracking the progress made with technologies for monitoring both the vadose zone and groundwater.

GOVERNMENT INITIATIVES FOR IMPROVING SUBSURFACE MONITORING

The numerous initiatives by DOE and other government agencies aimed at improving subsurface monitoring stem partly from the many lessons learned during the past three decades in the course of attempting to remediate contaminated aquifers at sites across the country. Additional motivators for these efforts are found in technological advances that make it possible to perform tasks that, though always desirable, may not have been possible a decade or two ago. Included in this latter category is the ability to collect and disseminate large quantities of data, much of which can now be shared in near-real time on the Internet.

A summary of several Federal Government initiatives that are advancing the science of subsurface monitoring is presented in Table I. This summary is not meant to be exhaustive; numerous additional efforts of a related nature are progressing within the federal system and under the auspices of state and local governments, academia, professional societies, and industry. Rather, the initiatives in Table I were selected for discussion in this paper because the techniques promoted by them are expected to have bearing on many of the issues that LM will deal with as a result of its commitments to site surveillance. It should be noted that the labels assigned to initiatives were arbitrarily selected by this author and may not match labels used by the government agencies supporting their respective programs.

The first initiative listed in Table I represents the culmination of a DOE-sponsored workshop on performance monitoring that was held in Butte, Montana [5] during summer 2005. The workshop participants comprised hydrologists, geochemists, geophysicists, and environmental researchers from EM and LM and technology developers, regulators, and end users of performance monitoring technology. The objective of the gathering was to identify current and promising technologies for (1) improving the monitoring of contaminated sites that have moved past an initial remediation stage and are subsequently transitioning to restoration while (2) reducing monitoring costs.

Many recommendations for monitoring resulted from the workshop, but six particular areas were identified as being key to taking environmental monitoring of the subsurface to a new and more advanced stage. These areas, stated as recommendations, are

1. Use integrated performance monitoring systems that coordinate technical and risk objectives, largely by using indicator (or surrogate) parameters and multiple methods for sensing subsurface conditions.
2. Use measures of mass flux to support mass balance approaches (in lieu of point measurements of concentrations) for demonstrating performance of groundwater remedies while accounting for system uncertainties through modeling and other techniques.
3. Employ geophysical and other methods that facilitate spatially integrated views of subsurface properties, processes, and features affecting groundwater cleanup.
4. Apply field-testing methods, such as push-pull tests, that better quantify subsurface transport properties and rates.
5. Implement objective- and uncertainty-based optimization methods for improving monitoring networks and reducing monitoring frequency.
6. Employ autonomous monitoring systems that provide real-time access to potentially large volumes of collected data.

The DOE Office of Cleanup Technology is expected to implement a technology development program that will address all these areas and incorporate guidance from environmental scientists, technology developers, end users, and regulators.

The Idaho National Laboratory (INL) has developed a strategy for optimally collecting monitoring data and maximizing the information drawn from those data.[6] Referred to as the Structural Approach to Performance Monitoring in Table I, the INL strategy seeks to overcome perceived inadequacies and inefficiencies in the ways that monitoring data are now collected, disseminated, and analyzed. The advocated approach is designed to minimize costs, account for risk, and provide the information desired by stakeholders (regulators, site owners, consultants, and scientists). Highlighted components of the INL system include (1) monitoring design based on well-defined objectives, (2) automated data collection systems using sensors, (3) optimal management of large volumes of data, (4) near-real-time sharing of data, (5) streamlined analysis tools that suit the specific needs of individual stakeholders, and (6) analysis of data by experienced professionals who understand the subsurface processes occurring at a site.[6] The INL strategy was described in some detail at a 2004 workshop on long-term monitoring of metals and radionuclides in the subsurface.[7] The concepts incorporated in this strategy were also presented at the summer 2005 workshop in Butte [5] and can be discerned in some of the areas emphasized as a result of the workshop.

Another DOE-sponsored initiative that LM is tracking is the Advanced Monitoring System Initiative (ASMI) [8] that is operated by the DOE Nevada Site Office and Bechtel Nevada. The overarching purpose of this initiative is to accelerate the development and application of advanced systems capable of detecting and monitoring radionuclides and metals in the subsurface. It emphasizes integrated development, demonstration, testing, and evaluation of sensors and monitoring systems that show promise for meeting DOE needs. AMSI promotes aggressive development of innovative monitoring technologies with the intent of having these technologies fully applied by end users. The AMSI actively pursues sensor and monitoring projects that, among other things, monitor tritium in the vadose zone and groundwater, technetium-99 and strontium-90 in groundwater, and moisture in landfill covers using unique testing facilities at the Nevada Test Site.[8]

In parallel with DOE initiatives, the NRC is overseeing the development of an integrated ground-water monitoring strategy (IGWMS) [9], a system that is expected to provide practical guidance for reviewing NRC licensees’ subsurface monitoring programs. A relatively new perspective is guiding the development of this strategy, wherein groundwater monitoring is used to specifically support performance assessments of nuclear facility sites. The strategy promotes approaches to monitoring that support performance assessment models based on the features, events, and processes that may occur at sites over long time periods.

The IGWMS is expected to be robust, producing monitoring schemes that will (1) assess the effectiveness of contaminant isolation systems or remediation activities, (2) inform stakeholders about monitored performance indicators through effective data management and analysis, (3) identify contaminant plumes and preferential transport pathways, and (4) identify and quantify system uncertainties.[10] Though the IGWMS is not being explicitly developed to assist the monitoring of sites under the purview of LM, it is expected that some of the techniques and monitoring technologies identified in the strategy (e.g., in situ sensors, geophysical monitoring methods, unsaturated zone monitoring techniques) will be helpful in monitoring radionuclide fate at some LM facilities.

Table I. U.S. Government Initiatives for Advancing the Science of Subsurface Monitoring at Contaminated Sites

Government Agency	Initiative	Description and Features
DOE Office of Cleanup Technology	Performance Monitoring Workshop [5]	Summary report from a DOE-sponsored workshop on performance monitoring. Emphasizes an integrated system combining technical and risk goals, mass flux and mass balance concepts, geophysics and other spatially integrated methods, push-pull tests, optimization, and autonomous monitoring.
DOE Idaho National Laboratory	Structural Approach to Performance Monitoring [6]	An integrated approach to performance monitoring designed to overcome current inadequacies and inefficiencies by clarifying monitoring objectives, automating data collection, optimally managing data, sharing near-real-time data, and using powerful analysis tools and appropriately experienced personnel.
DOE Nevada Site Office, Bechtel Nevada, and Ames Laboratory	Advanced Monitoring System Initiative (AMSI) [8]	Initiative seeks to accelerate development and utilization of advanced monitoring tools and sensors for radionuclides and metals in the environment, particularly for DOE needs. Unique field sites at Nevada Test Site facilitate the demonstration and testing of sensor technologies and other monitoring technology.
NRC Office of Nuclear Regulatory Research	Integrated Ground-Water Monitoring Strategy (IGWMS) [9,10]	NRC-centric monitoring strategy designed to support performance assessments of nuclear facility sites, particularly those of NRC licensees. Focuses on assessing effectiveness of contaminant isolation, informing stakeholders regarding performance indicators, identifying plumes and preferential pathways, optimally managing data, and quantifying system uncertainties.
EPA Office of Research and Development	Inorganics Framework Document [11]	An ongoing effort to develop a tiered approach to evaluating the feasibility of monitored natural attenuation (MNA) of metals and radionuclides and developing ways to monitor their attenuation. Attenuation of metals and metalloid levels occurs by immobilization.
EPA National Risk Management Research Laboratory	Performance Monitoring of MNA Remedies for Volatile Organic Compounds [12]	An EPA document that provides guidance for verifying MNA as a remedy for remediating aquifers contaminated with organic chemical solvents and fuel hydrocarbons. Focus is placed on monitoring systems that characterize three-dimensional plumes and the biogeochemical processes occurring in and near the plumes. Provides guidance on selecting horizontal and vertical locations for monitoring of biogeochemical indicator parameters.
DOD Air Force Center for Environmental Excellence	Monitoring and Remediation Optimization System (MAROS) [13,14]	A computer-based decision support system designed to reduce temporal and spatial redundancy associated with sampling of monitor wells. Methods available in the software include parametric and non-parametric trend analyses, techniques for evaluating plume stability, and a combined graphical and computational approach to identifying redundant monitor wells.
DOD Air Force Center for Environmental Excellence	Geostatistical Temporal/ Spatial Optimization [17]	A computer-based decision support system that uses statistical and geostatistical methods to identify ways of minimizing temporal and spatial redundancy in monitoring systems. The software facilitates data exploration for preparation of data sets that are amenable to geostatistical analysis.

Two EPA initiatives examine the assessment of monitored natural attenuation (MNA) at sites regulated under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) or the Resource Conservation and Recovery Act (RCRA). The Inorganics Framework Document encompasses ongoing efforts on the part of EPA to develop a tiered approach to not only evaluate the feasibility of MNA for metals and radionuclides but also to monitor the effectiveness of MNA systems for these inorganic contaminants.[11] With this approach, monitoring systems will be designed to demonstrate the long-term capacity and stability of contaminant attenuation mechanisms. The Inorganics Framework Document identifies constituent immobilization as the primary process for attenuating the concentrations of contaminant metals and metalloids. Nonradioactive elements considered in this initiative consist of seven metals, two metalloids, and the anions nitrate and perchlorate. The framework also focuses on MNA of 12 radionuclides.

The EPA initiative referred to as Performance Monitoring of MNA Remedies for Volatile Organic Compounds [12] provides guidance for verifying the efficacy of MNA in groundwater at sites contaminated by volatile organic chemical solvents and fuel hydrocarbons. Monitoring under this approach concentrates on delineating the three-dimensional nature of contaminant plumes and identifying and quantifying the physicochemical processes that effect contaminant attenuation within and along the borders of the plumes. In accordance with the emphasis on multi-dimensional characterization, guidance is presented for selecting vertical intervals for monitoring in addition to optimal locations downgradient of contaminant source areas. Because the bioattenuation of volatile organic compounds (VOCs) affects local geochemistry, this EPA initiative stresses not only the assessment of contaminant concentrations but also biogeochemical process indicators, such as measures of redox potential. The temporal and spatial variabilities of these surrogate parameters are considered important to demonstrate the sustainability of MNA. It is recommended that distinct remedial objectives and performance criteria for MNA are defined, and that objective quantitative tools be used to assess compliance with cleanup goals.

The recommendation from the 2005 DOE performance monitoring workshop [5] to use formal optimization methods for improving monitoring network design and reducing monitoring frequency reflects wide recognition that long-term surveillance of the subsurface at a large number of sites creates the potential for significant cost liability. The U.S. Air Force Center for Environmental Excellence (AFCEE) has spearheaded the development of two optimization tools that are representative of techniques LM can use to minimize monitoring costs at a site while meeting pertinent data quality objectives. It is important that the term “optimization” be clarified when considering the use of these tools. Rather than being based on “true” optimization, which implies searching an entire solution space for the single best result, the AFCEE methods are more like decision analysis techniques, in which a finite number of choices are evaluated. Also, these methods only take into account the sampling of an explicit network of monitoring wells, rather than being allowed to consider alternative networks or the use of monitoring technologies other than the sampling of wells.

One of the AFCEE initiatives has resulted in the Monitoring and Remediation Optimization System (MAROS) [13,14], a computer-based decision-support system that helps minimize locations and frequency of sampling for contaminant concentrations while continuing to ensure adequate monitoring of remedy performance. Temporal trends (parametric and non-parametric) in concentrations are analyzed with the MAROS software along with evaluations of plume stability to determine an initial recommended level of monitoring frequency (extensive, moderate, limited) for a site. These techniques assist in identifying temporal redundancy, in which samples are taken in time that are highly correlated with other samples in the same time series that provide little additional information about temporal trends. A relatively simple, combined graphical and computational technique (Delaunay triangulation method) is used to identify monitoring locations contributing to sampling redundancy (i.e., monitoring wells that contribute little additional information regarding plume characterization because of their spatial correlation with other monitoring wells).[13] A modified Cost Effective Sampling method is also available in MAROS for determining whether quarterly, semi-annual, or annual sampling is most appropriate for a site. MAROS is mentioned as a possible decision analysis tool in EPA's *Roadmap to Long-Term Monitoring Optimization.*[15] The performance of MAROS and another publicly available approach to optimizing monitoring programs at contaminated sites was recently provided as part of an EPA-sponsored demonstration of these tools.[16]

The AFCEE system referred to as Geostatistical/Spatial (GTS) Optimization [17] is similar to MAROS in that it helps identify optimal sampling locations and frequencies. However, the GTS software is distinguished from MAROS by its use of geostatistical methods (variogram analysis) to minimize temporal redundancy and a technique called multiple indicator local regression to minimize spatial redundancy. GTS Optimization also provides data exploration tools [17] that help facilitate the development of data sets that are amenable to geostatistical analysis. Though the software is relatively simple to apply, some formal training in the use of statistical and geostatistical methods is helpful in ensuring that logical decisions are made regarding sampling network design.

Several other approaches and methods for optimizing subsurface monitoring systems are available in the public domain. The American Society of Civil Engineers provides a relatively recent summary of the state of the art for long-term groundwater monitoring [18] with more discussion of the optimization tools that have been developed thus far.

Though the motives of the respective government agencies listed in Table I might differ, the initiatives they are sponsoring share several common themes regarding monitoring. These include the use of mass flux and mass balance concepts to demonstrate groundwater restoration, automated monitoring systems, indicator parameters reflective of subsurface chemistry, chemical- and process-specific sensors, monitor network optimization, optimal data management, geophysical and other spatially integrated characterization methods, and data analyses by qualified personnel.

ENHANCED UNDERSTANDING OF TRANSPORT PROCESSES

Biogeochemical Processes

It has long been realized that the fate of contaminants in groundwater can be affected by local aquifer geochemistry, both as a result of ambient background conditions and any changes in water chemistry induced by the introduction of contaminants into the subsurface. However, only during the past 10 to 15 years has greater attention been given to the effects of geochemical conditions on the performance of groundwater remedies. Many engineered remedies like pump and treat were designed decades ago using flow-and-transport models that did not accurately account for the chemical reactions that can occur in the subsurface and influence the mobility of contaminants. With heightened interest during the 1990s in more passive approaches to aquifer remediation, it became evident that a better understanding of geochemical processes in soil and groundwater was key to assessing the performance of such remedies. As the knowledge base regarding chemical reactions in the subsurface has expanded, new quantitative models have been developed with the intent of more accurately projecting and evaluating the efficacy of geochemically influenced remediation. Though many of these newer models are not commonly used to select a remedy, there is a greater awareness today as to why subsurface chemistry, particularly as affected by aquifer heterogeneity, might impede the progress of some pump-and-treat systems.

Much of the work dealing with geochemical effects on contaminant fate and transport has concentrated on abiotic reactions in the subsurface. Since the early 1990s, however, even keener interest has been generated in biologically mediated chemical reactions in porous media. Part of the interest in biogeochemical processes stems from the recognition that heterotrophic bacteria are capable of degrading many organic contaminants (i.e., biodegradation), which makes possible the natural attenuation of some organic species.[19] Additional enthusiasm has resulted from the use of organic chemical amendments to manipulate the redox state of contaminated zones, thereby affecting the mobility of inorganic chemical species. This latter type of remediation is a form of in situ biostimulation that typically relies on the biodegradation of organic amendments to produce anaerobic conditions in groundwater and concomitant reductions in redox potential. The creation of chemically reducing conditions causes many metal and radionuclide elements to convert to a less oxidized state, in which they tend to be less soluble.[20] The reductants in these cases are typically organic acids or hydrogen. Research on this form of bioremediation continues under the DOE-sponsored Natural and Accelerated Bioremediation Research (NABIR) Program.[21]

Significant research has been conducted on biogeochemical processes that affect the fate of uranium in the subsurface. Much of this work is driven by the possibility that uranium in groundwater can be immobilized in situ via biostimulation.[22] The mobility of uranium in the environment is largely determined by its oxidation state. Oxidized, hexavalent uranium, U(VI), is quite soluble and can readily migrate with groundwater, whereas reduced tetravalent uranium, U(IV), is highly insoluble and virtually immobile. Hexavalent uranium typically dissolves in water as uranyl anions (UO_2^{2+}) and tetravalent uranium precipitates as uraninite (UO_2). Thus, at sites contaminated by uranium, the potential exists to remove it from groundwater by creating subsurface conditions that reduce U(VI) to U(IV).[20,21] This process is typically accomplished through stimulation of iron-reducing and sulfate-reducing bacteria in contaminated zones. The amendments used to initiate this process are organic carbon sources that degrade to the reductants acetate and hydrogen.[22]

Biologically mediated uranium reduction is a straightforward concept that is relatively easy to understand. However, the biogeochemistry of uranium in some environments can be complex, making its immobilization sometimes difficult to achieve. Sorption of U(VI) to sediments can affect the bioavailability of uranium, and the presence of carbonate, which tends to complex with U(VI) in the aqueous phase, can affect its sorption.[23] In addition, nitrate, which is often a co-contaminant with uranium, must be removed from solution before U(VI) reduction can occur.[24]

Uranium biogeochemistry is also complicated by possible remobilization of U(VI) after biostimulation because of the reoxidation of U(IV) in uraninite. A study of induced microbial uranium reduction in nitrate- and sulfate-containing groundwater from a New Mexico tailings site indicated that reemergence of oxidizing conditions did not lead to significant remobilization of uranium.[25] However, more recent studies have suggested that uranium is readily remobilized in some circumstances [26], even under persistent reducing conditions.[23]

The varied findings regarding uranium geochemistry exemplify the complex transport behavior of most metals and radionuclides that occur as contaminants in groundwater. Consequently, much remains to be learned about the interrelated effects of biological and chemical processes in the subsurface and the mechanisms by which they can affect the mobility of inorganic contaminants in different hydrogeologic settings. The results of ongoing research in these areas will be helpful in assessing the progress of aquifer cleanup at any LM sites where biostimulation might be used to immobilize inorganic species and possibly at other sites where either natural processes or more aggressive remedies are used to attenuate contaminant concentrations.

Effects of Transient Flow

Though groundwater flow in most aquifers varies temporally, it is common in assessments of associated contaminant transport to assume the flow is steady and unidirectional. In aquifer systems that are affected by significant hydraulic stresses, this assumption may lead to inaccurate estimates of contaminant mass flux and plume attenuation. In recent years, studies of the effects of transient flow on contaminant transport in groundwater suggest that improved means of measuring transient flow fields and associated mass fluxes would better explain observed plume behavior and would enhance the assessment of remedy performance over long time periods.

The effects of transient flow on plume disposition are commonly observed in the form of enhanced mechanical dispersion.[27] When this enhanced dispersion is significant in directions transverse to the predominant direction of flow, the mixing of dissolved contaminants with uncontaminated water and sediment increases noticeably. This in turn leads to dilution of the contaminant mass in a plume and, in the case of many organic chemical contaminants, increased biodegradation by natural means.[27] The stable length reached by a plume that is susceptible to natural attenuation by dilution and biodegradation will be relatively small if effective transverse dispersion is significant and relatively large if transverse dispersion is minuscule.

Mechanical dispersion in porous media transport results from local variations in water velocity around a mean pore-water velocity.[28] Historically, these variations have been mostly attributed to nonidealities in aquifers that are observed at three different scales: microscopic (local scale), macroscopic (local-to-field scale), and megascopic (field-to-regional scale). The nonidealities at a microscopic scale, which comprise features like pore-size distribution and different pore geometries, make only a minor contribution to dispersion. The greatest amounts of dispersion associated with contaminant plumes are typically observed at a macroscopic scale, where the nonidealities mostly occur in the form of aquifer heterogeneity (i.e., spatially variable hydraulic conductivity). Thus, dispersion on a macroscopic scale is expected to be larger in a very heterogeneous aquifer than in a less heterogeneous system. Mathematical approaches to explaining macrodispersion predict that mechanical dispersion coefficients increase as a function of plume length.[29] Dispersion transverse to the predominant direction of groundwater flow is often assumed to be smaller than the mixing that occurs in the direction of flow (longitudinal dispersion).

It is helpful to view transient groundwater flow as adding to, or enhancing, the macrodispersion caused by aquifer heterogeneity alone. Such dispersion enhancement actually occurs because of contaminant advection in alternating directions, which tends to produce particle traces that repeatedly traverse a mean flow path (Fig. 1.). Erratic flow paths of this kind are sometimes observed at sites located in the vicinity of floodplains that adjoin rivers [4] or in response to transient mounding produced in unconfined aquifers from storm-related episodic recharge in hummocky terrain.[30] As a consequence, transverse dispersion coefficients used to characterize mixing along the flanks of a plume increase measurably [27], as do vertical dispersion coefficients in response to recharge events.[31] A recent study of effective dispersion induced by temporally fluctuating flow indicated that resulting transverse dispersion coefficients can be quite large and comparable in magnitude to the longitudinal dispersion coefficients associated with steady flow.[32]

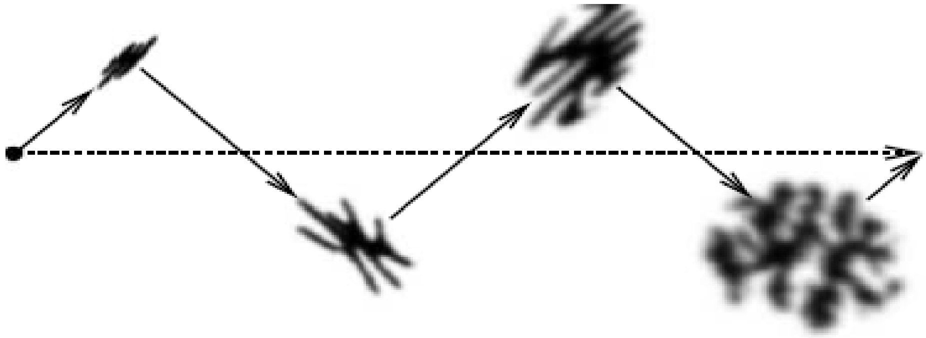

Fig. 1. Effect of changes in flow direction on transverse dispersion (from Ref. 27)

Because the processes contributing to natural attenuation of groundwater contamination can be both mass destructive (e.g., biodegradation, radioactive decay) and nondestructive (dilution), the eventual fate of contaminant plumes could be predicted more accurately if the relative magnitudes of these different forms of attenuation were better quantified. Given the potentially significant effects that transient groundwater flow fields can have on both types of processes, it stands to reason that improved means of measuring both short- and long-term variations in groundwater flow (direction and magnitude) would be helpful for this purpose.

RELATED ADVANCES IN MONITORING TECHNOLOGY

Geoelectric Methods

Literature describing state-of-the-art geophysical characterization methods indicates that significant advances are being made using geoelectric techniques to identify contaminant-related processes in the subsurface. Some of the more promising geoelectric tools make use of induced polarization (IP).[33] This is a class of electrical methods that measures electrochemical responses of subsurface materials to either a pulse of injected current or alternating current. The electrochemical processes induced by the current are measured in units of voltage between potential electrodes. Measured responses are affected by variations in the mobility of ions and, where metallic minerals are present, variations because of the change from ionic to electronic conduction.

During the past decade, use of a powerful IP method called complex resistivity has increased. This technique is used to measure the phase difference between real and imaginary parts of complex resistivity of subsurface materials [33], which may make it possible to reveal chemical reactions occurring in a contaminated zone. The idea is that pollutants may alter or influence ambient groundwater chemistry in such a manner that the complex resistivity response will be anomalous relative to unpolluted areas. Though this possibility has yet to be fully demonstrated, complex resistivity IP represents one of the few geophysical means of possibly performing noninvasive detection of chemical precipitation and other reactions.

Much of the current work with complex resistivity is performed at a laboratory scale. Some column studies are aimed at delineating zones where redox conditions have been altered by bacterial respiration of organic amendments, which in turn leads to the precipitation of metal sulfides.[34] Field applications of this technology are also being carried out through the NABIR Program at a former uranium mill tailings site in Colorado in hopes of detecting zones of microbially induced uranium reduction in groundwater. Additional laboratory investigations focused on the biodegradation of immiscible petroleum-related liquids have demonstrated how complex resistivity methods can be used to detect enhanced mineral weathering of sediments containing the contamination.[35]

Given that most current uses of IP for detecting subsurface contamination are in the research stage, it seems unlikely that complex resistivity could soon be employed to monitor contaminant plumes at LM sites. However, it is feasible that these and other geophysical methods might be available for monitoring at sites that involve decades or hundreds of years of LM stewardship.

Groundwater Flow Sensors

The technologies behind two different in situ sensors show promise for monitoring transient contaminant mass fluxes and identifying enhanced attenuation of contaminant plumes resulting from transient changes in groundwater flow. One of these, the passive flux meter, uses a sorptive permeable medium placed in a well to intercept contaminated groundwater and release a tracer embedded in the permeable medium. By measuring the masses of tracer lost and contaminant sorbed to the medium, quantitative estimates can be made of temporally averaged Darcy velocity in ambient groundwater and the associated contaminant mass flux. The passive flux meter can be used to gauge mass flux of a range of organic and inorganic contaminants.

A passive flux meter placed in a well can be fitted with segmented sorptive media to provide estimates of vertical variations in Darcy velocity and mass flux.[36] After time periods of a few to several days, the sensor is removed from the well, and the sorptive media are analyzed. The velocities and mass fluxes produced by this technique are horizontal in nature and represent cumulative quantities over the time period that the sensor was exposed to groundwater. The passive flux meter has been tested in both laboratory and field settings.

The second in situ technology, referred to as the in situ permeable flow sensor, uses measurements of heat flow past the sensor to estimate groundwater flow direction and magnitude (Darcy velocity).[37] This instrument differs from other flow measurement technologies because it is buried in direct contact with the materials in which the flow is measured rather than being suspended in a well. It is also distinguished by its capacity to monitor all three components of the three-dimensional Darcy velocity vector.

The basic operating principle behind in situ permeable flow sensor technology is to bury a thin cylindrical heater in the ground at the point where groundwater velocity is to be measured. A uniform heat flux is emitted from the cylinder, which results in a temperature distribution on the cylinder surface that varies as a function of the direction and magnitude of ambient flow.[37] The surface temperatures of the cylinder are transferred to a data recorder, and a numerical inversion algorithm is used to translate them into Darcy velocities in both horizontal and vertical directions. In relatively permeable aquifers, the average velocity during the course of a day can be discerned. These sensors have been tested in both the laboratory and the field.

Though they are still considered somewhat experimental, the passive flux meter and the in situ permeable flow sensor technologies represent significant improvements compared with conventional methods for estimating groundwater flow magnitudes and directions. Traditional approaches to computing Darcy velocity use hydraulic head measurements in a number of screened boreholes to determine hydraulic gradients, which are multiplied by estimates of hydraulic conductivity to estimate the velocity field between the boreholes. The resulting estimates are subject to a great deal of uncertainty [38] because of the uncertainties inherent in measuring heads at wells and hydraulic conductivity estimates based on aquifer tests. Thus, both sensor technologies produce more direct measures of groundwater flow than has typically been available, which can improve assessment of remedy performance.

Both flow sensor methods might be useful for confirming the presence and sustainability of natural attenuation processes at LM sites. The direct measure of contaminant mass flux provided by the passive flux meter would be most useful at sites where flow directions and velocities tend to be relatively steady. However, a fair amount of labor would be required to prepare sorptive media with resident tracers and subsequently analyze the information contained in the media. The passive flux meter does not appear well suited to recording relatively minor changes in flow direction or to monitoring short-duration changes in flux because the data collected are cumulative and time averaged.

In groundwater systems strongly affected by external hydraulic stresses like episodic and spatially variable recharge, the in situ permeable flow sensor would be helpful in identifying short-duration perturbations in flow that enhance contaminant attenuation. The in situ permeable flow sensor is uniquely suited to this purpose not only because it continually records flow phenomena when operating but also captures vertical flow components that might be crucial for the effective mixing of organic chemical species with oxidants, nutrients, and other reactants. Existing in situ permeable flow sensor deployments are sometimes limited by difficulties in establishing adequate contact between the sensors and surrounding aquifer material, and the sensor could be improved by finding ways to increase its operative life of about 1 to 2 years.

CONCLUSION

DOE-LM has adopted a strategic plan that facilitates the adaptation of advances in remediation science to long-term surveillance at DOE closure sites. Many of these advances are anticipated to be particularly useful for monitoring relatively passive approaches to groundwater remediation, such as remedies based on natural attenuation and phytoremediation. In accordance with its strategic plan, LM is tracking several formal initiatives that are likely to contribute to the monitoring of subsurface contaminant concentrations and associated transport processes at DOE facilities. Descriptions were provided for eight programs of this nature that are or will be the products of U.S. government agencies. Despite the varied motives behind these programs, many common themes are observed among them, including the use of mass flux and mass balance concepts, automated monitoring systems, indicator parameters reflective of subsurface chemistry, sensors, monitoring network optimization, optimal data management, geophysical and other spatially integrated characterization methods, and data analyses by qualified personnel.

In addition to the various initiatives focused on improving long-term monitoring of contaminated sites, advances in our understanding of the interrelated effects of physical, chemical, and biological processes in subsurface domains are expected to lead to more efficient monitoring of groundwater contamination at DOE sites over long periods of time. Examples of such advances are observed in studies of biogeochemical processes associated with uranium mobility and the effects of transient groundwater flow on contaminant attenuation. New technologies potentially suited to monitoring these subsurface processes include geoelectric methods for identifying subsurface zones of active, contaminant-affected chemistry and in situ sensors for tracking changes in groundwater velocity and contaminant mass flux.

Adaptation of advances in remediation science to subsurface monitoring is expected to reduce the costs of long-term surveillance at DOE closure sites while local human health and the environment remain protected. Decisions regarding the use of a new technology will depend on site-specific conditions and whether the benefits of implementing the technology justify its cost.

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