PROJECT TECHNICAL PLAN

Project 2: Environmental Remediation Science & Technology

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Principal Investigator:

Leonel E. Lagos, Ph.D., PMP®
Applied Research Center
Florida International University
10555 West Flagler Street, EC2100
Miami, FL 33174

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U.S. Department of Energy
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1000 Independence Avenue, SW
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FIU Applied Research Center
FLORIDA INTERNATIONAL UNIVERSITY

INTRODUCTION

Nuclear weapons production and other defense-related activities at the Hanford Site and Savannah River Site (SRS) have resulted in uranium, heavy metal, and radioactive contamination in the surface and subsurface environments. The U.S. Department of Energy's (DOE) Office of Environmental Management faces a number of environmental challenges with tremendous associated cleanup costs. The success of the DOE EM mission requires development and insertion of innovative approaches and novel technologies to address the significant challenges associated with the remaining cleanup of contaminated sites. A key focus of the research portfolio addresses data gaps related to the behavior and chemistry of radionuclides of concern as well as the co-mingling of these contaminants in groundwater, sediments and surface water at EM sites. This research is being conducted in collaboration with Pacific Northwest National Laboratory (PNNL), Savannah River National Laboratory (SRNL) and Savannah River Ecology Laboratory (SREL) scientists to support environmental remediation efforts at the Hanford Site and Savannah River Site (SRS), which are focused on cleanup technologies for contaminated soil and groundwater and the assessment of the fate and transport of contaminants in the environment. FIU is also teaming with scientists at Los Alamos National Laboratory (LANL) and the DOE Carlsbad Field Office (CBFO) to address contamination issues associated with the disposition and storage of large quantities of transuranic waste at the Waste Isolation Pilot Plant (WIPP), which originate from various DOE sites across the United States. The overall objective of the efforts under this project is to conduct basic science to fill knowledge gaps and validate potential remediation technologies to assist with environmental cleanup of the contaminated soil and groundwater. This project is conducted in close collaboration between FIU, PNNL, SRNL, SREL, and LANL scientists in order to plan and execute research that is synergistic with the work being conducted at the sites and supports the resolution of critical science and engineering needs which leads to a better understanding of the long-term behavior of contaminants in the subsurface. The knowledge gained through this research will be used to transform experimental and modeling innovations into practical applications deployed at the sites. The aim of FIU's research is to reduce the potential for contaminant mobility or toxicity in the surface and subsurface through the development and application of state-of-the-art scientific and environmental remediation technologies at DOE sites.

DOE EM (HQ) Contacts:
Genia McKinley, CA Technical Monitor, EM-3.2
Paul Beam, EM-4.12, Subsurface Closure
Skip Chamberlain, EM-4.12, Subsurface Closure
Kurt Gerdes, EM-4.12, Subsurface Closure
Matthew Zenkowich, SRS Field Liaison
Jeff McMillan, SRS Liaison Detail
Celinda Crawford, Richland Field Liaison

Hanford Site Contacts:
Christopher Bagwell, PNNL
Vicky Freedman, PNNL
Edmundo Placencia-Gomez, PNNL
Nik Qafoku, PNNL
Jim Szecsody, PNNL
Mike Cline, DOE Richland Field Office

SRNL/SRS Contacts:
Johnbull Dickson, SRNL
Carol Eddy-Dilek, SRNL
Elizabeth Hoffman, SRNL
Brian Looney, SRNL
Luke Reid, SRNL
Patrick Jackson, SRS
John Seaman, SREL

WIPP Contacts:
Donald Reed, LANL
Russ Patterson, CBFO

ARC Program Contact:
Leonel E. Lagos, PhD, PMP®
Principal Investigator, Director of Research
(305) 348-1810 E-mail: lagosl@fiu.edu

Applied Research Center
Florida International University
10555 W. Flagler St., EC 2100
Miami, FL 33174

During FIU Performance Year 8 (2017-2018), novel analytical methods and microscopy techniques will be used for characterization of various mineral and microbial samples prepared via laboratory-scale batch and column experiments. The data derived will provide relevant information for contaminant fate in natural systems and following remediation in the SRS F/H Area and the Hanford Site and for updating risk assessment models at WIPP. FIU will continue the development of a surface water model of the Tims Branch watershed at SRS to predict contaminant fate and transport during severe rainfall or storm conditions. Development of the Tims Branch hydrological model is supported by the application of geographic information systems (GIS) technology which serves as a foundation for management, storage, processing, analysis and visualization of spatiotemporal model configuration parameters and modeling results.

Collaborative relationships between FIU and the national laboratories have provided large benefits over the years to FIU, the national laboratories, the DOE complex, and the DOE EM mission. By working closely with the national laboratories, FIU research is not only closely aligned with the cleanup mission priorities at the DOE sites, but complements and supports the work at national laboratories. This coordination and leveraging of research efforts results in time- and cost-savings, and will accelerate progress of the DOE EM environmental restoration mission.

TECHNOLOGY NEEDS

Conventional site characterization methodologies provide limited understanding of the interactions between the hydrological cycle, contaminant mobilization and environmental impacts. This Project Technical Plan presents the use of laboratory-scale experiments to better understand and address fundamental questions regarding contaminant behavior in real sediment under natural conditions and during remediation, and the implementation of simplified systems that are representative of field-scale phenomena occurring at DOE sites. This project also uses conventional hydrologic and remediation analytical tools in combination with the latest scientific software (i.e., 2D and 3D numerical flow and transport models integrated with reaction kinetics and thermodynamic software) that are widely accepted by the U.S. Environmental Protection Agency (EPA), U.S. Army Corps of Engineers (USACE), and U.S. Geological Survey (USGS), to provide an integrated solution for better understanding of the mobility and fate of contaminants in soil, surface water and groundwater at DOE sites.

Task 1: Remediation Research and Technical Support for the Hanford Site

Legacy waste from the development of atomic weapons at the Hanford Site has left significant radionuclide contamination in soil and groundwater. There is a need to further investigate the environmental fate of uranium and technetium under natural conditions and following remediation. For example, a significant residual mass of uranium still resides in the deep vadose zone (VZ) following release of over 200,000 kg of uranium from improper waste disposal and accidental spills (Szecsody et al. 2013). Further, approximately 703 Ci of ^{99}Tc have been released to the ground from historical releases, spills and leaks (Serne, Rapko and Pegg 2014).

Previous uranium releases have created plumes that threaten groundwater quality due to potential downward migration through the unsaturated VZ. The mobility of uranium in the groundwater at the Hanford Site is relatively high (K_d 0.11 – 4 L/kg at pH 8) due to the presence of carbonate and oxidizing conditions (Zachara et al. 2007). Remediation of deep vadose zone contamination located near the waste tanks in the 200 Area and in the saturated zone near the 300 Area by the Columbia River can potentially be completed via *in situ* methods by converting mobile, aqueous U-carbonate phases to lower solubility precipitates that are stable in the natural environment. FIU's support to Hanford includes contributing to the understanding of Tc-99 chemistry and the fate and transport mechanisms of co-mingled contaminants including Tc-99, U(VI), Cr, and iodine (I). Research focus is also on *in situ* methods to sequester radionuclides in the deep vadose zone that are more cost effective as contaminants cannot be definitively extracted by traditional near-surface methods such as *ex situ* dredging.

Currently, DOE has no approved treatment technologies for subsurface iodine plumes. However, historical ^{129}I releases have resulted in massive, dilute plumes spreading to the scale of kilometers in the subsurface of the Central Plateau at the Hanford Site. The majority of ^{129}I concentration in the plumes are within the proximity of 10 pCi/L, which is above the drinking water standard (DWS) of 1 pCi/L. The aquifer also contains natural stable iodine (^{127}I) which has a similar chemical behavior as ^{129}I but is present at much larger concentrations in the groundwater, with $^{127}IO_3^-$ /$^{129}IO_3$- ratios ranging from 100 to 300 (Truex et al. 2015a). The mobility of iodine in the subsurface depends on many environmental factors such as speciation, pH, redox conditions, organic matter content, carbonate precipitation/dissolution and microbial activity. In addition, reducible co-contaminants such as nitrate and chromate can influence iodine speciation and sorption reactions (Kaplan et al. 2012, Truex et al. 2015a). Although the speciation of ^{129}I in Hanford groundwater has yet to be determined conclusively, the speciation of stable iodine (^{127}I) has shown that iodate (IO_3^-) is the major species followed by organo-iodine species with averages of 71% and 26%, respectively (Zhang et al. 2013). This task will investigate the effect of vadose zone environmental conditions such as pH and porewater constituencies, particularly silica content, on the iodine co-precipitation process with calcium carbonate in the presence of comingled contaminants.

Ammonia gas injection is currently being considered for uranium remediation at the pilot scale in the 200 Area of the Hanford Site. Previous work has shown that the injection of NH_3 gas to the vadose zone is a viable method to decrease uranium mobility in the contaminated subsurface via pH manipulation and co-precipitation processes (Szecsody et al. 2012a, Zhong et al. 2015). Further, it is an attractive remediation technology because it will not require additional liquid input into the vadose zone that could initially increase uranium flux to the groundwater.

It is expected that under the alkaline conditions caused by injection of the weak base, mobile uranium species will be transformed to low solubility uranium precipitates and/or additionally coated by non-uranium precipitates that are stable in the natural environment (Szecsody et al. 2012). However, there is a need for a better understanding of the formation processes leading to co-precipitation of uranium and the stability of the U-bearing precipitates. This information is necessary to accurately predict the fate of uranium in post-treated vadose zone soil.

Research on environmental remediation requires knowledge of deep vadose zone contaminant distributions that may be accomplished using geophysical techniques. Traditionally, the spectral induced polarization method (SIP) has been used to distinguish bulk phase changes in subsurface conditions, (e.g., rock/sediment/water, saturation, ionic conductivity). However, recent research indicates that this method shows sensitivity to changes in the presence of microbial cells and biofilms (Ntarlagiannis and Ferguson 2008). In Performance Year 7, FIU performed column experiments related to the SIP signatures of microbial activity using saturated columns. The goal of FIU Performance Year 7 experiments was to utilize SIP measurements to collect information on microbial activities affecting porewater composition and the formation of biofilm. Bacteria in the subsurface are seldom found as solitary mobile organisms; rather, most microorganisms form interconnected immobile colonies known as biofilms. These biofilms are supported by extracellular polymers, which serve to strengthen bacterial attachment to solid surfaces as well as to provide structural integrity to the biofilm. Biofilm formation can produce various changes in the physical and electrical properties of a porous medium. These changes can be due to clogging of pores (changes to porosity, permeability, and hydraulic conductivity); changes to overall shear strength and elastic moduli of media; production of proteinaceous extracellular appendages that facilitate electron transport and increase bulk electrical conductivity; alterations to pore fluid electrolyte concentrations; dissolution of minerals leading to increased surface roughness; and precipitation of magnetosomes (Atekwana and Slater 2009). There is a need for better detection of biofilms and microbial activities affecting ground and porewater quality in order to effectively implement any remediation technique. This can potentially be accomplished via geophysical methods like SIP. However, the feasibility of this approach can only be determined if system complexity is systematically controlled throughout the experimental phase by performing some basic studies.

Technetium-99 (Tc-99) is one of the major contaminants of concern at the Hanford Site. Tc-99 exhibits unique chemistry: when Tc is exposed to the atmosphere or any moderately oxidizing environment, it is found as pertechnetate (TcO_4^-) with valence state +7. Pertechnetate is highly soluble, does not sorb onto sediments and migrates at the same velocity as groundwater (Kaplan, Parker and Kutnyakov 1998), whereas under reducing conditions, technetium is found in the +4 valence state. Tc(IV) is expected to either sorb onto the sediments or precipitate as insoluble $TcO_2 \cdot nH_2O$ (Icenhower et al. 2008). Technetium migration is affected by the porewater and groundwater chemical composition and soil mineralogy. Hanford groundwater and porewater are rich in bicarbonates. Recent studies have identified the existence of stable, aqueous Tc(IV) carbonate-hydroxo complexes at circumneutral conditions, such as $Tc(CO_3)(OH)_3^-$ and $Tc(CO_3)(OH)_2$, (Eriksen Trygve et al. 1992, Paquette and Lawrence 1985, Alliot et al. 2009), indicating that despite Tc being reduced, it remains in the aqueous phase. Nevertheless, there is very limited data on the fate of those complexes and their interaction with soil components under reducing conditions. Therefore, technetium interactions with Hanford soil and pure minerals present in the Hanford Site, in the presence and absence of bicarbonates, need to be investigated. Furthermore, investigation on the stability of immobilized TcO_2, in the presence of bicarbonates, is important for designing effective remedial strategies for this contaminant.

Task 2: Remediation Research and Technical Support for Savannah River Site

Nuclear weapons production and other defense-related activities at the Hanford Site and SRS have resulted in uranium, heavy metals, and radioactive contamination in the surface and subsurface environments.

Humic substances (HS) are complex heterogeneous organic mixtures of polydispersed materials formed by biochemical and chemical reactions during the decay and transformation of plant and microbial remains. Humic substances account for 50-80% of the organic carbon in the soil or sediment and are known for their excellent binding capacity for metals, while being insoluble or partially soluble. This makes HS a strong candidate for remediation efforts to reduce the mobility of uranium (VI) in the subsurface. Humic acid, which carries a large number of functional groups, provides an important function in ion exchange and as a metal complexing ligand with a high complexation capacity being able to affect the mobility of actinides in natural systems.

Different types of humic substances such as unrefined humic acid, modified humic acid and commercial humic acid will be used in this research to study the sorption of humic acid on the sediment at different pH and its effect on uranium removal. Huma-K has potential as an amendment in the treatment of uranium in groundwater associated with the SRS F-Area seepage basins plume. In addition, it is thought that elevated silica concentrations in the acidic plume may enhance uranium removal when pH is increased by base injection. Understanding the synergy between humate and silica is important to developing an optimized pH adjustment to treat uranium in groundwater.

Task 3: Surface Water Modeling of Tims Branch

According to DOE EM's *Technology Plan to Address the EM Mercury Challenge, 2016* and the DOE EM Innovation and Technology Program, a number of issues still exist regarding mercury and other heavy metal and radionuclide contamination at SRS and other DOE EM sites. Utilization of Tims Branch as a test bed to develop a numerical modeling tool to evaluate hydrological impacts on the fate and transport of major contaminants of concern (e.g., Hg, U, Ni, radionuclides) will be beneficial to SRS, particularly if the tool developed can be applied to other streams at SRS as well as other DOE EM sites.

Hydrological models are simplified representations of the natural hydrological cycle. They are mainly used as a tool to understand hydrological processes and to predict the hydrological behavior of a natural system under various conditions. The best hydrology models are those that can describe a specific natural system and produce results close to reality with the lowest level of model complexity and the least amount of input parameters. Today, hydrological models are being widely used as a tool for environment and water resources management. In addition, surface hydrology is one of the key components in solute transport mechanisms. Therefore, developing a hydrological model that can simulate surface hydrology and estimate the flow components is essential in contaminant fate and transport modeling, particularly in an area such as SRS in South Carolina where both the surface water and groundwater have been contaminated from discharges associated with anthropogenic events at SRS process and laboratory facilities. The research under this task will directly support interpretation of historical data on the trends of contaminant concentration distribution in Tims Branch, and support planning and execution of future biota sampling in this important ecosystem, particularly considering the effect of extreme hydrological events on the stream flow and pollutant transport. In addition, the SRS Area Completion Project (ACP) is currently conducting additional characterization projects in Steed Pond to develop final plans for remediation, and this work will assist in developing cost effective remediation plans

GIS technology will be continuously utilized throughout the project to support the hydrological model development. An ArcGIS geodatabase has been developed by ARC researchers for SRS and the Tims Branch watershed as a foundation for management, storage, processing, analysis and visualization of environmental and hydrological parameters, and potentially building GIS-based water resources applications. The geodatabase possesses a spatial relational database management system (RDBMS) schema and relationship structure primarily based on the ArcHydro data model that is specific to hydrologic systems. This makes it a significant tool for conducting contaminant flow and transport analyses that require large amounts of high-quality spatial and temporal data in order to ensure reliability and validity of modeling results. ArcGIS tools significantly reduce the time needed for data preparation and improve overall efficiency by automating and batch processing model-specific geospatial and timeseries data via the development and implementation of process flow models. Utilization of the ArcGIS platform will continue to provide ARC researchers with a basis for management and geoprocessing of model configuration parameters, documenting process workflows, conducting geospatial analyses and visualization of model results. In addition, the SRS hydrologic geodatabase infrastructure enables linkage with other hydrologic modeling tools and applications to model hydrologic systems, and is scalable and replicable for implementation at other DOE sites.

Task 5: Research and Technical Support for WIPP

The current performance assessment (PA) for the Waste Isolation Pilot Plant (WIPP) recommends a K_d range of 20 – 400 mL/g for Pu(III) and Am(III) (Brush and Storz, 1996). However, reliable measurements have not been reported for actinide and lanthanide sorption to dolomite minerals especially in the presence of relevant ligands. There are several ligands that have been previously identified in waste being disposed of at the WIPP including EDTA and cellulose degradation products like isosaccharinic acid (Dunagan et al. 2007, Askarieh et al. 2000). Cellulose degradation products like isosaccharinic acid (the major degradation product formed under alkaline conditions) are also expected to form within a deep geologic repository and play a role in contaminant transport (Askarieh et al. 2000). There is a need to better understand the mobility of actinides and lanthanides under these conditions in order to develop more accurate risk assessment models for the WIPP.

FIU PERFORMANCE YEAR 8 PROJECT EXECUTION PLAN

The FIU Performance Year 8 tasks which are part of the main scope are identified in the table below. A detailed description is provided below for each project task.

Table 1. FIU Performance Year 8 Project Work Scope

Task No	Task
Task 1: Remediation Research and Technical Support for the Hanford Site	
Subtask 1.1	Remediation Research on Ammonia Gas for Uranium Treatment
Subtask 1.3	Investigation of Electrical Geophysical Response to Microbial Activity in the Saturated and Unsaturated Environments
Subtask 1.4	Contaminant Fate and Transport Under Reducing Conditions
Subtask 1.5	Stability of Contaminants in Carbonate Precipitates
Task 2: Remediation Research and Technical Support for the Savannah River Site	
Subtask 2.1	Interactions of Tc and I with soil from the Four Mile Branch Wetland
Subtask 2.2	The Synergistic Effect of Humic Acid and Colloidal Silica on the Removal of Uranium (VI)
Subtask 2.3	Humic Acid Batch Sorption and Column Experiments with SRS Soil
Task 3: Surface Water Modeling of Tims Branch	
Subtask.3.1	Modeling of Surface Water Flow and Contaminant Transport in the Tims Branch Ecosystem
Subtask 3.2	Application of GIS Technologies for Hydrological Modeling Support
Subtask 3.3	Data Collection, Sampling and Analysis in Tims Branch Watershed
Task 5: Research and Technical Support for WIPP	

Note: Task 4 was completed in FIU Performance Year 6.

PROJECT TASKS

This project is focused on environmental remediation of contaminated soil and groundwater at the Hanford, Savannah River and the WIPP sites. The aim is to reduce the potential for contaminant mobility or toxicity in the surface and subsurface through the development and application of state-of-the-art environmental remediation technologies at DOE sites. The project will be conducted in close collaboration between FIU, PNNL, SRNL, SREL, LANL and CBFO scientists in order to plan and execute research that is synergistic with the work being conducted at the sites, and supports the resolution of critical science and engineering needs which leads to a better understanding of the long-term behavior of contaminants in the subsurface. Research involves laboratory-scale studies which utilize novel analytical methods and microscopy techniques for characterization of various mineral and microbial samples. Tasks also include the implementation of hydrological models which help to predict the behavior and fate of existing and potential contaminants in the surface and subsurface. The following details the scope of work for the tasks under this project for FIU Performance Year 8.

Task 1: Remediation Research and Technical Support for the Hanford Site

Background

DOE EM has a critical need to understand the biogeochemical processes influencing the behavior of contaminants (U, I, Tc, and Cr) in Hanford Site's deep vadose zone that can impact groundwater. Research to address environmental risks and remediation challenges involving Tc-99 is a high-priority activity for the DOE EM complex. The deep vadose zone creates unique remediation challenges since contaminants reside at depths which are difficult to reach with near-surface remediation techniques. Manipulation of pH via ammonia gas is a potential remediation technology that can lead to incorporation of U(VI) into the sediments. In addition, the presence of carbonates and oxidizing conditions significantly increases the mobility of many contaminants, including uranium and technetium. Improving our understanding of geophysical responses with respect to contaminant behavior and remediation performance can assist with monitoring of remediation progress.

FIU ARC will collaborate and maintain communication with PNNL researchers to provide research on the following four subtasks under Task 1: the use of electrical geophysical response to measure geochemical changes in porewater chemistry due to microbial activity, fate and remediation technologies for uranium, iodine incorporation into calcite minerals, and technetium chemistry under reducing conditions with carbonate.

Subtask 1.1, Remediation Research of Ammonia Gas for Uranium Treatment, will include research on sequestering uranium at the 200 Area by *in situ* subsurface pH manipulation using NH_3 gas. This potential remediation technology is expected to transform mobile uranium species to lower solubility precipitates that are stable in the natural environment. Ammonia gas injection will raise the pH of the vadose zone porewaters leading to dissolution of silica-containing minerals such as quartz, montmorillonite, muscovite and kaolinite (Wan et al. 2004a, Wan et al. 2004b, Szecsody et al. 2013, Szecsody et al. 2012b). This will initially result in an increase in dissolved Si^{4+} and Al^{3+} as well as small increases in Na^{+}, K^{+}, $Fe^{2+/3+}$, Cl^{-}, F^{-} and SO_4^{2-} (Szecsody et al. 2013, Szecsody et al. 2012b).

Then, as ammonia leaves and the system returns to a neutral pH, U is expected to be immobilized as part of a complex co-precipitation process with cations dissolved from natural minerals in the first phase. There are two phenomena that are expected to decrease the mobility of U: 1) U (co)precipitation as solubility of Si, Al and similar ions decreases, and 2) Coating of U (co)precipitates with non-U, low-solubility precipitates. Some of the low solubility precipitates that are expected to form include cancrinite, sodalite, hydrobiotite, brucite and goethite (Bickmore et al. 2001, Zhao et al. 2004, Qafoku et al. 2004, Qafoku and Icenhower 2008).

Geochemical changes within the subsurface during remediation are often temporary unless they are moving the system towards its natural equilibrium. However, most of the coating and the co-precipitation processes removing uranium from the aqueous phase are expected to occur as the system returns to equilibrium (or neutral pH). Therefore, as long as the solid phases are relatively insoluble, uranium will be immobilized. It will be especially important to understand the coating processes of U co-precipitated with calcite as the solubility of calcite will increase as the system returns to a neutral pH.

Subtask 1.3, Investigation of Electrical Geophysical Response to Microbial Activity in Saturated and Unsaturated Environments, will continue tests initiated in FIU Performance Year 7 by focusing on basic, simplified experiments. FIU's experiments with saturated soil columns have suggested that the SIP signal is responsive to changes in subsurface conditions, but it is unclear how those SIP changes can be attributed to specific individual or co-occurring events. The primary assumption for planned basic studies is that all individual biogeochemical events have distinct geophysical signatures that would enable the use of SIP for subsurface diagnostics. However, there is a need for vigorous basic experimental testing to evaluate the contribution of all variables, beginning with simple saturated columns filled with SGW solution and then progressing into soil columns, followed by microbiological systems and then to uranium-bearing systems to evaluate for bioreduction. Without these basic studies there is no way to deconvolute the effects of many reactions that occur simultaneously on the measured SIP signal. Previous research has also suggested that the induced polarization method is sensitive to changes in the presence of microbial cells and biofilm accumulation (Ntarlagiannis and Ferguson 2008).

The focus of the experiments will be to measure the SIP signal in response to gradual changes in experimental conditions attributed to the specific biogeochemical events that have distinct geophysical signatures that could enable the use of SIP for remote diagnostics and monitoring of the subsurface.

This task will focus on laboratory-scale basic column experiments to show the potential use of SIP for remote sensing of microbial effects on geochemical changes indicative of bacterial activities in subsurface conditions at larger scales. SIP is capable of measuring effects related to polarization at the surfaces of grains and bacterial biofilms; however, it has never been applied at a field scale for this purpose.

Subtask 1.4, Contaminant Fate and Transport under Reducing Conditions, investigates the fate of Tc in conditions related to the Hanford Site and explores the effect of bicarbonates on redox transformations of Tc-99. Reduction of pertechnetate by Hanford soil and pure minerals relevant to the site, such as magnetite, will be studied in the absence and presence of bicarbonates. Magnetite is an Fe (II,III) oxide found in the Hanford Site (Xie et al. 2003) and due to its high ferrous iron content, it could potentially provide the necessary electrons for the reduction of pertechnetate (+7 oxidation state) to TcO_2 (+4 oxidation state). Nevertheless, the existence of soluble Tc(IV)-carbonate complexes under circumneutral conditions has been recorded (Alliot et al. 2009) and therefore, the fate of Tc-99 in soil containing ferrous iron minerals and bicarbonates is not well understood. Ferrous iron minerals may provide the necessary electrons for the reduction of pertechnetate to amorphous TcO_2, but on the other hand, the presence of bicarbonates may act antagonistically and retain Tc-99 in the aqueous phase in its reduced form. Furthermore, technetium under reducing conditions is expected to be in a poorly soluble Tc(IV) phase, forming ($TcO_2 \cdot H_2O$) (Lieser et al. 1987). The presence of bicarbonates, however, may affect its mobility significantly. In the anoxic porewater, bicarbonate ions may form soluble Tc(IV)-carbonato-hydroxo complexes of Tc(IV) that could potentially re-enter the aqueous phase (Alliot et al. 2009). For this reason, the stability of immobilized Tc-99 in the form of TcO_2 in the presence of bicarbonates needs to be investigated in an effort to identify if the presence of bicarbonates facilitates TcO_2 dissolution, especially since bicarbonate is a major ligand present in Hanford Site's porewater.

Subtask 1.5, Stability of Contaminants in Carbonate Precipitates. Because current scientific literature has limited information on remediation strategies for ^{129}I, this subtask investigates the potential for incorporation of iodine and other contaminants of concern into carbonate precipitates.

Calcite exists in the vadose zone at greater than 2% by mass in some areas of the Hanford Site and the groundwater is slightly saturated with respect to CO_2 gas (Xu et al. 2003). Studies conducted previously confirmed that iodine removal from the aqueous phase can occur through incorporation into calcium carbonate (Zhang et al. 2013). Calcium carbonate is also known to adsorb and incorporate metals and radionuclides such as chromate and uranium (Truex et al. 2015b, Szecsody et al. 2010, Truex et al. 2015a, Um et al. 2009).

Dissolved silica is present in all natural systems and previous research demonstrated the removal of silica from solution by calcium carbonate co-precipitation (Klein and Walter 1995). Si can also change the behavior of $CaCO_3$ precipitation and affect the nature of precipitating phases and their morphology (Lakshtanov and Stipp 2010). In addition, colloidal silica can be deposited on calcium carbonate crystals, creating a surface coating (Iler 1979) or form specific calcium silicate or calcium silicate-carbonate solid phases such as scawtite, $6CaSiO_3 \cdot CaCO_3 \cdot xH_2O$. The formation of those solid phases could affect radionuclide concentrations in solution; however, the relationships of silicon and calcium carbonate to the co-precipitation process of radionuclides, and specifically iodine, is unknown.

Another factor to consider is the pH of a mixture containing calcium carbonate and silica, as the behavior of the constituencies may vary greatly with only minor changes in pH. In addition to its relevance under natural conditions, there may be potential benefits for planned remediation via pH manipulation as this process promotes higher dissolution of Si, Ca and bicarbonate from soil minerals. This may result in the formation of different mineral phases including calcite, leading to sequestration of contaminants and reduction of contaminant flux to the groundwater (Szecsody et al. 2012b). However, there is limited data on how the vadose zone environmental conditions and porewater constituencies affect the iodine-calcium carbonate co-precipitation process in the presence of Si, which is one of the major elements in the porewater composition. In previous studies, Si was effective in the removal of uranium from synthetic bicarbonate and calcium bearing solutions, mimicking porewater compositions characteristic of the Hanford Site VZ after pH manipulation via ammonia gas injections (Katsenovich et al. 2016). An additional uncertainty of the process is the stability of the co-precipitated calcium carbonate contaminants with respect to dissolution.

Objectives

Subtask 1.1: The aim of this subtask is to understand the processes controlling U as the system returns to a neutral pH following NH_3 gas treatment. U will likely be adsorbed to mineral phases, co-precipitated with calcite, or complexed in the aqueous phase at high pH at low concentrations. At high concentrations of U, boltwoodites have formed prior to remediation following releases in Hanford sediments (Szecsody et al. 2010), but these will not be the major focus of this work as they are relatively insoluble compared to other phases of U present in the subsurface. However, the complex co-precipitation and coating processes for aqueous, adsorbed, and calcite-associated U occurring as the system returns to neutral pH must be understood. This task will conduct laboratory experiments and modeling to identify the processes leading to formation of insoluble precipitates in the presence and absence of calcite-forming conditions. Through this work, FIU will better understand the formation and stability of precipitates under controlled conditions following ammonia gas injection including: (1) coating of adsorbed U, (2) coating and/or dissolution of calcite-associated U, and (3) co-precipitation of U with dissolved cations from phyllosilicate minerals as the system returns to neutral pH.

Subtask 1.3: The objective of this subtask is to investigate the influence and corresponding electrical geophysical response of microbial activity on geochemical changes in simplified column experiments. This will advance knowledge of the technique under strictly controlled experimental conditions to get a better understanding of the microbial-driven changes within the subsurface.

Subtask 1.4: The objectives of this subtask are to:

a) Conclude the experiments on Tc partitioning between Hanford Site soil and pure minerals of relevance, such as magnetite, in the absence of bicarbonates and proceed with batch experiments under identical conditions in the presence of bicarbonates. The bicarbonate-free experiments aim to establish a "baseline" in pertechnetate reduction rate by magnetite in circumneutral conditions, which will eventually be compared to similar experiments in the presence of bicarbonates (e.g. low and high bicarbonate concentration). Furthermore, the potential formation of soluble Tc(IV)-carbonate complexes in the presence of bicarbonates under circumneutral conditions and their environmental fate will be investigated (e.g., identify potential interactions with the mineral or Hanford soil through sorption). The detection of soluble Tc(IV) species will be accomplished by the solvent extraction speciation from the supernatant solutions containing technetium with various oxidation states.

b) Identify if pertechnetate reduction by magnetite and Hanford soil in circumneutral conditions is a heterogeneous or homogeneous reaction by monitoring the concentration of ferrous iron released into the aqueous phase. Monitoring of ferrous iron in the aqueous phase will provide information on the electron donor (Fe^{2+}_{aq} versus Fe^{2+} of the mineral) contribution to pertechnetate reduction. This will be accomplished by monitoring the ratio of Fe^{2+}_{aq} and Fe^{3+}_{aq} as a function of time along with pertechnetate reduction.

c) Identify if the presence of bicarbonates facilitates TcO_2 dissolution, especially since bicarbonate is a major ligand present in Hanford porewater. This will be accomplished by suspending prior immobilized TcO_2 on magnetite and Hanford soil in bicarbonate solutions of different concentrations, and by measuring Tc(IV)/Tc(VII) in the aqueous phase through a solvent extraction process.

Subtask 1.5: The focus of this subtask will be to: (1) investigate co-precipitation of iodine with calcium carbonate and study the effect of silica content in the synthetic porewater composition on the co-precipitation process; (2) investigate the pH effect on the iodine co-precipitation with calcium carbonate; (3) investigate co-precipitation of iodine co-mingled with uranium and chromate contamination with calcium carbonate; (4) characterize produced solids; and (5) study the stability of contaminant-substituted calcium carbonate solids via sequential extractions and flow-through mini-column dissolution experiments. For FIU Performance Year 8, the goal will be to accomplish the research outlined in (1) above and initiate research described in (2).

Benefits

Subtask 1.1: Injection of reactive gases such as NH_3, to create alkaline conditions in the vadose zone, is an innovative technology that may be used to decrease uranium mobility in the subsurface. This task will improve understanding of the dissolution and secondary product formation of minerals during and after ammonia gas injection. In addition, it will identify major uranium phases and investigate the stability of solid phases formed during the remediation process. This will help to predict the long term effectiveness of this potential remediation technique.

This work directly complements ongoing experiments at PNNL including field-scale injection testing, laboratory-scale experiments determining U re-mobilization in contaminated sediments, ammonia partitioning and diffusion kinetics research, and investigations into co-precipitation of contaminants of concern with calcite. These data will especially complement the applied work at the field scale and with contaminated sediments as it will provide a more basic understanding of the dominant mechanisms controlling U fate in controlled, systematic experiments.

Subtask 1.3: This subtask will help to identify methodologies for tracking the remediation process within the subsurface with minimal impacts to the vadose zone through geophysics. Electrical geophysical techniques are useful due to their non-invasive nature as well as their cost effectiveness, especially when compared to the traditional methods of drilling boreholes and taking samples manually. Geophysical measurement systems can be set up to work remotely and take continuous measurements through automation.

Subtask 1.4: There is limited data on Tc interaction with iron minerals under reducing conditions in the presence of bicarbonates. Hence, the contaminant's fate in the environment is not well understood and bicarbonates are a major ligand in Hanford's porewater composition. Furthermore, immobilized Tc(IV) (through sorption on sediments or precipitation as Tc(IV)-oxide) may be extracted by carbonates and re-enter the aqueous phase in the form of the mobile $Tc(CO_3)(OH)_3^-$ and $Tc(CO_3)(OH)_2$ complexes. There is currently no information on the re-solubilization of Tc(IV)-oxide due to the presence of carbonates. The proposed task will provide new information on Tc(IV)-carbonate complexes as a potential mechanism for technetium migration in reducing geochemical environments by examining Tc-99 fate under conditions relevant to the Hanford Site.

Subtask 1.5: There is limited data on how vadose zone environmental conditions and porewater constituencies, particularly silica content, affect the contaminant-calcium carbonate precipitation process. In addition to its relevance under natural conditions, there may be potential benefits for planned remediation at the Hanford Site via pH manipulation as they may promote greater precipitation of calcium carbonate. This process may result in sequestration of contaminants leading to reduction of contaminant flux to the groundwater. The research conducted under this subtask will advance knowledge of the iodine co-precipitation process with calcium carbonate in the presence of silica and comingled contaminants, which has important implications for the Hanford Site with respect to contaminant fate and transport.

Technical Approach

Task 1 is a joint effort with the Pacific Northwest National Laboratory. Four subtasks have been identified and will be developed during FIU Performance Year 8.

Subtask 1.1: Remediation Research on Ammonia Gas for Uranium Treatment

FIU's research will focus on ammonia and uranium fate via batch and column experiments with synthetic porewaters and relevant minerals and sediments. These experiments have been designed based on results from FIU Performance Year 7.

During FIU Performance Year 7, experiments quantified partitioning of U and mineral dissolution up to 30 days in batch experiments prepared in the presence of 7.2 mM NaCl or synthetic groundwater of equivalent ionic strength with treatment via NaOH, NH_4OH or 5% NH_3/95% N_2 gas in the presence of a suite of minerals (kaolinite, montmorillonite, illite, muscovite, calcite, and quartz) or Hanford 300 Area sediments. These results show that base treatments generally result in greater U removal although it cannot be confirmed that one treatment was more effective than another. However, there is a more significant decrease in redox conditions with NH_3 gas treatment that could lead to a short term increase in U removal via reduction and precipitation. These data also show that greater U removal occurs in the presence of clays and in systems with aqueous Ca and carbonate. The greater removal in the presence of clays is likely due to mineral dissolution and secondary precipitate formation at elevated pH which may co-precipitate U. The greater removal in the calcium carbonate system is likely due to co-precipitation with calcite as the pH increases and calcite solubility decreases. Therefore, FIU Performance Year 8 will focus on understanding the dominant co-precipitation and coating processes occurring during and after base treatment via solid phase characterization and mineral dissolution experiments.

During FIU Performance Year 8, the scope of work will include the following studies conducted in collaboration with PNNL researchers.

- Equilibrium and kinetic batch experiments will investigate uranium partitioning and co-precipitation and mineral dissolution during and after base addition. Samples will include either simple NaCl, or NaCl with a similar bicarbonate content to the Hanford Sites's groundwater. The following conditions will be considered:
    - Batch samples will be equilibrated in a glovebag filled with 5% NH_3/95% N_2 (gas) and aged for varying amounts of time up to six months before stripping of gas with high purity air. Variable uranium concentrations and solid to liquid ratios may be used to investigate the effect on uranium speciation and precipitation, as previous studies suggest that higher U concentrations may lead to boltwoodite formation while lower U concentrations will lead to adsorption and co-precipitation with calcite (Szecsody et al. 2010). The solid phase will initially consist of clean sediments from the Hanford 200 Area or pure minerals relevant to the site (montmorillonite, illite, calcite, and muscovite).
    - Following base treatment and air stripping, solid materials will be subjected to additional batch desorption or flow-through dissolution experiments (miniature columns) to understand the stability of solid phases. Initial dissolution column experiments will also be conducted with minerals and sediments in the absence of U to quantify dissolution in the absence of secondary precipitation processes (as observed in batch data). These results will be directly compared to previous batch dissolution results from DOE Fellow Silvina Di Pietro's 2016 internship experience.
    - In addition, solids will be characterized to understand changes in mineralogy and morphology as well as the minerals with which U is associated at each time step (i.e., variable exposure periods to ammonia gas and following air stripping with re-equilibration up to one month). Conventional characterization techniques will be used including but not limited to TEM, SEM-EDS, EMPA, BET, XRD, and FTIR.

Subtask 1.3: Investigation of Electrical Geophysical Response to Microbial Activity in the Saturated and Unsaturated Environments

FIU will work with PNNL to investigate the influence and corresponding electrical geophysical response of microbial activity in a set of basic experiments to test the SIP signal stability and reliability before proceeding to the next more complicated level. The following experiments will validate the functionality of the SIP technique:

- Experiment 1: Set up soil-free SIP columns and operate with only autoclaved SGW;
- Experiment 2: Add autoclaved Hanford soil to the column and saturate with SGW. The SGW solution will be purged with oxygen to simulate aerobic conditions in the column, or nitrogen to ensure anaerobic conditions within column. Conditions within the columns will be kept aseptic; the SGW will be periodically changed to 10% bleach to flush the column between exchanges with SGW. To maintain sterile conditions, the experiments will not be run to an extended period of time.
- Experiment 3: Add heat deactivated microbial cells of known titer. Previous research has suggested that even inactive microbial cells cause an impact in the SIP signature of the media (Ntarlagiannis, Yee and Slater 2005).
- Experiment 4: Add active microbial cells of known titer. This experiment will address whether live cells produce different and distinct SIP signals. The results will be also compared to data obtained via experiments utilizing dead cells alone.
- The SIP signal measurements obtained will be evaluated for each experiment to answer if the signals are distinct for each of these contributing biogeochemical experimental conditions.

General test methods for the column set ups will follow the same approach as was used for FIU Performance Year 7. The set up will include one-dimensional PVC columns. Potential electrodes will be designed as in former experiments; a short silver wire encased in agar gel, to better facilitate contact with the soil. Current electrodes will be coiled Ag-AgCl and placed at either end. All sediments and solutions to be introduced to the columns will be autoclaved. Microbial cultures will be used as inoculum for sediments to investigate if the geophysical techniques have the potential to improve detection of microbial activities in the subsurface (note: this is still under discussion and could potentially be *Shewanella oneidensis* or a microbial consortia enriched at PNNL). Measurements will be taken using a National Instruments data acquisition card connected to a standard windows PC. Phase and conductivity will be measured at frequencies from 0.1 Hz to 100 Hz with measurements repeated five days a week. At the end of the experiment, sediment will be extracted to prepare samples for SEM/EDS analysis and to do chemical analysis after sediment centrifugation. The sediment samples will be also enumerated for bacteria via microscopy.

In FIU Performance Year 7 research, the columns were inoculated with microbial consortia enriched at PNNL and monitored over time using geochemical and SIP analyses. Porewater samples from these columns were analyzed for dissolved elements including U, Fe^{2+}, total Fe, Ca, Mg, and P. Work is still in progress to prepare samples from this experiment for uranium analysis via a KPA instrument. In addition, sample preparation for SEM/EDS analysis needs to be repeated since the first round of microscopy analysis has not shown the presence of microbial cells on the surface of sediment particles.

Subtask 1.4: Contaminant Fate and Transport under Reducing Conditions

During FIU Performance Year 8, FIU will continue the investigation by performing batch experiments of Tc-bearing solutions with Hanford Site sediment and pure minerals relevant to the site, such as magnetite, under reducing conditions. FIU Performance Year 7 experiments, in the absence of solid Tc-99 and several reducing agents in the aqueous phase, revealed no pertechnetate reduction, indicating the importance of a mineral presence that can act as an electron donor (Cui and Eriksen 1996). Furthermore, pertechnetate reduction experiments were performed under reducing conditions using different types of magnetite, namely micro- (325 mesh) and nano- (mean particle diameter 50-100 nm) magnetite, as well as Hanford sediment in circumneutral conditions. TcO_4^- reduction was faster at pH 6 compared to pH 8 for magnetite, whereas the nano-magnetite was able to reduce pertechnetate faster than micro-magnetite at the same pH (pH 8). Preliminary results with Hanford sediment at pH 8 indicated that pertechnetate reduction is slower compared to magnetite samples, despite the fact that all samples contain the same amount of magnetite. This experiment is still in progress and will be completed during FIU Performance Year 8, providing a clearer picture of the ability of each sample to reduce pertechnetate.

Hanford sediment and pure mineral suspensions at different Tc-bicarbonate concentrations at pH 8 will be prepared and introduced into the anaerobic glovebox. Micro- and nano-magnetite and Hanford sediment of mean particle diameter <300 μm will be used. The specific surface area of micro- and nano-size magnetite will be determined by Brunauer–Emmett–Teller (BET) analysis, which is available at the FIU Engineering Campus. The ferrous:ferric iron content of micro- and nano-size magnetite, as well as Hanford sediment, can be determined by mineral dissolution in sulfuric and hydrofluoric acid followed by ferrozine spectrophotometric analysis (Husler et al. 2011) and/or by means of XPS. The reducing conditions in the glovebox will be adjusted by purging the glove box with 95%:5% N_2:H_2. Aliquots from the supernatant will be isolated and the Tc concentration will be measured by means of liquid scintillation counting (LSC). Discrimination between Tc(VII) and Tc(IV) in the aqueous phase will be performed by a solvent extraction technique (TPPC in CH_3Cl). The effect of bicarbonate on the reduction of pertechnetate will be monitored as a function of time and will be compared to the reduction rate of bicarbonate-free experiments under identical conditions.

Total iron concentrations will be monitored closely by means of ICP-OES and ferrous iron will be determined spectrophotometrically. The ratio of ferrous:ferric iron as a function of time in the aqueous phase is a critical parameter, since it will provide experimental proof for whether the reduction of pertechnetate is a hetereogeneous reaction (solely contributed to the Fe content of the minerals) or if it is assisted by the presence of the electron donor (Fe^{2+}) in the aqueous phase. Furthermore, upon completion of pertechnetate reduction by Hanford sediment and magnetite, the aqueous phase will be replaced with a fresh solution of bicarbonates, in an effort to investigate the potential re-mobilization of immobilized Tc(IV) by Hanford sediment and magnetite. Different bicarbonate concentrations will be used (e.g., 5 mM and 50 mM) in order to identify if low or high concentrations of bicarbonate facilitate the dissolution of TcO_2. The dissolution experiments will take place in the anaerobic glovebox and the concentration of $Tc(IV)_{aq}$ and $Tc(VII)_{aq}$ will be determined using a solvent extraction technique (TPPC/CH_3Cl) monitored as a function of time (Yalçintaş et al. 2015).

In summary, Tc reduction will be studied under reducing conditions in the presence and absence of bicarbonate and the experimental results will test the hypothesis that bicarbonate affects the pertechnetate reduction by Hanford sediment and magnetite, a major iron oxide mineral at Hanford sediment, and consequently, whether there is a formation of Tc(IV)-carbonate complexes under circumneutral conditions. The monitoring and speciation of iron in the aqueous phase will test the hypothesis for the mechanism of pertechnetate reduction under circumneutral conditions: whether it is a heterogeneous reaction or it is affected by ferrous iron in the aqueous phase.

Subtask 1.5: Stability of Contaminants in Carbonate Precipitates

During FIU Performance Year 8, FIU will initiate studies on iodine incorporation into calcium carbonate precipitates in the presence of silica in the synthetic solution compositions. The first step in this research will be setting up a validated analytical method for measuring iodine in the ARC laboratory. Purchase of an ion chromatography (IC) coupled with inductively coupled plasma mass spectrometry (ICP-MS) is being considered to perform iodine separation at the parts-per-trillion level detection limits.

Previous analysis of groundwater samples from monitoring wells around the 200 Area suggested that iodate, IO_3^-, is the dominant iodine species accounting for 60-84% of total iodine (Zhang et al. 2013). A mix of iodine species also includes organo-I that is present on a level of 26% and a small amount of I^- (about 4%).

Based on this speciation analysis, the initial batch experiments promoting calcium carbonate precipitation in the presence of silica will utilize iodate. As a first step in understanding the interaction of iodine with calcium carbonate, a series of experiments will be conducted to investigate if the precipitation of calcium carbonate with the addition of sodium silicate in the solution composition produces calcite, which is the most stable polymorph of calcium carbonate. Calcium carbonate precipitation will be accomplished by mixing stock solutions of $CaCl_2$ and $NaHCO_3$ or Na_2CO_3 (Declet, Reyes and Suárez 2016). The reaction using $NaHCO_3$ will result in the formation of CaCO3 and the pH of the solution will be decreased by the following reactions:

$$Ca_2^+ + HCO_3^- \leftrightarrow CaCO_3(s) + H$$

The resulting pH of the solution mixture will be on the level of 8-8.5, which is relevant to Hanford Site conditions.

Experiments conducted at higher pH conditions will employ Na_2CO_3 for the precipitation of calcium carbonate. In the experiments investigating the effect of silica on the calcium carbonate precipitation process, the required quantity of metasilicate solution will be added to the sodium bicarbonate solution to create a silicate-carbonate mixture. This solution will be mixed with an iodate standard spiked to the desired concentration before the addition of a calcium chloride stock solution. All solutions will be prepared in DIW, which will be bubbled with N_2 prior to use to remove dissolved CO_2 and then stored in tightly sealed plastic bottles. Precipitation of calcium carbonate will be conducted in closed polypropylene vials in order to avoid silica contact with glass containers and prevent the uptake of atmospheric CO_2 during crystallization. The tested concentrations of silica in the solution composition will include: 0 mM, 0.5 mM, 2 mM, 5 mM and 20 mM. These Si concentrations were measured in natural porewater of Hanford sediment (4% water content) and sediment treated with NH_3 gas for uranium remediation in the vadose zone (Szecsody et al. 2012b).

The pH of the solution plays a decisive role on the formation of calcium carbonate particles by affecting particle morphology and nucleation rate (Yu et al. 2004). This might influence the co-precipitation process of iodate as calcium carbonate morphology changes with pH. To investigate the effect of pH, experiments will be conducted at pH 8.5 and 11, and if there are any observed differences in the removal of contaminants, the studied pH range will be extended to include values between pH 8.5 and 11. Solutions of 0.1M nitric acid and 0.1MNaOH will be used for the pH adjustments and, if required, efforts will be made to minimize the amount of acid for neutralization via sodium removal from sodium silicate using a cation exchange resin or use of silicic acid (Zaganiaris 2016). The synthesized calcium carbonate granules will be filtered, dried and characterized via XRD and SEM/EDS analysis. The concentration of iodine in the experiments will be varied up to 500 ug/L and iodate will be added to the solution mixture prior to mixing with calcium chloride. The aqueous concentration of iodate will be measured over a period of time to investigate any iodine changes. Experiments will also include the “late-spike” approach, where iodine and other contaminants are injected after carbonate-silicate solutions are mixed with calcium chloride. The “late-spike” experiment will provide information if there is any difference in the removal of iodine and other contaminants due to sorption or co-precipitation mechanisms. Studies will also involve speciation modeling via Geochemist’s Workbench® (GWB) software for the prediction of solid phases and soluble species.

Future work in FIU Performance Year 9 will study co-mingled contaminants such as uranium and chromate, and investigate the stability of contaminants substituted in calcium carbonate precipitates in the presence of silica via sequential extractions and flow-through mini-column experiments. Solids characterization studies will be conducted using higher concentrations of iodine and other co-contaminants which are consistent with XRD analysis to determine solid phase formations; SEM/EDS to evaluate surface morphology and elemental composition; and EPMA to investigate the relationship between element distribution maps. In addition, the percentage of silica incorporated into the formed $CaCO_3$ particles out of the total amount of SiO_2 added to the solution mixture will be calculated to supplement results on co-precipitation of iodine and other radionuclides. The research on this subtask is intended to be a topic for an FIU student’s Ph.D. dissertation.

Task 2: Remediation Research and Technical Support for SRS

Background

Approximately 1.8 billion gallons of acidic waste containing radionuclides and dissolved heavy metals were disposed of in SRS F/H Area seepage basins, which led to the unintentional creation of highly contaminated groundwater plumes consisting of radionuclides and chemicals with an acidic pH of 3 to 5.5. The acidity of the plumes enhances the mobility of several constituents of concern (COC) such as tritium, uranium-238, iodine-129, and strontium-90 for the F-Area plume and tritium, strontium-90 and mercury for the H-Area plume. Task 2 research is focused on uranium (VI), which is a key contaminant of concern in the F-Area groundwater plume.

During FIU Performance Year 7, FIU completed subtask 2.1, “Investigation on the properties of acid-contaminated soil and its effect on contaminant mobility.” The objectives of subtask 2.1 was to identify the morphological and physio-chemical characteristics of sediments that are affected by chronic acid leaching compared to the background soil and correlate the selected properties with sportive characteristics of the sediments for SRS contaminants of concern.

During FIU Performance Year 8, the scope of work under Task 2 will include three (3) technical subtasks conducted in collaboration with scientists at SRNL to support groundwater remediation at the SRS F/H Area. These subtasks will focus on the evaluation of remediation techniques for contaminated groundwater, as well as on the role of different environmental factors on the fate and transport of the contaminants of concern.

Iodine-129 and technetium-99 are among the most common contaminants related to radiological waste disposal sites. At SRS, radionuclides previously disposed of within the F-Area, including Tc-99 and I-129, are moving towards the Four Mile Branch Wetland with the natural groundwater flow, where they are subsequently interacting with organic materials present in the wetland. The fate and transport of technetium and iodine in the subsurface are controlled by their oxidation state and, consequently, speciation. Further, these anions interact relatively weakly with inorganic minerals above pH 4, but strong interactions are being reported with organic matter likely due to changes in oxidation and speciation (Emerson et al. 2014, Icenhower et al. 2008). Hence, a better understanding of the environmental conditions that affect these processes is critical.

Technetium (Tc) was previously produced at the site in large quantities as a fission product during the irradiation of ^{235}U-enriched fuel for plutonium for nuclear weapons. It exhibits unique chemistry: under oxidizing conditions it is found as soluble pertechnetate (TcO_4^-), whereas under reducing conditions, it is found in the insoluble TcO_2 state. In the natural environment, there is some of evidence for interaction between technetium and organic matter. Technetium retention by soils rich in organic matter has been reported in previous work. Nevertheless, the mechanism is not clear: organic materials rich in positively charged amino groups were found to be effective towards pertechnetate (Kim et al. 2004), whereas in other cases, the high content of organic matter resulted in pertechneteate reduction to insoluble TcO_2 (Maes et al. 2004).

The long-lived isotope of iodine, ^{129}I, is also produced during fission of ^{235}U. Iodine may exist in various oxidation states between -1 and +7, but the most common species in environmental systems are iodide, iodate and organo-iodine with organo-iodine being a significant fraction in the plume near Four Mile Branch at SRS (as much as 80% in the aquifer) (Kaplan et al. 2011, Emerson et al. 2014). In systems with organic matter present, iodine interacts strongly with it, and previous research suggests a strong association with aromatic structures of soil organic matter. However, they are still not well characterized (Emerson et al. 2014, Kaplan et al. 2014).

This task also involves expansion of FIU's research in the SRS F/H Area to investigate the possible synergy between colloidal silica and humic acid that may have an effect on the removal of uranium from contaminated groundwater. The research also evaluates the effects of different environmental variables such as pH and uranium concentrations on the process. Another study will include batch and column sorption experiments with humic acid, which simulate the creation of a sorbed humate treatment zone in the acidic groundwater contaminated with uranium. This data will be used for the modeling of the migration and distribution of natural organic matter injected into subsurface systems.

Objective

This scope for Task 2 assists in evaluating the mobility of actinides in natural systems in search of new remedial alternatives.

Subtask 2.1, Interactions of Tc and I with Soil from the Four Mile Branch Wetland. The objective of the proposed subtask is to investigate the binding properties of Tc and I to organic matter in the SRS Four Mile Branch Wetland under relevant environmental conditions. Natural organic matter (NOM) refers to a large pool of carbon-based molecules and is a heterogeneous and very complex entity. The aim is to determine the mechanism of technetium and iodine interaction with NOM by examining their interactions with organic substrates that model the main active groups of NOM, such as carboxyl-, amino- and phenol groups. Specifically, subtasks will:

a) Investigate the binding affinity of Tc and I with polygalacturonic acid (PGA), chitosan and lignin, which serve as substrates that model carboxyl-, amino- and phenol groups, respectively.
b) Investigate the binding properties by performing batch experiments at different pH values and ionic strengths under oxidizing conditions. Different pH and ionic strength values will determine whether the anions (Tc and I) bind to the active groups by electrostatic interactions.
c) Include studies of Tc and I interactions with well characterized humic substances under identical conditions, as with the previous experiments. The aim of this experiment will be to investigate the binding properties and mechanism of Tc and I on more complex substrates, where all the aforementioned groups partake in the binding of anions from the aqueous phase, before moving on to experiments using actual soil from the wetland area.

Subtask 2.2, The Synergistic Effect of Humic Acid and Colloidal Silica on the Removal of Uranium (VI). The SRS F/H Area soil consists of three major mineral phases such as quartz, kaolinite and goethite that account for 92%, 6% and 1%, respectively of the soil composition (Dong et al. 2012). These minerals can strongly affect uranium mobility in the subsurface, hence research is needed to better understand the mechanisms of interactions of soil minerals with uranium in the presence of humic acid. The objective of subtask 2.2 is to investigate the mechanisms of the synergetic interactions of humic acid and colloidal silica on the removal of uranium in the presence of pure minerals commonly found in soils of F/H area. Although previous studies have focused on the influence of various HA and uranium concentrations on percent uranium removal at varying pH conditions, it is important to understand how pure soil minerals affect uranium removal in the presence of HA and colloidal silica at variable pH conditions.

Subtask 2.3, Humic Acid Batch Sorption and Column Experiments with SRS Soil, will determine if humic substances containing humic/fulvic acids of different molecular weight can be used to control uranium mobility in acidic groundwater. Specifically, batch experiments will be conducted using humic substances (HS) such as Huma-K and Mod-HA materials, varying pH, contact time, and different concentration of uranium to evaluate the removal of uranium from acidic groundwater. The main objective of flow-through column experiments is to investigate the sorption behavior of Huma-K and Mod-HA materials under varying pH conditions and the effect of sorbed HA on uranium mobility in porous media.

Benefits

Subtask 2.1:

The benefit of the proposed research is that it will provide information on the interaction of the contaminants of interest (Tc and I) with natural organic matter. Because the interactions of Tc and I with NOM are currently not well understood, risk assessment models cannot accurately predict monitored natural attenuation processes without the further investigation proposed here. Furthermore, because the SRS wetlands are removing Tc and I from groundwater, an accurate risk assessment model may allow for decreased monitoring long term (and coincident cost savings) due to a reduced peak dose.

The logical pathway of the proposed subtask is to provide information on the binding and release of Tc and I with NOM by using simple systems that model the groups present in NOM, and subsequently perform experiments with well-characterized humic substances as well as soil from the Four Mile Branch Wetland under identical conditions. There is currently very little information on modeling the sorption of Tc and I with organic groups on a molecular level.

Subtask 2.2: The investigation under this subtask will evaluate the synergy between colloidal Si and humic acid on the removal of U(VI) via batch reactors by using three major pure minerals that are characteristic for F/H area soil and analyze post-reaction sediments for surface morphology and composition. This study will help to better understand the mobility of actinides in natural systems in the presence of colloidal silica and humic acid and the potential for colloid-facilitated transport of uranium in the SRS subsurface.

Subtask 2.3: This study will demonstrate if humic substances are viable amendments for in-situ remediation of uranium, and determine conditions for optimal U(VI) removal from aqueous phase. This study will also help determine if humic substances can be used as potential amendments at other DOE sites, where soil and groundwater conditions are less acidic compared to SRS. FIU will investigate via flow-through and batch experiments the sorption behavior of humic substances for groundwater remediation and the effect of sorbed humic substances on uranium removal. This subtask will also include coupling flow and transport of humic substances and contaminants in the subsurface to simulate the response of the system after the injection of humate. The outcome of these studies will help to determine approaches to deploy humate technology under varying site conditions.

Technical Approach

The scope of work under Task 2 includes three (3) technical subtasks which will be conducted in collaboration with SRNL scientists.

Subask 2.1: Interactions of Tc and I with soil from the Four Mile Branch Wetland

During FIU Performance Year 8, FIU will initiate batch experiments under oxidizing conditions with commercially available, model organic substrates, as well as background soil from the Four Mile Branch Wetland, with Tc-99 and I-125. Well-characterized organic materials will be used to mimic specific functional groups common to natural organic matter in a more simplified system. Natural substrates under consideration include chitosan and poly-galacturonic acid (PGA) which are rich in amino- and carboxyl groups respectively (Kim et al. 2004), as well as lignin, which is rich in phenol groups (Wallace and Fry, 1994). These functional groups are the most abundant groups in natural organic matter (NOM) and participate in natural attenuation phenomena by interacting with heavy metals and contaminants. Better understanding of the interactions of Tc and I with NOM will allow for more representative modeling of natural attenuation processes in the Four Mile Branch Wetland soil. Furthermore, well-characterized humic substances will be purchased from the International Humic Substances Society (IHSS) to consider materials with relatively high and low amino acid content for comparison to the more simplified components. Humic substances are another integral part of natural organic matter and are known to regulate contaminant mobility.

Batch experiments will be performed on the benchtop containing suspensions of PGA, chitosan and lignin initially with pertechnetate, iodate and iodine. Batch experiments will be performed at different pH values (3, 6.5 and 8) and constant ionic strength (0.001 M $NaClO_4$). The carboxyl-rich substrate is expected to develop a negative net charge at pH 6.5 and 8, whereas the amino- and phenol-rich substrates are expected to develop more positive net charge, as pH values increase. The development of different net charges should directly affect the ability of the substrate to bind anions from the aqueous phase, assuming that electrostatic interactions are dominating the binding mechanism. Identical experiments will be performed at higher ionic strength (e.g. 0.01M $NaClO_4$). Strong dependence of binding on pH, as well as ionic strength, will verify the retention of anionic contaminants by the substrate due to electrostatic interactions. The residual Tc-99 in the aqueous phase will be determined by means of liquid scintillation counting (LSC). Iodine, iodate and iodide can be separated through a C-18 acetonitrile/phosphoric acid column (Sajonz et al. 2006), an IC column, or an alumina column eluting iodide and iodate with $NaNO_3$ and $NaHCO_3$ (Machado et al. 2001). $^{125}I^-$ and $^{125}IO_3^-$ will be determined by LSC as well. Batch experiments with humic substances will be performed under identical conditions to those with model organic substrates. Humic substances will be characterized by means of potentiometric titrations and FTIR, both available at the FIU Engineering Campus, in order to identify qualitatively and quantitatively the surface functional groups. In summary, Subtask 2.1 will identify the role of each of the major functional groups found in NOM when interacting with Tc and I under oxidizing conditions by using simple, model organic group substrates and well-characterized humic substances, and the mechanism that dominates the phenomenon. This new information will enable better understanding of pertechnetate and iodine behavior in organic-rich environments.

Subtask 2.2: The Synergistic Effect of Humic Acid and Colloidal Silica on the Removal of Uranium (VI)

FIU previously conducted batch experiments to study the effect of synergetic interactions between humic acid and colloidal silica on uranium removal while varying the concentration of humic acid (10 to 50 ppm) and uranium concentration (0.5 to 30 ppm) in synthetic compositions with and without sediment. These studies suggested that the removal of uranium in the presence of only sediment is much higher than the removal of uranium in sediment containing humic acid and colloidal silica. This subtask will study the synergetic interactions between humic acid and colloidal silica on the behavior of uranium in the presence of pure minerals such as quartz, kaolinite and goethite, characteristic of SRS sediment composition. Humic substances are major components of soil organic matter and are known for their ability to influence the behavior and fate of heavy metals (Trevisan et al. 2010, Perminova, Hatfield and Hertkorn 2005). Studies have shown that humic acids (HA) function as important ion-exchange and metal-complexing ligands laden with a large number of functional groups that can greatly affect the mobility of actinides in natural systems.

During FIU Performance Year 8, FIU will study the effect of synergetic interactions between HA and colloidal silica on uranium removal by using pure minerals instead of SRS sediment. Batch synthetic groundwater samples will be prepared to mimic the contaminated groundwater at SRS, with pH adjusted in the range from 3 to 8. The following batch samples will be evaluated at each pH condition:

- Quartz, Kaolinite, Goethite + U(VI)

- Quartz, Kaolinite, Goethite + U(VI) + HA
- Quartz, Kaolinite, Goethite + U(VI) + HA + Si

Subtask 2.3: Humic Acid Batch Sorption and Column Experiments with SRS Soil

This subtask will study the mobility of uranium in the presence of humic substances (HS) via batch and column experiments. To understand and predict uranium mobility, U(VI) adsorption/desorption experiments will be performed using background (clean) F-Area aquifer sediments and sediment amended with humic substances. The migration and distribution of humate and its effect on U(VI) mobility will be studied via column experiments. Tests will be performed in the presence of (1) Huma-K, an agricultural amendment composed largely of humic acid and (2) a modified HA (Mod-HA) material, which is a commercially available agricultural amendment customized for groundwater remediation.

The interaction of uranium with sediment in the presence or absence of humic substances involves complex mechanisms that are not yet well understood. The interaction of U(VI) with humic substances can affect the adsorption of U on sediment, altering its mobility in the subsurface. To elucidate the complex environment created by the addition of humic substances (Huma-K and Mod-HA), comprehensive studies are needed to address key factors that control the adsorption of HS on Savannah River Site sediments and the removal of U(VI) using HS-coated sediments.

This study will evaluate the effect of contact time (kinetics), pH and initial uranium concentrations, as well as expand the investigation of U(VI) desorption via the following batch experimental design:

- Savannah River Site sediments + uranium
- Sediments coated with HS + uranium
- HS + uranium

The study will be conducted in the following manner:

For the kinetics experiment, an initial uranium concentration will be allowed to equilibrate with SRS sediment and SRS sediment coated with Mod-HA for different time periods at pH 4.

To study the removal of uranium by SRS sediments, a HS-free sorption experiment will be performed with different uranium concentrations (25-1000 ppb) added to 200 mg of SRS soil at pH 4. Samples will be vortex-mixed, placed on a platform shaker for seven days, and centrifuged. The supernatant will be analyzed by a kinetic phosphorescence analyzer (KPA).

To study the removal of uranium by SRS sediments coated with Huma-K, 20 mL of solution at pH 4 will initially be reacted with 200 mg of SRS soil for five days, after which samples will be centrifuged and the supernatant replaced by a fresh uranium solution with varying concentrations (25-1000 ppb) at pH 4. Samples will be vortex-mixed, placed on a platform shaker for seven days, and centrifuged. The supernatant will be analyzed by a KPA and UV-Vis spectrophotometer.

For the desorption of uranium previously adsorbed, a batch desorption experiment will be conducted at pH 4, where initially a known concentration of uranium will be sorbed to SRS sediment and SRS sediment coated with Huma-K at pH 4. After seven days of agitation, samples will be centrifuged, residual uranium concentration in the supernatant determined and the supernatant replaced with deionized water at different pH values (4 and 7). Samples will be agitated and centrifuged in the same way as previously described above. The desorbed uranium concentration in the aqueous phase will be determined by KPA analysis.

Furthermore, the use of a new modified humic acid, Mod-HA, as a potential remediation amendment will be explored and compared with Huma-K behavior in order to determine which more suitable for efficient removal of uranium and under what environmentally-relevant conditions. For this study, detailed characterization of the modified humic acid will be performed by means of scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM/EDS) analysis and fourier transform infrared (FTIR) spectroscopy. Additionally, the uranium removal at pH 4 will be conducted with SRS sediments coated with modified humic acid. These results will be compared with those previously obtained from Huma-K experiments in order to determine which amendment would be more efficient for the removal of uranium.

This research aims to understand the sorption of HS under varying pH conditions and the effect of HS on uranium mobility through porous media employing flow-through column experiments. For each of the column tests, a series of effluent samples will be collected at the column outlet and then measured to determine the breakthrough curves as a function of pore volume (PV). Analytical methods will be used to determine the sorption parameters and the interactions between U(VI) and HS. Previously, FIU tested unrefined HA known as Huma-K and a modified HA (Mod-HA). In FIU Year 8, the focus of these current experiments will be to evaluate the long-term effect of HA treatment technology on the mobility of uranium. An amount of 0.5 PV of humate (Huma-K or mod-HA) will be injected into the column filled with SRS sediment to elucidate humate migration through the column when fresh solution comes into contact with sorbed humate. This will help to understand the transport of humate with groundwater at the injection site. Sorption of uranium to sediment in the presence of HS depends on various key controlling variables such as HS concentration, soil mineral composition and environmental conditions (e.g., pH). This task will investigate the influence of HS on the sorption of U(VI) onto sediments collected from the F/H Area using a column experimental set-up. In addition, FIU will estimate the U transport parameters to better predict the mobility of uranium in the presence of various humate products.

Task 3: Surface Water Modeling of Tims Branch

Background

This task involves the development of an integrated, fully distributed hydrology and transport model to be used as a tool for assessment, evaluation and monitoring of the fate and transport of sediment and contaminants in Tims Branch at SRS. Tims Branch is a small stream-scale ecosystem located in the A and M areas of SRS that has received direct discharges of wastewater from on-site process and laboratory facilities. At various times, this wastewater contained uranium, nickel, aluminum, mercury, other metals and radionuclides, and organic solvents. In the lower portion of Tims Branch, currently discharging groundwater contains trace levels of organic solvent. A number of innovative treatment methods were deployed to limit the contaminant flux to Tims Branch, including a wetland treatment system (northern tributary in 2000) and a mercury removal system that uses a tin (II) reagent and air stripping (outfall tributary in 2007). Together, these treatments effectively eliminated all local anthropogenic mercury inputs to this ecosystem. The tin-based treatment has resulted in concomitant discharge of low-levels of inorganic tin (as small micro particles and nanoparticles). The controlled discharge of tin to Tims Branch as a known step function with high quality records on the quantity and timing of the release makes this stream-scale ecosystem an ideal testbed to study complex systems science in a relatively well defined ecosystem that experienced controlled changes in boundary conditions, and provides a unique opportunity for the released tin to serve as a potential tracer for sedimentation and particle transport processes in the stream.

During FIU Performance Year 8, FIU will continue to support SRS and DOE EM's Office Subsurface Closure goals by conducting a targeted stream-scale study in the Tims Branch ecosystem to monitor the fate and transport of sediment and contaminants in Tims Branch and examine the response of the ecosystem to innovative EM-developed remediation treatment technologies that have eliminated anthropogenic mercury sources from this watershed. Work for this year will primarily involve modification and integration of overland and stream flow models developed in FIU Performance Year 7 to simulate the hydrology of Tims Branch and its response to extreme hydrological events. FIU will also begin the preliminary development of the contaminant transport component of the integrated model.

Objectives

The principal objective of this task is to develop and test a comprehensive transport model using available hydrology software and geographical information systems (GIS) tools to examine the response of Tims Branch to historical discharges and environmental management remediation actions. Results from this study are key to evaluating the effectiveness of wetland treatment and tin (II)-based mercury treatment at the SRS site, and are also relevant to evaluating the potential of using water treatment and novel remediation technologies in other mercury-contaminated stream systems. A rigorous calibration and validation exercise is necessary to increase confidence in the models' ability to estimate spatial distribution of flow depth and velocity, and contaminant concentration over time. The main challenges in hydrological modeling, however, are finding observed/measured timeseries data for the model calibration and validation process. A secondary objective of this task, therefore, will be to identify data gaps and, where necessary, attempt to collect additional field data to support model validation. Any data collection, sampling or analyses will be incorporated as part of a student summer internship in coordination with SRNL and SREL.

Benefits

The research under this task will directly support interpretation of historical data on the trends of contaminant concentration distribution in Tims Branch, and support planning and execution of future biota sampling in this important ecosystem, particularly considering the effect of extreme hydrological events on the stream flow and pollutant transport. In addition, the SRS Area Completion Project (ACP) is currently conducting additional characterization projects in Steed Pond to develop final plans for remediation, and this work will assist in developing cost effective remediation plans. This research also fosters collaboration between the students and scientists at FIU and the scientists at the Savannah River National Laboratory and the Savannah River Ecology Laboratory.

In general, hydrological models are the standard tools used for investigating surface/subsurface flow behavior. They provide insights for water resource management and decision making, and evaluate the water quality, erosion, deposition, and transport. The MIKE SHE/MIKE 11 model being developed for Tims Branch can be used as a tool to better understand the effect of extreme weather on flow in Tims Branch. The results of the hydrology model will be used to assess the fate and transport of remedial by-products, such as tin dioxide or other existing solutes (uranium, plutonium), that may have direct or indirect impact on the environment in SRS. The outcome of such a model can determine spatial and temporal distribution of suspended particles or contaminants in the area when storms or heavy rainfalls occur

The MIKE SHE/MIKE 11 hydrological modeling package being used has a GIS user interface built into its system that can directly use spatial GIS databases (geodatabases) for model input parameters. The use of GIS data is significant not just for the spatial representation of hydrologic features, but particularly because of its integration with timeseries data attributes such as flow rates and directions, contaminant concentrations, water levels, precipitation, etc. Availability of data in this format shortens the time for model-specific data preparation and ultimately model development. The geodatabase provides an advanced spatial data structure needed to address the management, processing, and analysis of large GIS and timeseries datasets derived from multiple sources that are used for numerical model calibration, uncertainty analysis, and simulation of flow and contaminant fate and transport during extreme climatic events. The geodatabase developed is based on the ArcHydro and ArcGIS Base Map data models with modifications made for project-specific input parameters. The significance of this approach was to ensure its replicability for potential application at other DOE sites. Application of GIS tools will also aid in the pre-processing and analysis of hydrological model data; automation of repetitive geoprocessing tasks; and production of maps for visualization of the surface water hydrology of the Tims Branch watershed.

Performing simulations of extreme storm events provides DOE-EM/SRS with information that can assist in: (a) understanding the potential impact on flow depth and velocity in Tims Branch, (b) determining the potential for contaminant transport due to the resuspension and remobilization of sediment during such extreme events, and (c) identifying areas where sediment/contaminants might further be deposited.

Technical Approach

Figure 1 provides an outline of the modeling work scope for development of a hydrology and transport model for assessment, evaluation and monitoring of the fate and transport of sediment and contaminants in the Tims Branch watershed. Phase 1 was initiated in FIU Performance Year 5 and completed during Year 6. FIU completed a literature review and site characterization; developed a conceptual model of the Tims Branch watershed; created a geodatabase to store and manage the data being used for hydrological model development; and began preliminary development of the MIKE SHE hydrological model which included the simulation of overland flow, one of the main components of the MIKE SHE modeling system. During FIU Performance Year 6, FIU revised the model domain and implemented the MIKE SHE overland flow, evapotranspiration, unsaturated and saturated flow modules. Phase 2 was also initiated in Performance Year 6 and continued throughout Year 7, and involved the delineation of the stream network along the A-014 outfall tributary using ArcGIS and MIKE 11 tools and preliminary model calibration. FIU aims to complete the components of Phase 2 highlighted in red in Figure 1 below during FIU Performance Year 8, by modifying the model input parameters with actual field data (e.g. cross sections, depth, suspended particle concentration, etc.), completing the model calibration and verification process, and coupling the MIKE SHE and MIKE 11 models developed.

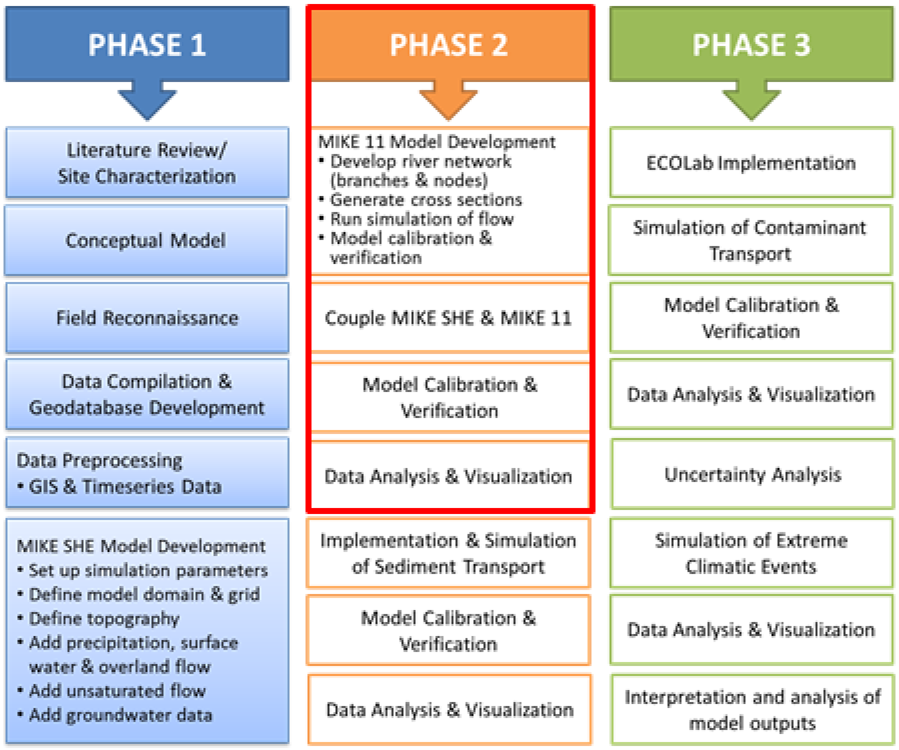

Figure 1. Hydrological modeling phases and detailed future plans.

Subtask 3.1: Modeling of Surface Water Flow and Contaminant Transport in the Tims Branch Ecosystem

The overall objective of this subtask is to develop an integrated hydrology and contaminant transport model to be used as a tool for studying the sedimentation and particle transport processes in the Tims Branch ecosystem at SRS. The Tims Branch ecosystem represents an important applied science opportunity as a result of significant past research by SRNL and SREL. Recent innovative cleanup technologies developed by DOE EM have eliminated anthropogenic mercury sources from Tims Branch watershed; however, a known quantity of relatively inert tin oxide tracer was introduced to the ecosystem. DOE EM has highlighted the need to track the tin and to understand the impact of frequent or extreme atmospheric events on its redistribution in Tims Branch. FIU will utilize the data available from the tin-based remediation technology to develop a model that can not only be extended to investigate other contaminants of concern (e.g., mercury, uranium, nickel, aluminum and other metals and radionuclides), but also be applicable to other nearby watersheds.

During FIU Performance Year 8, the hydrology models developed by FIU in Performance Years 6 & 7 will be fully calibrated and coupled. The software used has provided the flexibility to simulate overland flow and stream flow in either a stand-alone or coupled fashion, which can provide significant results in each case. The main activities will include the following:

- *Sensitivity analysis and calibration of the MIKE SHE overland flow model.*
    - FIU will complete the sensitivity analysis and calibration of the MIKE SHE overland flow model and conduct an updated literature review to determine reliable calibration methods, focusing on the most recent publications relative to MIKE SHE calibration and sensitivity analysis.

- *Sensitivity analysis and calibration of the MIKE 11 stream flow model of the A-014 outfall tributary.*
    - FIU will conduct sensitivity analysis and calibration of the existing MIKE 11 stream flow model developed by former DOE Fellow Natalia Duque. The simplified model of the A-014 outfall tributary will be reviewed and used to perform preliminary simulations and to train new DOE Fellow graduate students during this fiscal year.
- *Addition of existing man-made infrastructures to the A-014 model.*
    - There are several man-made hydraulic structures along the A-014 outfall tributary that were installed to control the flow velocity and erosion of the channel banks. These existing control structures must be included in the stream model to simulate the flow within the specific design of each structure. This requires creation of separate MIKE hydrodynamic files for each structure individually. These files contain the design specifications of each hydraulic structure. Simulations will be performed separately before and after each structure was installed to assess the effect of each structure on the simulation results.
- *Development of the MIKE 11 stream flow model of the main Tims Branch stream.*
    - This model is an exclusive stream flow model that simulates the flow characteristics within the Tims Branch stream. Tims Branch is highly affected by runoff, therefore it is very important to develop an exclusive flow model to estimate the flow depth and velocity after heavy rainfall occurs. FIU will delineate the main Tims Branch stream network using MIKE 11 and ArcGIS tools.
- *Sensitivity analysis and calibration of the MIKE 11 stream flow model of the main Tims Branch stream.*
    - As part of the model application and verification process, FIU will conduct a sensitivity analysis to find the calibration parameters. Multi-variable sensitivity analysis will also be considered to understand the model's response when two or three variables are changing simultaneously. This will increase certainty of the model output.
- *Scenario analysis.*
    - FIU will implement specific rainfall scenarios in each model to understand the models' behavior under various atmospheric conditions. Atmospheric scenarios will be determined based upon historical rainfall events and data provided by federal/state online databases or data provided by SRNL/SRNS.
- *Coupling of the overland flow and stream flow hydrological models*
    - The A-014 and Tims Branch stream flow models will each be coupled with the main overland flow model to increase the certainty of the overland flow model results. Coupling the 1-D stream flow and 2-D overland flow will create a comprehensive distributed surface water model that can be used as a tool to estimate hydrological components of the surface water under different scenarios.
- *Calibration of the coupled flow model*
    - Final calibration of the entire model will ensure the model's certainty and accuracy.
- *Data analysis and visualization*
    - MIKE and ArcGIS tools will be used for data analysis and visualization of model results.
- *Preliminary development of solute transport model*

  - FIU, with the support of DOE Fellow graduate students, will begin the literature review and assimilation of data to initiate the development of the solute transport component of the model using MIKE ECO Lab or other solute transport models.
- *Preparation of draft journal paper for publication.*
  - A draft manuscript will be prepared based on the calibration of the MIKE SHE model of the Tims Branch watershed for submission to a relevant peer reviewed journal, and due to the site specific nature of the research, the publication will be presented as a case study. In addition, a minimum of one peer reviewed journal paper on the stream flow model and flood assessment will be considered.

Subtask 3.2: Application of GIS Technologies for Hydrological Modeling Support

Application of GIS technology is a key component in hydrological modeling that helps to prepare data, display results and conduct further spatial analyses. The use of GIS technology has supported the development of a geodatabase to store and manage model-specific geospatial and timeseries data. GIS modeling tools have also been applied to perform associated geoprocessing of downloaded or model-derived data.

During FIU Performance Year 8, FIU will continue to support hydrological model development with pre- and post-processing of data. GIS tools will support the development of the flow and transport models for delineation of the stream network and generation of cross-sections and profiles of the major and minor tributaries of Tims Branch. Advanced geospatial and statistical analyses will also be conducted for the Tims Branch watershed. This will include an extreme hydrological event analysis to determine hyetographs for Tr = 2, 5, 10, 25, 50, 100 and 200 years for use in the integrated surface water model to simulate the spatiotemporal distribution of flow depth and velocity in Tims Branch under extreme hydrologic scenarios. FIU graduate and undergraduate DOE Fellow students will be mentored and trained on how to perform geoprocessing tasks, conduct geospatial analyses and generate maps and graphs for reporting purposes.

Subtask 3.3: Data Collection, Sampling and Analysis in Tims Branch Watershed

For application of the hydrology models being developed for Tims Branch, a rigorous calibration and validation exercise is necessary to increase confidence in the models' ability to estimate flow depth and velocity, and contaminant spatial distribution over time. The main challenges in hydrological modeling, however, are finding observed/measured data for the model calibration and validation process. It is therefore often necessary to collect additional field data to support model validation. During FIU Performance Years 6 and 7, field sampling and data collection in Tims Branch was initiated by ARC researchers and FIU DOE Fellow students with support from SREL. This effort included water sampling and analysis for tin, mercury, uranium and other inorganic constituents, and measurement of stream cross-section profiles and field environmental conditions such as flow velocity, suspended particle concentration and other water quality parameters along the A-014 outfall tributary and the main Tims Branch stream. During FIU Performance Year 8, sampling and *in situ* data collection will be continued by FIU students (DOE Fellows) as part of a student summer internship mentored by SRNL/SREL scientists, and any additional/follow-up fieldwork will be conducted by FIU students and FIU ARC researchers in collaboration with SRNL/SREL personnel. FIU's proposed sampling and *in situ* data collection protocol will include:

- Establishing long term monitoring station(s) (stage gauge) along Tims Branch and the A-014 outfall tributary to collect timeseries data of the following:
    - Depth of water/discharge
    - Water temperature
    - pH
    - Turbidity
    - Suspended particle concentration

  Deployment of a remote monitoring system in Tims Branch is planned for FIU Performance Year 8. A HOBO RX3000 Remote Monitoring System was purchased by FIU and will be tested and used to train DOE Fellow students prior to its deployment at SRS. This instrument is a water level data logger which has a web-based configuration so that data is stored and managed via the internet in the HOBOlink service cloud. HOBOlink allows the user to access current and historical data and manage and control the configuration of sensors, logging rates, alarm notifications and relay activations.

- Measurement of flow velocity in at least two locations upstream and downstream of Tims Branch and along A-014 outfall tributary at the same locations where data was collected during the fieldwork conducted in August 2016.
- Cross section profiling along the main Tims Branch stream
- Collection of samples (water, sediment and biofilms) from selected Tims Branch compartments and the A014 outfall tributary.
    - Analyzing the biota samples for possible contaminant deposit.
    - Sediment core sampling and thickness measurement at locations along the A-014 tributary and the main Tims Branch stream as site regulations permit.
- Laboratory analysis of contaminant concentrations (e.g., mercury, tin and uranium) in bulk water, sediment and biota samples. SEM/EXAFS/XRD analysis of isolated particulates (particle size and morphology, mineralogy and element concentration/distribution).

In situ field data will be used for model validation and to assess the Tims Branch ecosystem response (cleanup progress) to the implemented tin-based remediation technology

Task 5: Research and Technical Support for WIPP

Background

The current performance assessment (PA) for the Waste Isolation Pilot Plant (WIPP) recommends a K_d range of 20 – 400 mL/g for Pu(III) and Am(III) (Brush and Storz 1996). However, reliable measurements have not been reported for actinide and lanthanide sorption to dolomite minerals especially in the presence of relevant ligands. Previous experiments reported issues with oversaturation with respect to actinide and lanthanide solubility and often did not cover the range of conditions expected for the WIPP (Brady et al. 1999, Brush and Storz 1996, Perkins et al.1999). For example, the experiments cited for the PA from Brush and Storz (1996) were conducted in relevant brines, but they did not report pH for Am(III) and data is limited for Nd(III). Previous researchers have reported a range of K_d values from 200 – 10^6 mL/g for sorption of Am(III) and Pu(III) to calcite and dolomite minerals (Brush and Storz 1996, Dosch 1979, Higgo and Rees 1986, Lucero et al. 1998, Perkins et al. 1999, Shanbhag and Morse 1982).

There are several ligands that have been previously identified in waste being disposed of at the WIPP, including EDTA and oxalate (Dunagan et al. 2007). Cellulose degradation products like isosaccharinic acid (the major degradation product formed under alkaline conditions) are also expected to form within a deep geologic repository and play a role in contaminant transport (Askarieh et al. 2000). EDTA poses the greatest risk as it may form the strongest metal complexes (Brush 1990). Further, thermodynamic complexation constants have been measured previously for these compounds at high ionic strengths (Borkowski et al. 2001, Thakur et al. 2015, Thakur et al. 2014), although the effects of these ligands on the complex redox chemistry of the actinides is still not well understood.

Sorption of these ligand-actinide complexes for WIPP-relevant minerals and ionic strength has also not yet been conducted. Previous research showed significant complexation of Eu, Am, and Th by isosaccharinic acid in artificial cement porewater at pH 13.3 that led to a reduction in sorption to calcite (Tits et al. 2005). However, this work did not include carbonate in synthetic solutions or account for the presence of carbonate due to calcite dissolution in speciation modeling. Because of the strong effect of carbonate on actinide speciation, these must be represented in experiments conducted for the WIPP.

FIU ARC will collaborate with research scientists from the Actinide Chemistry and Repository Science (ACRSP) in support of Los Alamos National Laboratory’s field office located at the Carlsbad Environmental Monitoring and Research Center (CEMRC) in Carlsbad, New Mexico.

Objective

The overall objective of this task is to update experimental sorption data for actinides in the presence and absence of relevant ligands. This can be accomplished by using the actinide or an oxidation state analog with complementary batch and mini-columns experiments across a range of ionic strengths in the presence of relevant WIPP minerals and ligands. FIU Performance Year 8 will focus on understanding ternary interactions of the trivalent and hexavalent oxidation states (Am, U, and lanthanide analogs) with relevant minerals in the presence of relevant ligands including but not limited to oxalate, EDTA, and isosaccharinic acid.

Benefits

These experiments are expected to significantly reduce the uncertainty in the partitioning coefficients for the trivalent actinides in the presence of dolomite under WIPP relevant conditions. These experiments may allow the DOE to increase K_d parameters for the trivalent actinides as the current PA models assume a K_d range of 20 – 400 mL/g as compared to the reported range of 200 – 10^6 mL/g. This could lead to a significant cost savings in engineered barriers and environmental monitoring as an increased certainty in K_d values will likely decrease the need for additional engineered barriers and monitoring. Further, the impact of relevant ligands will also be taken into account.

There is synergy with this proposed work through current and future studies by Reed and Yalcintas investigating redox chemistry (including radiolysis effects) and complexation of uranium in the presence of EDTA and carbonate in the absence of minerals. In addition, ongoing research by Swanson and Reed will benefit from these results as microbial communities may be impacted by and be capable of influencing the formation and degradation of cellulose degradation products like isosaccharinic acid.

Technical Approach

Subtask 5.1:

During FIU Performance Years 6 and 7, research was initiated with the LANL ACRSP team to investigate the sorption of Nd to dolomite at variable ionic strength via mini column and batch experiments. Data has now been generated for ionic strength from 0.001 to 5.0 M in batch experiments with results highlighting an increase in removal from the aqueous phase with ionic strength. However, column experiments at 0.1 and 5.0 M ionic strength do not show significant differences. The working hypothesis is that co-precipitation and adsorption occurred in the batch experiments with a likelihood of greater co-precipitation at increased ionic strength due to greater solubility of dolomite. Moreover, co-precipitation processes did not occur in column experiments due to a shorter equilibration time. Therefore, we expect that adsorption is not dependent on ionic strength. During FIU Performance Year 8, a publication will be drafted and submitted to a peer-reviewed journal to finalize this task.

Subtask 5.2:

FIU has generated preliminary data on fate and transport of actinides and lanthanides (Nd, Th, and U) in the presence of EDTA in 0.1 M ionic strength (0.097 M NaCl + 0.003 M $NaHCO_3$) with relevant minerals. These results show that equilibrium is much slower in the presence of organic ligands. During FIU Performance Year 8, experiments will be conducted with dolomite or iron oxides at variable ionic strength (simplified brines in 0.01 to 5.0 M ionic strength in NaCl and $MgCl_2$), ligand concentration (including but not limited to EDTA and ISA), pH, and actinide/lanthanide concentration (Am, U, and lanthanides) to quantify the kinetics and equilibrium partitioning of actinides and their analogs in these ternary systems. Mini columns may be conducted for select systems based on the likelihood of transport in order to compare the impact of flow on these interactions.

PROJECT MILESTONES

Milestone No.	Milestone Description	Completion Criteria	Due Date
2017-P2-M1	Submit four draft papers to Waste Management 2017 Symposium	Acceptance notification by WM17 reviewers	12/15/2017
2017-P2-M2	Submit publication for review in peer-reviewed journal for sorption of Nd to dolomite at variable ionic strength (Subtask 5.1)	Submission of memo by Project Manager	1/15/2018
2017-P2-M3	Completion of experiments of pertechnetate reduction by magnetite in bicarbonate-free conditions (Subtask 1.4)	Submission of memo by Project Manager	1/31/2018
2017-P2-M4	Submit publication for review in peer-reviewed journal for partitioning of U following base treatment (Subtask 1.1)	Submission of memo by Project Manager	2/15/2018
2017-P2-M5	Completion of Tc-99 immobilized by magnetite dissolution kinetic experiments in the presence of bicarbonates	Submission of memo by Project Manager	2/28/2018
2017-P2-M6	Complete a set of column experiments using modified humic acid (Subtask 2.3)	Submission of memo by Project Manager	2/28/2018
2017-P2-M7	Complete sensitivity analysis of MIKE 11 stream flow model for A-014 outfall (Subtask 3.1)	Submission of memo by Project Manager	4/6/2018
2017-P2-M8	Complete batch isotherm experiments of uranium removal by HS sorbed on SRS sediments (Subtask 2.3)	Submission of memo by Project Manager	4/13/2018
2017-P2-M9	Complete coupling of MIKE SHE and MIKE 11 models (Subtask 3.1)	Submission of memo by Project Manager	6/15/2018

DELIVERABLES

Client Deliverables	Responsibility	Acceptance Criteria	Due Date
Draft Project Technical Plan	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	10/20/2017
Presentation overview to DOE HQ/Site POCs of the project progress and accomplishments (FIU Research Review)	Project Manager	Presentation to DOE HQ and Site POCs	4/6/2018**
Draft Technical Report on uranium removal isotherms by HS sorbed on SRS Sediments via Batch Experiments (Subtask 2.3)	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	5/18/2018
Draft Technical Report on the synergy between colloidal Si and HA on the removal of U(VI) (Subtask 2.2)	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	6/22/2018
Draft Technical Report on the surface water modeling of Tims Branch (Task 3)	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	8/10/2018
Monthly Progress Report	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	Monthly
Quarterly Progress Reports	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	Quarterly
Presentation overview to DOE HQ/Site POCs of the project progress and accomplishments (FIU Research Review)	Project Manager	Presentation to DOE HQ and Site POCs	9/28/2018**
Draft Year End Report	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	11/2/2018

**Final documents will be submitted to DOE within 30 days of the receipt of comments on the draft documents.*

***Completion of this deliverable depends on availability of DOE-HQ official(s)*

COMMUNICATION PLAN, ISSUES, REGULATORY POLICES AND HEALTH AND SAFETY

Communication Plan

Communication with the research collaborators and other stakeholders at the DOE sites, national laboratories, and DOE HQ is a critical component of the project, including the clients and relevant experts at DOE EM, PNNL, SRNL, SREL, LANL, and CBFO. The mode of communication will be e-mails, telephone/conference calls and meetings at the sites. Though site-specific contact persons have been identified, constant communication will be maintained with client stakeholders at DOE HQ and the DOE sites and to ensure all parties involved are aware of the project progress.

Information Item	Client Stakeholder	Schedule	Communication Method	Responsible Stakeholder
Status Update Teleconferences	DOE EM, PNNL, SRNL, SREL, LANL	Monthly	Phone	Project Manager
EM-HQ Status Update Phone Call	DOE EM	Bi-Weekly	Phone	Principal Investigator
Quarterly Report	DOE EM, PNNL, SRNL, SREL, LANL	End of Q1, Q2, Q3, Q4	E-mail	Principal Investigator
Annual Year End Report	DOE EM, PNNL, SRNL, SREL, LANL	45 working days after completion of performance period	E-mail	Principal Investigator/ Project Manager
Papers and presentations	DOE EM, PNNL, SRNL, SREL, LANL	As developed for conferences	E-mail	Project Manager
Deliverables/Milestone	DOE EM, PNNL, SRNL, SREL, LANL	At completion of deliverable/milestone	E-mail	Task Manager
Coordination of project activities	DOE EM, PNNL, SRNL, SREL, LANL	As needed to discuss issues and reach consensus	Phone, E-mails	Project Manager

Anticipated Issues

Project 2 receives significant support from DOE Fellows. It is anticipated that DOE Fellows will be supporting research related to this project (undergraduate and graduate) during FIU Performance Year 8. It is anticipated that research under this task may be used by students as the basis for a thesis or dissertation towards a graduate degree and would be impacted by a re-direction of the project task scope. FIU will communicate closely with DOE HQ and site contacts throughout the performance of the research tasks in order to accurately forecast the duration of the research tasks and minimize the potential negative impact of scope redirection on the graduate studies of any students working on that task.

Regulatory Policies and Health and Safety

All laboratory experiments and pertinent FIU on-site task activities will be performed in accordance with FIU-ARC's Project-Specific Health and Safety Plan (PSHASP). Standard health and safety issues normally associated with field activities and laboratory experiments will not directly apply to project work related to computer-based modeling and information technology development. Much of the environmental and GIS data used for hydrological model development will require security clearance from SRNL. As such, cyber security measures will be established to ensure that data integrity is maintained. In addition to the FIU-ARC firewalls and the built-in software and hardware security protocols, all computers used in this project must adhere to FIU's University Technology Services (UTS) Security and IT Policies which are outlined in detail at the following links: *http://it.fiu.edu/security/index.shtml* and *http://security.fiu.edu/Pages/policies.aspx*. Security measures such as password protection will also be implemented in addition to an effective security strategy for sharing the database via the internet with other project stakeholders such as DOE or DOE site contractors. Any field and laboratory work performed by FIU at the DOE sites will be conducted in accordance with the sites' required security and health and safety protocols.

No undergraduate student will perform research in a lab without direct oversight of faculty, staff, or a qualified graduate student.

The Department of Health and Safety at FIU also provides other training relevant to specific tasks or subtasks. Either FIU EHS or FIU ARC may request an audit by FIU EHS of safety documentation, lab set up and procedures when there are any concerns by any staff working on the task.

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