Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy.

Disclaimer:

Biogeochemical Gradients as a Framework for Understanding Waste Site Evolution

Miles Denham and Karen Vangelas
Building 773-42A
Savannah River National Laboratory, Aiken SC 29808

Abstract

The migration of biogeochemical gradients is a useful framework for understanding the evolution of biogeochemical conditions in groundwater at waste sites contaminated with metals and radionuclides. This understanding is critical to selecting sustainable remedies and evaluating sites for monitored natural attenuation, because most attenuation mechanisms are sensitive to geochemical conditions such as pH and redox potential. Knowledge of how gradients in these parameters evolve provides insights into the behavior of contaminants with time and guides characterization, remedy selection, and monitoring efforts. An example is a seepage basin site at the Savannah River Site in South Carolina where low-level acidic waste has seeped into groundwater. The remediation of this site relies, in part, on restoring the natural pH of the aquifer by injecting alkaline solutions. The remediation will continue until the pH up-flow of the treatment zone increases to an acceptable value. The time required to achieve this objective depends on the time it takes the trailing pH gradient, the gradient separating the plume from influxing natural groundwater, to reach the treatment zone. Predictions of this length of time will strongly influence long-term remedial decisions.

Introduction

In recent years there has been growing interest in monitored natural attenuation (MNA) as a remedy for sites contaminated with metals and radionuclides. This arises from an accumulating base of science that indicates long-term immobilization of these contaminants is feasible and an increasing effort to transition away from unsustainable remediation technologies. The growing acceptance that MNA is appropriate for many waste sites is marked by the release of guidance for assessing MNA recently published by the U.S. Environmental Protection Agency (EPA, 2007a; EPA, 2007b) and the formation of an Interstate Technology & Regulatory Council team dedicated to natural attenuation process for metals and radionuclides. The bar for demonstrating the viability of MNA as a remedy for metal and radionuclide contamination has been set appropriately high by the EPA guidance, but meeting this standard may seem intractable to many waste site managers. To address this, the U.S. Department of Energy's (DOE's) Office of Environmental Management is funding the Savannah River National Laboratory (SRNL) to lead a project to develop tools and guidance that will facilitate the use of natural-attenuation based remedies for sites contaminated with metals and radionuclides. A focus of this project will be new ways of understanding waste site evolution as a technical framework by which to develop a conceptual site model.

Understanding waste site evolution is critical to demonstrating the viability of natural attenuation-based remedies. These remedies include MNA and enhanced attenuation (EA). Enhanced attenuation for metals and radionuclides is similar to EA as defined by Wilson et al. (2007) for chlorinated solvents:

"...managing all or part of a contaminant plume in soil and groundwater by initiating and/or augmenting natural and sustainable decontamination and attenuation mechanisms and by documenting the resulting attenuation capacity."

The term sustainable takes on a different dimension when EA is used for metals and radionuclides because these contaminants may be required to remain immobilized for centuries, or in some cases, millennia. As a waste site evolves, the biogeochemical conditions change and affect the mechanisms responsible for contaminant immobilization. Thus, to demonstrate sustainability of a remedy requires evaluating attenuation mechanisms at conditions representative of those throughout the evolution of the waste site.

A contaminant plume is a transient perturbation of natural subsurface conditions that can change the chemistry, mineralogy, and microbiology within the aquifer as the plume migrates. Over time as the contamination source is depleted, or contained, the plume will eventually migrate to an exposure point or dissipate, and background uncontaminated groundwater will migrate through the zone traversed by the plume. Evolution of a waste site begins when the plume is introduced to the subsurface and ends when conditions have returned to near natural. Evolution of the waste site also includes all remedial actions, such as capping or removal of the source and any active treatment of the plume.

Understanding the overall biogeochemical evolution of a waste site is particularly important for sites at which active remediation is ongoing. It is this evolution that will dictate how long active remediation must continue before it can be transitioned to more passive remediation that relies predominantly on natural attenuation. Remediation is an additional perturbation of the original perturbation caused by the introduction of the contaminant plume. As such, remediation will also be affected by background water passing through the remediation zone, changing overall biogeochemical conditions. Thus, only by understanding the overall biogeochemical evolution can the question be answered of how long performance objectives can be sustained after active remediation is stopped. This, in turn, is key to remedial decisions about continuing active remediation or altering remediation processes to be more sustainable and cost effective.

The changes to the system caused by the plume itself and subsequent active remediation of the plume are a strong influence on waste site evolution. Typically, these are changes to the mineralogy and microbiology of the plume/remediation zone, although changes in flow paths are possible. Consider, for example, an acidic plume in a non-calcareous aquifer in which fine-grained surface active minerals have dissolved in the acid. This could cause changes in flow, but more importantly it causes a loss of adsorption sites. This, in turn, results in less adsorption of contaminants than would be expected as pH increases either naturally or from active remediation. This also results in a quicker return to natural pH values because there are fewer sites for H^+ adsorption and, hence, a loss of acidic buffering capacity. Thus, an understanding of overall waste site evolution must account for the plume induced and remediation induced changes to the aquifer.

Waste Site Evolution and Biogeochemical Gradients

One framework for addressing waste site evolution is to focus on the biogeochemical gradients induced by the contrasting chemical composition of a plume and the natural groundwater. Likewise, active remediation involving injection of reagents into the aquifer to immobilize contaminants has a similar effect. Biogeochemical gradients are defined by relatively abrupt changes in biogeochemical conditions and, thus, are often the locations of sharp contrasts in contaminant mobility. Away from these gradients, changes in contaminant mobility along the flow direction are relatively small. Certain biogeochemical gradients, such as pH and Eh, may control the migration of multiple contaminants. Thus, they are a way to make understanding the natural attenuation of multiple contaminants a tractable problem by minimizing the number of parameters needed to characterize the system and focusing the characterization on discreet portions of the plume system.

When a contaminant plume is introduced to the subsurface a leading biogeochemical gradient is created at the leading interface of the contaminant plume and natural groundwater (Exhibit 1). Dilution of the plume, reaction with aquifer minerals, adsorption of plume constituents, desorption of natural constituents, and changes in microbiology can all occur at this gradient. Different types of gradients move at different rates, although all are driven by the same hydrodynamic forces. Consider as an example that a leading gradient caused by dilution alone moves according to hydrodynamic forces and is unimpeded by chemical reactions. In contrast, a pH gradient is impeded by the buffering reactions associated with aquifer mineral dissolution and adsorption of free protons (H^+). Similarly, a leading redox gradient can be impeded by microbiological reactions and reaction with redox sensitive aquifer minerals.

Trailing gradients form where natural up-flow groundwater meets the infiltrating plume or enters the zone affected by the plume. As long as plume infiltration is relatively constant, the trailing gradient is stationary. Once plume flux from the vadose zone to the saturated zone is eliminated or substantially reduced, the trailing gradient migrates into and through the plume zone (Exhibit 2). Trailing gradients are controlled by hydrodynamic forces, dilution, reaction with plume-altered minerals, and the influx or elimination of nutrients to sustain microbial growth. Examples of reactions with plume altered minerals are desorption of free protons from plume zone minerals or oxidation of reduced minerals created within the plume zone.

One way in which consideration of biogeochemical gradients simplifies long-term prediction of natural attenuation is that contaminants can be grouped by how their migration is controlled. The mobility of many metals and radionuclides is sensitive to one or both of the master variables, pH and redox potential. Many plumes have extreme pH values relative to natural groundwater because the origins of the plumes are process solutions designed to keep the contaminants dissolved. Acidic plumes are also often associated with mining sites. Extreme redox values do occur in some waste streams, but in plumes they are as commonly caused by incidental co-disposal of organic compounds. Microbial degradation of the organic compounds in the subsurface then drives redox potential to reducing values. Exhibit 3 shows some common metal and radionuclide contaminants and whether their mobility is sensitive to pH, redox potential, or both. Most of these metals and radionuclides are sensitive to both, although the degree of sensitivity varies. Thus, at sites with multiple contaminants, tracking and understanding migration of these gradients is an efficient framework for evaluating attenuation of the contaminants.

The other way in which consideration of biogeochemical gradients simplifies long-term prediction of natural attenuation is that it compartmentalizes characterization and modeling into zones of importance. This is based on the recognition that large changes in mobility only occur across controlling gradients. It focuses characterization and modeling on the leading and trailing gradients, which are most important in controlling overall contaminant mobility. If a leading gradient can be identified, it is more important to characterize what is present at and down flow of that gradient than what is between the leading and trailing gradient. Likewise, it is more important to understand and model the processes occurring in those parts of the aquifer in the vicinity of the gradients and less emphasis can be given to parts of the aquifer between these gradients.

Exhibit 4 shows results of a simple 2-D reactive transport calculation illustrating the development of a pH gradient. The calculation simulates 5 years of acidic (pH=3) waste injection into an aquifer with a natural pH of 6. Exhibit 4 shows the plume with leading and trailing pH gradients 10 years after the injection stopped. The simulation was performed with The Geochemist's Workbench® (Bethke, 2005). The sharp leading pH gradient is caused mostly by adsorption of the free protons of the acid onto the ferric hydroxide, with very minor acid neutralization by dissolution of ferric hydroxide. The migration rate of the gradient is inversely proportional to the amount of ferric hydroxide in the aquifer. On the up-flow side of the pH gradient, the mobility of most cationic contaminants is higher than on the down-flow side. Thus, contaminants that are only mobile at low pH can migrate only as fast as the leading pH gradient migrates. Conversely, anionic contaminants will tend to be less mobile on the up-flow side of the gradient, but will become more mobile as the trailing pH gradient migrates through the plume zone, resulting in higher pH values.

Trailing gradients often migrate slower and are less defined than leading gradients because the chemical composition of natural up-flow groundwater is usually less concentrated than the plume composition. The trailing gradient in Exhibit 4 is created by the natural groundwater containing hydroxyl ions migrating into the plume zone and encountering minerals, in this case ferric hydroxide, with acidified surfaces. The natural water has a hydroxyl concentration that is nearly 5 orders of magnitude lower than the free proton concentration of the acid that created the plume. So it requires much more of the natural groundwater water to de-acidify mineral surfaces than it required plume water to acidify them. Hence, the diffuse nature of the trailing gradient.

Biogeochemical gradients are also a useful organizing principle for assessing sustainability of active remediation. Most in situ active remediation for metals and radionuclides is essentially installation of an artificial biogeochemical gradient. This can be a pH, redox, mineralogical, or microbiological gradient or a combination of these. Once installed, this artificial gradient evolves under the same influences that control evolution of the biogeochemical gradients associated with introduction of the plume into the subsurface.

Consider the generic active remediation of a plume shown in Exhibit 5. Some reagent is injected into the plume to render contaminants immobile in the treatment zone. The longevity of a single application depends, in part, on the mechanism of contaminant immobilization. However, the longevity also depends on how long the conditions that immobilized the contaminant are sustained in the treatment zone. This is controlled by how rapidly the trailing gradient, separating treatment zone conditions from plume zone conditions, advances through the treatment zone.

In a reductive treatment for metals or radionuclides, whether bioreduction or abiotic reduction, an artificial redox gradient is established between the treatment and plume zones. The trailing redox gradient advances through the treatment zone at the rate at which dissolved oxygen or other oxidizing constituents advance. This depends on how rapidly groundwater moves and the redox conditions of the plume and/or natural groundwater, but is also strongly dependent on how the reductive treatment affects aquifer minerals. The minerals in an aquifer can act as redox buffers, so that abundant ferric iron minerals can buffer attempts to reduce contaminants.

Likewise, successful reduction of ferric iron minerals to ferrous iron minerals can buffer re-oxidation of reduced contaminants. Exhibit 6 shows possible reactions of hematite during a reductive treatment and possible subsequent re-oxidation reactions. If the treatment reduces hematite to dissolved ferrous iron, then this flows out of the treatment zone and residual redox buffering capacity is lost. On the other hand, if hematite is reduced to other solid phases, these act as redox buffers that slow the advance of the trailing oxidation gradient. The degree of buffering capacity depends on what phases are created because it requires different amounts of oxygen to convert different reduced iron minerals into 1 mole of hematite. For the re-oxidation products shown in Exhibit 6, the relative buffering capacities are:

Pyrite > Siderite > Magnetite

Thus, the post-treatment mineralogy is a key factor in the rate at which a trailing redox gradient will migrate and, in turn, the longevity of a reductive active remediation.

Post-treatment mineralogy is also important for treatments in which a reagent is injected to induce precipitation of contaminants. An example is the addition of phosphate to cause contaminant metals or radionuclides to precipitate or co-precipitate as insoluble phosphate minerals. In this case dissolved phosphate gradients are created between the treatment zone and the plume zone. Within the treatment zone the dissolved phosphate concentration is high enough to stabilize the phosphate minerals precipitated during treatment. At the trailing treatment gradient the phosphate concentration is lower on the up-flow side. As this gradient advances through the treatment zone, phases precipitated during treatment may re-dissolve. If the only phases precipitated were contaminant phosphates there is little phosphate buffering capacity. On the other hand, if a sufficient mass of phosphate minerals of iron, aluminum, and/or calcium precipitate, their dissolution as the trailing treatment gradient passes may buffer the phosphate concentration,, slowing the advance of the gradient.

If the treatment moves biogeochemical conditions from those in the plume toward natural conditions, the end-point of waste site evolution, then two biogeochemical gradients are important. One is the gradient established between the treatment and plume zones. The other is the trailing gradient of the plume itself. Take, for example, an acidic plume treated with an alkaline solution to raise the pH. Initially, there is a pH gradient established between the treatment zone and the acidic plume. The rate of advancement of that gradient through the treatment zone is slowed by adsorption of free protons onto surface active minerals. It may be further slowed by dissolution of minerals, such as aluminum hydroxides, that were precipitated during the initial injection. Repeated injections may be necessary until the trailing pH gradient of the plume reaches the treatment zone. At this point active remediation may stop because conditions have returned to near natural and acid is no longer present to mobilize contaminants.

These examples demonstrate that understanding the evolution of biogeochemical gradients during and after active remediation is important for assessing how long current active remediation systems must operate before natural attenuation can be relied on to keep risk below acceptable levels. These principles are also important in evaluating the sustainability of various remediation options so that the most appropriate and cost effective can be chosen.

Field Study Site

The DOE’s Office of Environmental Management is funding SRNL to develop the applied science and tools required to facilitate use of natural attenuation-based remedies at DOE sites contaminated with metals and radionuclides. During this project, SRNL will evaluate the use of biogeochemical gradients as an organizing principal for better understanding waste site evolution and its control on contaminant remediation.

The study will focus on the waste site associated with the F-Area Seepage Basins at the Savannah River Site. At this site, approximately 7 billion liters of predominantly acidic aqueous waste from nuclear processing facilities were disposed in un-lined basins from 1955 until 1988. The belief was that most of the radionuclides would be bound in the soils beneath the basins and would not significantly pollute groundwater. This was true for many of the radionuclides disposed, including plutonium isotopes and Cs-137, but many, such as Sr-90, uranium isotopes, I-129, Tc-99, and tritium, are now in the groundwater.

The geology of the site is made up of heterogeneous poorly consolidated quartz sands and clays. The quartz sands contain varying amounts of surface active minerals made up mostly of kaolinite, goethite, and hematite. Other minor clay minerals are present as well. The plume is stratified within the water table aquifer moving mostly within a highly transmissive unit along the top of a clay that confines the aquifer below and cropping out at seeplines along a stream approximately 400 to 600 meters from the basins.

The plume contains a large number of contaminants, the most important from a risk perspective being Sr-90, uranium isotopes, I-129, Tc-99, tritium, and nitrate. Groundwater remains acidic, with pH as low as 3.2 near the basins and increasing to approximately 5 at the plume fringes. The Atlantic Coastal Plain aquifer sediments that underlie the F-Area have been bathed with acidic solutions for about 40 years, but changes to their mineralogy and texture from this remain unknown. The dominant natural attenuation mechanisms are adsorption throughout the plume and dilution at specific locations. The basins were closed and capped in 1991 and in 1997 a pump-and-treat remediation system began operation. 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. Interaction of the plume with the wall mixes the stratified plume and alkaline solutions are injected into the gates in an attempt to neutralize the acidic groundwater and further attenuate Sr-90 and uranium isotopes. Exhibit 7 shows a schematic cross-sectional drawing of the plume and treatment wall.

The alkaline solutions are injected periodically, guided by monitoring the pH of groundwater down-flow of the injection gates. Injections are performed until groundwater down-flow reaches a pH between 9 and 10. When down-flow pH drops below 5, injection resumes returning the pH back to the target range. This is intended to reduce the flux of uranium and Sr-90 reaching the seepline and stream. To be sustainable, the base injection cycle must continue until the pH coming into the gates from up-flow is near 5, in other words, when the pH gradient trailing the plume reaches the barrier wall. This could occur naturally as the vadose zone is depleted of acid and clean water migrates through the plume zone or additional neutralization could be undertaken near the basins themselves. The additional neutralization would accelerate the migration of the trailing pH gradient. Thus, prediction of the time it will take for the trailing pH gradient to travel from the basins to the treatment wall is a critical piece of information for planning final phases of remediation.

Trends in concentrations of pH, tritium, and I-129 with time in groundwater from a well adjacent to the down-flow edge of the seepage basins suggest that the pH gradient is now beginning to move from the vadose zone into the saturated zone. Time zero in these figures is the date, 2/24/1991, of the first available concentration data for groundwater from this well and the data run through day 6,346, 7/10/2008. The time trend for pH in Exhibit 8 shows that the pH has been steadily rising in groundwater from this well since day zero. The patterns for tritium and I-129 indicate two factors contribute to this. The early decrease in tritium concentration (Exhibit 9) likely reflects decreasing water flux from the vadose zone after capping of the basin, and, since about day 2,500, the flux of tritium from the vadose zone has been at a steady state. This is supported by the decrease in the elevation of the water table beginning around day 2600 (Exhibit 10). However, the I-129 flux has been increasing since day 2,500 (Exhibit 11) rather than remaining constant. I-129 exists as an anion in groundwater and tends to be more mobile as pH increases. The disparity between the time trends of the two contaminants suggests that a trailing pH gradient may be emerging from the vadose zone. So, the early rise in pH was likely the result of a reduced flux of water from the vadose zone. Yet, the pH continued to rise after day 2,500 even as tritium concentrations remained relatively constant. This is due to the emergence of the pH gradient from the vadose zone.

This information on the movement of the pH gradient together with information on the mineralogy of the aquifer will be used to predict the travel time of the pH gradient from the basins to the treatment wall. This will allow long range planning for the next steps in the remediation of the plume associated with the F-Area Seepage Basins.

Summary

An important aspect of evaluating natural attenuation-based remedies for metal and/or radionuclide contaminated sites is the biogeochemical evolution of the waste site. Natural attenuation mechanisms are usually sensitive to the prevailing biogeochemical conditions. These conditions change as the waste site evolves and, thus, the degree of natural attenuation of contaminants changes with time. This must be considered when evaluating natural attenuation-based remedies for a site. Building a conceptual model of waste site evolution around the migration of biogeochemical gradients created by the contaminant plume and in situ remediation efforts can facilitate understanding and predicting waste site evolution. The SRNL has begun a study of natural attenuation-based remedies for metals and radionuclides with the object of developing approaches and tools that facilitate evaluation of these remedies. The study is funded by the DOE and will use the contaminant plume associated with the F-Area Seepage Basins on the Savannah River Site as field study area.

References

Bethke, C.M. (2005). The Geochemist's Workbench®, Release 6.0, University of Illinois.

EPA (2007a). Monitored Natural Attenuation of Inorganic Contaminants in Ground Water: Volume 1 – Technical Basis for Assessment. EPA/600/R-07/139.

EPA (2007b). Monitored Natural Attenuation of Inorganic Contaminants in Ground Water: Volume 2 – Assessment for Non-Radionuclides Including Arsenic, Cadmium, Chromium, Copper, Lead, Nickel, Nitrate, Perchlorate, and Selenium. EPA/600/R-07/140.

Wilson, K., Sewell, G., Kean, J.A., & Vangelas, K. (2007) Enhanced attenuation: its place in the remediation of chlorinated solvents. Remediation, Spring, 39-49.

Contaminant	pH	Redox Potential
Tritium	No	No
Cr(VI)	Yes	Yes
Ni	Yes	Yes*
Cu	Yes	Yes
As	Yes	Yes
Se	Yes	Yes
Sr-90	Yes	No
Tc-99	No	Yes
Cd	Yes	Yes*
I-129	Yes	Yes
Cs-137	Yes	No
Hg	Yes	Yes
Pb	Yes	Yes*
Ra-isotopes	Yes	No
Uranium-isotopes	Yes	Yes
Np-237	Yes	Yes
Pu-isotopes	Yes	Yes
Am-241	Yes	No

* -- Yes, only if sulfide mineralization is involved

Exhibit 3. A list of metal and radionuclide contaminants and whether their mobility is sensitive to pH and redox potential.

Reduction of Hematite	**Re-oxidation to Hematite**
Hematite + $6H^+$ + $2e^-$ = $2Fe^{+2}$ + $3H_2O$	Aqueous Fe^{+2} flushed from treatment zone
Hematite + $0.67H^+$ + $0.67e^-$ = 0.67Magnetite + $0.33H_2O$	0.67Magnetite + $0.17O_{2(a)}$ = Hematite
Hematite + $4H^+$ + $2HCO_3^-$ + 2e- = 2Siderite + $3H_2O$	2Siderite + $2H_2O$ + $0.5O_{2(a)}$ = Hematite + $2HCO_3^-$ + $2H^+$
Hematite + $4SO_4^{-2}$ + $38H^+$ + $30e^-$ = 2Pyrite + $19H_2O$	2Pyrite + $4H_2O$ + $7.5HO_{2(a)}$ = Hematite + $4SO_4^{-2}$ + $8H^+$

Exhibit 6. Potential reactions for reduction and re-oxidation of iron minerals during evolution of a site at which a reductive technology was used; hematite is conserved.

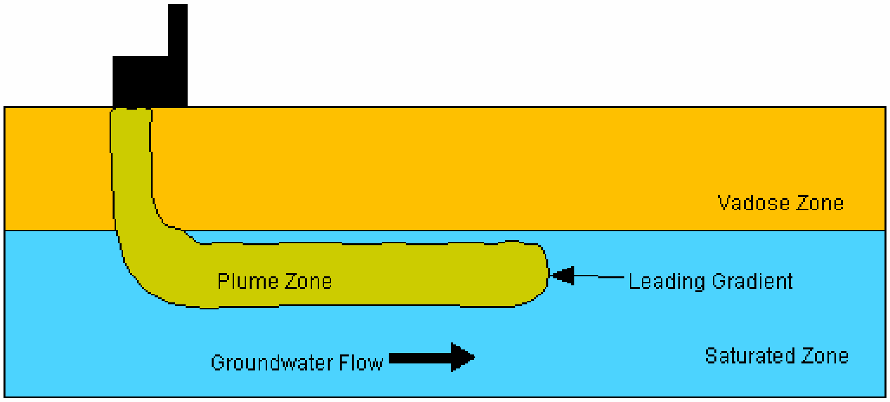

Exhibit 1. Depiction of the leading biogeochemical gradient at the front of a plume.

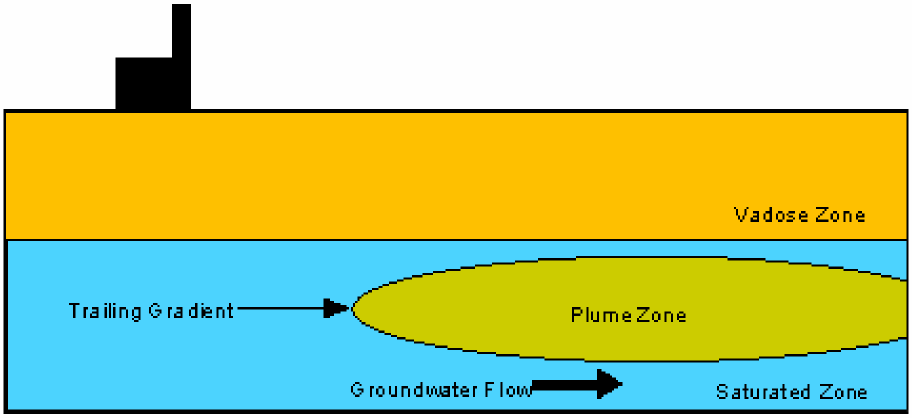

Exhibit 2. Depiction of a trailing biogeochemical gradient at the interface between natural groundwater and a contaminant plume following depletion or control of the contaminant source.

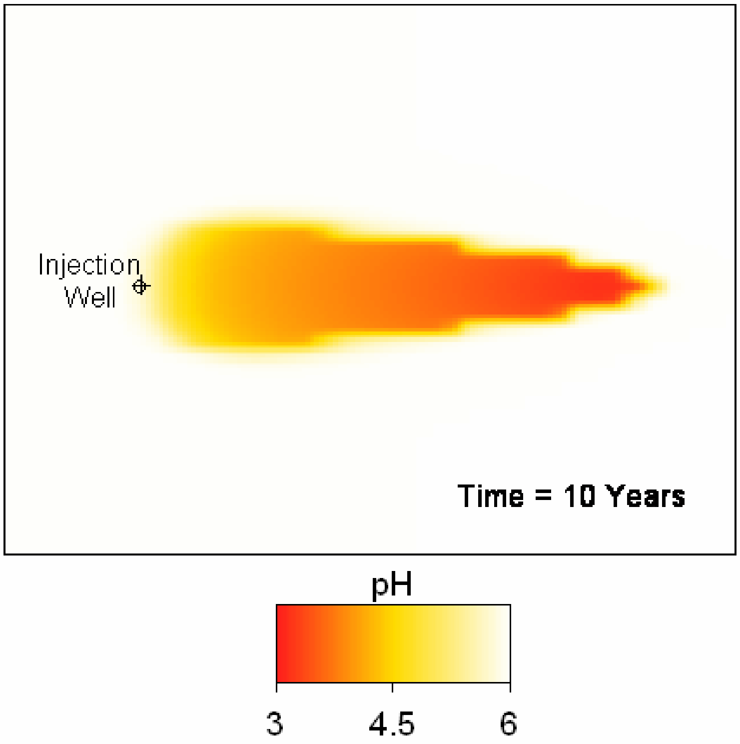

Exhibit 4. Simulation (2-D) of plume and pH gradient evolution from 5 years of injection of a pH=3 solution into natural groundwater of pH=5; planar view at 10 years following cessation of injection. Simulation done with The Geochemist's Workbench® (Bethke, 2005) with grid of 1 km x 1 km, porosity=30%, permeability=0.3 darcy, and ferric hydroxide content of 0.02 volume %.

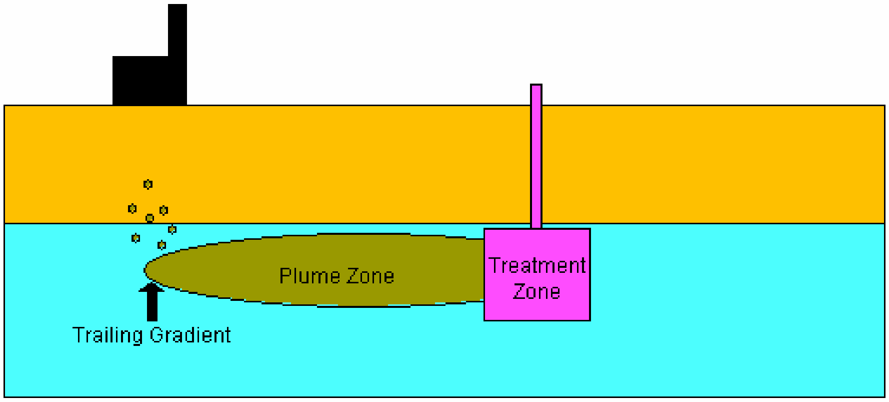

Exhibit 5. Drawing showing importance of the passage of the leading remediation induced gradient through the treatment zone and the passage of the trailing gradient of the plume through the treatment zone.

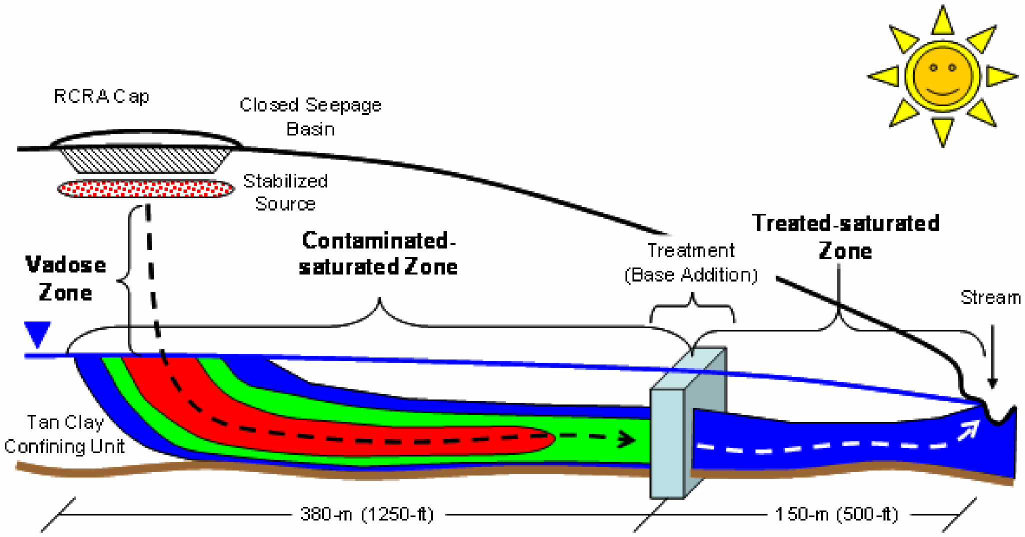

Exhibit 7. Cross-sectional depiction of F-Area Seepage Basins plume showing basins, plume, treatment wall, and stream.

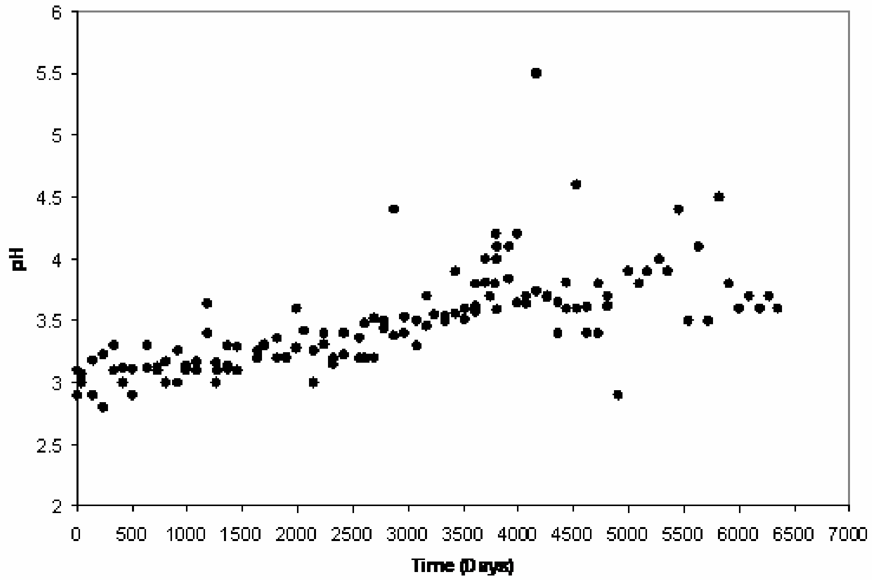

Exhibit 8. Time trend for pH in groundwater from a monitoring well adjacent to the down-flow edge of the basins. Time zero is 2/24/1991, the date of the first available data from this well.

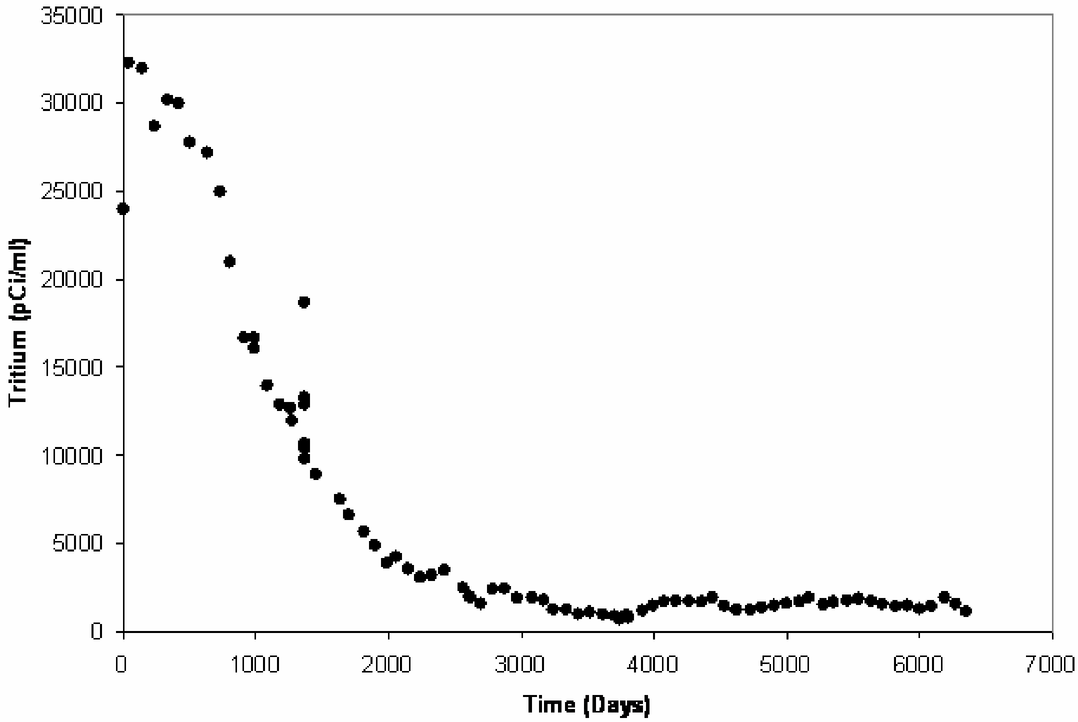

Exhibit 9. Time trend for tritium concentration (pCi/ml) in groundwater from a monitoring well adjacent to the down-flow edge of the basins. Time zero is 2/24/1991, the date of the first available data from this well.

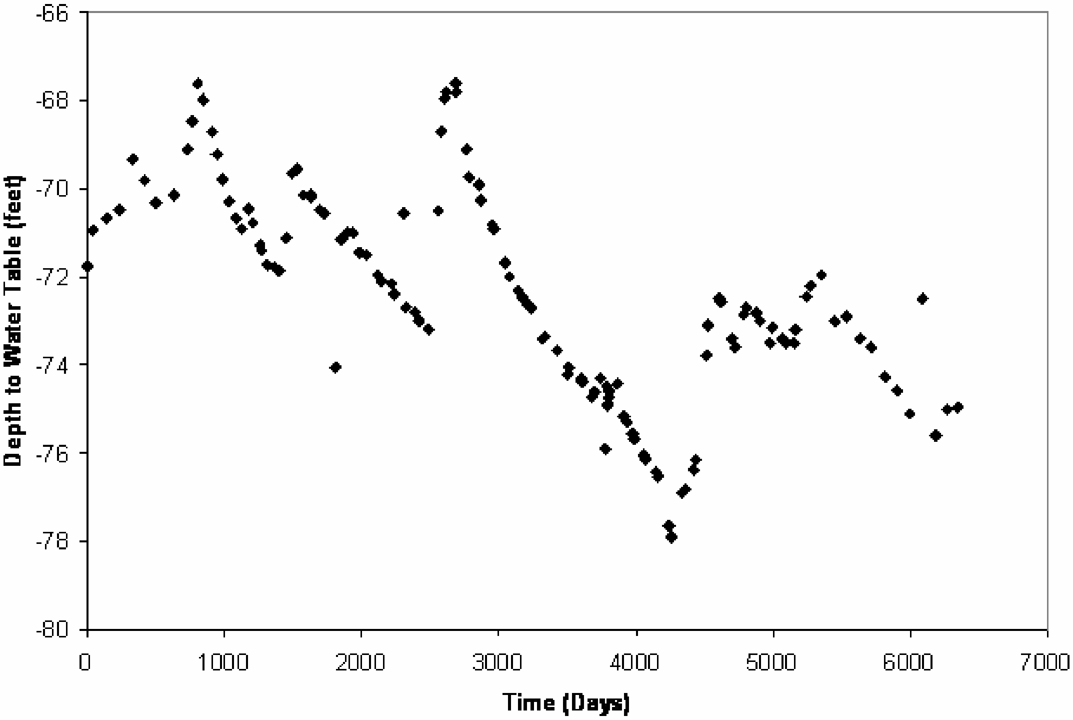

Exhibit 10. Time trend for the depth to the water table in a monitoring well adjacent to the down-flow edge of the basins. Time zero is 2/24/1991, the date of the first available data from this well.

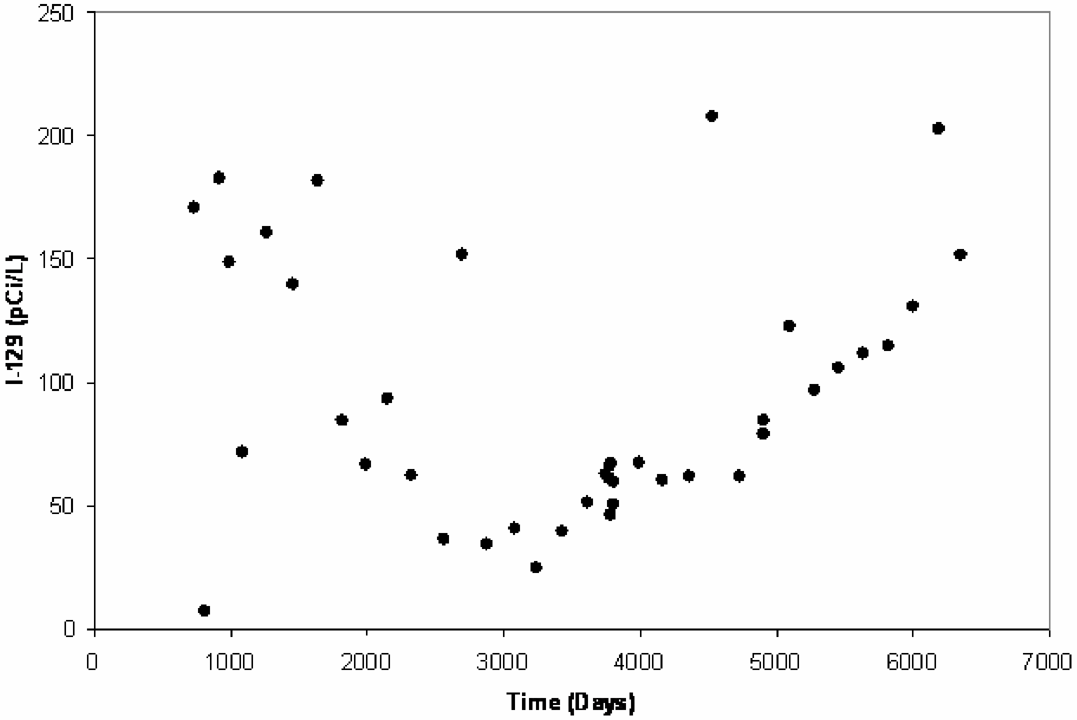

Exhibit 11. Time trend for I-129 concentration (pCi/L) in groundwater from a monitoring well adjacent to the down-flow edge of the basins. Time zero is 2/24/1991, the date of the first available data from this well.