

FINAL REPORT
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**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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EXECUTIVE SUMMARY

This project developed techniques for measuring globally distributed radionuclides that occur today in extremely low abundances (“fallout” from the era of atmospheric nuclear testing), and then applied 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. The goal in this project was to develop AMS analytical techniques for ^{129}I (fallout concentration: $\sim 10^6$ atoms/g) ^{99}Tc ($\sim 10^9$ atoms/g), ^{90}Sr ($\sim 10^7$ atoms/gram soil), and ^{93}Zr ($\sim 10^9$ atoms/g), and improved methods for ^{36}Cl ($\sim 10^0$ atoms/g). As a demonstration of the analytical techniques, and as an investigation of identified problems associated with characterizing moisture and radionuclide movement in unsaturated desert soils, we developed a vadose zone research site at the Nevada Test Site. Our findings can be summarized as follows: 1) The distribution of chloride and ^{36}Cl at the research site indicates that the widely-used “chloride accumulation” method for estimating moisture flux is erroneous; some mechanism for attenuation of chloride exists, violating an assumption of the accumulation method; 2) ^{129}I is fractionated into several soil compartments that have varying migration abilities; the two most mobile can be tentatively identified as Fe/Mn oxyhydroxides and organic acids based on our sequential leaching techniques; 3) These most mobile constituents are capable of migrating at a rate greater than that of ^{36}Cl , usually considered *the* most mobile solute in hydrologic systems; these constituents may be colloidal in character, of neutral surface charge, and therefore conservative in aqueous migration; 4) ^{99}Tc is readily measurable by AMS, as we demonstrate by the first AMS ^{99}Tc measurements of contaminated waters; extraction of ^{99}Tc from silicate soils is difficult, but can be done using the extended methods we have developed; 5) Most of the bomb-pulse ^{99}Tc observed in the soil profile at the EMSP research site was confined to the upper 50 cm; however, there is some indication that a fraction of the ^{99}Tc could move to the same extent as bomb-pulse ^{36}Cl ; and 6) The observed AMS sensitivity for ^{90}Sr was $^{90}\text{Sr}/\text{Sr} \approx 10^{-12}$, corresponding to about 20-200 mBq per sample, similar to the sensitivity of traditional decay counting; further work should improve the sensitivity by at least a factor of 10, but even now the AMS ability for sensitive, high throughput, fast turnaround, robust measurements using simple chemistry is an improvement over decay counting methods.

Although our results regarding the migration of these radionuclides in arid soils increase the scientific understand of contaminant migration in that environment, we believe the primary benefit of our EMSP research is the development of AMS analytical techniques for low-level radionuclide measurement. The advantages of this 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 VOC’s, 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. Our research is therefore designed to make the study of radionuclide migration simpler to do, simpler to interpret, and easier to apply to specific DOE sites. This will lead to a better understanding of the migration potential and ultimate fate of radionuclides, creating much less uncertainty regarding which remediative strategies should be employed. For any project, this will reduce its cost, shorten its schedule, and provide greater confidence in its final result, both for the DOE and for the general public. We feel this is a substantial contribution to the EM community.

RESEARCH OBJECTIVES

DESCRIPTION OF AND NECESSITY FOR THE RESEARCH

This project developed low-level analytical methods for the measurement of radionuclides by accelerator mass spectrometry. The contaminant radionuclides potentially measurable by AMS include: ^{14}C , ^{36}Cl , ^{59}Ni , ^{63}Ni , ^{90}Sr , ^{93}Zr , ^{99}Tc , ^{129}I , ^{239}Np , ^{239}Pu , and other actinides. We chose to concentrate on ^{36}Cl , ^{99}Tc , ^{90}Sr , and ^{129}I . These nuclides were globally distributed as fallout during the era of atmospheric nuclear testing, and occur today in almost every environment. They also are prominent contaminant nuclides at a variety of DOE sites. There is a need to develop these low-level methods to observe the migration of radionuclides in natural environments. There are at least three advantages of this: 1) the ability to conduct migration studies in locations most like those of concern to public health, e.g., a "far-field" environment; 2) migration research does not have to be conducted at sites of multiple contamination, e.g., by VOC's, which can produce hard-to-interpret results; and 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. Our approach of examining globally distributed, fallout radionuclides provides another advantage: 4) since the nuclides are globally distributed, migration research can be conducted in any chosen environment. Arid environments can be examined for purposes of nuclear waste storage; riverine systems can be examined for the effects of long-range transport; forested or agricultural regions can be examined for the effects of vegetative mediation; even accessible arctic regions could be examined to better understand the fate of radionuclides in remote northern Russia. The innovative aspect of this research project was that it developed methods by which field studies of radionuclide migration could take place virtually anywhere, making the research easier to conduct, less expensive, and better controlled scientifically.

Science is still in the process of trying to characterize the mechanisms by which radionuclides migrate in natural environments. It is only by understanding these mechanisms that improved methods for predicting contaminant radionuclide migration can occur. Improved predictions will reduce costs of remediation by indicating where remediative actions will be the most effective, by ensuring that the full extent of remediation required has been accurately determined, by eliminating the need for over-engineered solutions to the problem, and in some cases by demonstrating that natural attenuation near the release will decrease contaminant concentrations below regulatory maximum permissible concentrations (thus eliminating the need for *any* direct remediative action). Therefore, the development of AMS analytical techniques, which provide strong advantages for scientific characterization of radionuclide migration in all natural environments, thereby providing the means for improved predictive capabilities, will ultimately reduce remediative costs significantly.

ONGOING RESEARCH BY OTHERS

Use of Chloride and ^{36}Cl in Soil Moisture Movement Studies

Physical methods for assessing moisture flux in arid soils are inadequate. Chemical and isotopic tracers, such as chlorine and ^{36}Cl , that move conservatively with the moisture and therefore define flux by their distribution over time are preferred. Allison et al. (1994), in a review of available techniques for measuring moisture flux in the unsaturated zone, have pointed out that "[w]hen recharge rates are only a few millimeters per year or less, chemical and isotopic methods are likely to be more successful than physical methods, such as water balance methods,

which rely on measured or estimated values of water flux.....An advantage of tracers is that they integrate all of the processes that combine to affect water flow in the unsaturated zone". The most important tracers discussed by Allison et al. (1994) are chlorine and ^{36}Cl . A field scale tracer is also valuable because laboratory experiments are extremely difficult for dry soils. While soil column experiments are often conducted (e.g., Porro and Wieringa, 1993), there has been a growing realization that centrifugal devices are required to adequately simulate unsaturated moisture flow (Nimmo, 1990; Conca and Wright, 1992; Nimmo et al., 1994). However, these small devices are inadequate to assess field-scale phenomenon, such as lateral heterogeneity or preferential flow due to soil structure.

A number of assumptions are required when chloride is used as a field tracer of water flux: that all the chloride is all derived from atmospheric deposition and that current fluxes are representative of long-term averages, that chloride behaves conservatively during soilwater transport, that migration is by advection and dispersion, and that a piston-flow model applies to water movement. The mass balance of chlorine - the ratio of incoming chlorine ($\text{g}/\text{m}^2/\text{yr}$; through precipitation and dry deposition) to the soil chlorine concentration to a given depth (g/m^3) - gives the average rate of moisture movement to that depth (m/yr ; Allison and Hughes, 1978). This rate, combined with measurements of soil water content (g/m^3), gives the moisture flux for the soil (rate * moisture content = flux in $\text{g}/\text{m}^2/\text{yr}$), and by extrapolation recharge rate (Edmunds et al., 1988; Gee and Hillel, 1988; Sharma, 1988; Cook et al., 1992; Allison et al., 1994; Phillips, 1994). The amount of incoming chlorine may either be estimated, measured in precipitation, or derived from $^{36}\text{Cl}/\text{Cl}$ budgets (Scanlon, 1991).

Arid soil profiles commonly show changes in rate of chlorine accumulation with depth, producing an apparently temporal segmentation of the profile into times of high moisture flux and times of low moisture flux (Phillips, 1994). This has been regarded as an indicator of paleohydrologic and/or paleoclimatic conditions (Stone, 1992; Phillips, 1994). Accumulation of chlorine is due, of course, to evapotranspiration of incoming precipitation. Quantifying the accumulation of chlorine is thereby a means of quantifying evapotranspiration rates in arid regions (Matthias et al., 1986).

Two "varieties" of ^{36}Cl are used to characterize moisture flux: "bomb-pulse" ^{36}Cl and cosmogenic ^{36}Cl . Significant amounts of ^{36}Cl were produced during atmospheric nuclear testing from 1952 to 1958, and a well-defined "bomb-pulse" of ^{36}Cl was distributed globally (Bentley et al., 1986). That pulse has today migrated downward into the soil column, and can be measured at depth in desert soils (Phillips et al., 1988). The depth of penetration into the soil marks the extent of downward moisture movement since the 1950's, and a rate of moisture flux can be directly calculated (rate = depth/ ~ 45 years). Cosmogenic ^{36}Cl is produced by cosmic radiation in our atmosphere and enters the hydrologic system through precipitation. Changes in pre-1950's $^{36}\text{Cl}/\text{Cl}$ ratios observed in deep soil profiles below the bomb-pulse peak may be an indication of paleoclimate conditions (Phillips, 1994). The $^{36}\text{Cl}/\text{Cl}$ ratio (non-bomb-pulse) for chlorine deposited at any given time is the result of mixing of cosmogenic ^{36}Cl produced in the atmosphere with stable chlorine from ambient sources, most prominently the oceans (Nimz, 1998). Changes in atmospheric circulation and thus of the mixing of cosmogenic ^{36}Cl with marine chloride may produce a "secular variation" in $^{36}\text{Cl}/\text{Cl}$ ratios at depth. The rate of deposition of ^{36}Cl remains relatively constant over time (dependent on cosmic radiation flux), while the amount of incoming stable chloride fluctuates with climatic conditions. Low $^{36}\text{Cl}/\text{Cl}$ ratios in deep soil profiles may indicate periods of wet climates, whereas high $^{36}\text{Cl}/\text{Cl}$ ratios may

indicate very dry climates. Important climate fluctuations may occur on a several hundred-year timescale (Stine, 1994).

Research on Iodine and ^{129}I Transport in Soils

The difficulty in iodine soils research is due to the multiple oxidation states in which iodine can occur. Iodine occurs naturally, and abundantly, as iodide (I^-), iodate (IO_3^- ; 5+ oxidation state), periodate (IO_4^- ; 7+ oxidation state), and “elemental iodine” (I_2 ; covalent bond). Yuita (1992) examined Japanese soils and determined that ~86% of the iodine was iodate, and mostly complexed in the soil so as to be insoluble. However, under flooded conditions the iodine became soluble and, at least now in solution, was 87% iodide, 11% iodate, and 2% elemental iodine (I_2). Thus local redox condition is important for solubility of iodine, but “flooded” and “non-flooded” are rather wide extremes. Unsaturated soils fall somewhere in the continuum, and therefore iodine atoms will show rather complex behavior in unsaturated soils. Yuita did not extensively examine the nature of the iodate complexation. Other studies showing similar effects of iodine oxidation distributions are reviewed by Whitehead (1984).

The complications arising from multiple oxidation states has led several researchers to attempt to focus on anthropogenic ^{129}I in soils, using it as a tracer to elucidate the geochemical behavior of iodine. However, it is clear that difficulties exist here also. A case in point is the question of ^{129}I residence time in the upper several meters of soil. Kocher (1981) approached this question on the basis of a global iodine transport model. His results indicated that the most important parameter in estimating radiological impact in the first 10^4 years after release is the mean residence time of the ^{129}I in the upper one meter of soil. His predicted mean residence time for iodine in this compartment is 4000 years. Later, Kocher (1991) measured ^{129}I in surface soils from the vicinity of the Savannah River Plant in South Carolina and, using a diffusion model, obtained a residence time that agrees semi-quantitatively with his earlier prediction of 4000 years. However, this agrees poorly with the results of Schmitz and Aumann (1995), who conclude that iodine residence time in shallow soil is as short as 40 years in the vicinity of the Karlsruhe Nuclear Fuel Reprocessing Plant, Germany. While the latter study is in better agreement with some of our EMSP observations at the NTS research site (discussed below), the published residence-time disparities illustrate the general lack of understanding of the controlling processes of ^{129}I transport in soils.

Research on Bomb-pulse ^{129}I in Natural Waters

Pre-nuclear era background $^{129}\text{I}/\text{I}$ ratios were estimated by Fabryka-Martin (1985) to be about 6×10^{-13} , with only slight variations in all hydrosphere compartments. Within a factor of two this has been borne out by the few measurements that have been made from pre-nuclear sources. A pre-bomb-pulse very dilute groundwater sample from Clear Lake, California, had a $^{129}\text{I}/\text{I}$ ratio of 8.9×10^{-12} (Fehn et al., 1992), while iodine leached from marine sediment averaged a ratio of about 1.3×10^{-12} (Fehn et al., 1986). Bomb-pulse values measured in these studies were 8.3×10^{-11} (dilute groundwater) and about 8.5×10^{-11} (marine sediment). The groundwater sample contains chlorine with a bomb-pulse $^{36}\text{Cl}/\text{Cl}$ ratio of about 1.8×10^{-12} , which is a factor of 4 lower than the maximum ratio reported for very dilute groundwater at Yosemite, California (Nimz, 1998). If the iodine bomb-pulse value were to scale accordingly, the maximum precipitation $^{129}\text{I}/\text{I}$ bomb-pulse ratio in the western United States could be expected to be at least 3×10^{-10} , or about 3 orders of magnitude higher than background.

Contaminant $^{129}\text{I}/\text{I}$ ratios from nuclear production and reprocessing of course can be much higher. Seaweed collected near the La Hague, France, reprocessing plant had a ratio of 3.7×10^{-06} (Yiou et al., 1994). Depending on proximity to the release and the ambient stable iodine concentrations, $^{129}\text{I}/\text{I}$ ratios could be expected to range even higher than this by several orders of magnitude. A demonstration of potential $^{129}\text{I}/\text{I}$ values in very distal portion of contaminant releases was presented by Kilius et al. (1994), who measured a ratio of about 2×10^{-9} in algae near the mouth of the Columbia River. The source for the ^{129}I was the Hanford facility over 300 miles upstream.

The concentrations of several radionuclides, including ^{129}I , in the Snake River Plain aquifer at INEEL were examined by Beasley et al. (1998; the ^{129}I data were taken from Mann and Beasley, 1994). By comparing the concentrations of the nuclides at various locations away from the Idaho Chemical Processing Plant (ICPP; the source of the plume), relative degrees of attenuation could be seen in the migration of the nuclides. The least attenuated (most conservative) nuclides were ^{36}Cl and ^{99}Tc . The greatest attenuation was shown by ^{236}U and ^{237}Np . The fraction of ^{129}I present in the downflow direction relative to the initial concentrations was much less than those fractions observed for ^{36}Cl and ^{99}Tc , but greater than those observed for ^{236}U and ^{237}Np ; demonstrating a degree of attenuation for ^{129}I almost exactly intermediate between the extremes. At the farthest extent for which data exist, the concentration of ^{129}I relative to initial concentrations were an order of magnitude less than the concentration of ^{36}Cl or ^{99}Tc relative to their initial concentrations. The relative concentrations of ^{236}U were an order of magnitude lower than the relative concentrations of ^{129}I . Clearly something is retarding the migration of ^{129}I in the Snake River Plain aquifer.

Research on ^{99}Tc in Soils

Technetium-99 is a long-lived (2.1×10^5 a), high-abundance (6%) fission product which has been widely distributed in the environment through atmospheric testing, the nuclear fuel cycle, and nuclear medicine. It has a high potential for migration in the environment as the pertechnetate anion. This radionuclide is a weak beta emitter ($E_{\text{max}} = 292\text{KeV}$) which, combined with low specific activity (long half-life), makes it difficult to measure at low levels by decay counting methods. A number of mass spectrometric methods have been developed to address needs for low-level ^{99}Tc measurements, including thermal ionization mass spectrometry (TIMS; Rokop et al., 1990; Schroeder et al., 1993; Dixon et al., 1997), inductively-coupled plasma mass spectrometry (ICP-MS; Richter et al., 1997; Tagami et al., 1998; Eroglu et al., 1998), resonance ionization mass spectrometry (RIMS; Passler et al., 1997, Wendt et al., 1999). Recently, the feasibility of accelerator mass spectrometry (AMS) for ^{99}Tc measurements has been demonstrated (McAninch and Proctor, 1995; McAninch et al., 1998). Besides the instrumental obstacles, chemical extraction of Tc is difficult (cf. Tagami and Uchida, 1993; Gu et al., 1996), and requires a means of assuring that complete extraction (high chemical yield) occurs. Commonly $^{95\text{m}}\text{Tc}$ is added to the sample as a tracer, which is relatively expensive. We faced these same chemical-extraction problems for AMS analysis (see discussion below). Due to the analytical difficulty, there has been only limited research concerning concentrations of ^{99}Tc in natural samples, especially soils.

Technetium-99 was measured in rainwater in Texas in 1967, near the height of the bomb-pulse, as indicated by tritium in precipitation that has been measured yearly since the early 1950's. The concentration was about 0.2 mBq/L ($\sim 2 \times 10^9$ atoms/L; Attrep et al., 1971). Precipitation at our EMSP research site is about 17 cm/year , or about $170 \text{ L/m}^2/\text{year}$. The

calculated bomb-pulse signal would therefore be about 34 mBq/m²/year, or a total of about 360 mBq/m² deposited throughout the bomb-pulse era, assuming an instantaneous rise to peak values and a sinusoidal decrease in values over 20 years. If natural diffusion has distributed this peak through a meter thickness (at any depth), then assuming standard soil densities (1.4 g/cm³), the average concentration of ⁹⁹Tc in the bomb-pulse peak would be about 0.25 mBq/kg. Concentrations in water leachate solutions would then be about 0.35 mBq/L (using equal volumes leachate and soil). This is about 7 times the meaningful background for an AMS measurement, but is below the detection limit for ICP-MS. Thus AMS must be used for this work.

Very few other rainwater analyses have been made. Garcia-Leon et al. (1993) observed ~0.1 mBq/L in pre-Chernobyl rain in Spain. In comparison, ocean samples have been measured in the range 0.001 mBq/L (Momoshima et al., 1995) to 0.06 mBq/L (Holm, 1993).

No data exist on ⁹⁹Tc in soils that is clearly only bomb-pulse ⁹⁹Tc. Soil samples from Japan have been measured in the range 100-500 mBq/kg (Tagami and Uchida, 1993; Morita et al., 1993). This concentration is too high to be derived from the bomb-pulse, as the calculations above would indicate. It is unclear whether these samples have been affected by nearby releases from nuclear reprocessing.

Obviously very little is currently known about ⁹⁹Tc in the environment. One of the results of the EM Science Program was therefore to provide an analytical technique whereby more could be learned about this important contaminant radionuclide.

Research on ⁹⁰Sr in Soils

Like ⁹⁹Tc, research on environmental levels of ⁹⁰Sr has been difficult in the past. The primary reason for the difficulty is that radiochemical analysis of ⁹⁰Sr is typically done by use of its daughter decay product ⁹⁰Y, which is a superior analyte. To do this, the ⁹⁰Sr must first be “cleaned” of all of the ⁹⁰Y occurring in the sample. Then ⁹⁰Y is allowed to accumulate in the sample from ⁹⁰Sr decay for a defined time period (~30 days typically). The ⁹⁰Y is again separated from the sample, but this time is measured by beta counting rather than being discarded. The amount of ⁹⁰Y measured in the sample then indicates the amount of ⁹⁰Sr present. The entire process requires two episodes of chemical extraction and at least a month delay in the analysis. For low-level ⁹⁰Sr work, the delay time must be considerably extended to permit sufficient ⁹⁰Y to accumulate that the detection limit is well surpassed. Typical analytical problems that are encountered are an incomplete initial separation of ⁹⁰Y from ⁹⁰Sr (producing incorrectly high ⁹⁰Sr results), and loss of ⁹⁰Sr from the sample during the first chemical separation (producing incorrectly low ⁹⁰Sr results). Only one chemical separation is necessary for AMS ⁹⁰Sr analysis, which not only makes the process simpler and without a delay interval, but also avoids these analytical errors.

Strontium-90 representative of near-peak bomb-pulse was measured in rainwater from Texas in 1967 (same samples as the ⁹⁹Tc measurement, discussed above; Attrep et al., 1971). The concentration was about 40 mBq/L (5.3 x 10⁹ atoms/L). Following the same calculation strategy used above for ⁹⁹Tc at our EMSP research site, the total deposition would be about 7.2 x 10⁴ mBq/m². This compares to 6.3 x 10⁵ mBq/m² measured in uncontaminated soil at the Hanford site in Washington state (Price, 1991). The near order of magnitude difference may be partially offset by the increase in precipitation in eastern Washington relative to the 17 cm/year at our study site that was used for the calculation. Alternatively, the Texas measurement may be incorrectly low since it leads to an atomic ⁹⁰Sr/⁹⁹Tc ratio in the rainwater of about 10⁻². Fission

production of these two nuclides is very similar in magnitude, thus the fallout ratio might be expected to be about equal. There is no reason to suspect fractionation during fallout transport. The Hanford measurement is supported by Wilken and Diehl (1987) who found roughly the same amount of ^{90}Sr in soils in Germany. As with ^{99}Tc , very little information exists concerning ^{90}Sr in soils away from contaminated sites.

METHODS AND RESULTS

EXPERIMENTAL METHODS USED

The foundation of the experimental method used in this project is the ability to measure radionuclides that today occur in very small concentrations in virtually all natural surficial environments because they were globally distributed during the era of atmospheric nuclear testing in the Pacific Ocean. Their abundances are usually less than a million atoms per gram of soil. For ^{90}Sr , this means about 1 Bq/kg soil, or for a soil with 25 $\mu\text{g/g}$ stable strontium, a $^{90}\text{Sr}/\text{Sr}$ ratio of about 1×10^{-12} . One million atoms of bomb-pulse ^{36}Cl and ^{129}I lead to typical soil ratios of $^{36}\text{Cl}/\text{Cl}$ of about 1×10^{-12} and of $^{129}\text{I}/\text{I}$ of about 1×10^{-10} . These low ratios are only measurable by accelerator mass spectrometry (AMS). For ^{99}Tc , one million atoms is about 0.1 mBq, or about 2 fg. This quantity is difficult to measure by any means, but through the use of surrogate stable isotope (^{93}Nb) can be readily measured by AMS.

The reason AMS is superior to other forms of mass spectrometry in the measurement of these very low ratios is its ability to reduce background “noise” at the mass position of the analyte. This is accomplished by ionizing the atoms in the sample and accelerating the ions to sufficient energies (MeV energies) such that they can pass through a metal foil. The foil breaks up or simply blocks molecular species that become the “noise” detected by other techniques at the analyte mass position. Mass filters and spectrometric magnets provide further “purification” of the ion beam, and the acceleration permits a variety of types of very sensitive detectors to be used. The technique permits measurements as low as one radionuclide atom per 10^{15} atoms of a stable element (for example one atom of ^{129}I per 10^{15} atoms of ^{127}I). As a comparison, thermal ionization mass spectrometry has a “noise” background throughout the mass spectrum of at least 1 part in 10^9 , one million times less sensitive than AMS. It is only because of the extreme sensitivity of AMS that the bomb-pulse radionuclides can today be easily measured worldwide.

Chemical separations in this project were done using conventional means, although for ^{99}Tc and ^{129}I a very large effort was made to develop improved sample preparation techniques commensurate with AMS high-sensitivity analysis. These techniques are described in the body of this report.

A research method unique to this project was the development of a field research site that included a deep trench where the trench wall could be used to examine the migration behavior of radionuclides through the vadose zone. This method was believed superior to borehole studies that only provide a one-dimensional picture of radionuclide movement. Several new important observations were made in this project because of this approach. The most important of these will be discussed later in this report. We begin by describing this field research site and the baseline hydrologic/geologic measurements first, since this work provides a foundation for understanding the results from the AMS developmental work.

DEVELOPMENT OF A FIELD RESEARCH SITE AND BASELINE MOISTURE FLUX DETERMINATION

As a demonstration of the analytical techniques, and as an investigation of identified problems associated with characterizing moisture and radionuclide movement in unsaturated desert soils, we developed a field study site at the Nevada Test Site. The goal of creating the site was to enable sampling of vadose zone soils for physical and chemical characteristics, as well as the fallout radionuclides to be developed under the EMSP project. In particular, our goal was to create a site where specific sample positions could be observed and studied prior to sampling (unlike drillcore samples), and where the geologic/hydrologic context of each sample would be understood. The excavation of a trench at the study site allowed these goals to be met, and would also provide a location where further studies could be conducted (Figs. 1a-1e). The trench is approximately 5 meters deep by 20+ meters in length. Because we were interested in examining the affects of soil fractures on radionuclide movement, the site chosen for trenching was across an active geologic fault where the soil on either side contained parallel small-scale fractures of apparently different ages (some contain abundant calcite, others contain none).

The geology of the trench wall was mapped in detail, and careful attention was paid to soil fractures and root zones (Fig. 2). Six vertical profiles extending from landsurface to the base of the trench were chosen for sampling. These profiles were chosen so that samples within vertical fracture zones and root zones would be collected, as well as samples well away from these features. The profiles were also chosen so that all major stratigraphic units would be sampled. Samples were collected down the profiles at either 12.5 or 25 cm intervals (Fig. 2). At each sample location, two samples were actually taken, one for moisture content and soil physical properties, and one for chemical and radionuclide analysis. The first of these samples was tightly sealed to preserve the soil moisture. In total, 115 sample locations were selected (Fig. 2). As a cost saving analytical strategy, representative chemistry/radionuclide samples were chosen for analysis and approximately one third were archived for future analysis as needed. Soil moisture was measured for all samples. Particle size analysis, first-order mineralogical compositions, and soil moisture content were determined (Fig. 3).

Chlorine concentrations and $^{36}\text{Cl}/\text{Cl}$ ratios were determined on all samples (Fig. 4) This represents the greatest number of ^{36}Cl analysis from any single location, and nearly doubles the number of soil ^{36}Cl analyses worldwide made to date. It was important to achieve this sample and analytical density in order to reach four of the goals of this project: 1) determine the role of soil structures, especially fractures, in the preferential flow of soil moisture and radionuclides; 2) determine the effect of root zones in concentrating radionuclides in soils; 3) determine in two dimensions the relation between soil moisture, chloride concentrations, and bomb-pulse ^{36}Cl ; and 4) provide a framework by which the migration of other bomb-pulse radionuclides (^{99}Tc , ^{90}Sr , and ^{129}I in this project) could be compared. Goal number three was for the purpose of testing the validity of using chloride and ^{36}Cl as a tracer of soil moisture movement in arid unsaturated soils. Goal number four was important because even if soil moisture movement would not be known with certainty, at least migration could be known relative to ^{36}Cl ; other studies could then use this as a basis for assessing attenuation of radionuclides.

The results of the analyses are being readied for publication, but a short summary can be given here with reference to Figures 3 and 4. There is no strong evidence observed for preferential flow anywhere in the trench. Nor does there appear to be any extensive migration of chlorine or ^{36}Cl to areas of concentrated plant roots. The migration of ^{36}Cl appears to be uniform downward, with subhorizontal layers having similar values of $^{36}\text{Cl}/\text{Cl}$. Piston flow seems to be implied. The depth interval of peak bomb-pulse ^{36}Cl does not correspond to the level of greatest

soil moisture or chloride concentrations. Highest soil moisture contents are at about 3 meters depth, highest bomb-pulse $^{36}\text{Cl}/\text{Cl}$ values are at about 2 meters. In all of the profiles, the accumulated chlorine above the bomb-pulse ^{36}Cl peak was in excess of the integrated flux of chlorine to the Earth's surface over the last 45 years (the time since atmospheric nuclear testing). Thus some of the chloride above the bomb-pulse ^{36}Cl must have been deposited prior to the bomb-pulse ^{36}Cl . Some mechanism for attenuation of chlorine must be present. Our ^{129}I results, discussed below, lead us to feel that the attenuation is due to more than just an effect of wetting-drying. Further investigation of this phenomenon is continuing. These EMSP results clearly show, however, that the widely used "chloride-accumulation" method for estimating moisture flux in arid soils is erroneous, at least for the shallow soils (<20 meters) that are of most interest for low-level nuclear waste storage (see Phillips, 1994, for a discussion of the method).

DEVELOPMENT OF ^{129}I TECHNIQUES

The research completed on ^{129}I under this EMSP project can be divided into three parts: 1) development of chemical processing techniques specific to iodine; 2) development of improved AMS instrumental techniques for analyzing ^{129}I ; and 3) measurement of ^{129}I from soils at the NTS research site. The first of these can also be divided into iodine carrier method development and sequential leaching method development.

Iodine Chemical Processing Techniques

Iodine carrier method development

. Bomb-pulse ^{129}I presented several new analytical challenges beyond those encountered in previous ^{129}I work. Measurement of ^{129}I by AMS in rock and water samples has been done for several years (Fabryka-Martin et al., 1985, Fehn et al., 1992), but the measurement of bomb-pulse ^{129}I in soil samples had never been done until this EMSP project. Iodine concentrations in precipitation are very low, so exchangeable iodine concentrations in soils (i.e., iodine not bound in the primary mineral phases of the soil) are very low (<1 $\mu\text{g}/\text{g}$ soil). Bomb-pulse ^{129}I occurs as exchangeable iodine. In order to make an AMS measurement, which requires at least 1 mg of iodine, carrier iodine had to be added to the leachates that were used to remove the exchangeable iodine from the soil (the leachates would contain at most 0.25 mg). This became particularly important in this project because we were to use a sequential leaching technique, described below, that would extract not only the water leachable iodine, but also exchangeable iodine loosely bound to secondary phases in the soil (carbonates, oxyhydroxides, organic acids). In order that the carrier iodine and soil exchangeable iodine not be fractionated during subsequent chemical extraction, steps had to be taken to ensure that they were equilibrated, i.e., in the same chemical form and oxidation state. One of the goals of this project was to develop a technique to ensure this equilibration, and to extensively test the effectiveness of this technique.

After a certain amount of trial and error, a fairly simple technique was developed. A strong reducing agent was added to the carrier+sample solution that drives all of the iodine, regardless what original form to iodide (I^-). The carrier iodine added to the leachates is already in the I^- oxidation state, while the oxidation state of the ^{129}I in any individual leachate is unknown, but much of it was undoubtedly in iodate form (IO_3^-). After this reduction step, the I^- was subsequently oxidized to I_2 , which further equilibrated the iodine and placed it in a form suitable for chemical extraction. Although the developed technique was fairly simple, several weeks of testing were required, using stock solutions and actual leachate samples, to ensure equilibration always occurred and that the total iodine was extracted from the sample.

A second analytical challenge was to purify the final chemical iodine separate derived from the solvent extraction techniques. After considerable testing, including several AMS runs measuring blanks from the chemical procedures, we determined that three sequential extractions of the iodine into chloroform resulted in a “clean” sample. The organic extractions serves both to eliminate contaminants and to concentrate the iodine from several hundred milliliters to ~15 ml. Once the iodine is concentrated in a smaller volume more purification is possible. We have found that precipitation of AgI in an ammoniacal solution is desirable. After precipitation, the precipitant and the supernate are centrifuged and the supernate is decanted. The precipitant is washed with dilute HNO₃, following which the AgI is washed several times with ultra pure water.

In general the procedure described above produced pure AgI for AMS analysis. With the notable exception of the last leachate solution the chemical yields were good. The leachate designed to extract iodine from organic material is more problematic. The organic extraction of iodine into chloroform requires the iodine be present in an acidic, specifically nitric acid, solution as I₂. The addition of HNO₃ to the basic leachate results in an extremely volatile solution which must be allowed to evolve slowly. During this time iodine can be lost. An additional complication is the difficulty in oxidizing the I to I₂ in this reducing mixture. Iodine was recovered from these mixtures although the yield was less than optimal. We are presently exploring alternative extraction strategies designed specifically to both reduce the volatile nature of this leachate and increase our yields.

Sequential leaching method development

. There have been numerous suggestions regarding the siting of ¹²⁹I in soils (c.f. Kocher (1991) and Fuge and Johnson (1986)). In particular it has been suggested that ¹²⁹I is bound to clay minerals or organic phases. To investigate these processes a significant goal of the EMSP work was the development of laboratory procedures that would allow not only the determination of the spatial distribution of ¹²⁹I but also would enable an investigation of the siting of ¹²⁹I. Accordingly, we employed a sequential leaching procedure in which each successive leaching step attacks a particular constituent within the soil (Fig. 5). This procedure is based on those developed by Schmitz and Aumann (1995).

The first leachate was simply deionized, high-purity water, and was applied in order to extract water soluble, “exchangeable”, iodine. Following this step the soil was leached with a mildly basic solution (pH = 8.2) to extract exchangeable iodine that might be soluble under very non-acidic natural conditions (though not in pH-neutral waters). The next step utilized a mild acidic solution (pH = 2) to dissolve secondary, pedogenic. carbonates, and release any ¹²⁹I that may become associated with these phases. The following step used a strongly reducing acidic solution. This leachate primarily attacks Fe and Mn oxyhydroxides, which are common secondary minerals in arid soils. The final leachate was a strongly reducing basic solution. This leachate attacks organic acids, which in colloidal form are also common in soils (although *how* common in *arid* soils is as yet undetermined).

The strategy behind the chosen leaching sequence was to identify ¹²⁹I associated with specific constituents in soils that would either enhance or retard migration. The first step was to identify the water soluble ¹²⁹I that would be likely to migrate freely with soil pore water. This includes the very basic soil water that could exist in high-carbonate microenvironments (the second leachate solution). The next two leachates were for the purpose of identifying ¹²⁹I that may become bound to two common types of minerals that form quickly and abundantly in arid soils, carbonates and metal oxyhydroxides. It was our initial hypothesis that this ¹²⁹I would be

severely attenuated in migration, moving only when these secondary phases released the ^{129}I through dissolution or ionic exchange. We later realized the possibility that these phases could also occur in colloidal form and perhaps enhance the migration of ^{129}I (see discussion below). The final leachate solution was designed to release ^{129}I bound to organic acids in the soils, which are known to occur in colloidal form. Little is known about the transport properties of the organic acids in soils, but in groundwater systems they are thought to be associated with enhanced migration of radionuclides.

Improved AMS Instrumental Techniques for ^{129}I

At the same time the sequential leaching techniques were being developed, improvements were being made to our abilities to measure ^{129}I by AMS. At the beginning of this project LLNL possessed an elementary ^{129}I measurement capability. The beamline used at that time was not ideal for ^{129}I . Its major shortcoming was that the high-energy mass analyzing magnets could not effectively divert (“bend”) the ^{129}I beam. However, until a new beamline became available we could perform the tests needed to verify the efficacy of our chemical extraction techniques. In addition to performing these tests, this beamline served as a means for investigating various detector combinations. In particular we experimented with a time-of-flight detector in conjunction with a solid state surface barrier detector. For those energies available on this beam line, we were able to demonstrate complete resolution of the ^{129}I peak from scattered ^{127}I , however several problems were apparent. The most obvious was a continual loss of energy resolution in the barrier detector, probably resulting from radiation damage. Each detector could only be used for a maximum of two ^{129}I runs. A more serious shortcoming was the possibility that an isobaric contaminant, having the same velocity as ^{129}I and essentially the same total energy, was present. This contaminant would then be measured as though it were ^{129}I .

Approximately midway into the EMSP project a new beamline designed for heavy elements was installed and tested. This beamline allowed ^{129}I to be measured under more favorable conditions. Specifically, the new beamline allowed a terminal voltage of 8 MV rather than 3 MV, allowing the complete analytical resolution of ^{129}I from scattered ^{127}I .

This increase in ion energy also allows the detection of ^{129}I in a gas detector rather than a barrier detector. Accordingly, we designed and successfully tested a two-anode gas detector that provides both total energy and $\delta E/\delta x$ information (i.e., loss of energy as the atom moves through the gas field). This allowed us to verify and eliminate the interference which our previous work had demonstrated to be present. The interference does in fact have the same velocity and nearly the same total energy as the ^{129}I . However, it has substantially different $\delta E/\delta x$ properties. In fact, this interference arises from the arrival, in coincidence, at the detector of two fragments. The ^{129}I we detect is in the 5^+ charge state. One of the interfering fragments is in the 4^+ charge state and accordingly has approximately 4/5 the mass of ^{129}I . The other fragment is in the 1^+ charge state and has approximately 1/5 the mass. The sputtering process in the ionization source creates essentially all possible molecular species. Although the low-energy mass analyzing magnet injects ^{129}I it also injects all other species possessing the ^{129}I momentum/charge ratio, including molecules. These molecules are disassociated at the terminal of the accelerator, where everything passes through a stripping gas, but there is the finite chance that the fragments having just the right charge state will arrive in coincidence at the detector. The barrier detector, which could only measure the total energy deposited in the detector, could not detect the presence of two fragments. The $\delta E/\delta x$ detector, on the other hand, yields unequivocal evidence of these by virtue

of the energy loss properties. This permits us to avoid measuring the contaminant as though it were ^{129}I .

Realizing the physical nature of the contaminant aided in elucidating its origin. Its physical nature indicated that it was a chemical component derived external to the AMS instrument, as opposed to a component derived from the instrument itself or an artifact of atom scattering. Most AMS samples are mixed with a binder to enhance the sputtering yield of the material. In most instances this binder is Ag. We have determined that this is the source of the contaminant. We are now using Nb as a binder for ^{129}I measurements. So, not only did the new detector give us the capability to resolve the contaminant but it further enabled us to completely eliminate it. All measurements of samples from the NTS research site were performed on the new beamline.

Finally, a new low-energy injector was installed and tested as part of the EMSP project. This injector shares a mass analyzing magnet with the old injector but in addition has an electrostatic analyzer. This element suppresses interferences from sputter tails. This further improves our ability to measure low-level ^{129}I samples.

Measurement of ^{129}I From Research Site Soils

Following development of the sequential leaching techniques and AMS analytical methods, we began our analysis of samples of arid unsaturated soils from the field research site at the NTS. Soil profiles were measured from landsurface to the base of the trench. Figures 6 and 7 show the integrated release of all ^{129}I from each soil fraction in two of the profiles, P4 and P6. The most outstanding feature is that unlike the observed distribution of ^{36}Cl where only one peak was present, there are multiple peaks of bomb-pulse ^{129}I in the profiles. The main observations regarding the integrated ^{129}I profiles are that 1) a substantial fraction of ^{129}I is bound relatively close to the surface; 2) a substantial peak occurs at about the same depth interval as the ^{36}Cl peak; and 3) a very large fraction of the total observed ^{129}I has migrated to a depth even greater than the ^{36}Cl . The last observation is very surprising, since chlorine is generally considered to be *the* most conservative solute in hydrologic systems. These results imply either that a fraction of the total iodine is more conservative than chlorine, or that the migration of that fraction has in some way been facilitated in this system (for example by association with non-solute constituents such as colloids that enhance migration).

In all instances the ^{129}I concentration associated with the peaks are well above background levels. For many samples in the P4 profile aliquots of AgI were measured in two separate AMS runs, the runs being several months apart. These replicates agreed well and demonstrate the robustness of the AMS measurement. Further, other soil profiles from the research site show similarities in the distribution of ^{129}I .

The results of the sequential leaching methods suggest that non-solute constituents may control the deeper migration of ^{129}I at the research site. Figures 8 and 9 show the individual release patterns for the leachates from soil profiles P4 and P6. The ^{129}I in these profiles that is extractable from the soil in water only, the bulk is held close to the surface. Evidently a small fraction of this has followed the ^{36}Cl to greater depths. It is important to note that if water had been the exclusive method used for ^{129}I extraction, we would have concluded that the migration of ^{129}I was similar to that of ^{36}Cl (see P4 profile, Fig. 8) or slightly *retarded* relative to ^{36}Cl (see P6 profile, Fig. 9).

The ^{129}I released by the more aggressive leachates has a considerably different pattern from that of water leachable ^{129}I . Like the water exchangeable iodine, there is a fraction that resides close to the surface. In the P4 profile, a fraction also occurs at the depth of the ^{36}Cl peak (Fig. 8);

but in the P6 profile, this feature is absent (Fig. 9). In both profiles, however, the ^{129}I that occurs at a greater depth than the ^{36}Cl peak is found in the metal oxyhydroxide and organic acid leachates (Figs. 8 and 9). The association of this ^{129}I with such phases leads to a hypothesis that this ^{129}I may be associated with colloids. Once the ^{129}I is molecularly bound it is effectively “chemically inert” and accordingly transported to the depth of maximum moisture penetration (see moisture peak intervals on Figures 8 and 9).

Taken together, a coherent hypothesis for bomb-pulse ^{129}I is that in the near surface region the ^{129}I is partitioned into at least 3 components, each having different transport properties. One component is immobile and remains near landsurface (note that this “component” may in fact be several components, since all leachates contained ^{129}I at landsurface). A second component migrates in a similar manner to ^{36}Cl , and perhaps is in anionic form (iodide, iodate). The third component migrates to a greater depth than ^{36}Cl , and is associated with metal oxyhydroxides and organic acids. These can be hypothesized to be colloidal in form, and enhance ^{129}I migration by being completely chemically inert in the hydrologic system.

Although this hypothesis is suggestive and consistent with our leaching data, the leaching process itself offers no rigorous demonstration of the nature of the phases being attacked by the leachate solutions. What can be said with confidence, though, is that the work done to date demonstrates unequivocally that ^{129}I does not move monolithically through the unsaturated zone, but rather fractionates into at least three components. Although these components have distinct leaching characteristics the exact oxidation state of the iodine and its near molecular environment remains unknown at this time.

DEVELOPMENT OF ^{99}Tc TECHNIQUES

The research completed on ^{99}Tc under this EMSP project can be divided into three parts: 1) development of sample preparation techniques; 2) development of improved AMS instrumental techniques for measurement of ^{99}Tc ; and 3) measurement of ^{99}Tc from soils at the NTS research site.

Technetium Chemical Processing Techniques

A great variety of chemical processing techniques were tested, some published by other researchers, some taken from our own previous experience with soil processing. Over a period of a year, the following technique evolved. This proved satisfactory for stripping ^{99}Tc from all matrices tested, most importantly for this project, silicate soils.

Aqueous samples or leachates are reduced in volume to ~100 mL (small samples are diluted to ~100 mL) and boiled with peroxide to fully oxidize technetium and to destroy organics. Persulfate is added if necessary to generate a more aggressive oxidation. Calcium and barium are added for samples with high levels of dissolved salts to precipitate major matrix components. Supernatants are filtered at 0.2 μm and loaded onto a column containing 2 mL of a technetium-specific resin (Eichrom TEVA-Spec⁺). Following rinsing with 0.1 and 1 M nitric acid, Tc is eluted with 15 mL of 8 M nitric into a teflon vial.

For AMS analysis, a stable isotope of another element with similar ionization characteristics must be added to the sample to serve as a proxy for a stable technetium isotope. We found ^{93}Nb to work well. Therefore, elemental niobium (natural niobium is 100% ^{93}Nb) is added to the eluent as peroxoniobium (2 mg total Nb in concentrated peroxide/nitric acid solution). The vial is capped with a flow-through lid and the samples are dried under a dry nitrogen flow at low temperature on a hot plate. Once dried, the niobium oxide pellet is

transferred to a small borosilicate test tube and baked at 400° C for ~1 hr. The pellet is then crushed to improve sample homogeneity, and pressed into a standard LLNL aluminum AMS sample holder.

Technetium recovery is monitored using ^{95m}Tc as a tracer. Our ^{95m}Tc stock was extracted from a spallation target and contains high ^{99}Tc concentrations. To avoid this contamination in samples prepared for AMS analyses, separate splits were taken for recovery measurements. An alternative source of ^{95m}Tc , reported to produce ^{99}Tc -free material (Sekine et al., 1999), is produced by alpha bombardment of ^{93}Nb , which we plan to employ for future measurements. Results of the tracer work show typically high recovery (> 90%) for aqueous samples and mixed results for soil leachates, depending on the soil type. Transfers of pertechnetate onto and off of the column, and ultimately to the final sample pellet, are consistently quantitative.

AMS Instrumental Techniques for ^{99}Tc

AMS measurements are performed using the LLNL AMS spectrometer (Davis et al., 1990; Roberts et al., 1997). Negative ions are produced in the cesium sputter source and accelerated to 40 kV (Southon and Roberts, 1999). Injection of $^{99}\text{Tc}^{16}\text{O}^-$ and $^{93}\text{Nb}^{16}\text{O}^-$ ions into the accelerator occurs quasi-simultaneously (~3 Hz cycle; 1 ms $^{93}\text{Nb}^{16}\text{O}^-$; 300 ms $^{99}\text{Tc}^{16}\text{O}^-$). The high energy spectrometer is set to select $^{99}\text{Tc}^{13+}$ ions at 125 MeV energy, and $^{93}\text{Nb}^{13+}$ current is measured in an off-axis Faraday cup located after the first high energy analyzing magnet. Count rates are $\sim 5\text{s}^{-1}$ for samples containing 100 fg ^{99}Tc , and samples can be measured for >30 minutes, for a total efficiency $\sim 1\text{-}2 \times 10^{-5}$ detected counts per sample atom. Extracted $^{93}\text{Nb}^{16}\text{O}^-$ currents are typically 1-2 μA , and stripping yield in the 13+ charge state is 4-5%.

Ion counting is performed using a gas ionization detector filled to 110 Torr with P10 (90% argon, 10% methane). Differential energy loss is measured in 3 anodes. Two dimensional spectra (first anode v. third anode), gated on the second anode, are used for particle identification. Ruthenium-99 and ^{99}Tc peaks are not fully resolved at the energies available with the 10 MV LLNL accelerator. Separate Tc and Ru windows are placed on the spectra, with ~85% of the Tc events and ~25% of the Ru events occurring within the Tc window. For quality control, a third window is included to monitor for Mo events which are occasionally evident in the spectra. The detected Mo rate is nearly always negligible compared to the Ru rate for environmental samples. Corrected Tc, Ru, and Mo counts are determined analytically from the gated events. Counting uncertainties and systematic uncertainties in the deconvolution (caused by small gain shifts in the detector) are included in the corrected results. The parameters (the fractions of Tc, Ru, and Mo events in each cut) for the deconvolution are determined by repeatedly running blanks, high activity Tc standards, and spiked Ru samples as part of the measurement protocol.

Ratios of Tc counts to Nb integrated charge, corrected for electronics deadtime and ^{99}Ru background, are computed for each sample. This ratio is converted to total sample ^{99}Tc by normalizing to the same ratio as measured for ^{99}Tc standards, then multiplying by the amount of Nb carrier solution added.

Measurement of ^{99}Tc From Research Site Soils, Standards, and Other Samples

We have measured ^{99}Tc in soil leachates from the EMSP research site and other locations, as well as fresh and sea water samples. Sensitivity of 10- 20 fg is typical for each sample type, and low-level standards containing 20 fg ^{99}Tc are readily measurable above background. Three difficulties have been encountered in these measurements. These are: variability in the measured

ratios; matrix material which is not removed during sample preparation; and relatively high ruthenium levels in some samples.

To evaluate our methods, we measured ^{99}Tc concentrations in the reference material IAEA-381, Irish Sea water. A ^{99}Tc activity of 217 ± 11 mBq/kg was reported in the IAEA report on this material (Provinec et al., 1999). Figure 10 shows the results for a set of 20 IAEA-381 aliquots which were included as part of a set of ~120 environmental samples (plus associated blanks, standards, and tests) measured over a 3 day period. The average of the AMS results is 190 mBq/kg, with a standard deviation of $\pm 14\%$. No correction for chemical recovery is included in these results. If the two most extreme outliers are removed, the average remains 190 mBq/kg and the standard deviation drops to $\pm 10\%$.

The variability observed in the IAEA-381 results is typical of that seen in samples and standards. The source of this sample-to-sample variation is time-dependence in the Tc/Nb ratio measured for an individual sample over the course of the measurement. This time-dependence has also been reported by the AMS group at the Australian National University, where Tc/Rh ratios are measured (L. K. Fifield, pers. comm., 1998). This variability may be caused by differences in the sputtering rates of Tc and Nb or sample inhomogeneity. The effect of this time-dependence can be reduced by integrating the measurement over a longer time, and assuring that the integration time is as similar as possible for different samples. Presently this represents the major limitation to our measurements.

Fresh water samples (some radionuclide contaminated) from the Nevada Test Site were measured by us for the DOE-EM UGTA project (McAninch et al, 2000). Figure 11 shows the results of replicate analyses. Nine samples were measured with detectable ^{99}Tc , with very good replication of results for concentrations above 2 mBq/kg. Based on the relative ease of sample preparation for water samples, samples as large as 1 L should be easily measurable with an expected sensitivity of ~ 0.01 mBq/kg (~ 0.3 fCi/L). This work is a clear indication of the range of usefulness of our ^{99}Tc capabilities developed under the EM Science Program.

Soil leachates have been measured in arid soils from our EMSP research site for samples up to 250 g. A difficulty in the largest samples (and in some ~ 100 mL freshwater samples) is the presence of significant quantities (milligrams) of non-volatile material (presumably soluble salts) which are not fully removed by the sample chemistry. For quality control, each pellet is weighed after baking. The primary effect of this material is dilution of the niobium and technetium, resulting in low or undetectable signals — no interferences from this material are observed in the detector spectra. Since it is not known how this dilution might affect the measured Tc/Nb ratio, these samples are flagged as suspect. Efforts to fully identify and remove this remaining material is ongoing. Initial experience shows that precipitation steps using calcium and barium, combined with additional rinse volumes of the column prior to elution, can reduce this material to acceptable levels in most cases.

Figure 12 shows the ^{99}Tc profile in the soils at the EMSP research site trench. The average and standard deviation of 18 baseline samples was 1 ± 11 fg per sample. The surface concentration from global fallout of 0.1-2 mBq/kg was readily measurable above background. A near surface sample was also readily measurable above background, with a value of 15 fg ^{99}Tc in a 120 g aliquot. Although most of the ^{99}Tc appears to be present within 50 cm of landsurface, a small amount appears to be present in the 220-300 cm interval, about the depth of the ^{36}Cl peak (Figure 12). Some ^{99}Tc therefore may migrate as conservatively as chloride. Because ^{99}Tc occurs as the TcO_4^- anion, it was long felt to be capable of significant migration. Our results suggest that while this does not appear to be the case with the bulk of the bomb-pulse ^{99}Tc present,

fractionation similar to that observed with ^{129}I may occur, allowing some of the ^{99}Tc to move to greater soil depths. We still consider these results preliminary because we feel the need to gain more confidence in our techniques through analysis of standards and replication of these data, but these results demonstrate the sensitivity of the method. We are pursuing opportunities to investigate the possible component fractionation of ^{99}Tc in arid soils.

DEVELOPMENT OF ^{90}Sr TECHNIQUES

During FY00 we performed tests to examine the value of AMS for routine ^{90}Sr determinations. In a general sense, the motivation for pursuing AMS as an analytical tool for ^{90}Sr is the potential for sensitive, high throughput, fast turnaround, robust measurements using simple chemistry. Low level measurements of ^{90}Sr are traditionally performed indirectly, by measuring the ingrowth of the ^{90}Y daughter. This approach is time-consuming (~4 weeks for ingrowth), accuracy can be limited (the chemical yields of three separate chemical extractions must be high and well determined), and backgrounds from other radionuclides can interfere. More specifically to this project, we were interested in ^{90}Sr migration because, like ^{129}I and ^{99}Tc , it is a high abundance fission product which is present in worldwide fallout and is of significant importance at a number of DOE sites. In addition, the chemistry of Sr is sufficiently different that hydrogeologic information in the vadose zone could be determined by contrasting the relative migration of the ^{36}Cl , ^{129}I , ^{99}Tc , and ^{90}Sr fallout peaks.

The primary issues in developing ^{90}Sr AMS are rejection of interference from the stable isotope ^{90}Zr , and conversion of sample ^{90}Sr to a form which is acceptable for AMS analyses. The first of these is somewhat easier than in the case of $^{99}\text{Tc}/^{99}\text{Ru}$. Although ^{90}Zr is much more abundant in the environment than ^{99}Ru , Zr and Sr are sufficiently different in chemical behavior that chemical separation is easily obtained. Also, the Sr and Zr are separated in atomic number by 2 units, greatly improving the separation which can be obtained using the AMS gas ionization detector. Our preliminary tests showed that instrumental ^{90}Zr backgrounds were sufficiently low, and that reasonable separation of ^{90}Sr and ^{90}Zr peaks in the energy loss spectra could be obtained.

To allow measurements of environmental samples, we developed a simple and convenient chemical preparation. Soil leachates were combined with stable strontium, which served as carrier and for yield monitor. The solution was taken to dryness, and the residue was taken up in 8M nitric acid, which was loaded onto a strontium-specific column (0.7 g Eichrom Sr-Spec) for concentration, purification, and removal of Zr. The Sr-containing fraction was taken to dryness twice in the presence of concentrated hydrofluoric acid, converting the sample to SrF_3 , which can be used directly for AMS analysis. Following the drying of the leachate, the entire procedure takes only a few minutes per sample.

We applied these methods to a set of IAEA reference soils, a set of Marshall Islands soils which measure separately by the standard radiometric technique, and a set of the NTS trench samples. Overall results were mixed. Backgrounds from Zr were elevated in these soils from what had been seen in preliminary tests, which significantly limited sensitivity and in some cases prevented quantification. Stable Sr currents were also low in many samples, indicating that elements other than Sr are not being adequately separated during the chemical extraction. For most of the samples, the observed sensitivity was $^{90}\text{Sr}/\text{Sr} \approx 10^{-12}$, corresponding to about 20-200 mBq per sample, similar to the sensitivity of traditional decay counting.

Our conclusion from this work is that AMS analysis of low-level ^{90}Sr is indeed possible, but will require improved Sr purification. Very likely, this will only require one or two additional passes through Sr-Spec columns, and not additional chemical procedures. This will add only a

few minutes to the preparation time and could be done by robotics. Stabilization of the AMS Sr beam may take longer to develop, since identification of the contaminants has not been made yet. However, it is clear from this work that the potential for simplicity and speed, and the expectation of an additional factor of 10 improvement in sensitivity, merits further work. We would conservatively estimate that 2-3 additional months of work would bring ^{90}Sr fully on-line.

RELEVANCE, IMPACT, AND TECHNOLOGY TRANSFER

RELEVANCE

Relevance to DOE Needs

. On the EMSP website listing site needs (http://emsp.em.doe.gov/focus_area.htm), seven areas of research needs are listed under Environmental Restoration. Of these, we believe there are three that our research directly addresses. They are (quoting verbatim from the website):

- * Fundamental improvements in the abilities to characterize contaminant geologic settings and chemistry, to assess data, and to predict the movement and fate of contaminants.
- * Better understanding of the vadose zone processes which are complicated by the possibility of multiphase flow (e.g. water, air, contaminant), by competition between fluids for wetting of surfaces, by effects of alternating wet and dry periods and other factors.
- * Basic data or methods to support long-term decisions and to understand processes that affect the validity of remediation decisions and long-term effectiveness of remediation activities.

The first of these is the basic goal of this research project. Our results provide of means of not simply measuring a group of radionuclides that are very difficult to measure without AMS, but also of measuring them in almost any type of environment worldwide. This greatly facilitates the ability to perform work that is intended to determine the movement and fate of contaminants in the far-field environment, near human receptors. The second listed need is addressed by our research by improving the mechanisms for determining moisture flux in the vadose zone. As mentioned earlier, chloride and ^{36}Cl are important tools for determining moisture flux. Our research has shown that these tools cannot be used indiscriminately. We believe that the course of our research is heading towards an understanding of how chlorine and ^{36}Cl actually do migrate in unsaturated soils, and therefore how they can best be used to track moisture movement. Further, our ^{129}I results suggest that there may be even better ways of tracking moisture movement in the vadose zone. The third need is again addressed very directly by our research. The primary result of this work is to produce the basic data on ^{36}Cl , ^{90}Sr , ^{99}Tc and ^{129}I and contaminant transport in any environment (we focused on the vadose zone) that is required in order to assess the expected relative effectiveness of alternative remediation strategies, and to make good technical decisions when planning remediation activities.

Reducing costs, schedules, and risks

. As discussed earlier, previous research has shown that there is a serious lack of knowledge regarding the migration potential and ultimate fate of anionic nuclides like ^{99}Tc and ^{129}I . This leads to uncertainty in how to remediate DOE sites, both from the standpoint of which actions really need to be taken (and which do not), and with regard to how effective various actions might be. This uncertainty leads to an inefficiency in assessing actual public health risks and in communicating those risks to the public. A result of this is over-designed projects that are

not only costly to implement, but have protracted planning stages that are costly. Remediation schedules become lengthy due to uncertainty of action and the need for trial-and-error remediation procedures. Our research is designed to make the study of radionuclide migration simpler to do, simpler to interpret, and easier to apply to specific DOE sites. This will lead to a better understanding of the migration potential and ultimate fate of radionuclides, creating much less uncertainty regarding which remediative strategies should be employed. For any project, this will reduce its cost, shorten its schedule, and provide greater confidence in its final result, both for the DOE and for the general public.

Bridging the gap towards needs driven technology development

. This research is not intended to provide the technology to remediate DOE sites contaminated with radionuclides. Rather, it is intended to provide the basic information that someone would need in order to adequately develop a technology for this remediation. At present, this information is lacking, and so therefore the technology is lacking. Further, in the future these technologies will require a means of assessing their effectiveness in actual field operation. Our research is intended to provide a sophisticated and straightforward technique for making these assessments.

IMPACT

This project developed new capabilities within the DOE complex to measure low-level radionuclides (^{90}Sr , ^{99}Tc , ^{129}I) by accelerator mass spectrometry. These nuclides are difficult to measure in any abundance, and the developed techniques permit a new ease of analysis. But more importantly, we believe, the techniques allow migration research concerning these nuclides to occur in almost any environment worldwide (because of the globally-distributed bomb-pulse). This will be a means of gaining valuable and needed information regarding radionuclide migration. It provides a tool for scientists to use at any DOE site, or other site where nuclide migration is of issue, in order to characterize the migration of a set of very important radionuclides. The nuclides that we focused upon in this project (^{129}I , ^{99}Tc , and ^{90}Sr) were specifically chosen because of their key importance at DOE sites. All sites where uranium or plutonium production or reprocessing were carried out, and where contamination from this occurs, will be sites where these particular nuclides are important. This prominently includes the Hanford and INEEL sites. Therefore we anticipate that our results will have a large impact on future radionuclide assessments at these sites.

Besides advancing scientific analytical capabilities, the applied side of our research produced three significant advances in the understanding of moisture and radionuclide movement through unsaturated soils. First, it suggests that in arid soils, preferential moisture flow and associated preferential radionuclide migration are not a common phenomena. Despite a variety of conditions at our research site that would be thought to be conducive to preferential migration of both moisture and radionuclides, preferential movement was not observed. Second, the commonly used “chloride accumulation” method for estimating moisture flux is erroneous. The distribution of chloride relative to bomb-pulse ^{36}Cl at our research site clearly shows that the movement of chloride is in some way attenuated in the soil column. This leads to an accumulation of chloride that is not a direct function of the flux of chloride to the Earth’s surface, and so is not a direct function of the duration of this flux. Third, our research has demonstrated that migration of ^{129}I can be enhanced relative to ^{36}Cl in arid soils, and that this enhancement is related in some way to metal hydroxide and organic acids phases in the soil. We hypothesize that these phases are colloidal and that ^{129}I is affected by colloidal transport in arid

soils. A secondary observation in this regard is that this fraction of the ^{129}I (and/or perhaps the colloids) are a much better measure of moisture flux in arid soils than either chloride or ^{36}Cl . These three advances should have a significant impact on future research in both moisture flux and nuclide migration in soils, both arid and non-arid. Once published in the scientific literature, these findings should therefore find broad use both by researchers attempting to further vadose zone science, and by scientists assessing migration potential from known contaminated sites.

Much research needs to be done in this area. Larger-scale projects that are designed to better understand how in general nuclides migrate in soils, and how in particular iodine moves in arid soils are needed. We believe ^{129}I may be key in understanding the role of colloids in nuclide, or even nutrient, movement in soils. This may well extend to an understanding of the role of colloids in saturated groundwater systems. We are pursuing ways of extending this research.

TECHNOLOGY TRANSFER

The results of this project can be applied to DOE-EM problems immediately. We have developed fast and relatively easy methods for analyzing ^{99}Tc , ^{90}Sr , and ^{129}I , and improved methods for the analysis of ^{36}Cl in arid soils. We are using the techniques to analyze ^{99}Tc in waters at the Nevada Test Site (through the DOE-EM UGTA project), ^{36}Cl for the Yucca Mountain Project, and ^{36}Cl for the DOE-EM Site 300 (LLNL, California) remediation efforts. We are in contact with personnel at both the Hanford and INEEL sites to use both ^{36}Cl and ^{129}I at them, and we anticipate that ^{99}Tc will be analyzed by AMS at these sites in the near future also. When we more fully develop our own data base of ^{90}Sr results, such that our capabilities are fully demonstrable, we expect to add ^{90}Sr characterization efforts within the DOE complex as well.

A hurdle that must be overcome in order for the DOE complex to make full use of the products of our EMSP project is the development of a mechanism for communication between ourselves and those who could profitably use the products. We are able to find adequate ways of contacting other researchers, but not those who could use the capabilities in the field to help with the remediation effort.

PROJECT PRODUCTIVITY

The project accomplished most of its proposed goals. AMS analytical techniques were developed for ^{90}Sr , ^{99}Tc , and ^{129}I , and the desired improvements in the methods for ^{36}Cl analysis were completed. The field research site in arid soils (Nevada Test Site) was developed and used for the measurement portion of the research. The results of this research are discussed above. Two of the original goals of the project were not realized: soil profiles of ^{90}Sr concentration at the NTS research site, and the development of AMS analytical techniques for ^{93}Zr . The difficulties we encountered in the development of ^{99}Tc consumed too much time and project funding to allow us to complete these tasks. In our original EMSP proposal, we had stated that the development of ^{93}Zr would be a lower-level priority, and might not be doable in the timeframe of the project if unforeseen problems arose.

The workplan was never revised. We stayed on schedule with the ^{36}Cl , ^{129}I , and research site development portions of the project. Only the ^{99}Tc , ^{90}Sr , and ^{93}Zr portions of the project, which for technical reasons had to be accomplished in this order, fell behind schedule. We found significant problems in extracting technetium from silicate soils. We believe previous researchers encountered this problem as well, without completely realizing it. This may be because our

increased analytical sensitivity allowed us to see variations in Tc yield that were unnoticed using less sensitive techniques.

We are satisfied with the productivity of our project, and feel well-positioned to carry the work beyond that which was proposed in the original 1996 EMSP funding proposal. We are currently making use of our increased capabilities and expertise on EM-related and other projects. The EMSP program provided us a wonderful opportunity to complete a significant body of scientific research.

PERSONNEL SUPPORTED

The following is a list of the primary personnel that were supported by this EMSP project, and an approximation of the work time devoted to the project (percent of yearly time). All are employees of Lawrence Livermore National Laboratory (except the student, B. Bergquist).

Gregory Nimz (PhD Geochemist, Principal Investigator). Project time: 40%
Marc Caffee (PhD Physicist, Principal Investigator). Project time: 40%
Jeff McAninch (PhD Physicist, Principal Investigator). Project time: 25%
Robert Finkel (PhD Chemist). Project time: 10%
Alfredo Marchetti (PhD Chemist). Project time: 10%
Roger Martinelli (Laboratory chemistry technician). Project time: 10%
V. Jan Brown (Laboratory technician). Project time: 33%
Bridget Bergquist (Student and post-graduate researcher). Project time: 10%

PUBLICATIONS

Caffee, M.W., Nimz, G.J., Roberts, M.L. (1999) Measurement of iodine-129 in unsaturated soils: Transport properties and distribution of iodine-129 in depth profiles. EOS: Transactions of the American Geophysical Union, AGU Fall Meeting, San Francisco, CA.

McAninch, J.E., Marchetti, A.A., Bergquist, B.A., Stoyer, N.J., Nimz, G.J., Caffee, M.W., Finkel, R.C., Moody, K.J., Sideras-Haddad, E., Buchholz, B.A., Esser, B.K., and Proctor, I.D. (1998) Detection of ⁹⁹Tc by accelerator mass spectrometry: preliminary investigations. *J. Radionanal. Nucl. Chem.*, 234: 125-129.

Bergquist, B A;Marchetti, A A;Martinelli, R E;McAninch, J E;Nimz, G J;Proctor, I D;Southon, J R;Vogel, J S. (1999) Technetium measurements by accelerator mass spectrometry at LLNL. Lawrence Livermore National Laboratory Report UCRL-JC-136204. Submitted for publication to *Nuclear Instruments and Methods*.

Nimz, G.J., Caffee, M.W., and McAninch, J.E. (2000) Distribution of ³⁶Cl, chloride, and moisture in an arid unsaturated soil: Implications for the "chloride accumulation" soil chronology method. In preparation for submission to *Water Resources Research*.

Caffee, M.W. and Nimz, G.J. (2000) Bomb-pulse ¹²⁹I profiles in an arid unsaturated soil and its dependence on secondary phases. In preparation for submission to *Geochimica et Cosmochimica Acta*.

INTERACTIONS

Meetings, workshops, conferences

. The following presentations concerning our EMSP work were given at scientific meeting, workshops, and conferences. Because presentations on topics other than our EMSP work were also given, trip costs to foreign meetings were not charged to EMSP.

8th International Conference on Accelerator Mass Spectrometry, Vienna, September, 1999.

Poster: "Technetium-99 measurements by accelerator mass spectrometry at LLNL", B.A.

Bergquist, A.A. Marchetti, R.E. Martinelli, J.E. McAninch, G.J. Nimz, I.D. Proctor, R. Southon, J.S. Vogel

8th International Conference on Accelerator Mass Spectrometry, Vienna, September, 1999.

Poster: "Three Dimensional Distribution of ^{36}Cl and Cl in Arid Soils: Implications for Their Use as Indicators of Moisture Flux", Gregory J. Nimz, Marc W. Caffee, Jeffrey E. McAninch, Robert C. Finkel

8th International Conference on Accelerator Mass Spectrometry, Vienna, September, 1999.

Talk: "Sequential leaching and AMS measurement of ^{129}I from unsaturated soils", Caffee, M.W., Nimz, G.J., and Roberts, M.L.

American Geophysical Union Annual Meeting, San Francisco, December, 1999.

Application of Accelerator Mass Spectrometry to the IAEA Safeguards and Environmental Sampling Program, International Atomic Energy Agency, Seibersdorf, September, 1999.

Invited talk: "AMS measurements of actinides and technetium at LLNL", J.E. McAninch

Workshop on Standards, Intercomparisons and Performance Evaluations for Low-Level Environmental Mass Spectrometry and Atom Counting, National Institute of Standards and Technology, Gaithersburg, April, 1999.

Invited talk: "Accelerator mass spectrometry for the measurement of long-lived radionuclides", J.E. McAninch

Technetium-99 Workshop, Southampton, England, April, 1998.

Talk: "Application of accelerator mass spectrometry to Tc-99 measurement", J.E. McAninch

International Conference on Methods and Applications of Radioanalytical Chemistry - Marc IV, Kona, April, 1997.

Invited talk: "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

211th National American Chemical Society Meeting, New Orleans, March, 1997.

Talk: "Accelerator Mass Spectrometry at LLNL: Prospects for the near-term future"

J.E. McAninch, M.L. Roberts, M.W. Caffee, L.J. Hainsworth and I.D. Proctor

Environmental Management Science Program Workshop, Chicago, July, 1998.

Poster: "Hydrologic and Geochemical Controls on the Transport of Radionuclides in Natural Undisturbed Arid Environments as Determined by AMS Measurements", Gregory J. Nimz, Marc W. Caffee, Jeffrey E. McAninch, Robert C. Finkel

Consultative or advisory functions

. Our EMSP work has served as the foundation for advisory work concerning ^{36}Cl in the vadose zone for the proposed Ward Valley low-level radioactive waste site in southern California. We met several times with both Department of Interior personnel (including Bureau

of Land Management, and the U.S. Geological Survey), and with personnel from the State of California, to provide scientific advice related to the use of ^{36}Cl to judge moisture flux in unsaturated soils. The original request that LLNL personnel provide this service came from Barbara Boxer, U.S. Senator from California.

Our EMSP work also served as a foundation for advisory work concerning ^{36}Cl for the Yucca Mountain Project. We have provided consultation for Martha Kohler of the YMP at LLNL, and for the U.S. Geological Survey, Denver (contact: Zell Peterman). Advisory work as well as ^{36}Cl analytical work is currently ongoing.

Collaborations

. Time did not permit active scientific collaborations during the course of this project. However, we are actively beginning collaborations with L. DeWayne Cecil (USGS-WRD, Idaho Falls) regarding a number of DOE sponsored or facilitated projects involving radionuclides, especially ^{129}I . We are seeking scientific collaborations related to our EMSP research at this time, and are certain that several will develop over the next few years.

TRANSITIONS

This project results in a body of data and scientific interpretation that are needed for at least three contaminant site activities: 1) public health risk assessment; 2) remediation design; and 3) monitoring design (both pre- and post-remediation). Because our findings will be published in peer-review literature, they will be available to workers involved with all three of these activities. It is common for them to consult peer-review literature in the course of their work.

Although our project is basic research, it is also applied research in the sense that it provides information immediately usable at several DOE sites, most prominently Hanford, INEEL, and the Nevada Test Site. Our work provides a blueprint for radionuclide migration studies in arid soils. We anticipate that it will indicate what to look for and where, and what factors are not of concern. This will streamline applied R&D at these DOE sites, and should reduce the costs of investigations leading to remediation designs and budget allocation decisions.

FUTURE WORK

There are three avenues for future work: completion of ^{90}Sr data base, development of analytical techniques for other radionuclides by AMS, and determination of the causes of the attenuation of chloride migration and the enhancement of ^{129}I migration in arid unsaturated soils.

Strontium-90 Database

. Samples from our trench research site were archived for analysis of ^{90}Sr . As discussed above, project time did not permit us to begin analysis of the profiles for ^{90}Sr concentrations. We are seeking ways to complete this work. It would form a scientifically important data set, along with the other measurements at the research site. We are particularly interested in building a data base of AMS ^{90}Sr analysis that demonstrate both our capability and the relative ease of ^{90}Sr analysis by AMS.

Additional AMS Radionuclide Techniques

. Many other radionuclides can be analyzed in low-level abundances by AMS. These include ^{59}Ni , ^{63}Ni , ^{79}Se , ^{236}U , ^{239}Np , ^{239}Pu , and other actinides. A natural extension of our EMSP work is to extend the range of nuclides that could be used in migration studies of this type.

Attenuation of ^{36}Cl and Enhanced Migration of ^{129}I

. Two of the most important results of our EMSP research were the observation of attenuated movement of chloride and enhanced migration of ^{129}I relative to ^{36}Cl . Because of the importance of chloride to understanding moisture flux in arid soils, and because of the hypothesized mediation of colloids in ^{129}I migration, each of these observations needs to be examined for their causes.

ACKNOWLEDGEMENTS

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Figures 1a-1d. Excavation of the EMSP research site trench. Note the soil fractures visible in 1a (upper left). This location was chosen for trenching because the soil fractures are potential sites for preferential moisture flow.



Figure 1a. Soil trench at the Vadose Zone Study Site

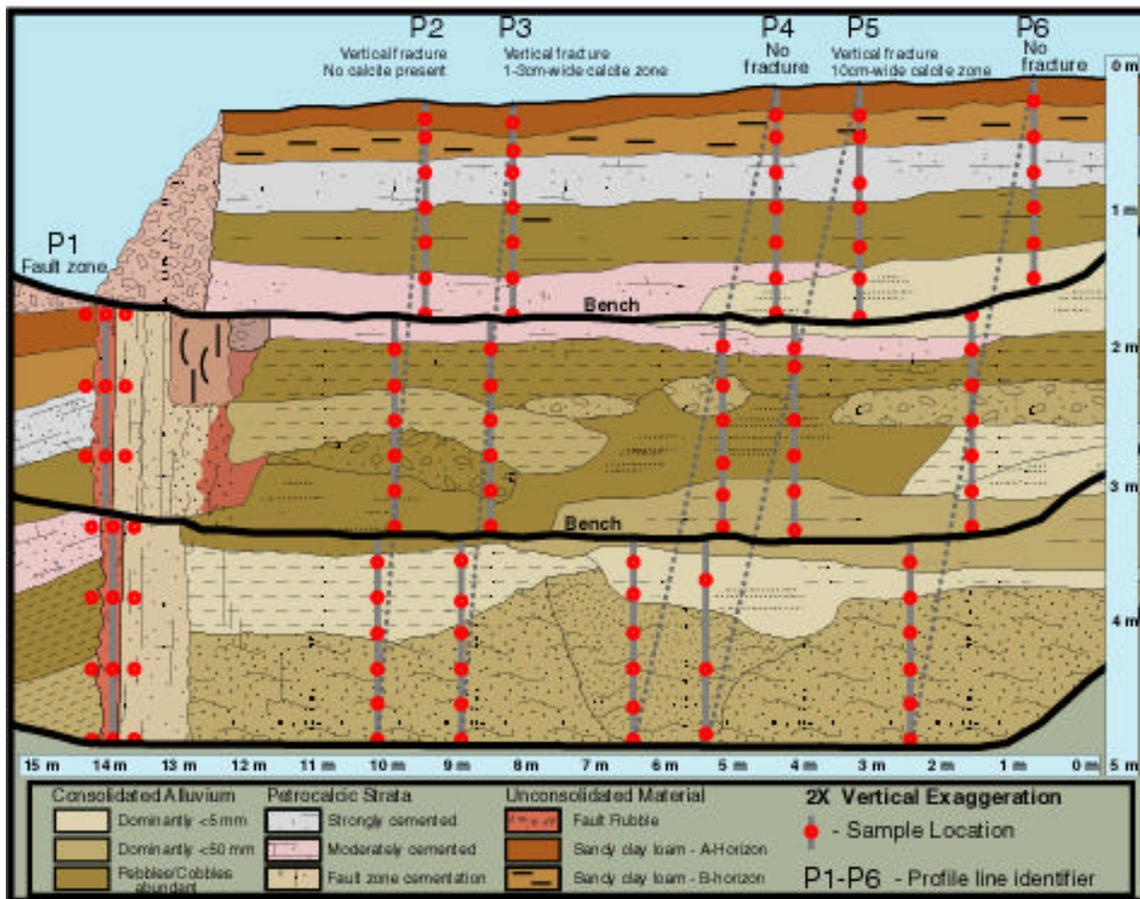


Figure 2. EMSP trench geology, showing sample profiles and locations.

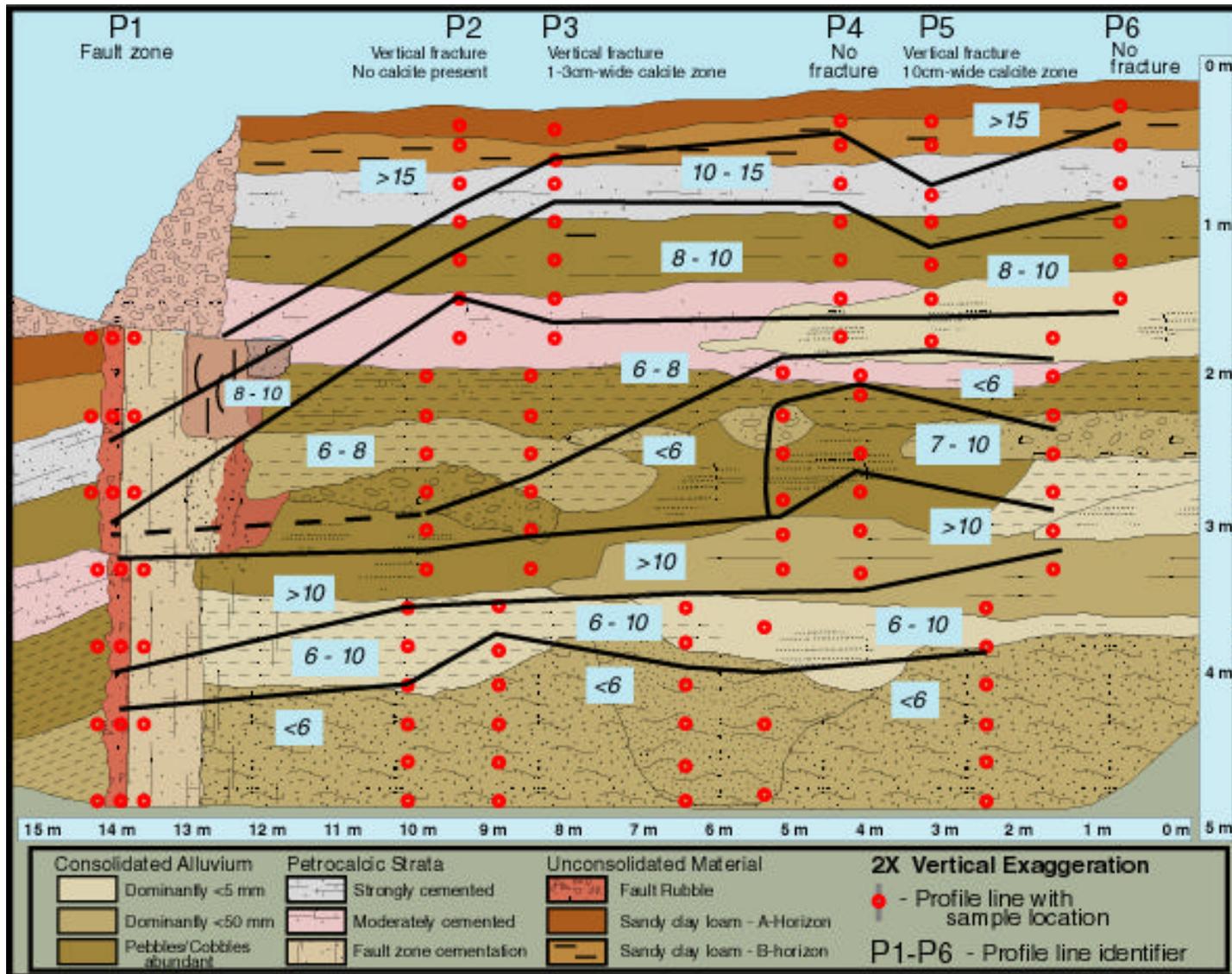


Figure 3. Soil moisture distribution in the EMSP trench. Values are weight % water content.

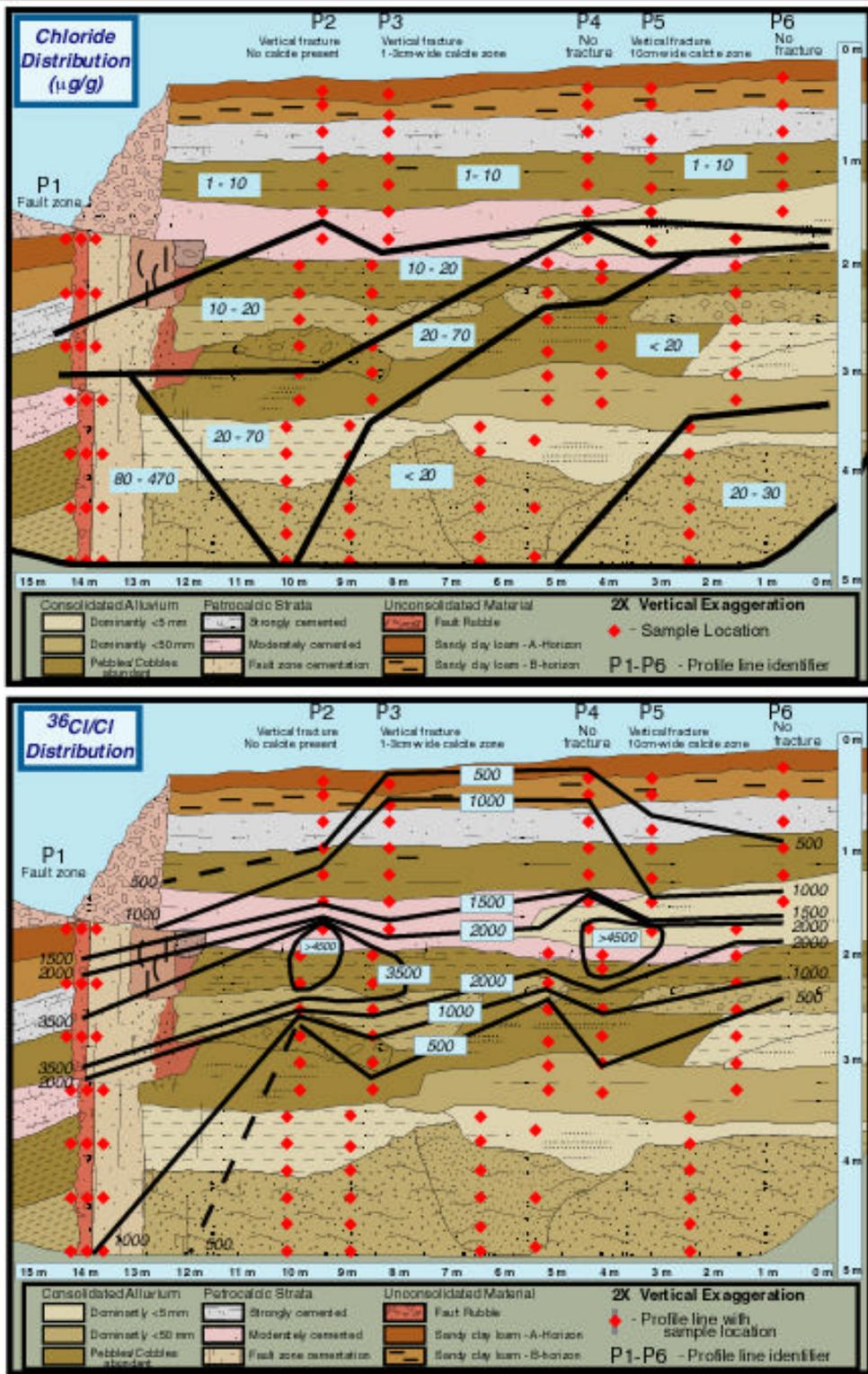


Figure 4. Chlorine and $^{36}\text{Cl}/\text{Cl}$ distributions in EMSP trench.

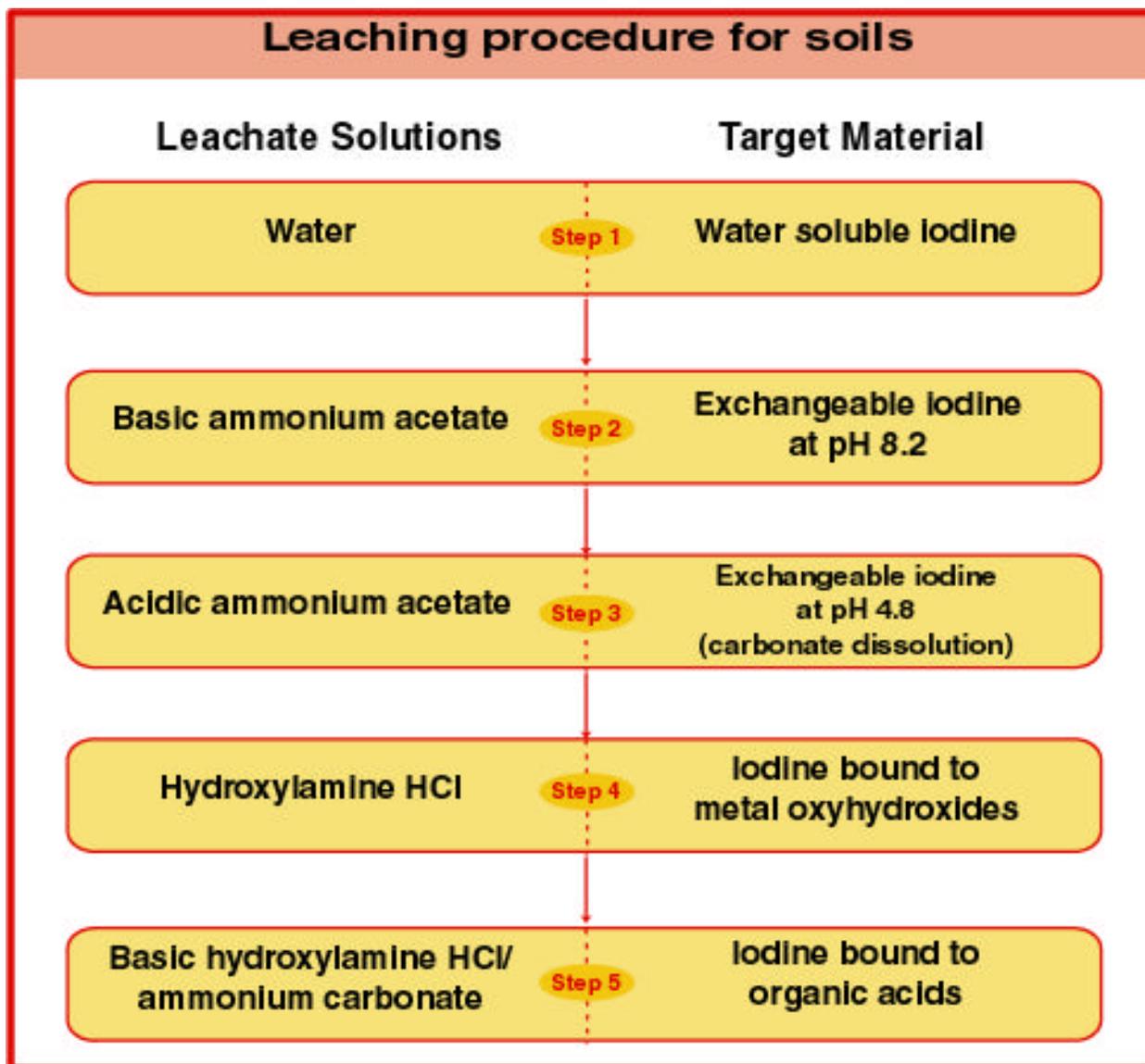


Figure 5. Procedure used on soils to extract ^{129}I from various soil compartments. The soils are leached in five steps with the leachate extracted and analyzed for ^{129}I at each step.

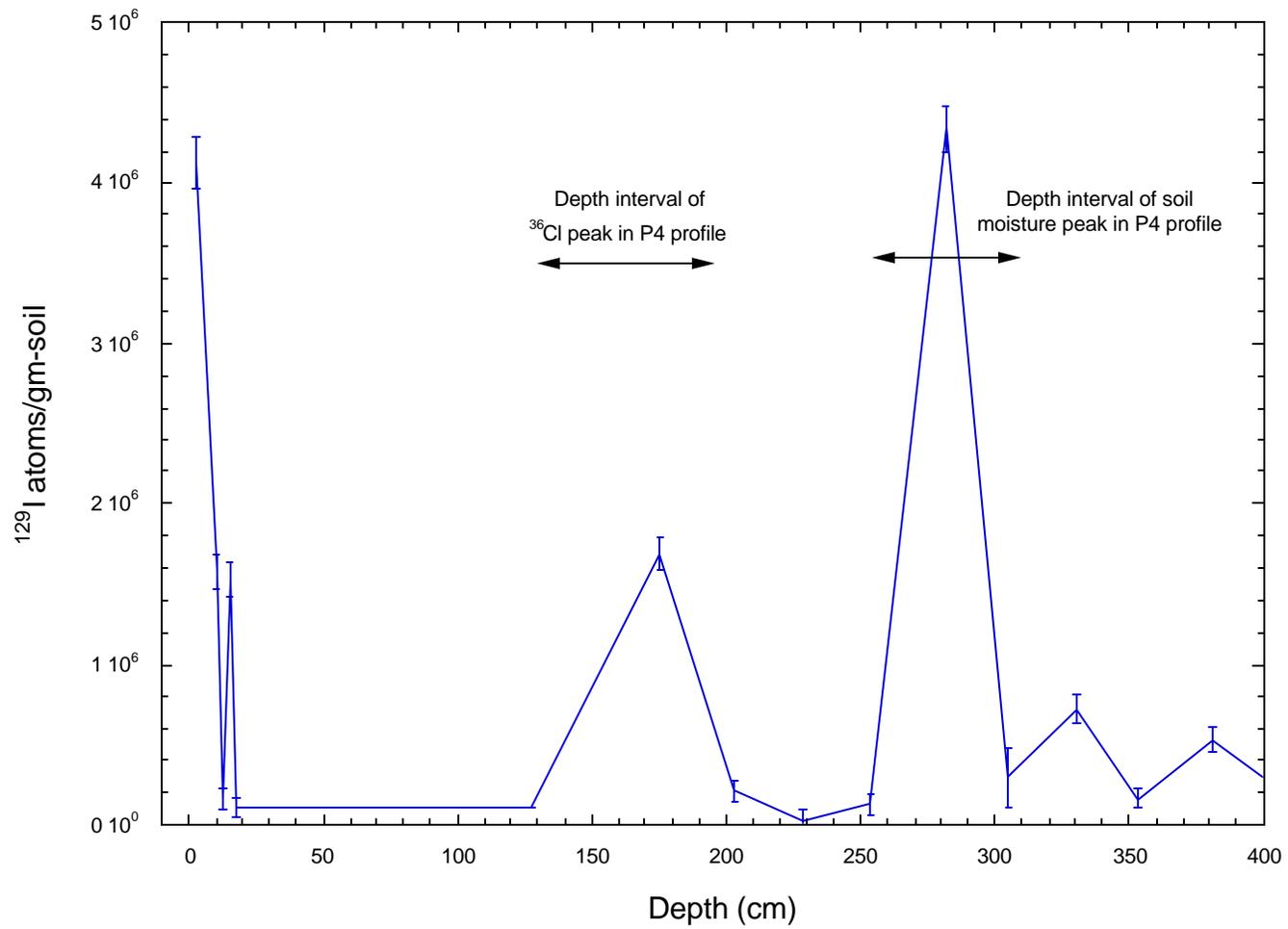


Figure 6. Iodine-129 in the P4 Profile. Summation from all leachate fractions.

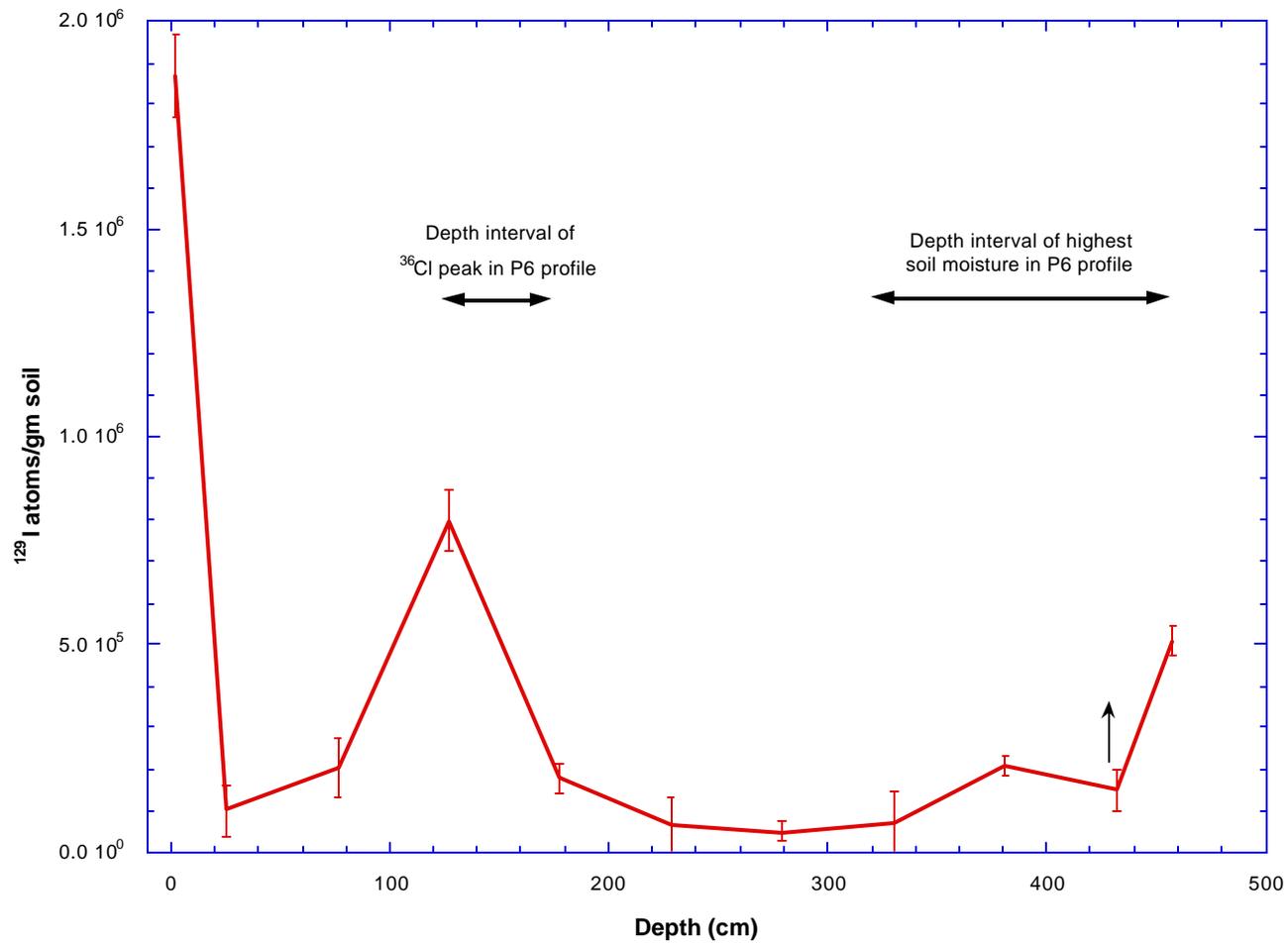


Figure 7. Iodine-129 in the P6 profile. Summation from all leachate fractions.

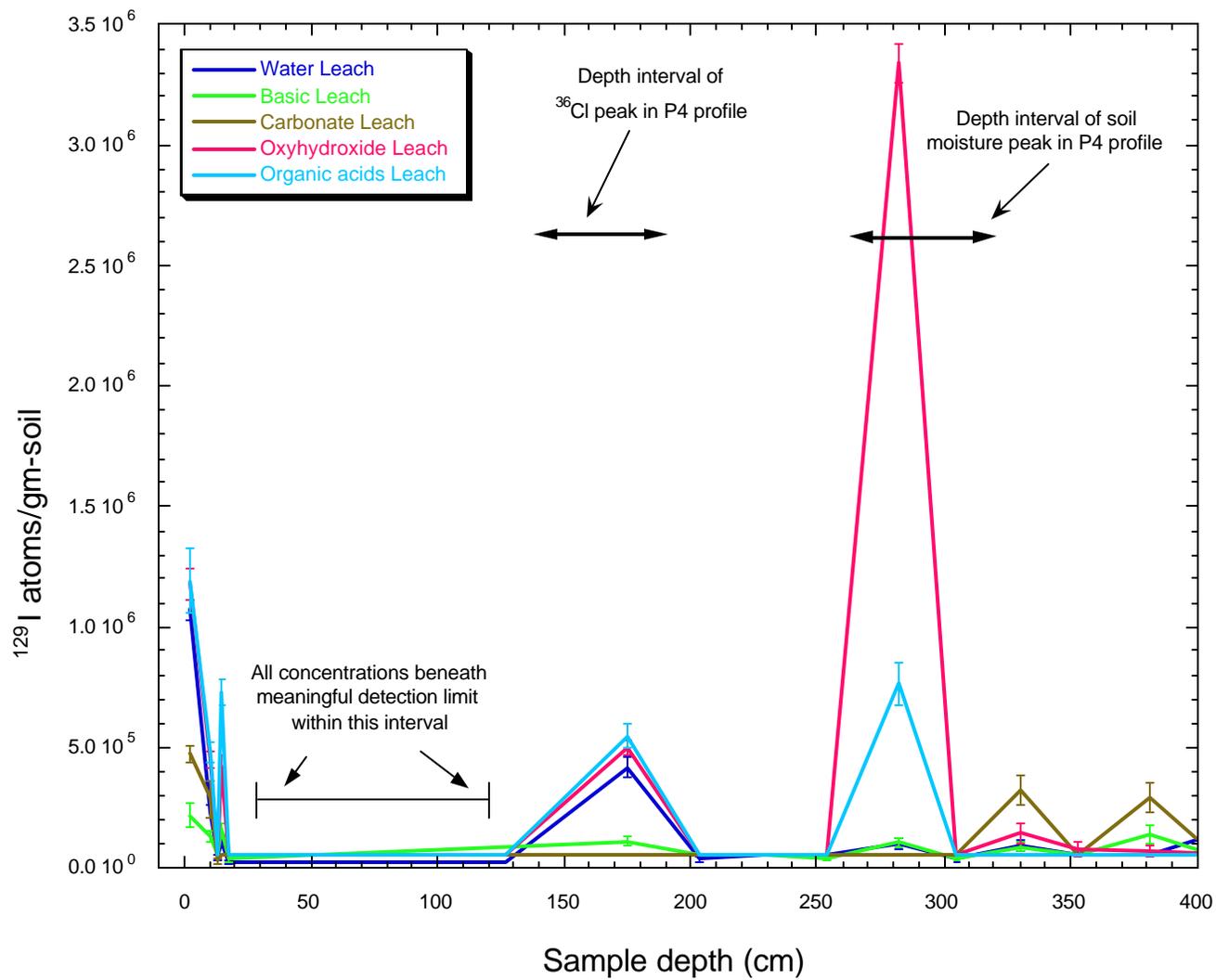


Figure 8. Iodine-129 from leachate fractions in soil profile P4.

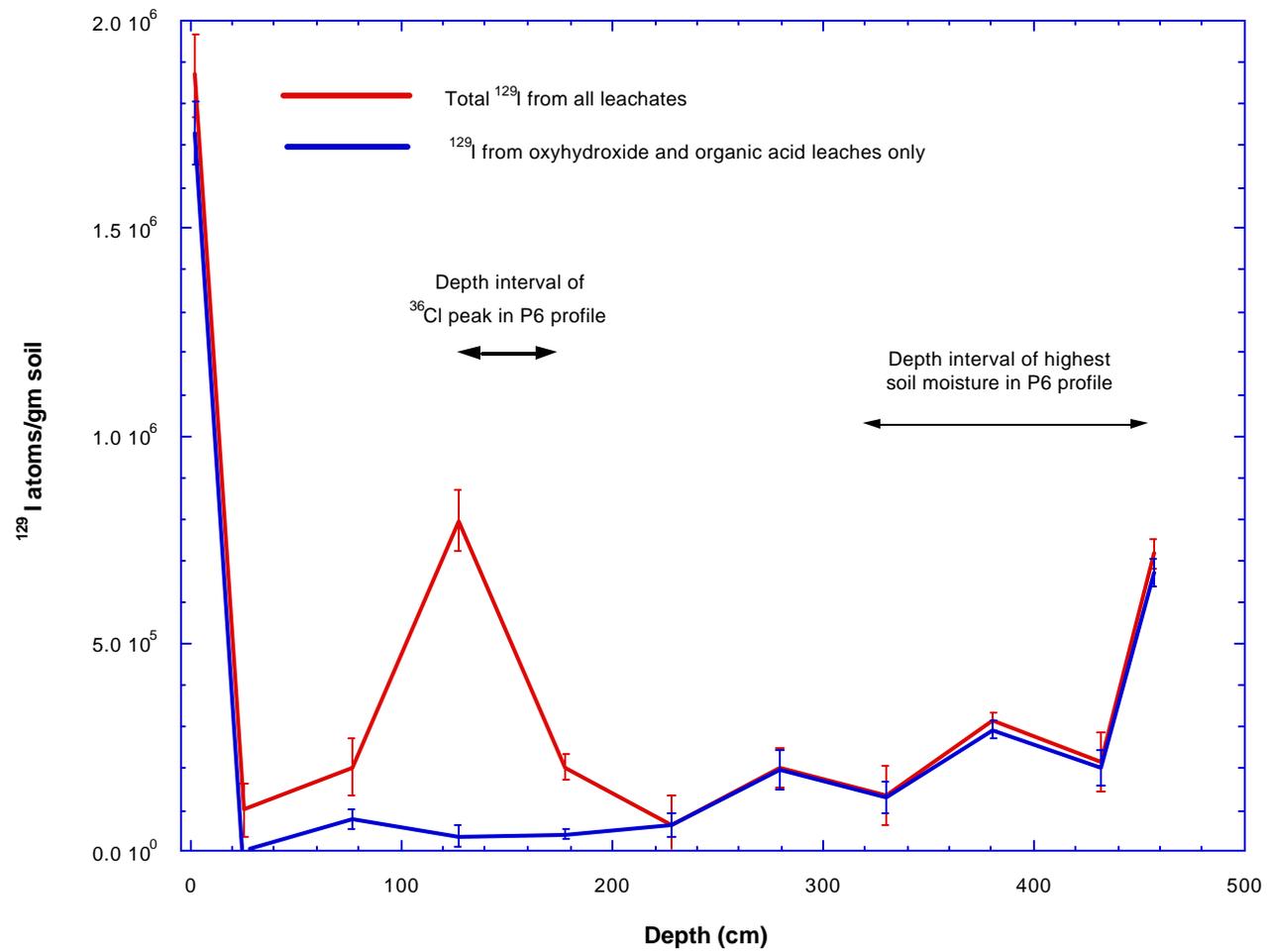


Figure 9. Iodine-129 from leachate fractions in soil profile P6

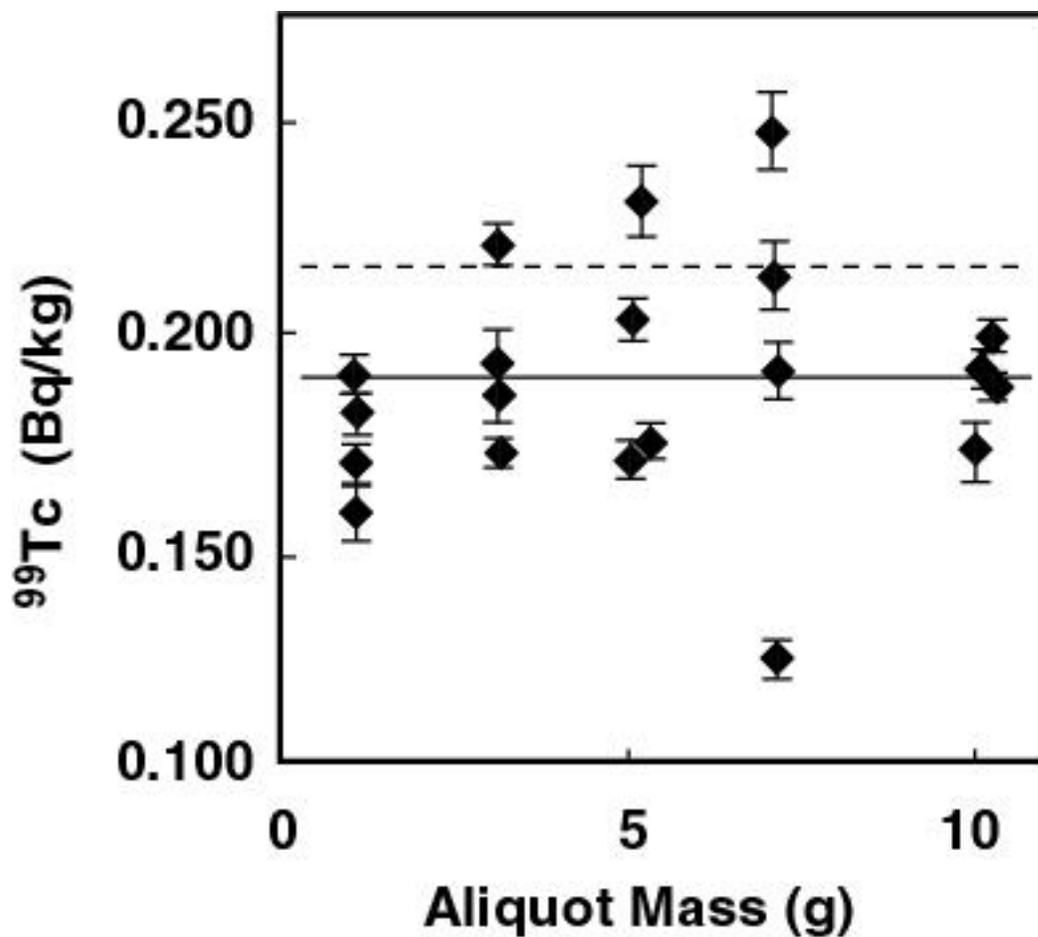


Figure 10. AMS measurements of ^{99}Tc in IAEA-381, Irish Sea Water. For comparison, the IAEA report on this material lists a single reported ^{99}Tc concentration of 217 ± 11 mBq/kg (dashed line) (Provinec et al., 1999). For the present work, 20 aliquots (1-10 g) were prepared as described in the text, then then analyzed with other samples over the course of 3 days. The average of all values (solid line) is 190 mBq/kg with a standard deviation of $\pm 14\%$. When the two most extreme outliers are excluded, the average remains 190 mBq/kg, and the standard deviation drops to $\pm 10\%$. These AMS results should be considered preliminary.

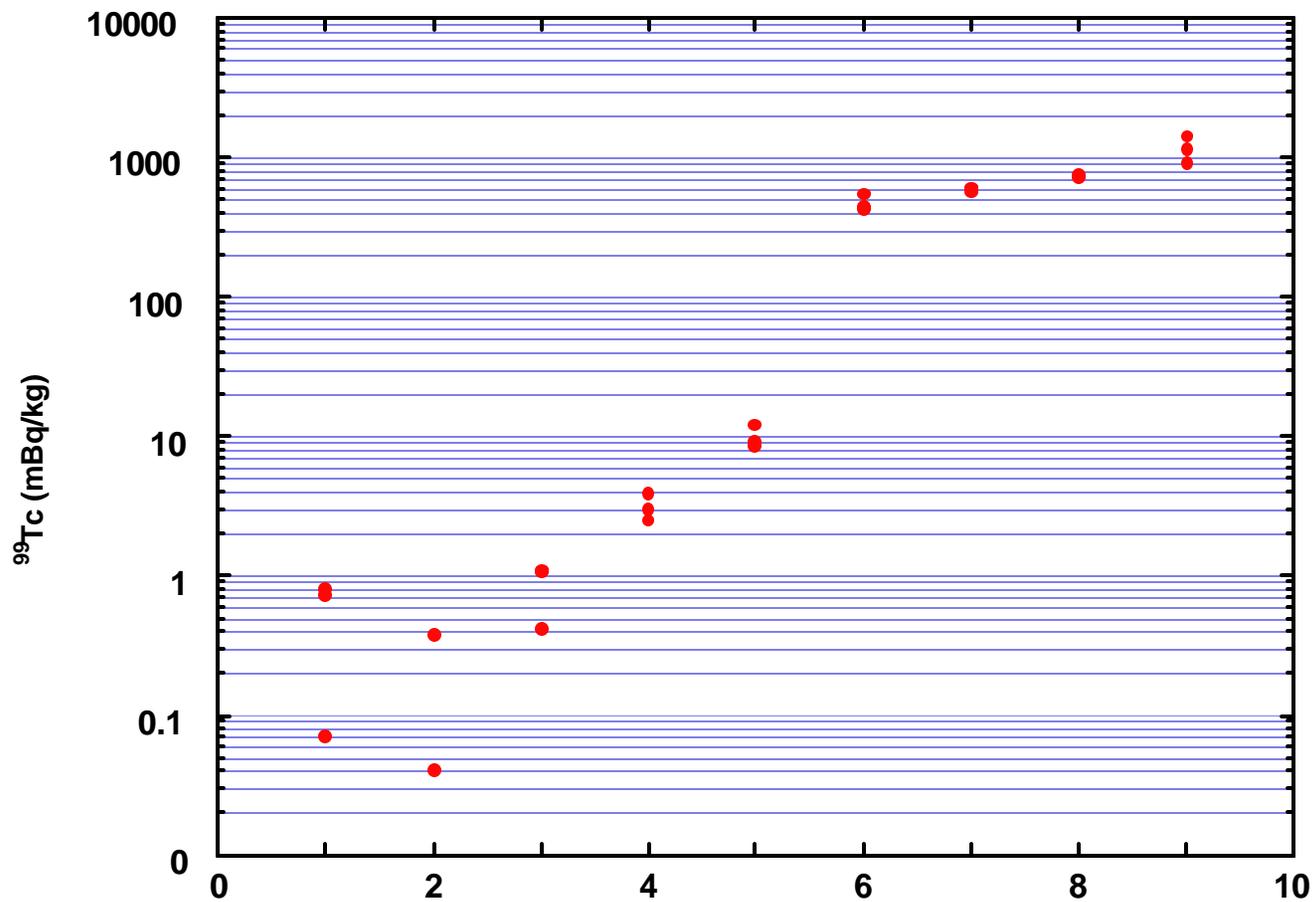


Figure 11. Water samples from the Nevada Test Site. Three replicates were run for each of nine samples. The agreement between each of the replicates is very good at concentrations above 2 mBq/kg.

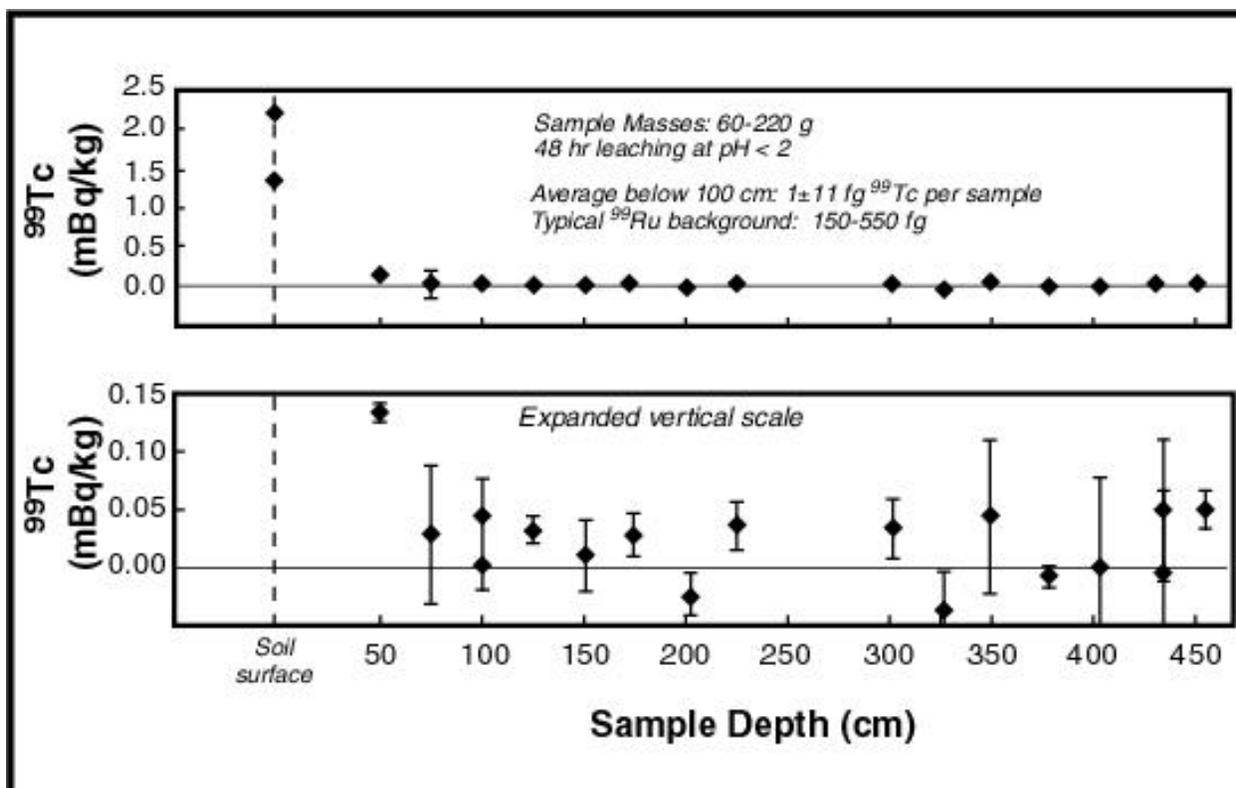


Figure 12. AMS measurement of soils from the EMSP research site. Samples of 60-220g were leached for 48 hours at pH < 2, and the leachate was prepared and measured as described in the text. The average measured ^{99}Tc for samples below 100cm depth is 1 fg per sample with a standard deviation of ± 11 fg. These results should be considered preliminary.