

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

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Considerations in Selection of Sample Matrix/Normalization Isotope

Our initial choice for sample matrix was rhodium

Advantages

- + A single stable isotope - ^{109}Rh
- + Good negative ion yield
- + Low natural abundance
- + Easily converted from dissolved to metal
- + Good homogeneity when co-precipitated with Tc

Disadvantage

- + Very high Ru levels in all commercially available pure Rh stock solution
- + Ru is the isobaric interference for measurement of ^{99}Tc
- + Oxidation-distillation using persulfate was successful in lowering Ru levels by 10^4 but this was still not sufficient

The optimum sample matrix/normalization isotope is niobium

An additional challenge is the presence of an interference from sulfur

Problem

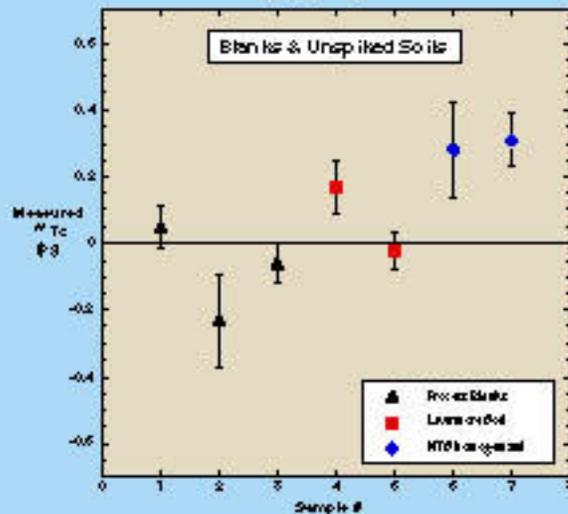
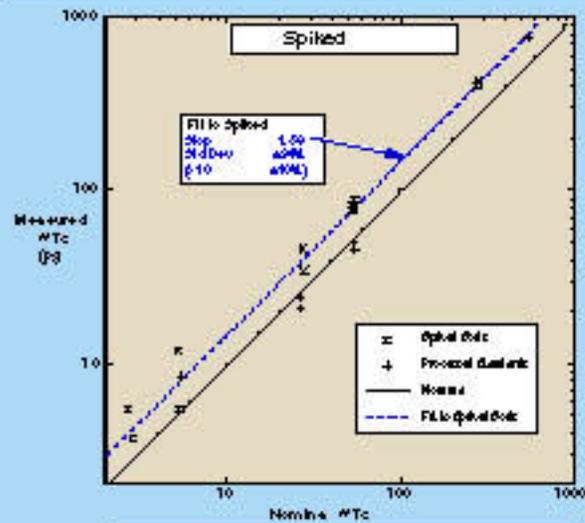
- + Sulfur ions have a high probability of injection into the accelerator at mass 99 as $^{99}\text{Zn}^{99}\text{S}^-$ and $^{99}\text{Cu}^{99}\text{S}^-$. A fraction of the individual fragments exit the accelerator with the exact velocity and magnetic rigidity as Tc ions, and are transmitted to the detector.
- + Sulfur ions reaching the detector then interfere with Tc because of an overlap between the S K-lines and the Tc L-lines

Solution

- + Rejection of sulfur was achieved by the addition of a thin gas ionization detector in front of the x-ray detector, allowing clean discrimination by differential energy loss
- + Injection of $^{99}\text{Tc}^{16}\text{O}^-$ molecules into the accelerator dramatically suppressed the S count rate relative to Tc

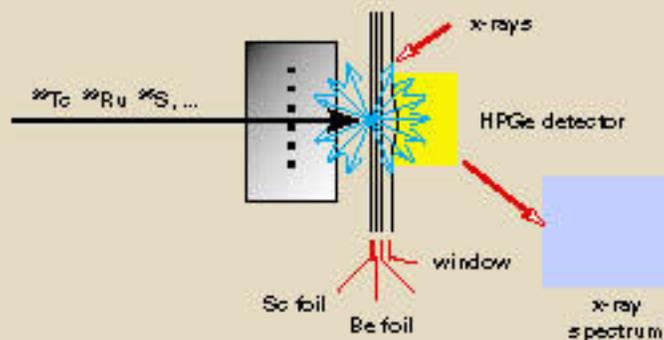
Results of AMS Measurements of ^{99}Tc in Spiked Soils

- + Soil from the trench area (homogenized, then split into 25g aliquots) was spiked with ^{99}Tc
- + Following centrifugation and filtering, hydrogen peroxide was added to fully oxidize Tc. Solutions were boiled to remove remaining peroxide, then passed through a TEVA-Spec column (Eichrom Industries) to concentrate the Tc



- + All spiked soils from NTS were measurable
- + No problems related to sample matrix were encountered
- + Reproducibility for those soils with higher ^{99}Tc concentrations was 10% (1 σ)

Characteristic Projectile X-rays for Ion Identification



After transmission through the spectrometer, the high energy ions are passed through a thin foil. As the ions slow in the foil, inner shell vacancies are produced in the ions, which then emit x-rays. The x-ray energies, which are atomic number dependent, are measured in a high purity germanium detector (HPGe), providing elemental identification.

- + Measured Tc L-lines provide a detection efficiency of 5-10%
- + Tc and Ru are unambiguously identified
- + The ^{99}Ru contribution is measured directly so background subtractions do not require assumptions about stable Ru isotope ratios in the sample
- + A thin ΔE gas ionization detector has been added to measure differential energy loss in coincidence with the x-ray measurement, further reducing certain interferences.

This Project is the First Concerted Attempt to Measure ^{99}Tc Using AMS

Research Issues

- + Will ^{99}Ru produce sufficient negative ions?
- + Given adequate negative ion yield are the ion transmission and detection efficiency sufficient for precise measurement?
- + Can isobaric interferences be resolved?
- + What is the optimal choice for a sample matrix that can serve as a proxy for an abundant stable isotope?
- + How accurate and reproducible are the measurements?

Results

- + ^{99}Tc produces considerable negative ion current
- + The combined system efficiency is sufficient to allow robust measurement of typical environmental samples
- + The utilization of characteristic projectile X-rays allows the resolution of ^{99}Tc from ^{99}Ru in most instances
- + Initial tests indicate rhodium sulfides as a sample matrix

Methods to Measure ^{99}Tc in Environmental Samples are being Developed

- Technetium-99 ($T_{1/2} = 2.1 \times 10^5 \text{ a}$) is an abundant long-lived fission product and is widely distributed in the environment
- The fate and transport of ^{99}Tc in the environment is an issue of considerable societal importance
- The transport of ^{99}Tc may differ from that of ^{137}Cs and ^{131}I because of its different chemical properties
- Because of its long half-life and weak radiation (292 keV β^-), ^{99}Tc is difficult to detect at low levels by decay counting.

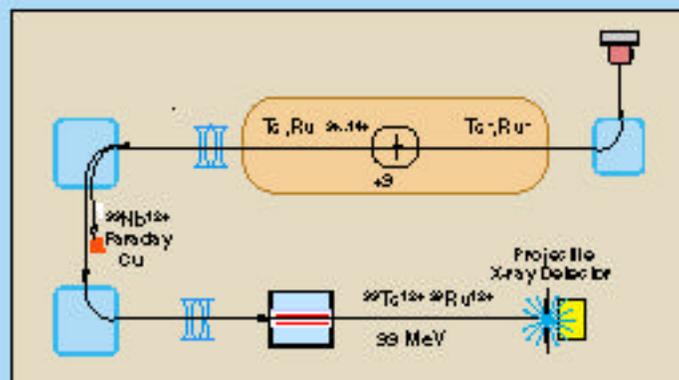
Goals

- $\sim 10 \text{ fg}$ (6×10^7 atoms) detection limit
- 10% precision
- Simple, cost effective sample preparation

Problems

- The long half-life and weak β^- emission (292 keV) make ^{99}Tc difficult to detect at low levels using traditional decay counting

Present configuration for ^{99}Tc AMS at LLNL



Results and Interpretations for ^{129}I

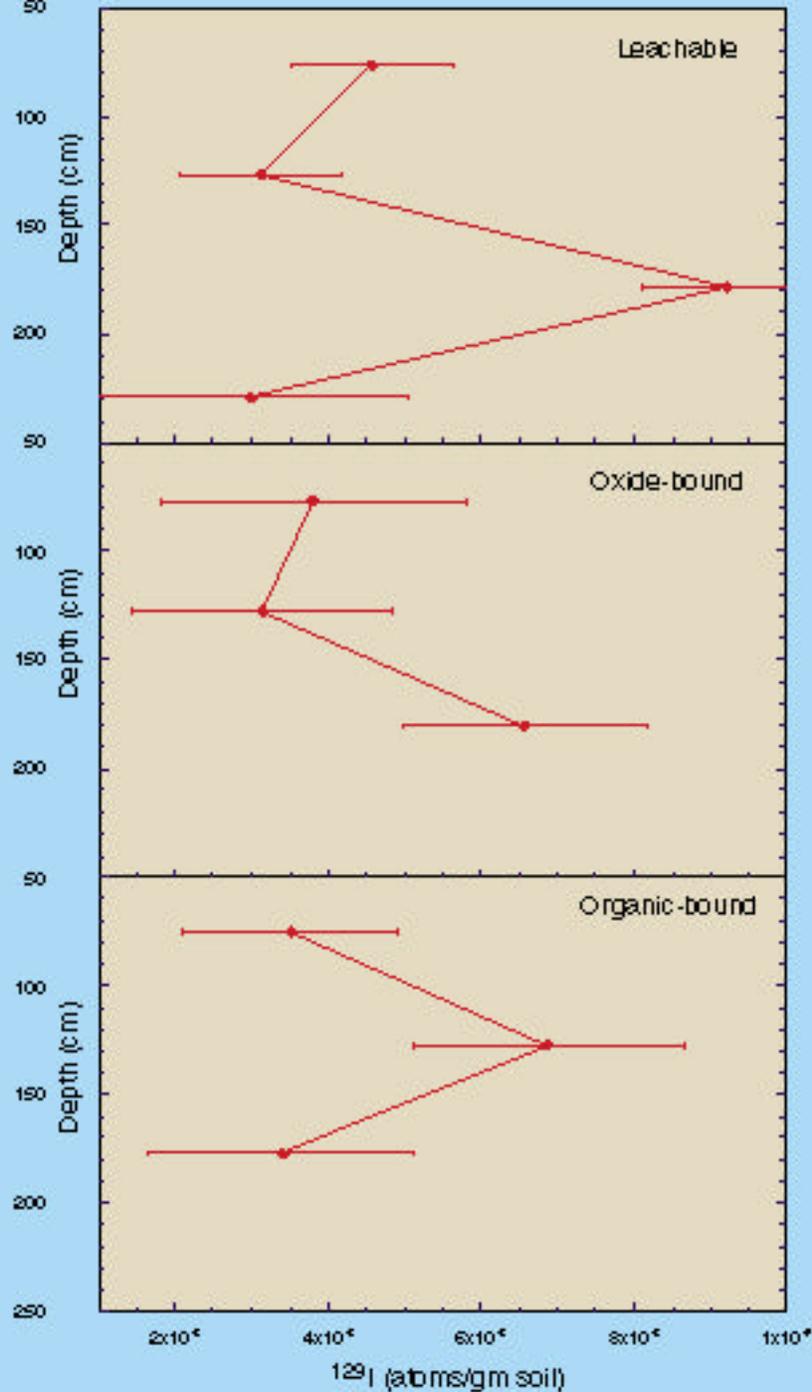
Summary

^{129}I has been measured in aliquots of Chernobyl soils. The ^{129}I concentration is consistent with that measured by other techniques.

Initial results indicate that the measurement of ^{129}I in environmental samples utilizing the new ionization detector on the heavy isotope beamline is successful.

Separation chemistries for the extraction of ^{129}I in environmental samples have been developed. Techniques utilizing sequential extraction and total dissolution have been tested.

Samples collected from the NTS have been analyzed.



- + Results from the sequential leaching of soils from the NTS indicate
 - Bomb pulse ^{129}I is partitioned into exchangeable and bound fractions. The bound fractions are located on oxides and organics.
 - There is a concentration increase in both total ^{129}I and the exchangeable ^{129}I at approximately the same depth as peak in ^{36}Cl concentration.
- + Verification of these observations would indicate that solute transport is an important mechanism in the transport of a fraction of the total ^{129}I inventory
- + More analyses will further illuminate the transport of ^{129}I



Project Description

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

The contaminant radionuclides potentially measurable by AMS include ^{59}Ni , ^{63}Ni , ^{90}Sr , ^{93}Zr , ^{99}Tc , ^{129}I , ^{233}U , ^{235}Np , ^{239}Pu , and other actinides. Under the EM Science Program, we are developing AMS analytical abilities for ^{90}Sr , ^{93}Zr , ^{99}Tc , and developing improved AMS methods for ^{36}Cl and ^{129}I .

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 have developed a field study site at the Nevada Test Site.

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Technical Issues to be Resolved

- + Sensitivity and linearity need improvement for samples containing low (< 1 pg) ^{99}Tc
- + Solutions include
 - use of Nb stock from previous supplier (5 x less Ru)
 - improvements in data acquisition software to reduce sensitivity/gain shifts
 - operation of ion source at full output will increase count rate fivefold
 - better characterization of backgrounds

Status of ^{99}Tc Development

- + The technical feasibility of low level detection of ^{99}Tc utilizing AMS has been demonstrated
- + Unanticipated technical challenges were dealt with successfully - the projected target capability is within reach
- + First pass measurements of trench samples will begin in the coming weeks
- + Focus will then turn to the matrix related issues and methods validation
- + Plans for a complete set of measurements will be based on the results of the first pass and the methods validation

Project Summary

- This project develops analytical techniques for analyzing radionuclides by accelerator mass spectrometry, and then applies them to address questions of radionuclide migration in arid soils.
- While initial efforts are focusing on ^{90}Sr , ^{95}Zr , ^{99}Tc , and ^{129}I , AMS analysis can potentially include ^{59}Ni , ^{63}Ni , ^{233}U , ^{239}Np , ^{239}Pu , and other actinides.
- Progress to date includes successful development of analytical capabilities for ^{99}Tc and ^{129}I , improved AMS methods for ^{36}Cl , and development of a field study site at the Nevada Test Site that includes a deep trench in alluvial soils.
- We have observed and documented variations in the migration of stable chlorine and ^{36}Cl in trench soil profiles, which indicate that chlorine may not be as direct and simple an indicator of moisture migration as has been commonly supposed.
- Results from the trench profiles indicate that significant concentrations of ^{129}I are bound within organic compounds and secondary oxide phases, but a larger fraction is water leachable, and appears to migrate at a rate similar to the bomb-pulse ^{36}Cl .
- Results from the ^{99}Tc spike leaching experiments indicate that present AMS capabilities provide a detection limit of >150 fg, and 10% reproducibility with linearity at higher levels.

Project Future Activities

Trench soil samples will now be analyzed for ^{99}Tc , and the peak bomb-pulse position - the extent of migration since the era of atmospheric nuclear testing - will be located.

The concentration profiles of ^{129}I will be completed for the trench samples, including the characterization of iodine complexing in soils.

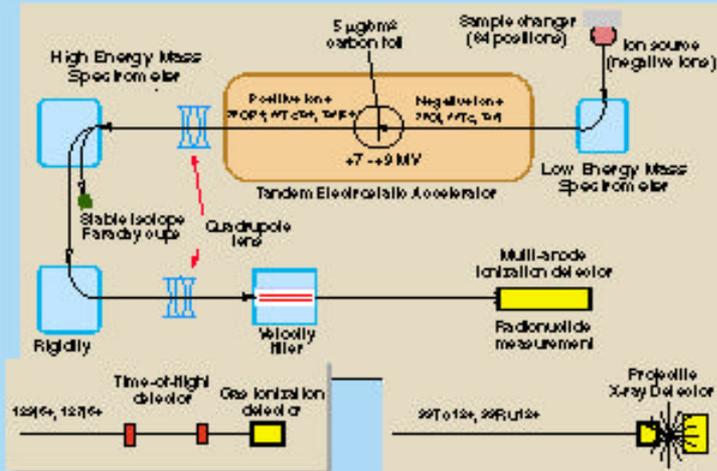
AMS analytical methods for ^{90}Sr and ^{95}Zr will be developed, and archived trench samples will be analyzed for these radionuclides.

A computer model, based on the NUFT computer code, will be developed to simulate the observed distribution of soil moisture, chlorine, ^{36}Cl , and the other AMS radionuclides. Particular attention will be paid to the relationship between moisture and chloride flux in an effort to make chloride a more reliable and robust indicator of moisture movement in arid soils.

The overall result will be an ability to conduct radionuclide migration studies using nuclides globally-distributed by atmospheric fallout from nuclear testing. The advantages of this include the ability to conduct the work in location of most concern to public health, sites of multiple contamination can be avoided, study samples are not themselves radioactive hazards, and the research can be conducted in any environment since the nuclides were globally dispersed.

Development of New Instrumental and Chemical Techniques for the Measurement of ^{129}I

Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory



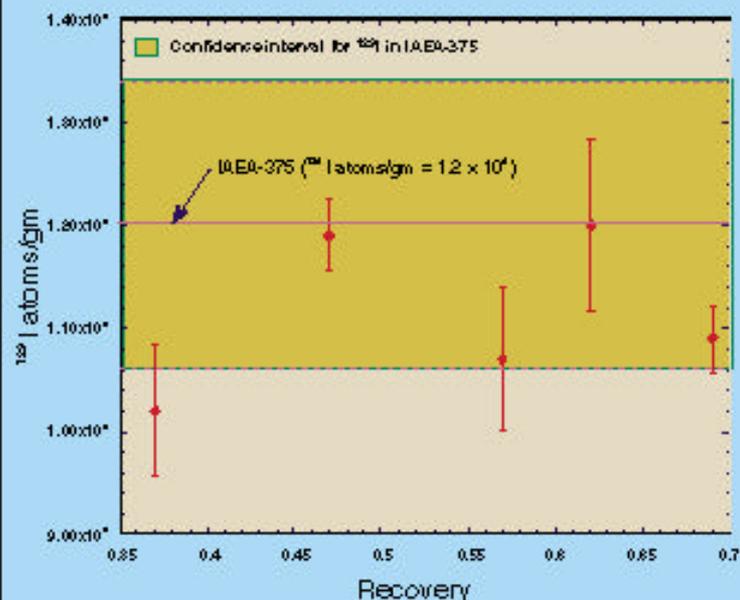
Advantages of Accelerator Mass Spectrometry

- Molecular interferences are eliminated or greatly reduced by stripping at the terminal
- Acceleration to high energies allows the use of detectors capable of rejecting isobaric interferences
- Isotopic ratios of $< 10^{-12}$ can be readily measured

Development of chemical separation techniques for measurement of ^{129}I in environmental samples

- The preparation of ^{129}I in environmental samples for AMS measurement is complicated by the relative volatility of I and its ability to readily change oxidation states during chemical preparation
- The transport of I in the vadose zone may be heavily dependent on its ability to partition into different reservoirs in the soil column
- A successful understanding of the cycling of I within and transport of I out of the vadose zone requires understanding the bio-geochemical cycling of ^{129}I

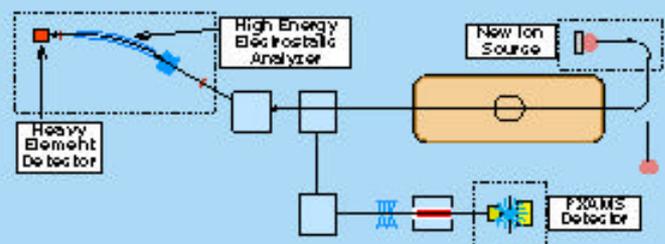
Measurement of ^{129}I in samples of "known" concentration from Chernobyl

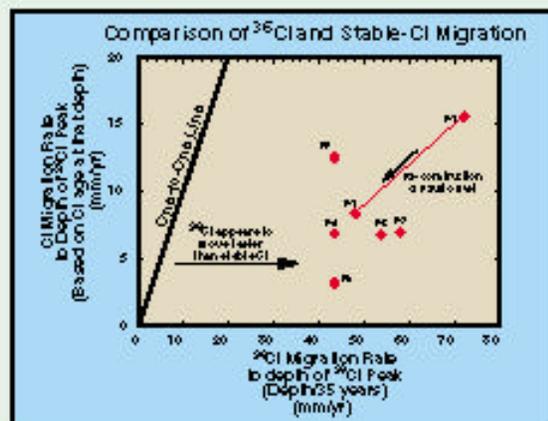
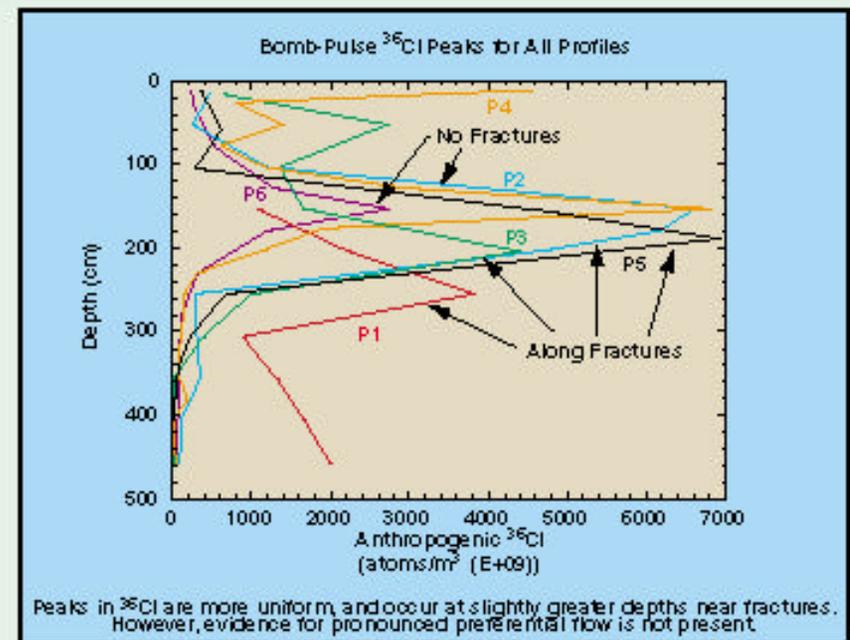
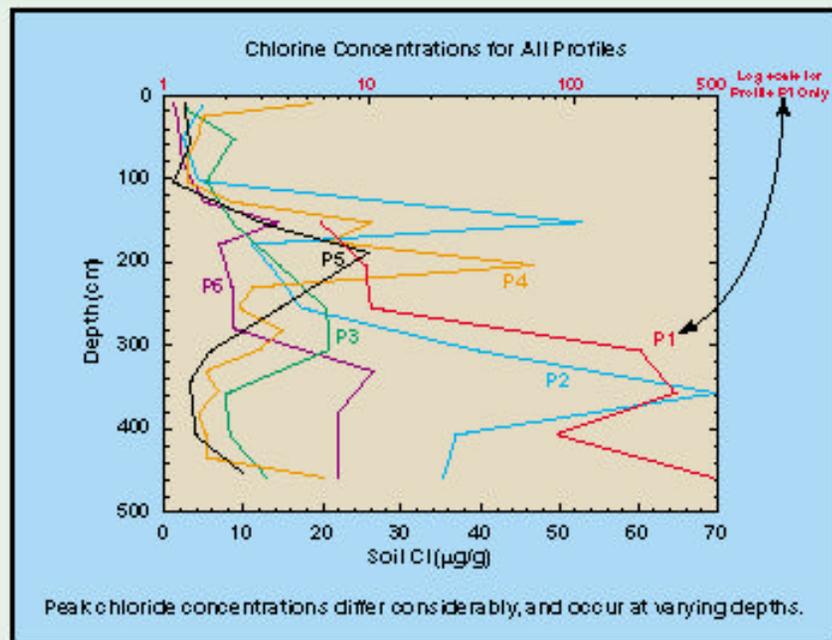
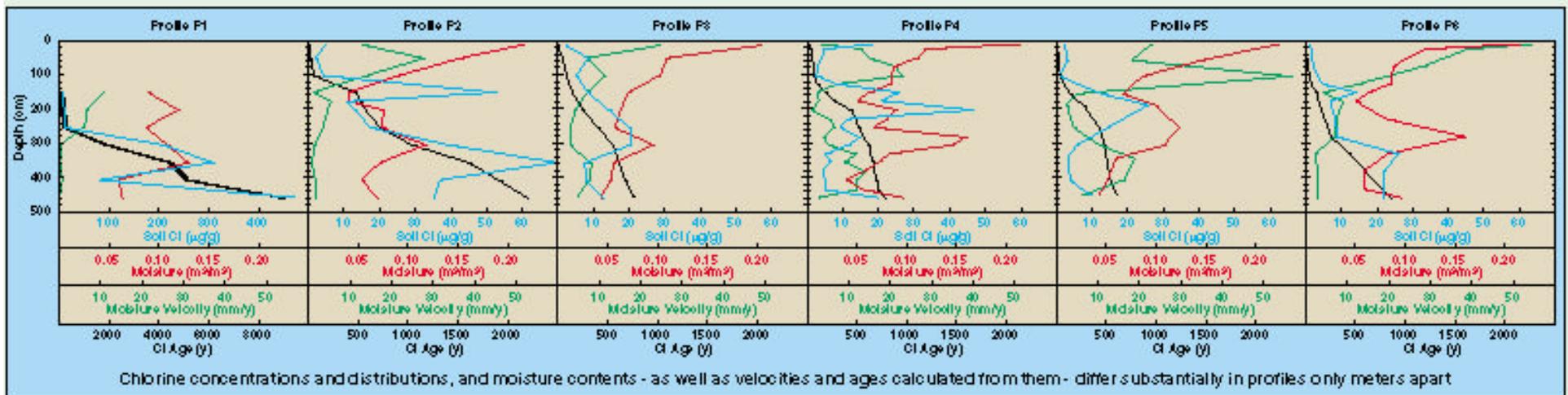


- Samples collected from the vicinity of the Chernobyl nuclear power plant have exceedingly high ^{129}I concentrations and have been measured using other techniques
- An extraction technique based on acid dissolution and distillation of the iodine was utilized to separate ^{129}I from the sample
- The concentration of ^{129}I was measured in numerous samples using AMS. These concentrations agree with the accepted values.

Reliable ^{129}I Measurements Required the Construction of a New Beamline and Detection System

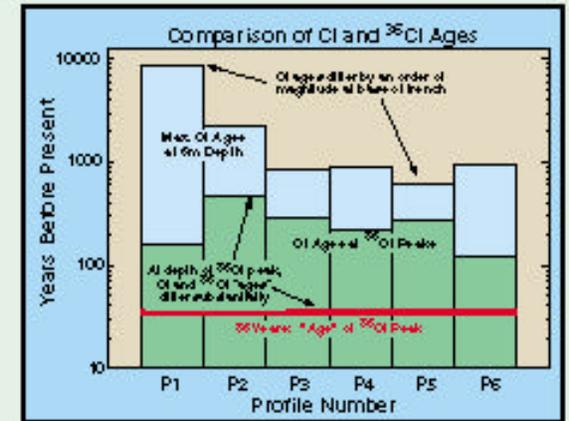
A New Beam line Optimized for Heavy Elements was Built and Tested





Chlorine, ³⁶Cl, and Moisture Flux

- In arid soils, physical data indicating moisture flux are uninformative. Instead, chemical data are used. Under the assumption that chlorine moves conservatively with soil water, Cl and ³⁶Cl ages within the soil column are regarded as the most useful indicators of moisture movement.
- Cl Age: Based on a constant Cl flux to Earth's surface and the accumulated concentration profile to depth.
- ³⁶Cl Age: Based on the peak in atmospheric weapon testing (1963) and the location of bomb-³⁶Cl at depth.
- However, moisture movement calculated from chloride concentrations does not agree with that calculated from ³⁶Cl. [SEE DIAGRAM AT LEFT]
- Also, distributions and ages of chlorine at depth appear to be very unsystematic. [SEE DIAGRAM AT RIGHT]

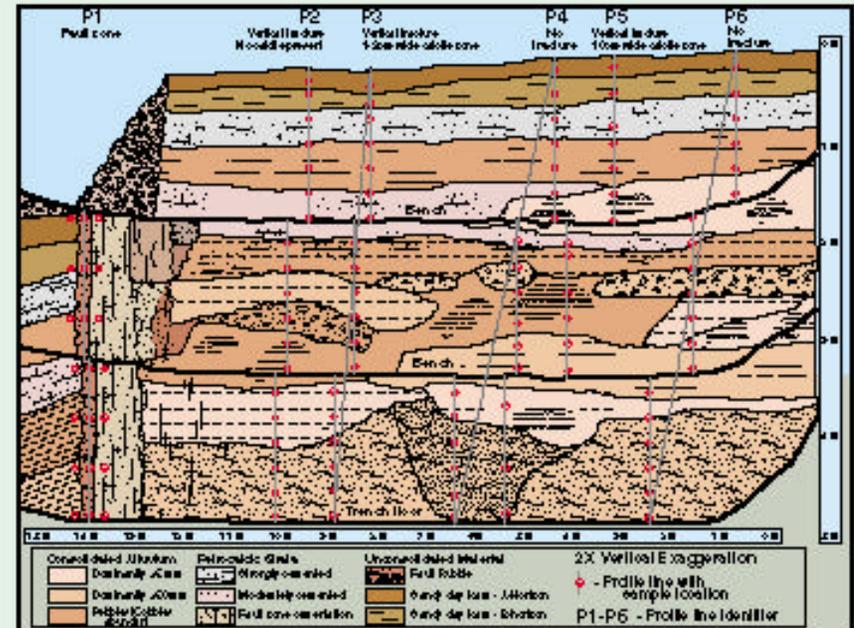


Conclusion: The systematics of chloride migration in arid soils must be better understood before chloride flux can be used as a reliable indicator of moisture flux. This is a prerequisite to the interpretation or prediction of radionuclide migration in unsaturated soils of arid environments.

+ This is not a widely recognized problem within the scientific or regulatory communities +

Application Site

Initial application of the AMS techniques is occurring at a trenched study site in arid unsaturated alluvial soils



Site Description and Sampling

- The purpose of trenching was to allow complete access to the soil column and to permit observation of all soil structures and stratigraphy.
- The trench was located across a geological fault in an attempt to see evidence of preferential moisture and radionuclide movement. Previous work had documented pervasive soil fractures, both modern and ancient, adjacent to the fault. Such fractures might provide pathways for preferential flow. Fault movement creating the currently visible landsurface offset occurred in 1970.
- Several near-vertical fractures are observed in the walls of the trench, and soil samples were systematically collected along vertical profiles (P1-P6) both within the fracture zones and safely away from them. Samples were also collected within the main fault zone.
- Samples were collected for: ⊕ global fallout ("bomb-pulse") radionuclide concentrations, and ⊕ supporting data used to interpret the observed radionuclide concentrations (moisture content, particle size analysis, mineralogy, chlorine and ³⁶Cl concentrations as indicators of moisture flux, and other physical and chemical measurements).