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Mid-Award Progress Report for Department of Energy Office of Science Graduate Student Research Program

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DOE Office of Science Graduate Student Research Program Progress Report For Mary Kathryn Hoffman

Guidelines for this section: Please follow the template and provide information for all fields unless it is specified as "optional". The information you provide should be a narrative on meaningful progress and/or accomplishments in achieving the research goals and objectives of the SCGSR project proposed at the time of application. The content of your narrative should be written at a level for readers who are not necessarily subject matter experts, but do have general scientific or technical knowledge and research experience. Do not assume the reader knows your terminology. Spell out all acronyms the first time they are used.
Note: Figures and Equations should not be included in the narrative section below. If they are necessary in illustrating important research concepts and/or approaches, all Figures and Equations must be placed into one single PDF document in a well-organized manner and uploaded as part of the report template under the "Uploading Additional Materials" section.
The content, data, and/or figures provided in your progress report are considered confidential and will not be shared with outside parties. For program management purposes, the mid-year reports will be viewed by the DOE SCGSR program manager and may be made available to your Collaborating Laboratory Scientist and Graduate Thesis Advisor.

Research Goals and Objectives

List the major goals of the project as stated in your SCGSR research proposal at the time of application, including the scientific and technological objectives of this effort. Describe the proposed technical approach to obtain those goals. Briefly describe how the project is contributing to your doctoral thesis/dissertation. If your SCGSR research proposal listed milestones/target dates for important activities or phases of the project, identify these dates and show actual completion dates or the percentage of completion.
Generally, the goals will not change from one reporting period to the next and are unlikely to change during the final reporting period. However, if the SCGSR program approved changes to the goals during the reporting period, list the revised goals and objectives. Also explain any significant changes in approach or methods approved by the SCGSR program. *[Max character count: 5000]*

The purpose of the work proposed for this study is to investigate the behavior and transport mechanisms for cesium-137 in soils collected from contaminated sites with distinct source release scenarios. More specifically, this study aims to determine with which elements and minerals cesium-137 associates in these various environments to more reliably predict its migration in the subsurface. This will be achieved using a state-of-the-art analysis technique available at Lawrence Livermore National Laboratory (LLNL) known as NanoSIMS. Nano-scale secondary ion mass spectrometry, or NanoSIMS, is a destructive surface analysis technique in which positive secondary ions are generated from the surface of a sample and then quantified based on their mass-to-charge ratio (m/z) using mass spectrometry. The data collected about the secondary ions can then be used to create isotope-specific spatial maps with a resolution of a few hundred nanometers and depth profiles that show the variation of the secondary ion intensity with sputtering time. This should be an ideal technique for locating cesium-137 in a sample, as cesium is an easily ionized element, meaning the yield of secondary cesium (Cs) ions produced should be high and making the identification of cesium-137 straight forward.

The first goal of this project is to develop a reliable method for NanoSIMS analysis of cesium-137 in contaminated soils. The plutonium work done previously by the Subsurface Biogeochemistry of Actinides Scientific Focus Area (SFA) team led by Annie Kersting and Mavrik Zavarin at LLNL will be the framework for the analyses in this project, but cesium does not behave the same as plutonium. The sample preparation and NanoSIMS methods will need to address the unique challenges associated with Cs and the soil matrix. Matrix-matched standards, where a known amount of cesium is sorbed to a solid material that has a similar or identical composition to the sample soil, will be used to develop and test these methods. To help prepare these standards and to complement the NanoSIMS analysis, experiments will be set-up to measure the rate of sorption and desorption of cesium-137 to and from bulk sample soils.

The second goal for this project is to use the developed NanoSIMS methods to analyze soils from several locations around the world with varying environmental conditions. Soil from the Marshall Islands will be the first focus of analysis, and other samples from locations such as Fukushima may be analyzed later. Each sample will likely have a unique composition that will require the method to be altered, especially with regards to any unique mass interferences for cesium-137 also originating from the soil. The NanoSIMS results of each sample will be compared with the depositional history at that site as well as with the results from other sites.

The final goal for this project is to compare and correlate the collected NanoSIMS data with data from other analytical techniques such as scanning electron microscopy (SEM), x-ray diffraction (XRD), and digital autoradiography. These other techniques will be used to analyze the samples before the NanoSIMS is used, which will identify areas of focus for the NanoSIMS analysis. For instance, XRD will be used to characterize the elemental composition of the bulk soil, which could help identify the size fraction of the soil with the most cesium-137 activity. SEM will also be used to characterize elemental composition of the sample, but at a micro-scale, helping to identify individual particles of interest. Autoradiography will be used to image the radioactivity of both the bulk soil and the prepared NanoSIMS samples to identify area of elevated cesium-137. These techniques may also be used after the NanoSIMS analysis to verify and compliment those results. By combining these techniques, we can draw conclusions about the behavior cesium-137 in the subsurface.

Like the proposed project, the focus of my thesis is characterization of radioactive contamination in the environment. My thesis relates the behavior of the radionuclide cesium-137 at a macro-scale in bulk soil to the behavior at the micro-scale. While there are some experiments I can accomplish at the University of Cincinnati (UC), like a sequential extraction and a morphological analysis by SEM of bulk Marshall Islands soil, our tools for measurement and expertise with cesium sorption are limited. Coming to LLNL to complete work for my thesis enables me to use state-of-the-art instruments like NanoSIMS and get assistance from experts in the field, both of which I would not have access to at my home institution. This project will ultimately produce more accurate and reliable results that will elevate the quality of my thesis as a whole.

Project Progress in Accomplishing the Research Goals and Objectives

For the period from the beginning of the SCGSR project till the time of this report, describe what was accomplished under the major goals of the project. More specifically, describe: 1) major activities; 2) specific objectives; 3) significant results or key outcomes, including major findings, developments, or conclusions (both positive and negative); and/or 4) other achievements. Include a discussion of stated goals not met. [Max Character count: 10000]

The work on the project so far has addressed multiple proposed goals. The activities have fallen into two categories: micro- or nano-scale characterization and bulk characterization of Marshall Islands soil. Micro-scale characterization has included use of nano-scale secondary ion mass spectrometry (NanoSIMS), scanning electron microscopy (SEM), and digital autoradiography. The primary aim of these activities has been identifying cesium-137 in small amounts and even individual particles of soil. Bulk characterization has included desorption experiments using dialysis membrane. The aim of these other activities has been measuring the rates of adsorption and desorption of cesium-137 from large amounts (~100g) of soil. Characterizing the soil at both the micro-scale and bulk level will provide a better understanding of the overall behavior of cesium-137 and dividing the activities accordingly allows for a clearer description of the aims of each experiment.

SEM analysis was one of the first activities and the results have assisted most with the micro-scale characterization of the soil samples. The technique SEM is generally used to investigate elemental composition and morphology of materials, which can be very useful before and after a NanoSIMS analysis. For this project, SEM was used to characterize Marshall Islands soil samples that had been analyzed by NanoSIMS before the start of this award period. [Preliminary experiments were performed earlier to determine the feasibility of using NanoSIMS for this purpose.] The soil had been size fractioned, but had not undergone any chemical processing, maintaining a composition representative of the current conditions of the environment at the time of sample collection. The previous NanoSIMS results showed discreet areas within the soil grains with elevated counts at mass 137. These “hot spots” were analyzed by energy-dispersive X-ray spectroscopy (EDS) on the SEM and the predominant elements were those expected to be in that environment (i.e. calcium and magnesium carbonates). No cesium was observed by SEM, likely because the concentration of cesium in the sample was below the detection limit of the instrument. There was, however, an unexpected element present: tin. These SEM results were used to guide the strategy for the next NanoSIMS analysis, which occurred in June 2017 and was also categorized as micro-scale characterization.

The overall consensus from previous NanoSIMS sessions and from the SEM measurements described above was that the mass calibration of the NanoSIMS for cesium-137 needed to be confirmed prior to further analyses, largely because the presence of cesium could not be confirmed by EDS. To facilitate this process, samples with a higher cesium-137 activity per gram were analyzed next by NanoSIMS. These new soil samples that were provided had a different chemical composition than the previous samples. A chemical dissolution had been used to remove a large percentage of the mineral phases present in the soil as a way to raise the activity per gram from the raw soil that was analyzed earlier. SEM-EDS analysis showed the composition of these new samples included significant amounts of aluminum, silicon, potassium, iron, calcium, and sodium, as well as smaller amounts of chromium, chlorine, titanium, manganese and tin.

As the preliminary SEM work was completed for these newest samples, the plan for the next NanoSIMS session was finalized. For NanoSIMS and most other types of mass spectrometry, data can only be collected for a finite number of mass values each session. As a result, only the following isotopes/mass values would be measured: silicon-30, potassium-39, titanium-48, iron-54, tin-118, calcium-44, cesium-133, mass 137, and barium-138. Other than cesium and barium, these isotopes were chosen because they were observed during SEM-EDS of the samples. The primary objective of this NanoSIMS session was to search and analyze any cesium-137 present, but tin was also of special interest because it was unexpectedly seen during SEM-EDS.

The results of the NanoSIMS analysis from the end of June have proven to be a turning point in this project, but not necessarily a positive one. Areas with elevated counts of mass 137 were once again observed. This session however, it was also observed that in every instance of elevated 137 counts, there was a corresponding elevation in tin-118 counts. This result indicates that tin, which has several naturally occurring isotopes, is a likely interference for the mass 137. This means that tin ions were combining with other ions present and creating a species that has a mass not easily resolved from cesium-137. Based on natural abundances, the most likely option is tin-120 plus an oxygen-16 and a hydrogen-1. Although only a preliminary result during the NanoSIMS analysis, this was a strong indicator than no cesium-137 had been measured yet by this technique in the two previous sessions with other Marshall Islands samples. It should be noted that this was the first session in which any tin isotopes had been measured. Further inspection of the NanoSIMS data only confirmed the preliminary conclusions: any counts of 137 correlated in a 1:1 ratio with counts of tin-118.

Once this tin theory had been established, the next step was to confirm the presence of tin in the samples by another technique. Once again, SEM was used for characterization. Both the samples from the June session and the earlier (April 2017) session were reexamined, specifically at all the locations where elevated counts of 137 had been observed. Tin was detected in each spot, in varying quantities. This confirmed that tin was an interference for NanoSIMS analysis of these samples. There is still a possibility that some of signal detected at mass 137 was produced by cesium, but identification of the analyte was no longer straight forward.

Autoradiography was then employed as another micro-scale characterization technique, specifically to determine if radioactive cesium was actually present in the samples analyzed by NanoSIMS. In autoradiography, radioactive decay being emitted from a sample alters the molecules on a film or plate that is coated with a radiation-sensitive substance, in such a way that an “image” is created. This film is then developed like in photography, or the plates are digitally scanned. The image produced through this process is effectively a map of the radioactivity present in the sample, where darker areas correspond to more radioactivity. The samples prepared and analyzed by NanoSIMS are the only samples that have been imaged with this technique. Results have shown that there is radioactivity present in the NanoSIMS samples and based on previous gamma measurements, the only significant source of radioactivity is cesium-137. It is still unclear why no cesium-137 has been detected by NanoSIMS if it is observed in the sample using other techniques.

Bulk characterization experiments have also been conducted. The aim of these experiments has been to determine the behavior of cesium in the environmental conditions of the Marshall Islands, which is different from the micro-characterization techniques. Based on work done previously in the SFA group at LLNL, we have started sorption experiments with raw, unprocessed, bulk Marshall Islands soil. These experiments use dialysis membrane devices known as Float-a-lyzers to physically separate the sample soil from a cesium sink—the mineral illite, which has a high affinity for cesium—but still allow cesium-137 ions to move freely between the two solids in a surrounding aqueous solution. The movement of the cesium-137 between the two solid phases can then be monitored easily by removing the Float-a-lyzer periodically and measuring the cesium-137 via gamma counting. Progress so far has included testing the experimental set-up, testing various parameters by spiking in known amount of cesium-137. Results from these initial experiments have shown that the experimental set-up does work—the activity outside the float-a-lyzer is decreasing and the activity inside the float-a-lyzer is increasing over time. This is happening on a much slower time scale than expected however. Next steps will include using the conditions we've optimized so far and moving on to contaminated Marshall Islands. These experiments will help us calculate rates of desorption which can be compared to any NanoSIMS results to draw conclusions about behavior in the environment

The work thus far has related to each of the three major goals in the proposal. We have started to develop a method for NanoSIMS analysis of Marshall Islands soil, but have encountered a major detection issue in the form of a tin interference. This issue has been partially investigated with SEM and autoradiography, but a solution has not been discovered yet. A solution will be necessary to fully develop this method. We have also already analyzed some Marshall Islands soil and these soils are in fact the current focus of our method development. Cesium-137 has not been measured by NanoSIMS yet, but hopefully more method adjustments will make this possible. We also haven't analyzed soil from any other locations like Fukushima for comparison. Once the method has been optimized for Marshall Islands soil, we will work to alter it for soil collected from other locations. Finally, other instrumentation—specifically SEM and autoradiography—has been an integral part of method development for NanoSIMS and this technique will continue to be important as we start to solve the issues and measure cesium-137 successfully. Ultimately we are approximately halfway to achieving each of the goals set out.

Use of DOE Laboratory Facilities and Research Capabilities

Please describe the major DOE laboratory research facilities and/or research instrumentation or capabilities at the DOE laboratory that you used as they were an essential part of your SCGSR research project. [Max Character Count: 500]

NanoSIMS 50 – Nano-scale secondary ion mass spectrometer at LLNL is being used to spatially map cesium-137 contamination on individual particles of soil. Identifying the elements with which this radionuclide associates will help to predict future migration in the subsurface.

Nuclear Counting Facility – All gamma counting is being performed in the NCF at LLNL. Gamma counting is the preferred method to measure cesium-137 and the NCF provides low-level counters that are ideal for measuring environmental samples with low activities.

What do you plan to do for the remaining period of your SCGSR project until the ending date to accomplish the goals and objectives? [Max character count: 5000]

The first goal of this project was to develop a method for analyzing cesium-137 using the NanoSIMS and this will continue to be a goal until the end date, but the focus will shift to solving a specific analysis issue. The presence of tin in the soil samples analyzed so far has prevented reliable interpretation of the results. Soil samples that have been processed differently than previous samples will be analyzed by NanoSIMS, looking for cesium and tin isotopes specifically. Other aspects of the analysis including sample mounting techniques and instrumental settings may also need to be altered. Matrix-matched standards with varying concentrations of the analyte will also be examined to help determine a radioactivity detection limit for different types of soil. By the end date, the objective is to reliably replicate cesium-137 detection and analysis on standards and samples alike.

To assist with this method development, autoradiography will continue to be used as a means to screen for radioactivity. Thus far, it has been used verify the presence of radioactivity after NanoSIMS analysis, but for the future, we will also hopefully use it to locate areas of higher radioactivity before a NanoSIMS analysis. More samples will be imaged by autoradiography including the matrix-matched standards, raw unprocessed Marshall Islands, and any other relevant materials that are also being analyzed by NanoSIMS. New sample mounting techniques will also be tested, including spreading soil into an even layer on a grid so that locating the particle for further analysis is less difficult. The objective is to have "hot" particles or a smaller mass of soil identified to use for NanoSIMS analysis.

Other analytical techniques will be used to survey and characterize soil, including SEM and XRD. SEM will continue to be used to analyze samples before and after NanoSIMS analysis as it is much more cost effective technique. XRD will be used to analyze the bulk elemental composition of any new soil samples, including samples from other locations. The data from these techniques will continue to be used to guide and help understand the implications of NanoSIMS results.

Lastly, the Float-a-lyzer desorption experiments that have been tested will be used to analyze contaminated soil from the Marshall Islands and any other samples of interest. Thirteen new samples from the Marshall Islands have already been acquired for these experiments and we will continue to look for others. Materials that can be used as a benchmark for comparison will also be investigated such as pure calcium carbonate or a well characterized mineral. These results will then be correlated with any NanoSIMS results that have been collected and conclusions will be drawn about the implications of the data on the geochemical behavior of cesium-137 in the subsurface.