FY97 Annual Report for the Department of Energy Environmental Management Science Program

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

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Summary of FY97 Accomplishments. During FY97 this study has developed unique accelerator mass spectrometry (AMS) analytical techniques for measurement of ^{99}Tc and ^{129}I, which compliments an improved capability for measurement of ^{36}Cl. The ability to measure these nuclides in natural soil samples has been demonstrated through analytical results obtained during FY97. Methods to determine the distribution of these nuclides in their natural setting, which will vary depending on site-specific chemical conditions, have also been developed. Spatially well-characterized soil samples have been collected from the vadose zone to a depth of -5 meters at the Nevada Test Site. To do this, a deep trench has been excavated and the geological setting for the soils has been well documented. Physical, chemical, and isotopic analysis of these soil samples during the course of this research project will result in a numerical computer model for moisture and radionuclide migration in arid soils that is valuable to nuclear waste storage, site remediation, and groundwater recharge concerns.

Project Description. This research identifies and quantifies geochemical parameters controlling the migration of key radionuclides (^{36}Cl, ^{90}Sr, ^{93}Zr, ^{99}Tc, and I) in undisturbed vadose zone soils. The radionuclide measurements use newly developed techniques employing accelerator mass spectrometry (AMS), which permits this work to be conducted for the first time. There are four research components: (1) developing ^{90}Sr- ^{93}Zr-^{99}Tc-^{129}I AMS methods; (2) improving AMS ^{36}Cl and chlorine methods for determining moisture flux in arid soils; (3) measuring the distribution of ^{90}Sr-^{93}Zr-^{99}Tc-^{129}I relative to the moisture flux in a vadose zone as defined by chloride and ^{36}Cl movement; and (4) developing a numerical model simulating the migration which produced the observed distribution. The research results enable the long-term assessment of nuclear waste facility performance, public risk from past contaminant releases, and recharge to desert aquifers. Previously available quantitative information is insufficient for these determinations.

The initial phase of this study particularly focuses on the problem of defining soil moisture movement based on chloride and ^{36}Cl distribution. Direct physical methods of measuring moisture flux in arid soils are insufficient due to the inability to accurately measure in-situ moisture contents and potentials at very low levels. Therefore chemical methods employing ^{36}Cl and chloride must be used. The use of chloride and ^{36}Cl to mark moisture migration requires the assumption that flux occurs by piston flow. Data from several studies suggest that solutes such as chloride may move through the vadose zone not by piston flow but via preferential pathways. This

would tend to invalidate the use of chloride for moisture flux determinations. It may be the case that over geologically long durations, and on a macro scale, pulses of preferential flow average out to mimic piston flow. However, studies have not yet been conducted to demonstrate this, or to understand the preferential flow processes well enough to diagnose their occurrence when one-dimensional (borehole) analytical strategies are employed (as has thus far always been the case). The purpose of excavating a trench in this study is to be able to "map" the migration of chloride, ^{36}Cl, and the other nuclides, in two and possible three dimensions. This will provide evidence of preferential flow, long-duration averaging of preferential flow, and the mechanisms by which such flow occurs. This will also provide the necessary data, and with sufficient spatial resolution, to create a well-constrained numerical model for moisture and radionuclide flux through the vadose zone in arid regions.

Project Timetable. The project goals for FY97 were: 1) development of AMS analytical techniques for measurement of ^{99}Tc and ^{129}I in environmental samples, 2) development of capabilities for reliable and replicable AMS analyses of ^{36}Cl and ^{129}I from soil samples, 3) excavation of a -5 meter deep trench in the vadose zone (alluvium) at the Nevada Test Site, the walls of which would provide soil samples for the determination of moisture and radionuclide flux (^{36}Cl, ^{90}Sr, ^{93}Zr, ^{99}Tc, ^{129}I), 4) AMS measurement of the concentrations of '"Cl, ^{129}I, stable chlorine and iodine, and related chemical components in samples from the trench wall, 5) characterization of the soil samples for moisture content, grain size distribution, secondary mineralogy, and related parameters to be used in subsequent numerical modeling of moisture and radionuclide flux. The projected work for FY98 includes the completion of ^{129}I analyses begun during FY97, complete analyses of ^{99}Tc in the soils, development of AMS analytical techniques for ^{90}Sr and ^{93}Zr, initial analysis of ^{90}Sr and ^{93}Zr in trench samples archived for this purpose, and the creation of a conceptual model for moisture and radionuclide flux at this site. The projected work for FY99 includes completion of AMS analyses of ^{90}Sr and ^{93}Zr, development of a numerical model for moisture and radionuclide flux using the LLNL NUFT computer code, and publication of the results of this study.

FY97 Accomplishments.

Development ofAMS ^{129}I Techniques. A significant amount of work during FY97 went into the AMS instrumental analytical procedures needed to measure ^{129}I. Sufficient improvements were made on sputtering efficiency, maximizing beam current, detection efficiency, and elimination of isobaric interferences that we now feel reliable ^{129}I analyses can be made at a background level of $^{129}I/I \approx 10^{-13}$. This is more than adequate to measure natural ambient $^{129}I/I$ levels in arid soils, and certainly adequate to measure anthropogenic (bomb-pulse or contaminant) levels. To demonstrate this, we performed two experiments. First, we measured ^{129}I concentrations in a soil with "known" ^{129}I concentrations. Measurement of ^{129}I at levels comparable to those achievable with AMS is so rare that it was difficult to locate "standard" samples to demonstrate our techniques. One sample that is available contains ^{129}I concentrations that overlap the levels measured by neutron activation and AMS. It is a soil collected in the vicinity of Chernobyl and distributed by the IAEA, denoted IAEA-375 Neutron activation techniques have determined the ^{129}I concentration to be 1.2 x 10^9 atoms/gram (20% uncertainty). Figure 1 shows the results of our AMS determination of the ^{129}I concentration of this soil obtained in the last year.

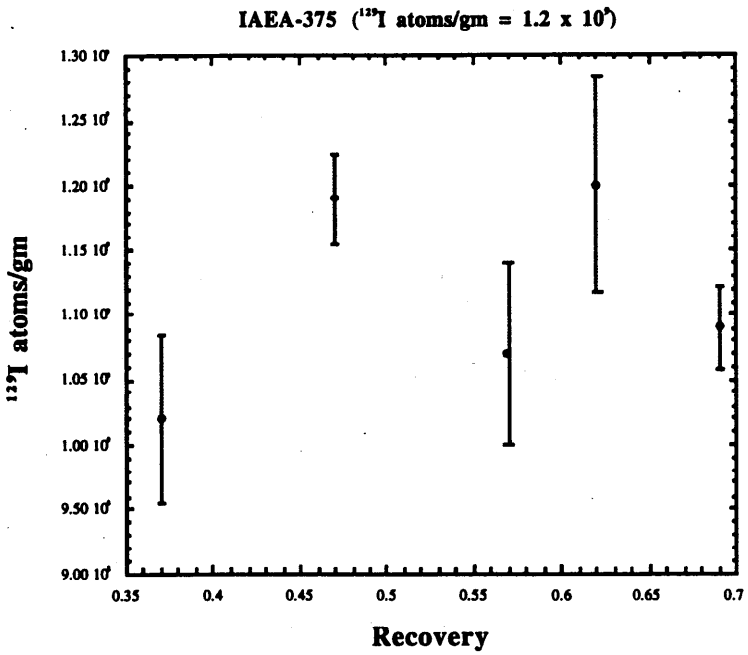

Figure 1

Iodine-129 ratio of IAEA-375 soil sample as determined at LLNL by AMS. Abscissa indicates the fractional yield of iodine in the five separate sample aliquots. All analyses agree with the IAEA accepted value (1.2 x 10^{9}) within twenty percent.

Within analytical uncertainties there is good agreement between our AMS measurements and those determined by neutron activation. These results demonstrate both the reliability of the AMS measurement itself and the chemical extraction method employed to release the ^{129}I from the soil. For this set of experiments a distillation technique in which the sample was boiled in HNO_3 and H_2SO_4 was utilized. The *I concentrations obtained for this soil were reproducible independent of both the chemical form of the added stable iodine carrier and chemical yield. These clearly indicate complete isotopic mixing of the carrier iodine and the ^{129}I indigenous to the sample.

The second set of experiments to determine the adequacy of our methods to measure natural levels of ^{129}I involved "garden variety" soil samples. Figures 2 shows the results of ^{129}I measurements on a soil sample collected in the vicinity of Liver-more, California.

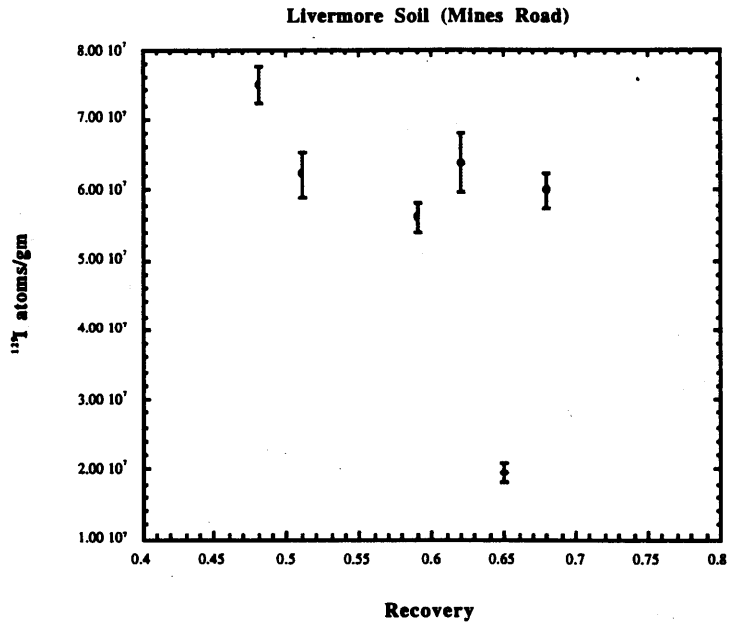

Figure 2

Iodine-129 in a natural soil sample from Livermore, California area. Abscissa indicates the fractional yield of iodine in the six separate sample aliquots. No accepted value for ^{129}I concentration is known for this sample, but close agreement in analyses at about 6x10' suggests this value. No attempt to homogenize sample aliquots was made, thus the single low value may represent sample diversity rather than an incorrect analysis.

This soil serves as a proxy for the soils collected at the NTS. With the exception of one anomalous result, these analyses indicate that reliable ^{129}I results can be obtained on natural samples. It is worth noting that for this soil sample no particular attempt was made to homogenize the various constituents. It is not unreasonable that some variability among aliquots occurs. Thus we believe each of the analyses is a reliable indication of the ^{129}I concentration in that sample.

Although the purely instrumental or machine-analytical aspects of this study are both time consuming and of central concern to the project goals, a second major component of this work is the identification of the processes influencing the mobility of ^{1} I in the vadose zone. Factors such as the binding of iodine to clays or organic material probably play an essential role in its mobility. No matter how reliable our mass spectrometry techniques are, valuable results depend on being able to analyze the appropriate samples in the appropriate manner. We are developing two complimentary techniques to identify the factors influencing iodine mobility in the vadose zone: sequential leaching of iodine from soils and physical separation of potentially significant components within soils.

Initial tests of a sequential leaching technique indicate that not all of the iodine in arid soils occurs in the same chemical setting. Conceptually, the iodine resident in soils is either leachable (residing in pore waters or loosely adsorbed on the grain surfaces), fixed (strongly sorbed on clays or in humus or plant tissues), or insoluble. Different soils may be expected to have different proportions of these various constituents. Our initial results on the proxy soil from Livermore indicate that < 20 % is leachable in water. This result is somewhat surprising since iodine is regarded as a "conservative" species that readily migrates with water. Further tests indicate that

smaller proportions are leachable in basic or mild acid solutions. Although these are only initial results, it may be the case that considerable ^{129}I in this particular soil resides on clays or in organic matter. Further tests in the near future are designed to address this question and should clarify the siting of ^{129}I in these samples.

Physical separation of samples for ^{129}I analysis is not as trivial as sieving or optical separation, followed by AMS analysis. Any significant processing or handling of samples can cause of mechanical separation of ^{129}I from its in-situ locality. From this perspective, the sequential leaching experiments, conducted on samples with minimal handling, were easier to conduct and the most appropriate starting point. The determination of the extent to which physical handing of ^{129}I samples can bias scientific results is a goal of the work planned for FY98. Our intent is to compare results from samples with this type of physical handling to samples with only sequential leaching processing. The benefit of developing physical separation techniques is that ^{129}I siting can be better examined because the phases can be isolated, and the precise site locations can be known with greater confidence.

In summary, we have demonstrated our capability to reliably analyze environmental levels of ^{129}I. The challenges of understanding the natural behavior of this geochemically complex element, and how this affects the distribution of anthropogenic ^{129}I in arid soils, lie ahead. This will be the focus of work during FY98.

Development of AMS ^{99}Tc Techniques. During early FY97 we performed preliminary tests which demonstrated the technical feasibility of AMS for the detection of ^{99}Tc. This feasibility work has been followed during the remainder of FY97 by more extensive development work on the AMS and ion detection parameters, detection sensitivity, and methods for the extraction of ^{99}Tc from soils.

The lack of a stable technetium isotope presents a number of technical challenges for AMS measurements which are not present for other AMS isotopes, such as ^{129}I, in which the stable isotopes serve multiple roles as yield monitor, chemical carrier, and sample matrix. Measurements of radioactive-to-stable isotope ratios (e.g., $^{129}I/^{127}I$) are then implicitly corrected for time- and sample-dependent variations in a number of factors such as chemical recovery, ionization efficiency, acceleration efficiency, and ion transport through the spectrometer. To allow AMS measurement of ^{99}Tc, some other element (or collection of elements) must be used as a sort of proxy, to fill these same roles. The requirements of this proxy are: a stable isotope near, but not at mass 99; reasonable negative ion production; good thermal and electrical conductivity; and a chemistry as near as possible to that of Tc. We have explored two candidates for this, silver and rhodium, both of which have positive and negative features.

By far the largest uncertainty going into this project was whether it would be possible to get reproducible ratios between isotopes of different elements when there are several factors in chemistry, negative ion production, and ion acceleration that could lead to large degree of fractionation between isotopes of the different elements. A further challenge is presented by interference from Ruthenium-99, a stable isobar of ^{99}Tc. This interference cannot be removed using the spectrometer, and must be chemically separated from the technetium in the sample and from the matrix material. An advantage of AMS in this respect is the high energy to which the ions are accelerated, which allows the use of nuclear physics particle detection techniques for post-spectrometer particle identification (Figure 3).

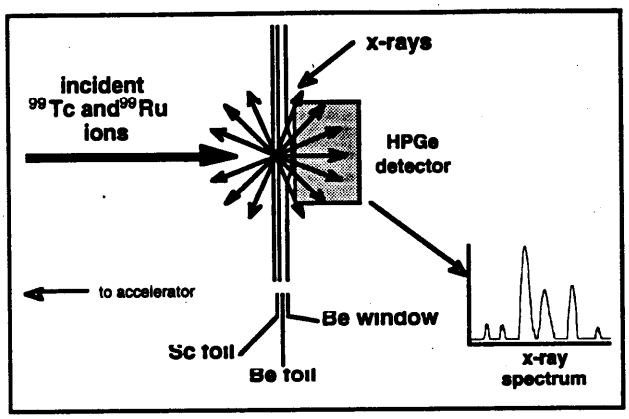

Figure 3

Detection of ^{99}Tc ions using characteristic projectile x rays. Following analysis in the AMS spectrometer, the ions are incident on a target foil. The induced x rays are detected with a HPGe detector. A Be absorber is included to stop the ions and to attenuate low energy x rays.

This enables additional rejection of certain interferences, including atomic isobars, easing the requirements for the chemical separation and reducing the ambiguity present in identifying ions by mass only.

During FY97, preliminary tests were performed to address the following questions: 1) the behavior of technetium and rhodium in the ion source, including the intensity and efficiency of the negative ion production; 2) the charge states and energies accessible for mass 99 using the LLNL AMS spectrometer; 3) the detection efficiency for mass 99 ions and the rejection of Ru-99 using characteristic projectile x-rays; 4) the potential existence of unanticipated interferences; and 5) the reproducibility of measured ^{99}Tc/^{103}Rh ratios.

The results of these tests showed acceptable ^{99}Tc negative ion currents from the cesium sputter source, high detection efficiencies using characteristic projectile x-rays, and reasonable ^{99}Tc/^{103}Rh ratios which were reproducible at the 10-15% level over time and for standards-varying by over an order in ratio (Figure 4).

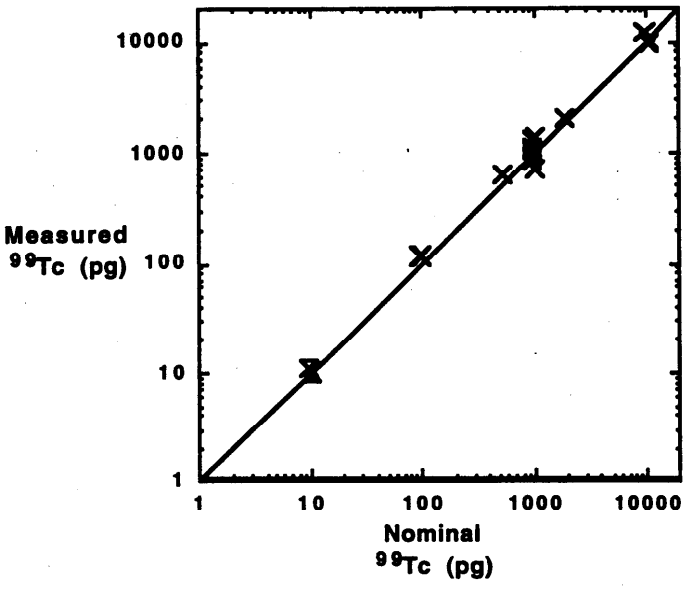

Figure 4

Measurement of ^{99}Tc in standards by AMS using rhodium carrier.

We believe this work was the first demonstration of significant Tc current from a cesium sputter source. Overall detection efficiencies sufficient to allow the detection of ~10 fg of ^{99}Tc in 10-15 minutes were observed. In addition, we found that the present AMS facilities at LLNL were sufficient to accelerate, transport, and analyze mass-99 ions at useful energies and-charge states. Finally, no unanticipated interferences were observed at the level of sensitivity of the preliminary tests.

Our preliminary work was presented in an Invited Talk and associated paper at the International Conference on Methods and Applications of Radioanalytical Chemistry - Marc IV, April, 1997:

> "Development of AMS for detection of ^{99}Tc: Preliminary Investigations"
> J.E. McAninch, A.A. Marchetti, B.A. Bergquist, N.J. Stoyer, I.D. Proctor, G.J. Nimz, M.W. Caffee, R.C. Finkel, K.J. Moody, E.Sideras-Haddad, B. Buchholz and B.K. Esser
> Invited talk presented at the International Conference on Methods And Applications of Radioanalytical Chemistry - Marc IV, April, 1997. Paper submitted to the Journal of Radioanalytical and Nuclear Chemistry as part of the conference proceedings.

Two significant problems were uncovered during the development work — unacceptably high ruthenium levels in the ultra-pure rhodium stock material, and the presence of an interference from sulfur which could not be removed using the characteristic x-ray detector. The natural abundance of ruthenium in the environment is quite low, and most materials should not have a sufficiently large ruthenium content to represent a problem in our measurements. However, an exception to this is rhodium, which is typically found in connection with ruthenium in nature. The rhodium stock material that we purchased for our work, which is ultra-pure by normal standards, had several orders of magnitude more ruthenium than was acceptable.

To reduce the level of ruthenium in the rhodium stock solution, we developed a chemical purification procedure which involves oxidizing the ruthenium to the volatile species ruthenium tetraoxide, then removing it by vacuum distillation. The process is simple and effective, reducing the ruthenium to within a factor of 10 of the required level, which is ~10 ppb Ru/Rh. A number of options are available that we can try either to further reduce the ruthenium level, or to reduce the amount of rhodium carrier which is required.

A second unanticipated problem was the discovery of an interference from sulfur, which has an x-ray line which overlaps with the technetium x-rays. The preliminary tests indicated that this interference could be eliminated by the proper choice of ion charge state and accelerator parameters. In addition, the production of these x-rays is very much suppressed relative to the technetium x-rays. However, with the experience and improved sensitivity which was gained during the development work, it became clear that this interference would not continue to be a problem.

To address the sulfur interference, we are now using a hybrid detection system, in which a thin gas ionization detector is placed in front of the characteristic x-ray detector. This system very cleanly discriminates against sulfur and other interferences which are well separated from Tc in the periodic table. The next most favorable alternative to rhodium as a carrier is silver. Silver has several advantages over rhodium — it is significantly less expensive, is more readily available, and is inherently orders of magnitude cleaner of ruthenium. The major disadvantage is that silver is much farther from ^{99}Tc in both atomic number and mass, increasing the possibility for widely varying measured ratios. In addition, we avoided silver during the early development work because the silver isotopes produce overwhelming interferences at the charge states which minimized the sulfur interference.

A byproduct of the hybrid detection system is that, because it so cleanly discriminates against sulfur and other interferences, it has allowed us to explore charge states in which silver is not an interference. In our first tests with silver, we have demonstrated reproducible ratios for standards (Figure 5), and have shown that

stock silver from the chemical supplier is cleaner of ruthenium than our processed rhodium, and appears to be sufficient for use as is.

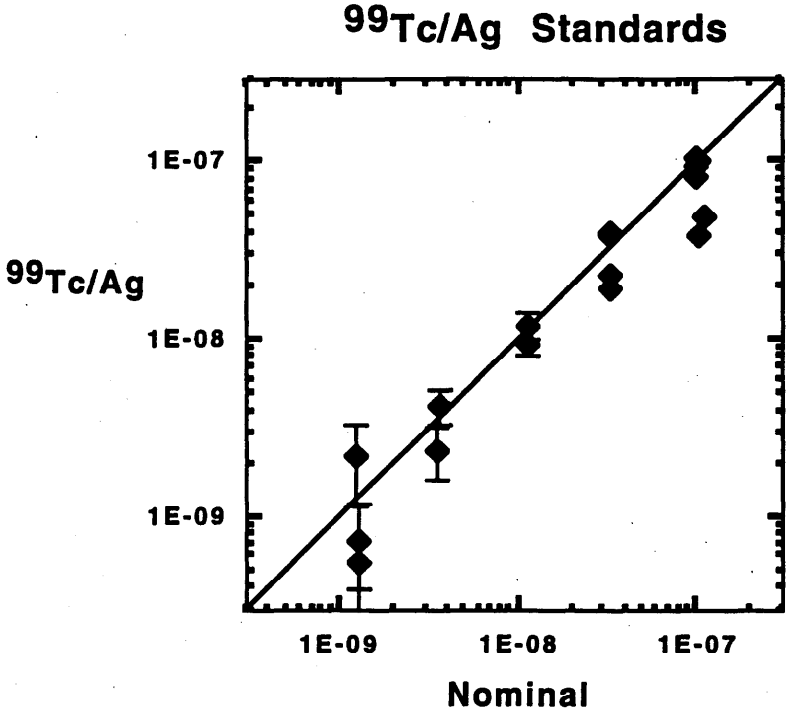

Figure 5

Measurement of ^{99}Tc in standards by AMS using silver carrier. The observed deviations for the highest standards were caused by a drift in the accelerator conditions. The deviations for different standards were consistent, and the overall deviation was removed with correction of the accelerator conditions.

In summary, we have demonstrated sub-picogram detection sensitivity for ^{99}Tc using both rhodium and silver carriers. We are currently optimizing the methods using silver carrier and the hybrid detection system, and expect to reach the necessary sensitivity using this combination in early FY98. We have also been working for the past few months on methods for the extraction of ^{99}Tc from spiked soil samples, using up to a few hundred grams of soil. Chemical recovery is so far somewhat low (-60% soil-to-measured-sample), but still sufficient for AMS analytical work and seemingly reproducible at this level. The lack of soils with known concentrations of ^{99}Tc (i.e., "standard" soils) hampers this work, but is an unavoidable problem when developing state-of-the-art analytical techniques.

Excavation of a Deep Trench for Soil Sampling. We chose to trench on the Nevada Test Site because we believed some of the logistical problems of this moderate-scale construction project could be more easily overcome at this well-used site. Still, NEPA documentation, archeological clearances, OSHA regulations, cost estimations, site "ownership" questions, and simple manpower deficiencies delayed excavation for several months during FY97. The trench was finally completed in September, the trench wall was mapped for geological structure, stratigraphy, and soil composition, and more than 150 soil samples were collected. Additionally, approximately 30 rock samples (cobbles) were collected from the trench wall for the purpose of exposure-age dating that could help to better define the depositional history of the trench sediments. The trench was located in Area 2 of the NTS, adjacent to the Carpetbag

geological fault. Trench dimensions are approximately 5 meters deep, 14 meters long at this depth, and 12 meters wide. It required approximately two days with a bulldozer and grader to excavate the trench. The south trench wall was benched at approximately 5 foot intervals for OSHA safety, and this permitted ease of sampling. The north trench wall was sloped to prevent collapse and was not sampled. Each end of the trench was ramped to allow easier access. The trench will remain open for several months to allow the further sampling planned in this study, and is available for any other scientific use that will not interfere with this sampling. We have contacted DOE-NV (Las Vegas) inquiring about any interest they would have in using this trench, or in collaborative work.

Samples were collected in six vertical transects from land surface to the bottom of the trench. Samples were taken every 25 cm, 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 transects were "baseline" transects that intersected no structural features of the soil. The other four transects sampled obvious fractures in the soil, one containing abundant carbonate infill, one containing, moderate carbonate, one free of carbonate, and the final transect along the "contact" of the carpetbag fault vein infilling and the non-carbonate soil external to the fault zone proper. If there are preferential pathways to moisture and radionuclide migration, it is believed they would be along sites such as these.

Planned FY98 Work. Because trench excavation could only take place late in the fiscal year, more emphasis in FY97 was placed on developing ^{99}Tc analytical techniques, and on methods for understanding the geochemical siting of ^{129}I in soils, than was originally planned. This work was slated for FY98 and will now be replaced by ^{36}Cl, ^{129}I, and the supporting chemical/mineralogical analytical work on the soils collected during FY97. The ^{129}I analytical work will likely continue throughout FY98 because of its difficulty and because of its experimental nature as discussed above. The soil characterization, ^{36}Cl, and soil chemistry work will occur quickly during the first three months of FY98. This work is more routine and the scientific community has more experience with its results. This will produce the initial conceptual model for soil moisture and solute flux at the site by the end of the first quarter of FY98. It is upon this that an analytical strategy for ^{99}Tc and ^{129}I will be developed (it is too expensive and wasteful to analyze all samples for these nuclides). Thus these analyses should be completed by mid-FY98. Creation of a conceptual model for moisture and radionuclide migration at the trench site and development of ^{90}Sr and ^{93}Zr analytical techniques, which will be more difficult that those thus far developed, will occupy the remainder of FY98.