Environmental Management Science Program

Project ID Number 55148

Hydrologic and Geochemical Controls on the Transport of Radionuclides in Natural Undisturbed Arid Environments as Determined by Accelerator Mass Spectrometry Measurements

Gregory Nimz
Lawrence Livermore National Laboratory and Center for Accelerator Mass Spectrometry
Mail Stop L-219
P.O. Box 808
Livermore, CA 94550
Phone: 510-423-2766
E-mail: nimz1@llnl.gov

Marc Caffee
Lawrence Livermore National Laboratory and Center for Accelerator Mass Spectrometry
Mail Stop L-202
P.O. Box 808
Livermore, CA 94550
Phone: 925-423-8395
E-mail: caffee1@llnl.gov

Robert Finkel
Lawrence Livermore National Laboratory and Center for Accelerator Mass Spectrometry
Mail Stop L-219
P.O. Box 808
Livermore, CA 94550
Phone: 925-422-2044
E-mail: finkel1@llnl.gov

Jeffrey McAninch
Lawrence Livermore National Laboratory
Mail Stop L-397
P.O. Box 808
Livermore, CA 94550
Phone: 925-423-8506
E-mail: mcaninch1@llnl.gov

June 1, 1998
Hydrologic and Geochemical Controls on the Transport of Radionuclides in Natural Undisturbed Arid Environments as Determined by Accelerator Mass Spectrometry Measurements

Gregory Nimz, Lawrence Livermore National Laboratory and Center for Accelerator Mass Spectrometry
Marc Caffee, Lawrence Livermore National Laboratory and Center for Accelerator Mass Spectrometry
Robert Finkel, Lawrence Livermore National Laboratory and Center for Accelerator Mass Spectrometry
Jeffrey McAninch, Lawrence Livermore National Laboratory

Research Objective
This research develops techniques for measuring globally distributed radionuclides occurring today in extremely low abundances ("fallout" from the era of atmospheric nuclear testing), and then applies these techniques to better understand the mechanisms by which radionuclides migrate. The techniques employ accelerator mass spectrometry (AMS), a relatively new analytical tool that permits this work to be conducted for the first time. Because the nuclides addressed in this project originated from thermonuclear events, they are generally those of most concern when assessing the extent of and risk from actual or potential radioactive contamination. The advantages of our approach include: 1) the ability to conduct migration studies in locations most like those of concern to public health, e.g., a "far-field" environment; 2) sites of multiple contamination, e.g., by VOCs, can be avoided; 3) it becomes unnecessary to collect research samples that are themselves radioactive waste and are therefore difficult to handle and dispose of in the laboratory; and 4) since the nuclides are globally distributed, migration research can be conducted in any chosen environment.

Research Progress and Implications
This report summarizes the research progress through the first 16 months of a 3-year project. It discusses the work completed and in progress on the development of AMS techniques for $^{99}$Tc, $^{129}$I, $^{36}$Cl, and the development of a demonstration field site chosen for this project in arid unsaturated soils.

Development of AMS $^{99}$Tc Techniques. Prior to our EMSP work, no group to our knowledge had rigorously attempted to develop AMS for $^{99}$Tc measurements. This lack of precedence, and some specific technical difficulties related to the lack of a stable Tc isotope, presented a number of challenges and questions. We have shown that acceptable Tc- negative ion currents can be produced in the AMS cesium sputter source (ionization efficiency of about 1E-03). We have also demonstrated an ability to reject $^{99}$Ru, a stable isobaric interference, using our characteristic projectile x-ray detection system. An unanticipated problem was discovered in this process: S ions can combine with Cu or Zn ions to create isobaric interferences in the AMS system. We have addressed this in two ways. First, we added a thin gas ionization detector immediately before the x-ray detection system. Only masses with the appropriate energy loss ($\delta$-E) and x-ray emission for Tc are measured. Second, we now use TcO-, rather than Tc-, as the ion injected into the accelerator, which reduces the background by approximately two orders of magnitude. This significantly improves the sensitivity of our detection limit. In full analytical mode, we anticipate detection limits in the range of 10-100 femtograms of Tc.
Currently, our efforts center around the choice of an appropriate analytical matrix and dilution reference isotope, and the conversion of Tc in solution to a solid form for introduction into the ion source. We have tried and rejected both Rh and Ag as analytical matrices, although we have determined that either may be suitable with the planned implementation of new system control options. We are now using Nb for a matrix which shows good promise in initial tests. Preliminary results with Tc spikes showed ±20% reproducibility over two orders of magnitude, and for 5 widely varying sample preparation procedures. The standard deviation for blanks was equivalent to ±10 fg, and was dominated by trace Ru in the Nb stock. The background was 40±9 fg for a 1mg Nb sample. Correction of the results to account for the Ru is expected to further lower both the standard deviation of the blanks and the background. We have removed and detected 99Tc from spiked soils from the field area by these methods, and are now in the phase of this project of debugging and streamlining certain steps in our analytical method.

Development of AMS 129I Techniques. We have made significant improvements in iodine sputtering efficiency, beam current maximization, detection efficiency, and elimination of isobaric interferences. We now believe reliable 129I analyses can be made at a background level of 129I/I = 1E-13. This is more than adequate to measure natural ambient 129I/I levels in arid soils, and certainly adequate to measure anthropogenic levels. To demonstrate this, we performed two experiments. First, we measured 129I concentrations in soil sample IAEA-375 originating from Chernobyl, and having a 129I concentration of 1.2E09 atoms/gram (as determined by neutron activation to 20% accuracy). Within analytical uncertainties there is good agreement between our AMS measurements and those determined by the IAEA. Unfortunately, no “standards” exist that contain 129I concentrations in the low AMS range (i.e., below neutron activation capabilities). Therefore for a second experiment we made repeated measurements of a soil sample that serves as a proxy to those at our field site. It contains fallout 129I in concentrations measurable only by AMS. Because no “accepted” value for 129I concentration exists for this soil, we cannot judge the accuracy of our measurements. However, we can judge the precision of the measurements, and this is very good. Four of the 6 measurements agree within analytical error, and a fifth agrees within 20 percent. A sixth measurement was considerably lower than the others, but we believe this could be attributed to soil heterogeneity.

We are particularly concerned with the physical location of the iodine within soil samples. Speciation and complexing can result in either retardation or enhancement of migration. We have therefore conducted a series of sequential leaching experiments employing ammonium acetate (pH=8.2; pH=4.7), hydroxylamine hydrochloride, acetic acid, and ammonium carbonate. The soils undergo a sequence of 5 leaching steps. Initial results indicate that <20% of the 129I is leachable in water alone. This low result is somewhat surprising since iodine is regarded as a “conservative” species that readily migrates with water. Further, even smaller amounts are leachable in either mild base or acid solutions (strong solutions completely strip the 129I). Although these are only initial results, it may be the case that considerable 129I in the soil is fixed on clays or in organic matter.

Development of the Field Site: Unsaturated Zone Trench. Rather than taking samples from drillhole cores, we chose to excavate a 5m deep trench (20m length, 18m width) and sample from the trench wall. This provides the ability to sample adjacent to soil structures that might affect soil moisture flux and radionuclide transport. The trench is located on the Nevada Test Site, adjacent to the Carpetbag geological fault. This site was chosen because previous work had shown the existence of significant structural features in these soils, probably due to fault activity. Samples were collected in six vertical profiles from land surface to the bottom of the trench. Samples were taken every 25cm, which allowed both thorough spatial coverage and a complete sampling of all levels of soil stratigraphy. All soil units were sampled by this strategy. Two of the profiles were “baseline” profiles that intersected no structural features of the soil. The other four profiles sampled obvious fractures in the soil: one containing abundant carbonate infill, one containing moderate carbonate, one free of carbonate, and the final profile - along the “contact” of the carpetbag fault - was a carbonate/soil interface. The two fractures not filled with carbonate contained abundant plant roots.

Moisture Flux at the Field Site: Cl and 36Cl Distribution. The trench method of sampling provides very good geologic/hydrologic control for the distribution of the parameters that determine moisture and radionuclide flux. Concentrations of Cl at the field site are uniformly low, about 5-10 times lower than most similar arid sites. Maximum Cl values occur at depths between 2 and 3.5m, which is
1-3m shallower than similar sites in the region. The depths are not obviously correlated with soil structures. The lower concentrations result in calculated Cl ages that are 5-10 times younger at a comparable depth than similar sites regionally. Soil moistures are similar to those regionally, except for the zone <3 meters which is ~1.5 times the other sites. The moisture profiles combined with low Cl concentrations results in calculated moisture flux values significantly higher than regional expectations. The peak in fallout 36Cl occurs between 1.5-2.2m, with profiles along fractures consistently deeper. These are similar depths to those reported in other studies. Neither Cl nor fallout 36Cl appears to be correlated with soil particle size; although further particle characterization is continuing. As with almost all such published profiles, the Cl age at the depth of the fallout 36Cl peak is significantly higher than the 40-50 year age of the 36Cl peak. In order to reconcile the age disparity, the regional flux of Cl to the Earth’s surface must be increased by a factor of five. Given current best estimates of atmospheric 36Cl production, this seems unreasonable. The only other alternative appears to be a decoupling of Cl migration, with some Cl (here represented by the fallout Cl) migrating at a different rate than other Cl (here, the non-fallout Cl). While apparently enhanced by soil structure, the cause of the decoupling seems unrelated to all soil parameters measured or observed thus far. The existence of such decoupling would have significant implications for estimates of both moisture and radionuclide flux in arid soils. This will be the focus of further field work, numerical modeling of the flux, and the other radionuclide measurements to be made in this project.

**Planned Activities**

We now have the framework and confidence in our analytical techniques to begin 99Tc and 129I measurements on soils from the field site, with completion expected within a few months. We then will begin development of techniques for AMS measurement of 90Sr and 95Zr (or actinides). We are also now in a position to begin constructing a numerical model, using the NUFT unsaturated transport code, simulating the observed movement of moisture and fallout radionuclides at the field site. Full completion of this model is not expected until mid- to late-1999.