

GROUNDWATER REMEDIATION SOLUTIONS AT HANFORD

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ABSTRACT

In 2006, Congress provided funding to the U. S. Department of Energy (DOE) to study new technologies that could be used to treat contamination from the Hanford Site that might impact the Columbia River. DOE identified three high priority sites that had groundwater contamination migrating towards the Columbia river for remediation. The contaminants included strontium-90, uranium and chromium.

A natural systems approach was taken that uses a mass balance concept to frame the problem and determine the most appropriate remedial approach. This approach provides for a scientifically based remedial decision. The technologies selected to address these contaminants included an apatite adsorption barrier coupled with a phytoremediation to address the strontium-90 contamination, injection of polyphosphate into the subsurface to sequester uranium, and a bioremediation approach to reduce chromium contamination in the groundwater. The ability to provide scientifically based approaches to these sites was in large part due to work the Pacific Northwest National Laboratory developed under previous DOE Office of Science and Office of Environmental Management projects.

INTRODUCTION

Congress provided funding to the U. S. Department of Energy (DOE) to study new technologies that could be used to treat contamination from the Hanford Site that might impact the Columbia River. The contaminants of concern are primarily metals and radionuclides, which are byproducts of Hanford's cold war mission to produce plutonium for atomic weapons.

Remediating a natural system is a complex undertaking, particularly near a river. The work requires incorporating biological, physical, and chemical factors into conceptual and deterministic models to first understand and then develop methods to minimize the impacts of contamination. Processes such as complexation, oxidation/reduction, adsorption, and precipitation along with the movement of water through the vadose and saturated zones control the rate and extent of contaminant mass distribution in natural systems. The mass balance between contaminant loading and the degree of attenuation in soil and groundwater is critical for assessing both the need for, and approach to, any remediation measures.

The DOE Pacific Northwest National Laboratory (PNNL) brought together a multidisciplinary team of geologists, biologists, chemists, and engineers to investigate to develop advanced remediation techniques for cleaning up radionuclide and metal contamination. Three of these approaches are highlighted here.

HANFORD SITE BACKGROUND

A microcosm of the nuclear weapons industry, the Hanford site was built in an arid portion of the United States' Pacific Northwest to produce plutonium for the atomic bomb during World War II and the Cold War. The site contained nuclear fuel fabrication facilities, nine nuclear reactors, reprocessing buildings, a plutonium conversion plant, and a host of laboratories.

The site also contained, and is working to remediate, a variety of storage systems. These include 177 underground tanks, containing more than 50 million gallons of radioactive waste. The site also contains dozens of infiltration trenches and facilities that were used to dispose of effluent waste to the ground.

It is estimated that 1.7 trillion liters (450 billion gallons) of liquid waste has been released to the ground over the past half century and some of it has reached the groundwater. This waste is complex, containing nearly half of the elements on the periodic chart. Radioactive plumes affect about 80 square miles of the site. Almost all of the plumes are flowing toward the Columbia River and some have reached it.

OVERALL STRATEGY

This paper highlights three sites along the Columbia River that have contamination in the subsurface posing a threat to the river. These sites include (1) 100-D Area chromium contamination, (2) 100-N Area strontium-90 contamination, and (3) 300 Area uranium contamination (Figure 1). Each of these sites had interim remedial actions that were either not the final remedy or were not working as well as planned. A natural systems approach was taken at each of these sites to develop a remediation strategy that would minimize or eliminate the threat to the river.

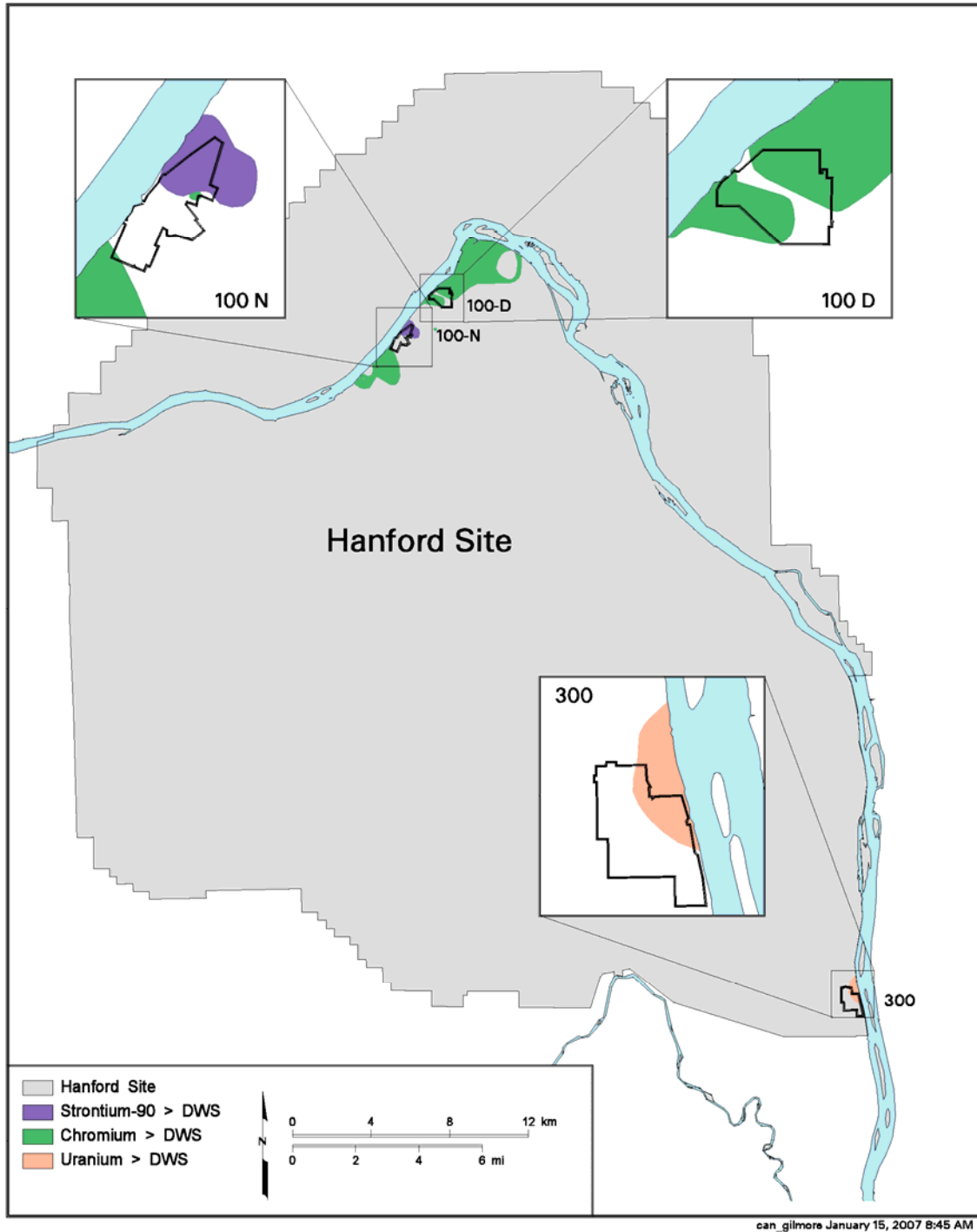


Fig. 1 Hanford Site map

The natural systems approach requires a scientific understanding of how the natural system and contaminants interact. A great deal of this knowledge was developed through previous scientific research studies regarding the movement of contaminants in the environment as well as research studies to develop remediation technologies. The DOE has invested in research for these areas through the Offices of Science and Environmental Management programs. PNNL is using the

results of these studies to develop a natural systems approach for remediating the threat of contamination entering the Columbia River.

The approach at the 100-N Area illustrates the natural systems approach and how it is critical to use a scientific approach for developing an effective and efficient remediation strategy. A similar approach was also used at the 100D and 300 Areas and an overview of these sites will be given.

NATURAL SYSTEMS APPROACH AT 100-N AREA

One of the locations identified as having contamination threatening the river is the site of a former reactor near the river called 100-N Area. This area received large volumes of contaminated water discharged to the ground through trenches during reactor operations between 1964 and 1991. A strontium-90 plume migrated from the trenches to the Columbia River driven by the large volumes of water during disposal. There is a continuing source of strontium-90 contamination to the groundwater from residual sorbed strontium-90 distributed in the aquifer and vadose zone.

A key aspect of formulating an appropriate remedial action was to frame the problem in terms of contaminant loading, movement and attenuation of the contaminants within the system and the resulting output (Figure 2). In this case the output was at the Columbia river. This “natural systems approach” is essentially formulating the problem in terms of a mass balance. [1] The mass balance of the system can be either observed (empirical approach), or formulated in terms of the physical, chemical, and biochemical processes and solving equations for each contaminant (deterministic approach). [2]

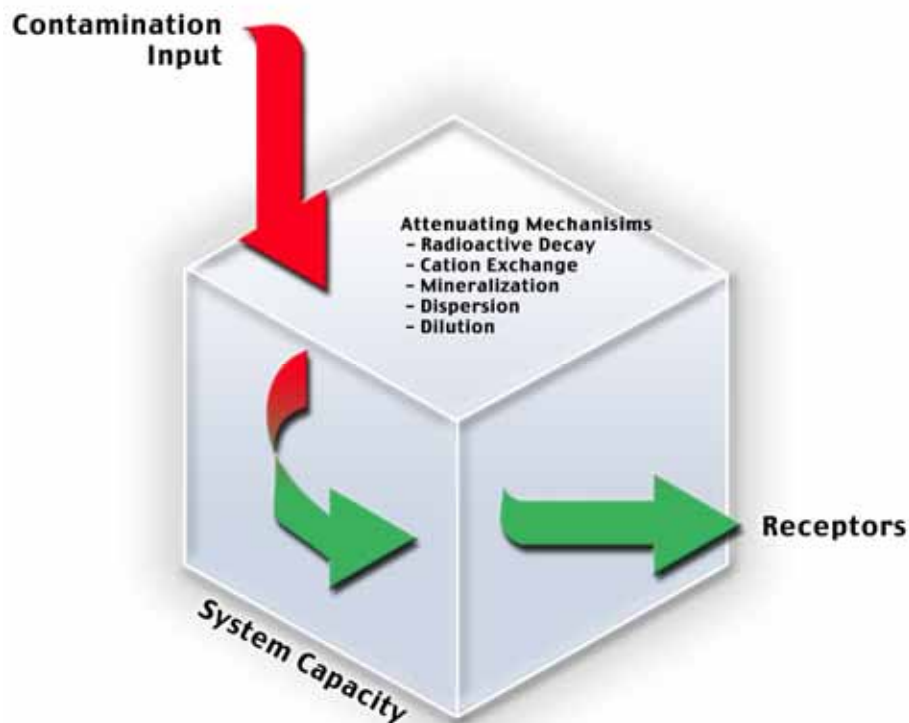


Fig. 2. Mass balance concept.

The groundwater flow conditions at 100-N Area are highly transient near the river and a deterministic approach was needed to interpret field measurements and empirical analyses. Each component of the mass balance for a plume, the source loading (inputs), attenuation, and the releases (outputs) are quantified independently and the mass balance calculated as a coupled fate and transport equation. This provided a means to quantify the natural system and identify key factors impacting the contaminant flux to the receptor. For 100-N Area the key factors are the equilibrium partitioning coefficient of strontium-90 that controls the rate of movement in the system and radioactive decay.

The equilibrium partitioning coefficient (K_d) for strontium-90 is on the order of 15 mL/g. [4] The high partitioning coefficient means that the concentration of strontium-90 on the sediments is much higher than the concentration in the groundwater, and the sorbed-phase contamination can serve as a source to groundwater over a relatively long period of time. The release of strontium-90 is controlled in large part from the rise and fall of the river stage. At high river stage, the water table moves up into the unsaturated zones and releases some of the sorbed strontium-90 on the sediments releasing them into the groundwater.

For radionuclides, radioactive decay can be a dominant attenuation mechanism that occurs at a constant and known rate regardless of environmental conditions. Therefore, the speed at which a radionuclide moves through the environment before reaching a receptor relative to the decay rate is critical in determining remediation opportunities. The high partitioning coefficient also slows the movement of contaminants through the system allowing the contaminants to attenuate before reaching a receptor. For the shorter lived isotopes, such as strontium-90 (half life of ~29years), if the material moves slowly enough (ie. has a high K_d value) the isotope may decay sufficiently to reduce the flux to the receptor over time.

This analysis identified that the near-river portion of the aquifer is a significant source of contamination to the river because of the high water flux through this zone due to the circulation of water in and out as the river stage moves up and down (Figure 3). The inland portions of the plume, however, do not have a significant impact on the contaminant flux to the river despite the fact the sorbed concentrations of strontium-90 are higher inland. The limited impact of inland strontium-90 is due to the slower water flux through these areas in comparison to the near-river area which allows the strontium-90 to significantly decay before reaching the river (Figure 4).

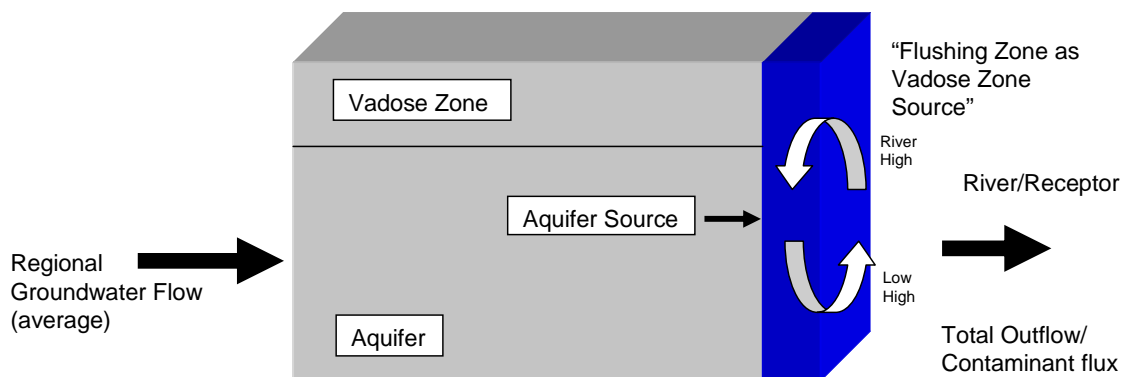


Fig. 3. Box diagram conceptual model for strontium-90 plume cross section.

The focus of the remediation should, therefore, be in the near river zone of high water circulation. The extent of the zone most significantly impacting the river is within approximately 91 m of the river and along a 365.8 m length of riverfront. The portions of the plume further inland (>91 m) can be left to naturally decay.

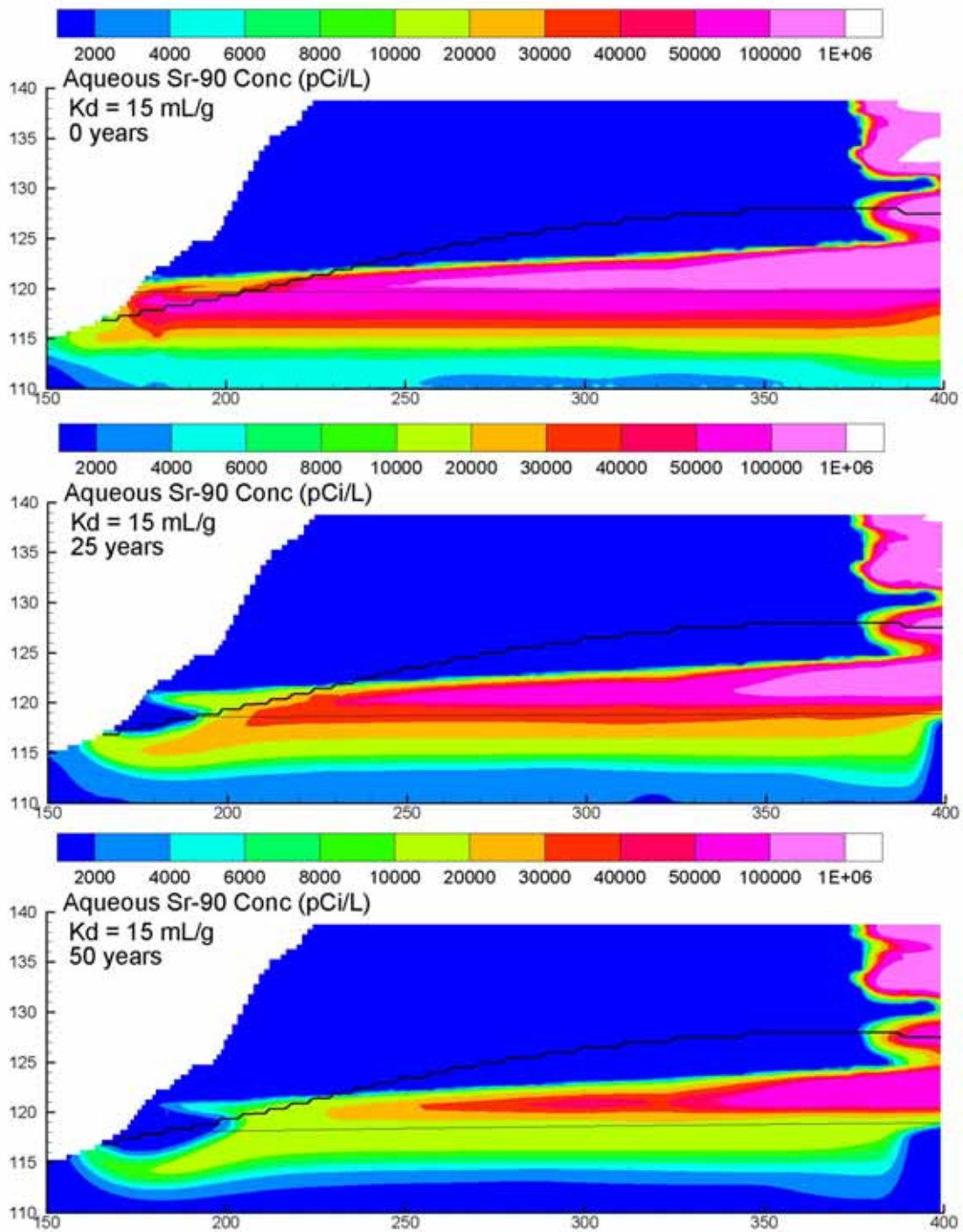


Figure 4. Strontium-90 Simulations showing decay over 50 years

Remediation at 100-N Area

A strategy was developed that focused on increasing the attenuation capacity of the sediments along the river shore through the emplacement of apatite. Apatite effectively increases the K_d value of strontium-90 in the aquifer, decreasing its mobility, and allowing for natural decay to occur before impacting the river.

Apatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] is a natural calcium phosphate mineral that is very stable and practically insoluble in water. [3,5] The substitution of strontium for calcium in the crystal structure is thermodynamically favorable and substitution in natural apatites can be as high as 11%. [6] A unique method for emplacing apatite by aqueous injection was developed by researchers at Sandia and the Pacific Northwest National Laboratories. [7,8] In this technology, a calcium-citrate and phosphate solution is injected into the subsurface. The citrate delays the formation of the apatite until it is in the subsurface. Relatively slow biodegradation of the calcium-citrate complex (days) allows sufficient time for injection and transport of the reagents to the areas of the aquifer where treatment is required. As calcium-citrate is degraded, the free calcium and phosphate combine to form amorphous apatite. The formation of amorphous apatite occurs within a week and crystalline apatite forms within a few weeks. The strontium-90 adsorbs to the apatite, which then recrystallizes with strontium-90 substitution for calcium.

In conjunction with the apatite emplacement, a phytoremediation approach will also be used as a complementary “polishing” step to the apatite. The phytoremediation approach will use the indigenous Coyote willow to draw strontium-90 laden water from the near-river aquifer and incorporate the contaminant into its plant structure. The willows will be periodically harvested and the plant material disposed. Phytoremediation will minimize the release of Sr-90 during the time when apatite is being formed in the subsurface and begins incorporating the Sr-90 into its crystal structure.

100-N Area Discussion

A detailed understanding of the natural system at the 100-N Area was needed before an effective remediation strategy could be developed. The conceptual and deterministic model of the site helped to identify the specific areas where remediation should be focused and validated the remedial approach to augment the system’s attenuation capacity through increased strontium-90 adsorption.

Additionally this work provides the technical basis to place an interim-action pump-and-treat system that was installed in 1995 on stand-by. The system was installed in the inland portion of the plume as a result of negotiations with regulators and stakeholders and was intended to provide a hydraulic barrier to the movement of strontium-90 to the river. A detailed analysis of the system, however, has shown that due to strontium-90 adsorption and radioactive decay, only the strontium-90 in the near river bank poses a risk to the river; the contamination farther inland would naturally decay before impacting the river. Therefore the pump-and-treat system could be placed on stand-by without impacting the strontium-90 flux to the river and the remediation focus should be on the near river sediments.

The apatite barrier combined with a phytoremediation approach is promising potential final remedy for the 100-N Area site.

100-D AND 300 AREAS

Similar approaches to what was described above for the 100-N Area were applied at the 100-D and 300 Areas.

At 100-D Area, hexavalent chromium, a highly toxic metal that was used to prevent corrosion in aluminum fuel elements during plutonium production at Hanford, is moving through the groundwater at the site. A reducing zone was created near the Columbia River that intercepts contaminated water before it reaches the river. This barrier was based on the In-Situ Redox Manipulation (ISRM) technology. ISRM relies on chemically reducing the sediments in the subsurface. The chemical sodium dithionite is injected into the subsurface where it reacts with the iron in the sediments, changing the iron to a more reactive chemical state. The chemically altered sediments can then reduce the chromium Cr(VI) to Cr(IV). The loss of electrons changes the chemistry of the chromium, resulting in a less toxic precipitate, thus stopping the contaminant from spreading. However some portions of the barrier are reoxidizing before anticipated limiting the effective lifetime of the barrier in protecting the river.

One approach to lengthen the barrier life is to remove the competing electron donors in the groundwater namely nitrate and oxygen upgradient of the barrier.

Bioremediation to Promote Barrier Life

The lifetime of the entire barrier can be lengthened by removing the primary oxidizing constituents (nitrate and oxygen) in the groundwater upgradient of the barrier. Nitrate and dissolved oxygen in the groundwater consume reducing capacity and consequently reduce the barrier lifetime relative to the contaminant of concern, chromium. By removing these constituents from the groundwater before they reach the barrier, the efficiency of the barrier will be increased.

Focusing on the microbes already present in the soil at Hanford, scientists plan to stimulate them by injecting a food source into the subsurface. As the microbial community grows and is sustained, it uses up oxygen and nitrate in the water, changing the oxidizing environment to a reducing one. This technique of biostimulation was previously demonstrated at another Hanford location under a DOE Office of Science funded program in a project managed by PNNL.

Polyphosphate Injections at the 300 Area

At the 300 Area the contaminant that is threatening the river is uranium. The 300 Area is similar to the 100-N Area in that the groundwater contamination is controlled in part by fluctuations in river stage. Uranium is widely dispersed in the soils and groundwater at 300 Area; when the river stage rises, the water table extends up into the vadose zone releasing uranium sorbed on the sediments. Unlike the strontium-90 at the 100-N Area, however, uranium will not radioactively decay in a reasonable period of time. In addition, uranium poses a toxic threat as a metal. Therefore, remediation of uranium requires that it is permanently sequestered from the environment. A technique developed by PNNL under an Office of Science program uses soluble long-chain polyphosphates that, when combined with calcium that is present in the subsurface, forms an insoluble uranyl phosphate, autunite $[\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}]$. Because autunite sequesters uranium in the oxidized form, U(VI), rather than requiring the reduced state

of uranium, the possibility of re-oxidation and re-mobilization is eliminated. Precipitation of phosphate minerals occurs when the injected polyphosphate compounds break down in water due to hydrolysis. The longer the polyphosphate chain, the slower the hydrolysis reaction. In essence polyphosphate provides a time-release molecule that can be controlled depending on where in the aquifer the material needs to form.

The current approach is to inject the polyphosphate into the “hot spots” of the contaminant plume, thereby reducing the overall contaminant loading to the aquifer. The intent is to reduce the uranium flux enough to meet the regulatory requirements for uranium concentration in the groundwater and moving into the river. As such, this approach focuses on increasing the attenuation capacity of the aquifer and is consistent with a natural systems and mass balance approach.

SUMMARY

A natural systems approach uses the mass balance concept to frame the problem and determine the most appropriate remedial approach. To use this natural systems approach, a detailed understanding of the natural system is needed including contaminant loading and the attenuation capacity of the system. This scientifically based approach allows an effective remediation strategy to be developed that includes guidance on where to focus remediation efforts and what remediation approaches are likely most effective. When appropriate a deterministic evaluation within the natural systems approach also provides predictions for the duration of remediation and supports design of an efficient and effective monitoring.

The 100-N Area analysis identified that the contaminant flux to river (receptor) was primarily from contamination located in the near-river zone of the aquifer where water circulates through the aquifer due to river stage variation. Based on this analysis, remedial actions are most effective when targeted in this near-river zone of the aquifer. Due to the attenuation capacity of the aquifer, inland areas of the aquifer do not significantly contribute to the contaminant flux to the river (receptor) and, therefore, natural attenuation alone may be sufficient to address the inland contamination. The deterministic analysis also provided a projection of how the contaminant flux to the river will diminish over time because radioactive decay and outflux of contaminant to the river will deplete the source and associated plume concentrations. This information is useful for determining whether the rate at which the contaminant flux to the river is sufficient to meet goals for protecting this receptor. The information also provides a timeframe over which remedial actions must be applied to if they are necessary to meet the remediation goals.

A natural systems approach requires upfront investment, but yields crucial information to select the most effective and efficient remediation strategy. The applications at Hanford illustrate how previous investments in environmental research by the DOE are being applied to protect the Columbia River. In addition, these research investments can be leveraged for use at other sites. It is also important to note that the scientific approach is not a purely laboratory-based approach. A step process of pilot and field-testing is an effective means to reduce technical uncertainty before large-scale application.

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