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Iodine-129 AMS for Earth Science, Biomedical, and National Security Applications

Technique and Application Development

G.J. Nimz, T.A. Brown, S.J. Tumey, A.A. Marchetti, and A.K. Vu

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LAWRENCE LIVERMORE NATIONAL LABORATORY

Executive Summary

This Laboratory Directed Research and Development project created the capability to analyze the radionuclide iodine-129 (^{129}I) by accelerator mass spectrometry (AMS) in the CAMS facility at LLNL, and enhanced our scientific foundation for its application through development of sample preparation technology required for environmental, biomedical, and national security applications. The project greatly improved our environmental iodine extraction and concentration methodology, and developed new techniques for the analysis of small quantities of ^{129}I. The project can be viewed as having two phases, one in which the basic instrumental and chemical extraction methods necessary for general ^{129}I analysis were developed, and a second in which these techniques were improved and new techniques were developed to enable broader and more sophisticated applications. The latter occurred through the mechanism of four subprojects that also serve as proof-of-principle demonstrations of our newly developed ^{129}I capabilities. The first subproject determined the vertical distribution of bomb-pulse ^{129}I (^{129}I distributed globally as fallout from 1950's atmospheric nuclear testing) through 5 meters in the upper vadose zone in the arid southwestern United States. This characterizes migration mechanisms of contaminant ^{129}I, or ^{129}I released by nuclear fuel reprocessing, as well as the migration of labile iodine in soils relative to moisture flux, permitting a determination of nutrient cycling. The second subproject minimized the amount of iodine required in an AMS sample target. Because natural iodine abundances are very low in almost all environments, many areas of research had been precluded or made extremely difficult by the demands of sample size. Also, certain sample types of potential interest to national security are intrinsically small – for example iodine on air filters. The result of this work is the ability to measure the ^{129}I/^{127}I ratio at the 2E-07 level or higher in a sample as small as a single raindrop. The third subproject tested the feasibility of using bomb-pulse ^{129}I in shallow groundwaters in the Sierra Nevada to determine the source of waters entering into the Merced River. The sources of water and their time (age) within the hydrologic system is crucial to understanding the effects of climate change on California waters. The project is in collaboration with faculty and students at the University of California – Merced, and is now the subject of a follow-on Ph.D. dissertation project funded by the LLNL-URP University Education Participation Program. The fourth subproject examined the requirements for using the decay of ^{129}I to date pore waters associated with continental shelf methane hydrate deposits. Understanding the age of formation and the historical stability of these hydrates is important in determining their response to climate change. Thawing of the world's methane hydrates would quickly and dramatically increase greenhouse gases in the atmosphere. The calculations and testing performed on this project have led to a follow-on project that selectively implants ^{127}I to the exclusion of ^{129}I, creating an analytical iodine carrier with a substantially lower ^{129}I background than is available from natural sources. This will permit measurement of ^{129}I/^{127}I ratios at sub-10^{-14} levels, thereby providing a method for dating hydrate pore waters that are tens of millions of years old.

I. Introduction

Iodine-129 is a high-yield fission product of uranium and the transuranic elements, and is also produced by spallation of xenon. It occurs naturally in small quantities (derived primarily from ^{238}U in the solid Earth, and from xenon in the atmosphere) but is abundantly released to the environment during nuclear reprocessing and similar activities. It is radioactive, with a half-life of 16 million years – long compared to the other important iodine radionuclides, ^{123}I (13 hrs), ^{125}I (60 days), ^{126}I (13 days), and ^{131}I (8 days); the only stable iodine isotope is ^{127}I. Iodine has complex chemical systematics, including volatility, that allow easy migration in the environment and also makes ^{129}I extremely difficult to contain during nuclear processing activities. For this reason, it is not only a significant contaminant at the DOE Hanford Reservation and INEEL site, but is also a good alert that clandestine nuclear activities are or have been occurring in an area. The effluent from the European Sellafield and La Hague nuclear reprocessing facilities can be traced into the north Atlantic and Arctic oceans. Because iodine accumulates in animal thyroids, elevated ^{129}I contents can be long-term markers of past exposure to environments associated with nuclear materials. I-129 in tree rings can be used to date the timing and duration of releases. Bioaccumulation has also permitted iodine isotopes to be used for biomedical research, particularly for Iodine Deficiency Disorder (IDD) and fetal brain development, and this will be improved by the use of longer-lived ^{129}I and smaller dosage permitted by AMS measurement. Natural pre-anthropogenic $^{129}I/^{127}I$ ratios are in the 10^{-12} range. Extreme anthropogenic $^{129}I/^{127}I$ ratios can exceed 10^{-2}. The higher values can be measured by ICP-MS ($> \sim 10^{-6}$), but most applications require measurement of moderate to low ratios. This can only be accomplished using AMS – which is capable of measurement below natural background levels.

II. Development of the AMS Analytical Method

Instrumental and Chemical Preparation Procedures

The development of ^{129}I AMS capabilities at LLNL required optimization of several interrelated aspects of the analytical process, including determinations of beam optics, transmission charge states, detector design and configuration, and ionization target materials. It also required development of chemical extraction techniques to provide pure low-background iodine separates free of analytical interferences.

The LLNL AMS Heavy Isotope Beamline. Figure 1 shows a schematic of the AMS system used for ^{129}I analysis. Iodine is ionized by sputtering with cesium in the ion source. The negatively charged ion beam is steered through two 90-degree turns by first a low-energy electrostatic deflector and then a 90-degree magnet which create a mass spectra from which the iodine masses (127 and 129) are selected. The negative beam (I^-) is then accelerated in two stages in the tandem accelerator, first to a positive potential where it is stripped of electrons creating several charge states (I^{3+} to I^{8+}) which are then accelerated out of the tandem to the high-energy beamline and the Heavy Isotope Spectrometer (Fig. 2). Further mass separation can be accomplished by a 30-degree analyzing magnet and further energy separation by a 45-degree electrostatic analyzer (ESA; Fig. 3). The beam current of the stable isotope (^{127}I) is measured in an off-axis Faraday cup located between the 30-degree magnet and the ESA, and ^{129}I is measured by

ion counting in a two anode gas ionization detector. The beam is steered (bounced) between the Faraday cup and the detector by electrostatic switching at the low-energy end (prior to entering the accelerator).

Run Parameters. The initial instrumental challenges were to select and optimize the parameters to be used for the various functions along the beamline from the ion source to the detectors. The goal is to maximize beam current, transmission through the accelerator, and mass and energy separation for iodine ions. Optimization was eventually achieved by selecting charge state 5+ for analysis at an accelerating potential of 8MV (for an ion energy state of 48MeV). At a nominal gas stripping pressure of 9.6E-08 torr, this produced 12% beam transmission through the accelerator (Fig. 4). Iodine-129 in charge state 5+ was guided to the ion detector by operating the high-energy ESA at ±110kV. Detector ionization gas pressures were optimized by means of ion trajectory modeling using the TRIM computer program. Maximum transmission to the second detector anode was achieved without ion rebound from the back plate of the detector (Fig. 5).

For a sample iodine mass of 1 milligram in the AMS cathode target, iodine beam currents measured in the off-axis Faraday cup were approximately 20µA. As will be discussed later in this report, high quality [129]I/[127]I ratios could be measured with currents as low as 100nA. Removal of isobaric interferences was complete; even from the most complex natural matrices such as seawater and geothermal brines, only [129]I could be observed in the detector (Fig. 6).

Standard Chemical Extraction Procedures. Iodine for analysis was prepared by extraction from aqueous solution through precipitation as silver iodide (AgI). Efforts to increase ionization by precipitation with palladium (PdI_2) were unsuccessful, both because ionization was not increased and because the palladium solution increased [129]I background (blank) levels by about an order of magnitude. Commonly for AMS analysis, the sample as AgI is mixed with commercially-obtained silver powder and then pressed into a small hole drilled into the center of a cathode for analysis (Fig. 7). Through experimentation with various metal powders, we realized that mixture with Nb powder, in an approximate 5:1 ratio (Nb:AgI) produced a stable beam current with significantly increased ionization. Nb powder also proved to reduce [129]I backgrounds. A cathode loaded with only Nb (no AgI) produced only 20 ion counts at mass 129 over a 1000 second sputtering interval. In comparison, iodine with a 2E-14 [129]I/[127]I ratio producing a beam current of 16µA would yield about 1500 ion counts in 1000 seconds. Thus even at this very low [129]I level, the contribution from Nb would be only about 1%.

Commonly, milligram-size amounts of iodine are required for AMS analysis. This not only produces a large enough "target" in the cathode for sputtering by the cesium beam, but also provides enough bulk to make the AgI sample capable of handling in the lab and loading into the cathode. Static electrical charges on lab equipment make small masses hard to control. However, most natural materials contain iodine at the µg/g level and obtaining and processing enough material to produce a milligram is difficult or impossible. Therefore the sample is bulked by the addition of carefully measured amounts of iodine that is almost pure [127]I. This iodine "carrier" is usually Woodward iodine, which will be discussed below. The addition of carrier obviously lowers the [129]I/[127]I ratio of the sample and a correction to the measured value must be made by subtraction of the known amount of carrier added. However, it is possible to add too much carrier such that the natural ratio of the sample is swamped and becomes

indistinguishable from the ratio of the carrier, which while very low is not zero. For the analysis of many natural materials, such as shallow groundwater, this becomes a major problem. Therefore one of the important subprojects in this LDRD, discussed below, was comprised of attempts to circumvent this problem and permit analysis of small quantities of iodine.

The AMS system is tuned (i.e., beam optics and currents optimized) using nA-level beam currents that can be continuously transmitted through the accelerator. Like small natural samples, this amount of iodine is too small to adequately handle during cathode preparation and must be increased in bulk. This was accomplished in tuning samples by addition of AgBr or AgCl. The presence of AgCl produced higher iodine beam currents by almost a factor of 5, but led to potentially interfering masses surrounding 127. These are thought to be combined species of Cl isotopes (35 and 37) with Nb at mass 93 (producing masses 128 and 130). If the peaks at these masses became large enough they could interfere with the ^{127}I peak. We therefore felt it to be safer to use AgBr and accept the lower currents.

Cathode Materials. In the early stages of this project we encountered a problem that had been mentioned in publications on AMS analysis of iodine. When initially loaded in the cathode, the samples were dry and solid. After a number of hours – often beyond the time when the cathodes were loaded into the ion source for analysis – the samples would become deliquescent with bubbling and visible moisture gain. These sample would understandably run poorly and sometimes give no beam current at all. Other facilities addressed this problem by minimizing the time between sample loading and analysis. Out of a concern that imperceptible oxidation of aluminum could be producing a chemical battery-like reaction involving AgI, we changed to using stainless steel cathodes. Although more expensive than aluminum, using stainless steel completely eliminated the deliquescence problem. Sputtering on an empty stainless steel cathode in the ion source produces no mass 129 ion counts, eliminating our initial fear of higher backgrounds. Although switching from aluminum was a simple, and, in hindsight obvious, change it produced a major advancement in ^{129}I analysis by AMS.

Analysis of Standard Materials

The primary indication of success in analyzing iodine by AMS is obviously being able to make measurements with low backgrounds, correctly analyze analytical standards, and correctly analyze natural materials with known ^{129}I/^{127}I ratios ("known unknowns"). Backgrounds can be checked with iodine derived from 90+ million year old brines from the Anadarko basin commercially sold by Woodward, Inc. The National Institute of Standards and Technology (NIST) produces a standard solution of iodine, SRM4949c, with a certified ^{129}I concentration. Dilutions of this standard can be used to test analytical accuracy. A number of natural materials have been measured at other facilities and those with the most certain values can be used as known unknowns.

Analysis of Woodward Iodine. Woodward iodine has been measured at other AMS facilities to have a ^{129}I/^{127}I ratio of 2E-14. No other natural material has ever been found to have a lower ratio. Thus not only is this material used to test instrumental backgrounds, it is the only available material at present for use as an iodine carrier during chemical separation of iodine from low abundance samples. Woodward iodine was analyzed repeatedly during the course of this project and typical analytical results are

shown in Figure 8. An instrumental measured ions/charge (i.e., ion detector [129]I counts relative to [127]I charge deposited in the Faraday cup) value of 0.00002 is taken to represent the 2E-14 value of Woodward iodine. This is confirmed by use of a calibration curve generated by dilutions of NIST standard SRM4949c, discussed below. During the course of this project, Woodward measurements ranged from 0.00002 to about 0.0002, indicating that sometimes during chemical processing an [129]I background contamination ("blank") is added to our samples. The level is generally insignificant relative to the [129]I/[127]I ratio of our sample, which are usually in excess of 10^{-12}. It is standard procedure for us to process a Woodward sample at the same time we process other samples. We then subtract the blank observed in the Woodward sample from the other sample prepared at the same time.

Analysis of NIST SRM4949c. We created a standard calibration sequence from 2E-14 to 1E-10 by dilution of SRM4949c with varying amounts of Woodward iodine solution (the 2E-14 value is of course pure Woodward iodine). This allowed us to produce calibration curves for use in determining the ratio in natural samples. The calibration curve was measured on many different occasion; Figure 9 shows one example. Excellent linearity was consistently achieved (r^2 value of 0.9999). This permits us to use only one of the dilutions (1E-11 is usually chosen) for determination of the ratio in actual samples. The instrumental measured value of ions/charge in the unknown sample is compared to the ions/charge value measured during the analytical run for our 1E-11 standard, thus determining the [129]I/[127]I value in the unknown sample.

Known Unknowns: Expected vs. Measured Values. Even though our calibration standards were created from NIST SRM4949c, our dilution process could have generated errors which while producing an internally consistent calibration curve, nonetheless leads to inaccurate [129]I/[127]I ratios for actual samples. Therefore the calibration curve needs to be tested by measuring known unknowns, natural samples that have been measured in other facilities. Figure 10 shows the results of these tests. For most of the materials, our measured value was the same as the expected value. The only sample not within 1 sigma analytical uncertainties of the expected value was a soil sample, which we believe may contain variable amounts of [129]I. The soil was not collected in large volume and homogenized, as is standard practice for common soil standards, including the only soil standard available for [129]I, the IAEA-375 standard (on Figure 10). Repeated analysis of IAEA-375 consistently produces [129]I contents within the range certified by the IAEA (Figure 11). Other soil standards for which iodine concentration are certified, but [129]I/[127]I ratios are not (NIST SRM2709 and SRM2711) also produce consistent results with respect to 1 sigma analytical uncertainties (note the log scale on Figure 11). Because no certified [129]I value exists for these soils, and to our knowledge they have not been analyzed at other facilities, they cannot be treated as known unknowns. While replication of the analyses of these soils was generally good, like the NTS soil we do not know if they are in fact homogeneous with respect to [129]I. In summary then, the good agreement shown in Figure 10 between expected and measured values gives us confidence that our SRM4949c calibration sequence provides correct analyses.

III. Developmental and Proof-of-Principle Subprojects

The activities detailed above leading to a reliable analytical capability for [129]I/[127]I analysis required about two years of this project. During the second year, and then

continuing into the third year, attention was turned to proof-of-principle projects that while demonstrating our analytical capabilities, also provided the opportunity to improve our techniques. Particular attention was paid to the problem that iodine occurs in microgram abundances in nature, but milligram abundances are required for AMS analysis. A central theme in all of the subprojects was the attempt to drive down the analytical requirement of a milligram of iodine to a requirement of perhaps only a few micrograms. This would open up a wide variety of new research opportunities.

Anthropogenic ^{129}I *Migration in Arid Soils*

The first subproject was the measurement of the distribution of anthropogenic (bomb-pulse) ^{129}I in arid soils at a site on the Nevada Test Site (NTS). The NTS was originally chosen not because of nuclide deposition, in fact little ^{129}I deposition occurred on the site, but because of the difficulty in excavating a 20+ meter long by 5 meter deep trench (Figure 12). For this, bulldozers and scrapers were required, which were available on the NTS but not easily available to us elsewhere. The trench was excavated through a project from the DOE Environmental Management Science Program (EMSP). As part of this project the distributions of soil moisture, chloride, and ^{36}Cl were determined, as well as soil stratigraphy and physical properties. The ^{129}I/^{127}I measurements made in this LDRD project were on archived soils from the EMSP project. The ^{129}I results can be compared to the soil moisture, chloride and bomb-pulse ^{36}Cl distribution previously determined.

The movement of soil water in arid soils is very difficult to measure., It has been generally believed that the best indication of moisture flux is the distribution of meteoric chloride, because chloride moves (infiltrates) conservatively with soil water. Bomb-pulse ^{36}Cl was deposited during a very short interval between 1953 and 1960. It occurs as a discrete peak in ^{36}Cl/Cl ratios in the soil column (Fig. 13). At the project site, the peak maximum occurs at about 1.8 meters depth. Pre- and post- bomb-pulse values are also observable in the soil column, and are about 5E-13. For the NTS region, this represents the natural non-anthropogenic ^{36}Cl/Cl ratio that can be measured in rainfall. Under the assumption that bomb-pulse ^{36}Cl moves conservatively with soil moisture, it can be inferred that the center of mass of water infiltrating since the bomb-pulse era is centered at about 1.8 meters depth. That is to say, infiltration has occurred at the rate of 1.8 meters in about 50 years, or about 3.6 centimeters per year. This value can then be used to estimate contaminant migration rates in arid soils, as well as groundwater recharge rates in desert environments.

The measurement of ^{129}I in the soils is accomplished through extraction of iodine by high temperature combustion of 1 to 5 grams of soil. The soil sample is placed in a ceramic boat and positioned within a quartz-glass tube within a double furnace array (Figures 14 and 15). A flow of oxygen is passed continuously over the sample while the furnaces are heated to 1000°C. The outflowing oxygen is then bubbled through a solution of 0.1M KOH and Na_2SO_3. Iodine liberated from the soils by combustion flows as a volatile with the oxygen and is trapped in this solution. This iodine is subsequently extracted from the solution by precipitation as AgI. The efficiency of the combustion-extraction techniques was thoroughly tested by repeated extraction of iodine from two soil standards, SRM2709 and SRM2711, for which NIST certified iodine concentrations

are available. Complete removal of iodine is achieved in the combustion apparatus after about 90-120 minutes.

The results of our ^{129}I/^{127}I analyses of two soil profiles at the study site are shown in Figure 16. There are two surprising results. First, unlike chlorine, iodine would generally not be expected to move conservatively with infiltrating soil water. Iodine has a high affinity for sorbing onto organic substances (plant debris, or soil organic acids) and this would retard the downward migration of iodine. While this effect can be seen by the high concentration of ^{129}I at land surface, a peak of ^{129}I is clearly present at the level of the bomb-pulse ^{36}Cl peak. This implies that a considerable amount of iodine is unexpectedly moving conservatively with the infiltrating water. The second surprising result is that while ^{36}Cl shows only one prominent peak at about 1.5-2.0 meters depth, there is a second ^{129}I peak in both profiles at a greater depth, about 2.75 meters. At this depth, ^{36}Cl/Cl values have returned to the background value of 5E-13 (cf. Figure 13), implying that little water from the bomb-pulse era has infiltrated to this depth. The distribution of bomb-pulse ^{36}Cl would suggest that the infiltration front has just reach 2.75 meters. The lower ^{129}I peak implies that some of the bomb-pulse ^{129}I is moving at a faster rate than bomb-pulse ^{36}Cl, or that a proportionally larger amount of ^{129}I is moving with the infiltration front rather than the center of mass of the water (as ^{36}Cl is behaving).

These two surprising results imply that a significant amount of iodine is very mobile and moves easily with soil water. However, we also tested the distribution of water-leachable ^{129}I in the P4 soil profile (Figure 17). Fifty grams of soil were placed in 200 milliliters of deionized water (18 megaohm resistivity) and shaken on a continuously moving shaker table for 24-48 hours. Iodine was then extracted from the leachate and analyzed for ^{129}I/^{127}I and iodine concentration. A peak in leachate ^{129}I concentration was observed at 2 meters depth, coinciding with the peak observed by whole-soil combustion. But no peak was present at a lower depth. The elevated ^{129}I observed at 2.75 meters is apparently not readily soluble in water. The further observation can be made from Figure 17 that the amount of leachable ^{129}I present is usually about 2-5% of the total in the soil. However, the leachable ^{129}I at the depth of the ^{36}Cl/Cl peak is much higher, almost 30%. This seems to suggest that the ^{129}I present at 2 meters is moving conservatively with soil water, whereas water solubility is not the key factor for the ^{129}I at 2.75 meters. There is apparently another mechanism by which ^{129}I can migrate in arid soils, and this mechanism causes the iodine to migrate primarily with the wetting front.

Minimizing Sample Size Requirements for ^{129}I Analysis by AMS

As discussed above, for many research applications the requirement to have one milligram of iodine is limiting. During the first year of this project, we observed linearity between sample mass in the cathode target and beam current measured (Figure 18). This suggested that stable, measurable, cathodes could be produced with 2-3 orders of magnitude less iodine than is generally used by the AMS community (i.e., 1 milligram). We therefore undertook a subproject designed to minimize the amount of iodine required for our AMS analyses.

Our initial efforts produced sub-milligram samples (down to 0.3 μg) by mechanical dilution with Nb. AgI and Nb powder were mixed in ratios producing targets that contained as little as 0.3 μg of iodine. This allowed us to observe a ^{129}I/^{127}I dependence on sample size that was likely due to background ^{129}I contamination (Fig.

19). Ratios at the 1E-10 level were unaffected by this contamination (i.e., the contaminant [129]I was swamped by the sample [129]I), but ratios at the 2E-14 level (Woodward iodine) were affected for sample masses less than 200 μg. The effort to determine the true level of the contamination, and thereby define the lowest unaffected sample mass at ratio levels between 2E-14 and 1E-10 was hampered by the problems in controlling the homogeneity of the Nb-AgI mixtures. Therefore this Nb-dilution method was eventually abandoned.

Our next efforts were with co-precipitation of AgI and AgBr or AgCl. Solutions of chloride and bromide were added to our samples such that the precipitate formed was Ag(Cl+I) or Ag(Br+I). By doing this the mass of iodine present in the sample could be carefully controlled while the total mass of precipitate would be sufficient for use in the AMS cathode targets. This was not initially regarded to be a desirable method because it was felt the commercially-purchased Br or Cl would contain high levels of [129]I, producing high backgrounds. High backgrounds were in fact observed with Br, but Cl allowed us to measure samples at the 1E-12 level down to 20μg without increases in the [129]I/[127]I ratio due to contamination. Levels smaller than 20μg however showed effects of background [129]I (Fig. 20).

Calculation of the amount of [129]I contamination present, based on measured [129]I/[127]I at various ratio levels, suggested that the added background [129]I was not derived from our chemical preparation process, but was in the Cl solution itself – probably derived from the commercially-purchased NaCl powder used to make the solution. This suggested that a commercial source might be found with lower [129]I contents. NaCl powders were obtained from several different commercial sources. Analysis of all of them showed them to be largely free of [129]I. Samples were then prepared at the 100 μg iodine level using our older Cl solution and one of the new solutions. The results are shown in Figure 21. There is a strong dependence between [129]I/[127]I ratio measured and the amount of Cl in the target for the older Cl solution, but no dependence when using the new solution. Although it is possible that the older NaCl used to make our initial solutions had higher [129]I contents when purchased, it is also possible that the powder became contaminated by volatile [129]I while on the shelf. We did not have a record of when the NaCl was purchased, which indicates that it was several years old when used.

Further work on this subproject was beyond the abilities of this LDRD project, given the need to progress on the other subprojects. However, we feel we have achieved a present capability of high quality [129]I/[127]I analyses at the 1E-12 level (the natural background level) with 10μg of iodine and 0.5 mg of chloride (new NaCl) in the cathode target. This results in a sample mass of about 2 mg Ag(I+Cl), which is very easy to manipulate in lab and load into a sample cathode. This is a reduction in the amount of sample required for analysis by two orders of magnitude.

What does this added capability permit? Rain contains very little iodine, about 2 ng/g. A 10μg sample with [129]I/[127]I of 1E-12 contains about 50,000 atoms of [129]I. If we are interested in measuring iodine with [129]I/[127]I of about 1E-07, as might be the case in monitoring direct airborne releases from nuclear reprocessing plants like Sellafield, we would require only one raindrop (0.025 mls) to make this measurement! The 10μg requirement would be met by addition of carrier, resulting in a 1E-12 measured ratio. The calculation is linear, so only 0.25 mls ("ten raindrops") would be needed for a ratio of about 1E-08, and so on. To measure the natural pre-anthropogenic background ratio in

the Sierra Nevadas (~5E-12), only 500 mls is required. Present-day values (~1E-11) require only 250 mls.

Analysis of iodine from air filters is another application – for example to monitor windblown particulates from the coast of the north Atlantic affected by the effluent from Sellafield and La Hague. The sole requirement is that approximately 5E+04 ^{129}I atoms are captured by the filter. For a ^{129}I/^{127}I ratio of 1E-09, this would be about 10 ng of captured iodine.

Another potential application is the measurement of ^{129}I in tree rings. Our 10 µg capability has the potential to make important measurements in small tree cores, rather than slices, thus permitting live trees to be used. Trees commonly contain about 150 ng/g iodine, The ^{129}I/^{127}I ratio of iodine contained in a 0.5 cm wide ring obtained from a 0.25 cm radius core from an oak tree (0.7 g/cm^3 density) could be measured to the 1E-09 level. Tree slices would of course permit analyses to even lower levels.

A final suggested application is the dating of crude oils to determine the locations of their source rocks for oil exploration. The difficulty of extracting iodine from oil demands that the sample be as small as possible. For a 40 million year oil with an initial, t=0 ratio of 1.5E-12 (i.e., having a present-day ratio of about 2.6E-13) and an iodine concentration of 1 µg/g (common for oils), only 40 grams would be required for analysis.

Other examples could be mentioned, nut the above examples make the point. The sample minimization subproject considerably broadened our potential applied and basic research capabilities for ^{129}I. The methods have facilitated the soils projects discussed above, and will be used in the UEPP continuation of the Sierran surface waters subproject discussed next.

Dating and Sourcing Sierran Surface Waters Using ^{129}I

This subproject tested the feasibility of measuring ^{129}I in Sierra Nevada river waters for this purpose of determining the sources of groundwater entering the river. The sources can be distinguished by their age – spanning the past few decades – which potentially can be discriminated using anthropogenic ^{129}I. This subproject is in collaboration with Professor Martha Conklin of the University of California – Merced, and her Ph.D. student Glenn Shaw. Our work indicates that using ^{129}I for this purpose does seem feasible, and this project will continue for the next two years with funding for Glenn Shaw from the LLNL-URP University Education Participation Program (UEPP).

The principle being used for this project relies on the post-1950's distribution of ^{36}Cl and ^{129}I in precipitation. During the bomb-pulse era both ^{36}Cl and ^{129}I were elevated in precipitation. Water recharged into aquifers at that time would today still contain elevated levels of both. After about 1965, levels of both nuclides in precipitation dropped significantly. But since that time levels of ^{129}I have increased in worldwide precipitation due to nuclear fuel reprocessing (mainly Sellafield and La Hague). Thus present-day precipitation has background (non-anthropogenic) ^{36}Cl contents, but elevated ^{129}I contents. In theory this should allow the discrimination of water recharged prior to the 1950's (background ^{36}Cl and ^{129}I), water recharged during the bomb-pulse era (elevated ^{36}Cl and ^{129}I), and water recharged very recently (background ^{36}Cl, elevated ^{129}I). These relationships are shown in Figure 22.

The feasibility ^{36}Cl and ^{129}I results are shown in Figure 23. In the Merced River proper, both ^{36}Cl and ^{129}I are elevated. Pre-anthropogenic ^{36}Cl/Cl would be about 3E-13,

and $^{129}I/^{127}I$ would be about 1E-12 to 5E-12. The tributaries of Yosemite Creek and Bridalveil Creek have ratios elevated even beyond those of the main river. This indicates that there is more than one source of water in the main river and that that source is different from the source of water in the tributaries. The feasibility of using ^{36}Cl and ^{129}I in Glenn Shaw's research is shown both by the presence of elevated levels and by the variation shown in the main river and tributaries. We have measured the $^{36}Cl/Cl$ ratios in recent precipitation (snow collected by Shaw) to be about 3E-13. During FY07 Shaw will measure the $^{129}I/^{127}I$ ratio in these same samples, an effort made possible because of the sample minimization subproject of this LDRD.

As mentioned, this project is continuing for two years under UEPP funding. At that time Glenn Shaw should be able to finish his Ph.D.. This project will therefore result in a Ph.D. dissertation and at least one major publications of the ^{129}I and ^{36}Cl findings.

Dating Pore Waters Associated with Methane Hydrates

Through researchers at the Navel Research Laboratory Scott Tumey, a post-doctoral researcher working on this LDRD, obtained aliquots of pore waters collected for the purpose of characterizing methane hydrates. Other research has suggested that such pore waters are several tens of millions of years old – i.e., that they have been trapped within the pores of the sediments containing the methane hydrates for that period of time. This finding, if confirmed, would be very important because it indicates that the methane hydrates themselves are that old and that they have had stability over these long geologic timescales. Because there is a fear that global warming may melt the hydrates and release large quantities of methane into the atmosphere, information on the range of stability of methane hydrates is very important.

Pore waters are not abundant nor easily collected. The samples obtained by Tumey are only a few milliliters in size. The iodine concentrations are low (<100mM). Therefore this served as an important part of the instigation for the sample minimization subproject – some of this minimization work could be described as an effort on our part to be able to measure the $^{129}I/^{127}I$ ratios in these pore waters. Unfortunately, if these pore waters are indeed several tens of millions of years old, they will have ratios in the low 10^{-13} range. Presently, we can still not make these measurements. The AgCl bulking technique that permits measurement of 10 µg of iodine at the 1E-12 level is still insufficient for the measurement of these samples.

However, this situation has instigated a new line of efforts to create an iodine carrier that would be used as the bulking material that would contain virtually no ^{129}I. Through collaboration with the LLNL Chemistry, Materials, and Life Sciences Directorate, Scott Tumey is investigating the possibility of implanting ^{127}I separated from ^{129}I into metal foils in sufficient quantities to be used as carrier iodine. If the iodine can be stripped from the foils – for example by chemical digestion of the metal – without imparting environmentally ambient ^{129}I to the separated ^{127}I, a ^{129}I-free carrier could be created. This presents the possibility of ultra-low $^{129}I/^{127}I$ measurements in the range necessary for measurement of our now archived pore waters.

IV. Publications and Future Directions

Two of the three years of this project were devoted almost exclusively to instrumental and chemical extract methods development. Thus the public dissemination

of the results have so far only been on the analytical techniques (Brown et al., 2005, Nimz et al., 2005). However, programmatic measurements enabled by this project have been published with the PI on this LDRD as a co-author (Zhao et al., 2006). A manuscript presenting the analysis of ^{129}I and ^{36}Cl in arid soils is being prepared (Nimz et al., 2007a), as is a manuscript using the soil ^{129}I results (and other ^{36}Cl results) to discuss the origin of chlorine and iodine in soils and shallow groundwaters (Nimz et al., 2007b). When the UC-Merced dissertation research has been completed, two papers are anticipated regarding ^{129}I in dilute surface waters – one describing the analytical methods development specifically for these waters, and one discussing the use of bomb-pulse ^{129}I as a hydrologic tracer and dating tool in the Merced River drainage. It is also believed that ^{127}I implantation research that was founded by this project will result in two papers, one discussing the implantation techniques and the other presenting the results of the analysis of methane hydrate pore waters. We believe this project has been very fertile in instigating publication-quality research focused upon ^{129}I. As a techniques-development project, it will require some time to come to fruition as published research.

Brown, T. A., Marchetti, A. A., Weyhenmeyer, C. E., Knezovich, J. P., Hamilton, T. F., and Nimz, G. J. (2005) Developments in the measurement of actinides and ^{129}I at LLNL by accelerator mass spectrometry. 45th Annual Meeting of the Institute of Nuclear Materials Management. UCRL-CONF-209000.

Nimz, G., Brown, T., Marchetti, A. and Tumey, S. (2005) Analysis of I-129 on the LLNL Heavy Isotope AMS Spectrometer. AMS-10 Conference, Berkeley California, September 5-8, 2005.

Zhao, P., Hu, Q., Rose, T.P., Nimz, G.J., and Zavarin, M. (2006) Distribution of 99Tc and ^{129}I in the Vicinity of Underground Nuclear Tests at the Nevada Test Site. Methods and Applications of Radioanalytical Chemistry. UCRL-CONF-220859

Nimz, G.J., Brown, T.A, Tumey, S., Marchetti, A.A., and Vu, A.M. (2007a) Distribution of bomb-pulse ^{129}I in arid soils in relation to bomb-pulse ^{36}Cl, soil moisture, and iodine concentrations. In preparation for submission to Environmental Science and Technology.

Nimz, G.J., Brown, T.A, Tumey, S., and Vu, A.M. (2007b) ^{36}Cl and ^{129}I evidence for the origin of chloride and iodine in soils and shallow groundwater in arid and semi-arid regions. In preparation for submission to Applied Geochemistry,
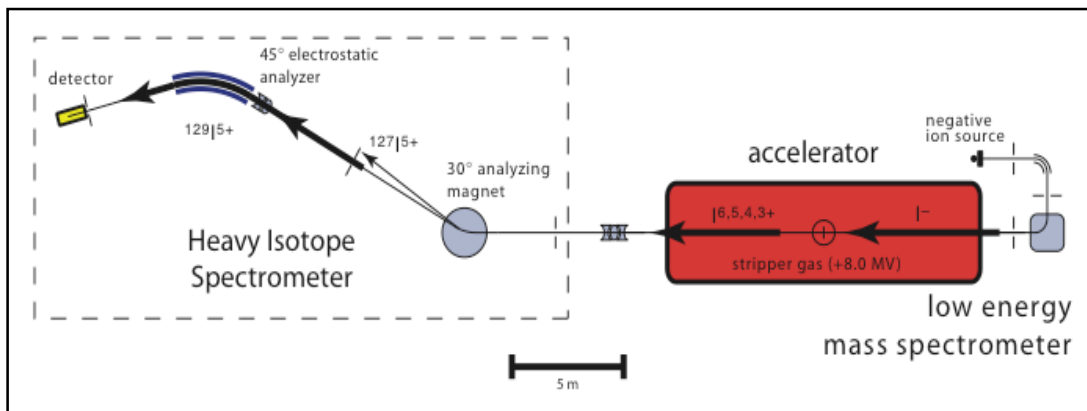
Figure 1. Schematic of the LLNL accelerator mass spectrometry facility showing beam flight path for [129]I and [127]I. Note the 5 meter scale bar at bottom.
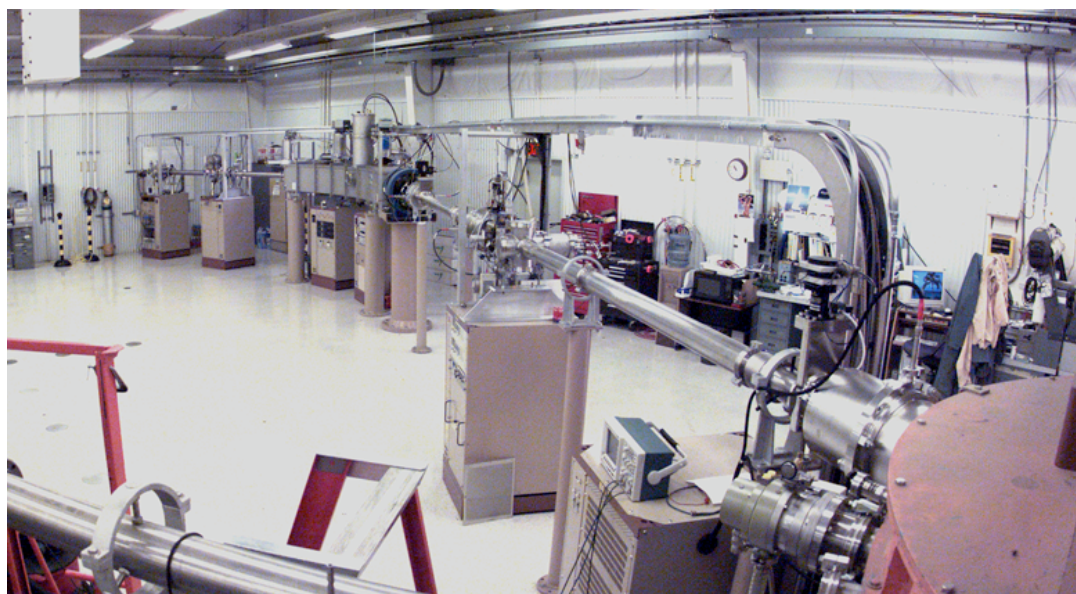

Figure 2. Photograph of Heavy Isotope Spectrometer beamline. The 30 degree analyzing magnet is at the lower right. Ion detector is in the distance at the left.

Figure 3. Close up of the high energy electrostatic analyzer without top cover plate. Note door to right for scale. The two curved plated to each side of the center beamline carry the positive and negative charge that deflects the ion beam and creates an energy spectra further isolating [129]I.
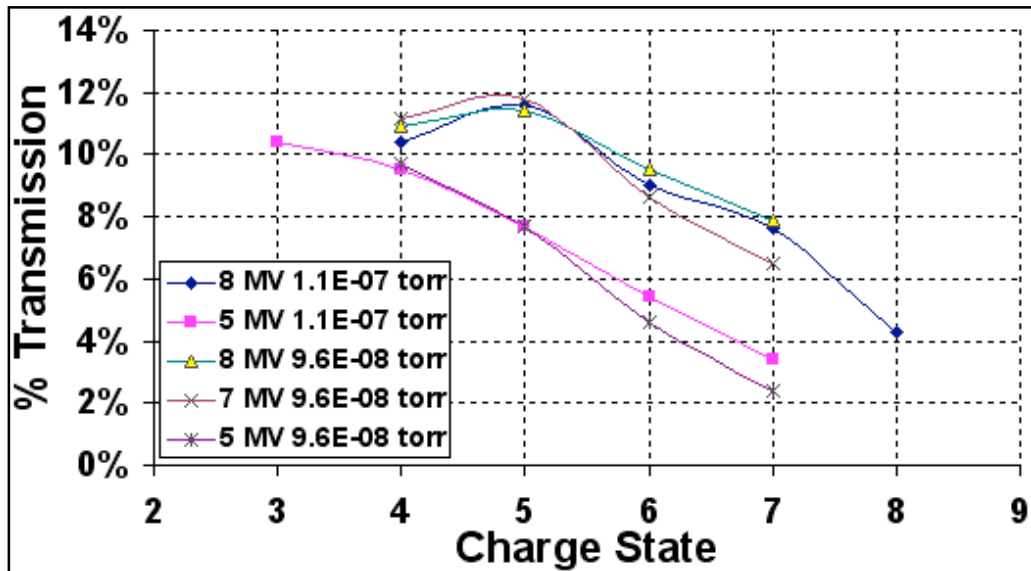
Figure 4. Beam current transmission through the accelerator at different ion charge states and stripping gas pressures. Maximum transmission occurs at the 5+ charge state with little difference between 5, 7, and 8 MV, although sensitivity to gas pressure is significant.

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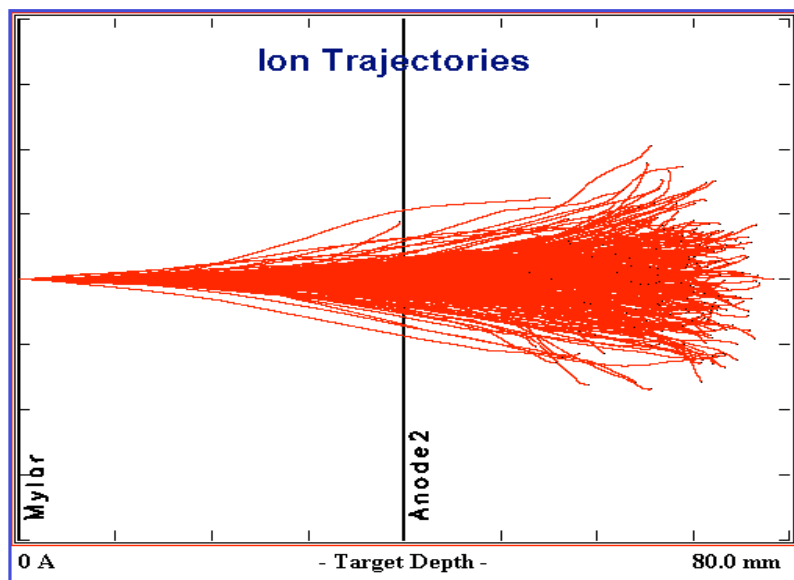
Figure 5. Result of TRIM modeling of the ion trajectory in [129]I ion detector. Beam enters detector at left and is scatter and stopped by the ionization gas in the detector. Optimum gas pressure occurs when trajectories pass completely through the detector but do not rebound off the back of the detector at right.
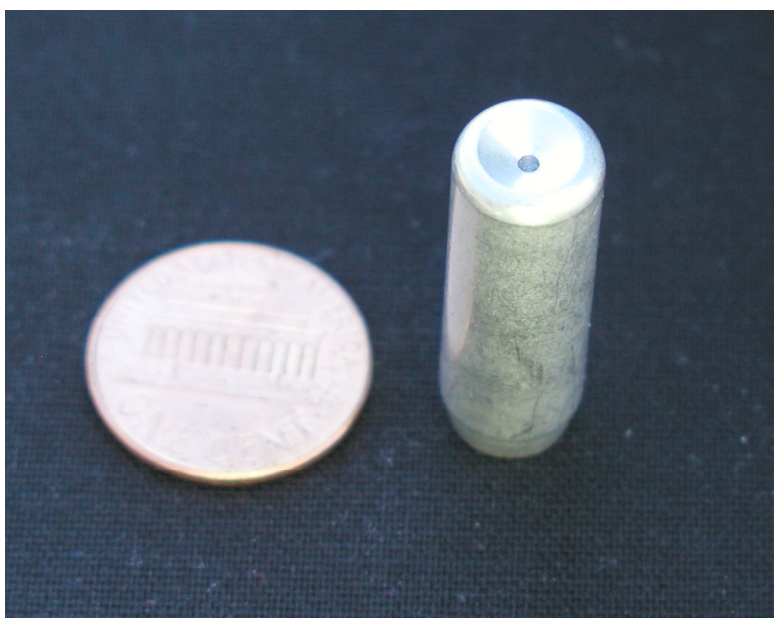
Figure 6. Photograph of cathode target used for [129]I AgI samples. The AgI+Nb mixture is pressed into the small hole in the center of the cathode. Penny is used for scale.
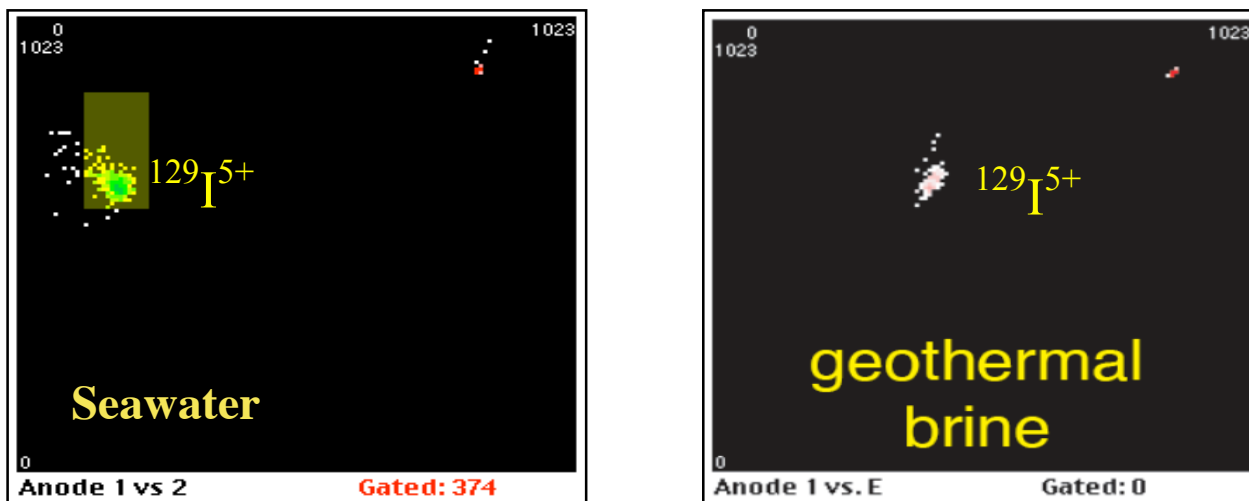
Figure 7. Computer screen shots of the ion energy spectra of [129]I from seawater and a geothermal brine. The seawater spectra shows detector anode 1 versus anode 2. The brine shows anode 1 versus total energy. In neither case are other ion energies present that would cause analytical interference. These are examples of complex natural matrices for which interferences might be expected.
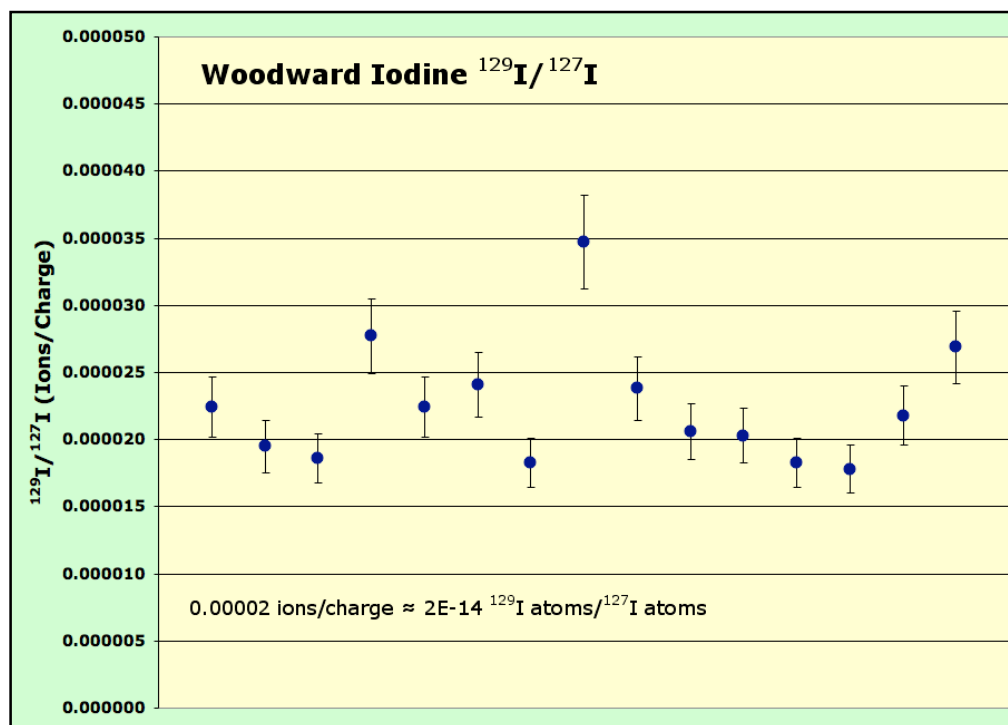
Figure 8. $^{129}I/^{127}I$ analyses of different Woodward iodine samples over time.
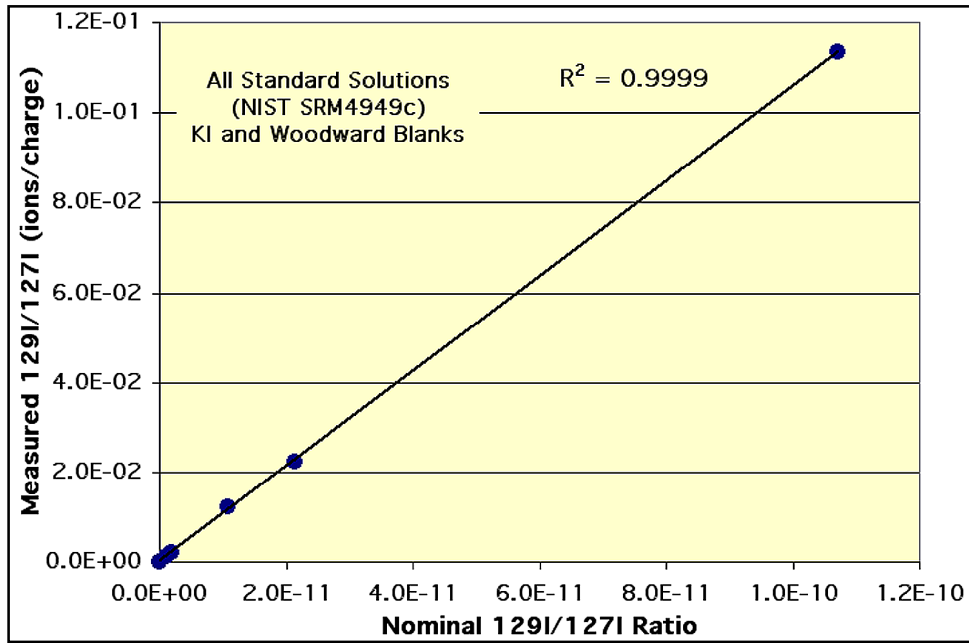
Figure 9. Calibration curve for instrumental parameters of [129]I ion counts relative to [127]I charge deposited in the Faraday cup versus the [129]I/[127]I ratio for dilutions of NIST [129]I standard SRM4949c ranging from 1E-13 to 1E-10, and including Woodward iodine at 2E-14 and a commercial KI solution at 1E-13.
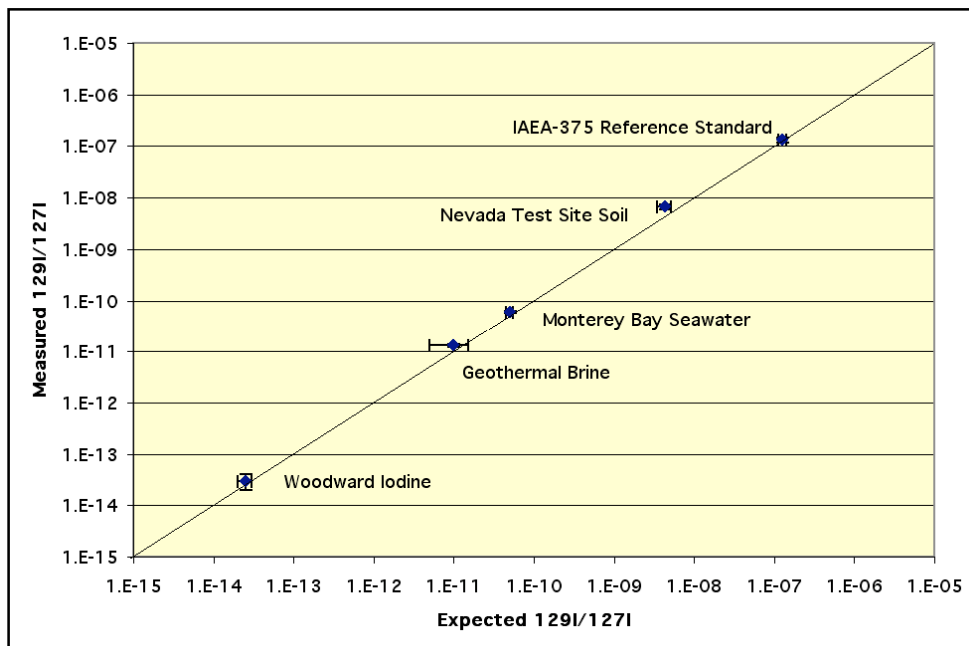
Figure 10. Analyses of known unknowns. Compares of our measured [129]I/[127]I values relative to those measured elsewhere. Analytical uncertainty bars are for 1 sigma.

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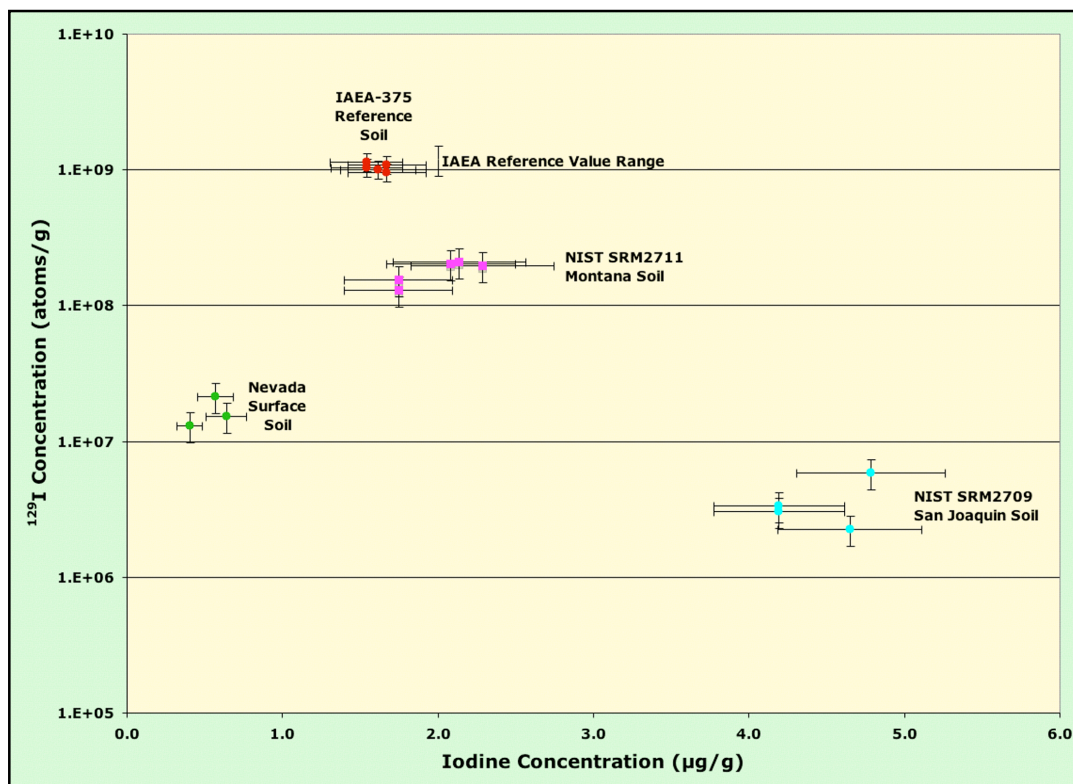
Figure 11. Replicate analyses of 3 soil standards and an in-house check standard extracted from a Nevada soil. Only the IAEA-375 reference soil has a certified ^{129}I concentration. The NIST standards have certified iodine concentration values only. Iodine concentration analyses were done by gas chromatography.

Figure 12. Photograph of vadose zone trench at the NTS from which samples were collected for $^{129}I/^{127}I$ and $^{36}Cl/Cl$ analyses.
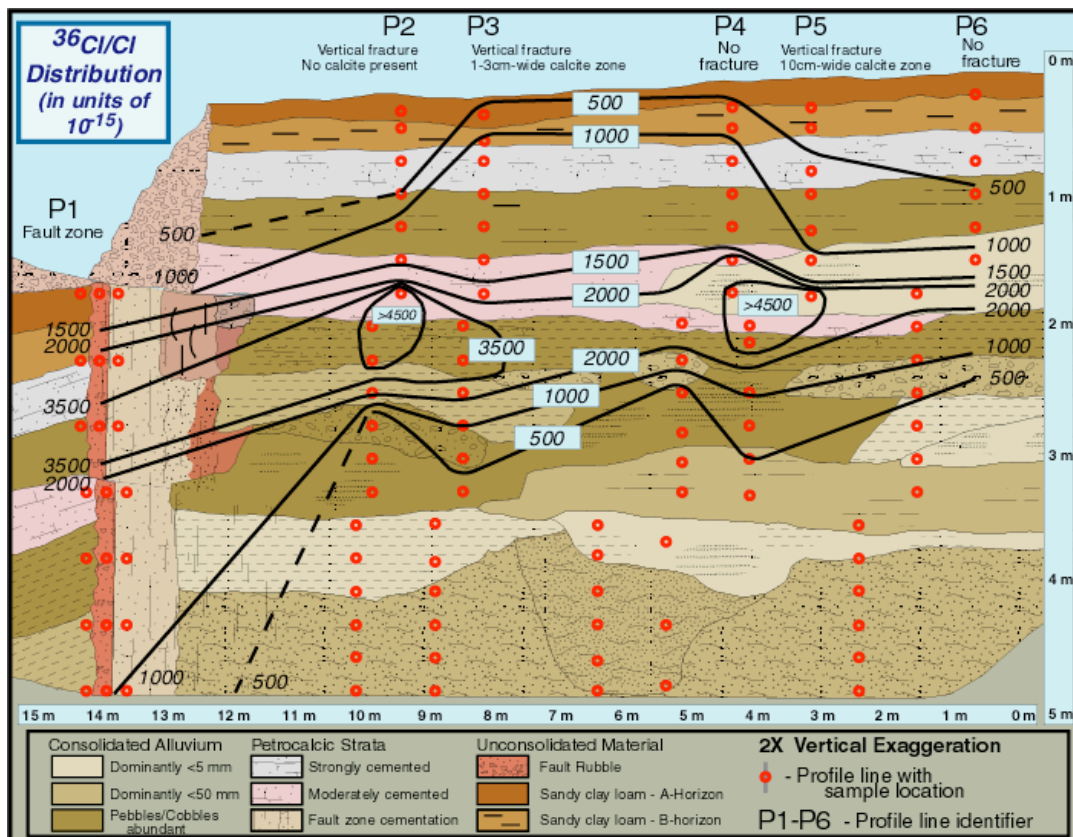
Figure 13. Cross section of vadose zone trench showing soil stratigraphy and measured distribution of $^{36}Cl/Cl$. Sample locations shown with red circles. Offset of sample profiles (P1 to P6) due to bench of trench seen in Figure 12.

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Figure 14. Photograph of the double furnace array used for combustion of soils to extract iodine. Sample placement can be seen within the glass tube in open furnace to left. Oxygen is passed through the tube from the left and the iodine is trapped in the solution in the flask to the right.

Figure 15. Ceramic boat used to hold soil sample in combustion furnace. Expended soil sample can be seen in the boat. The boat is approximately 3 inches long.
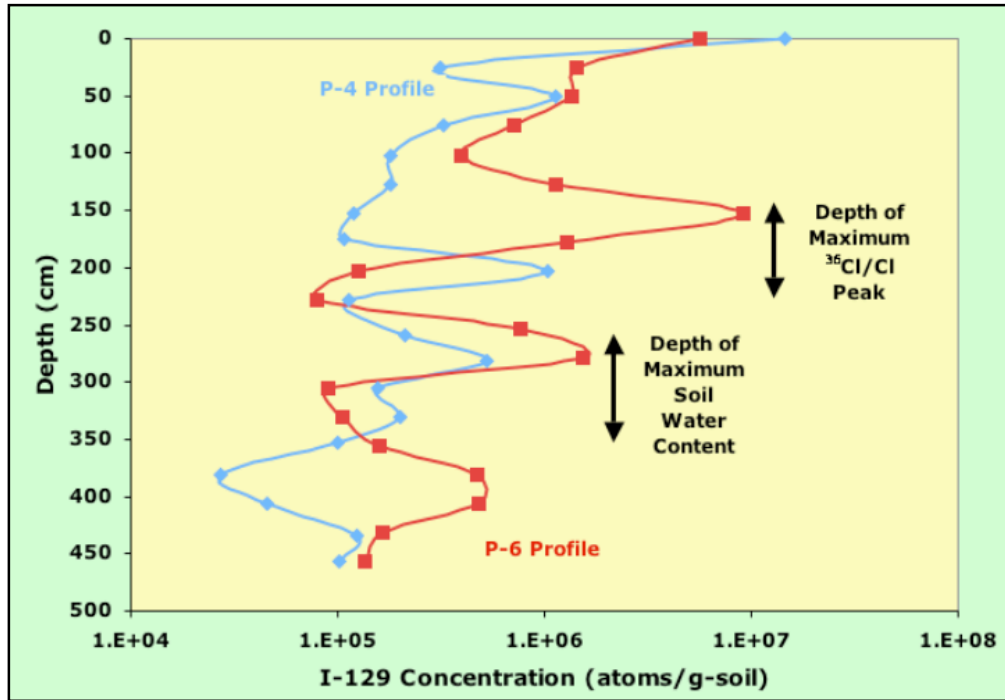
Figure 16. ^{129}I concentrations versus depth in soil samples from the vadose zone trench.
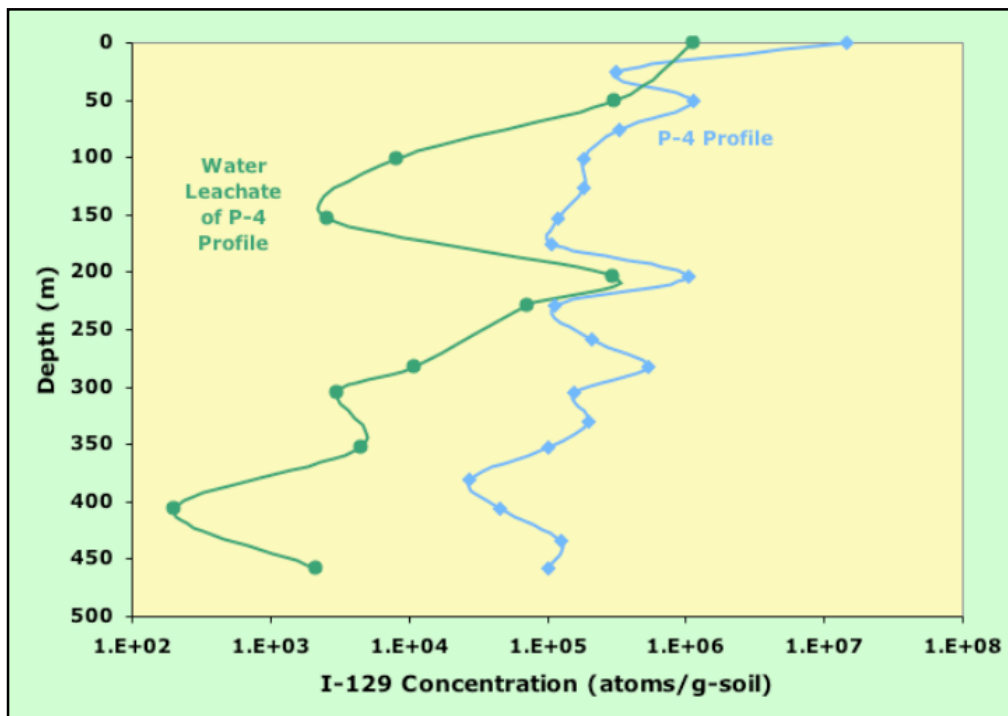
Figure 17. ^{129}I concentrations from the P4 soil profile in Figure 16 and a water leachate from soils in this profile.

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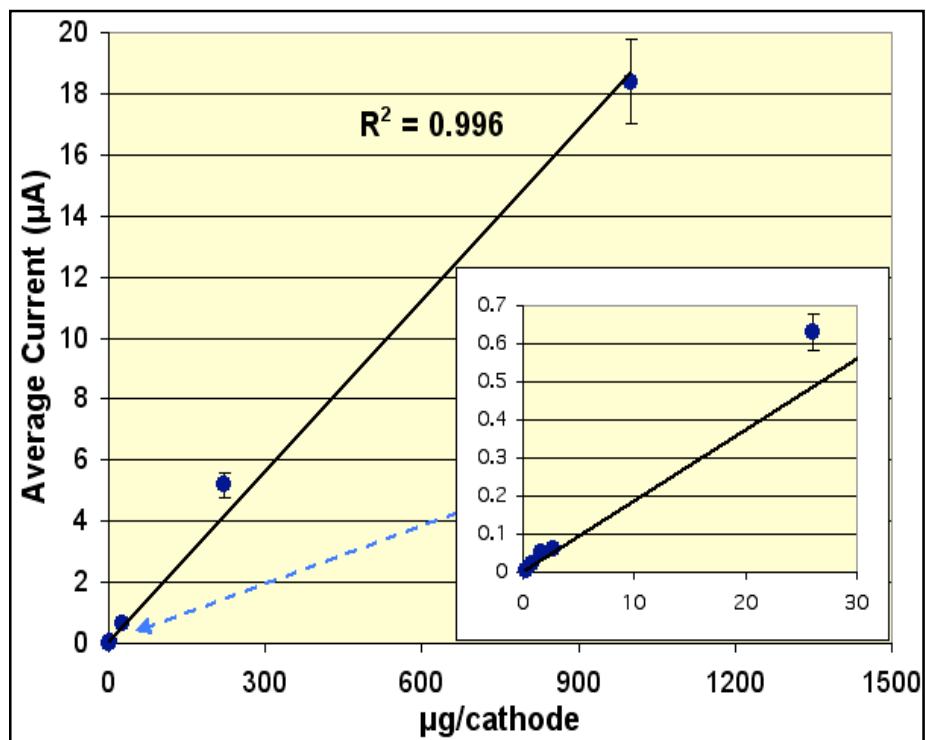
Figure 18. Relation between measured [127]I current in the off-axis Faraday cup and the amount of iodine (in µg) present in the cathode target.
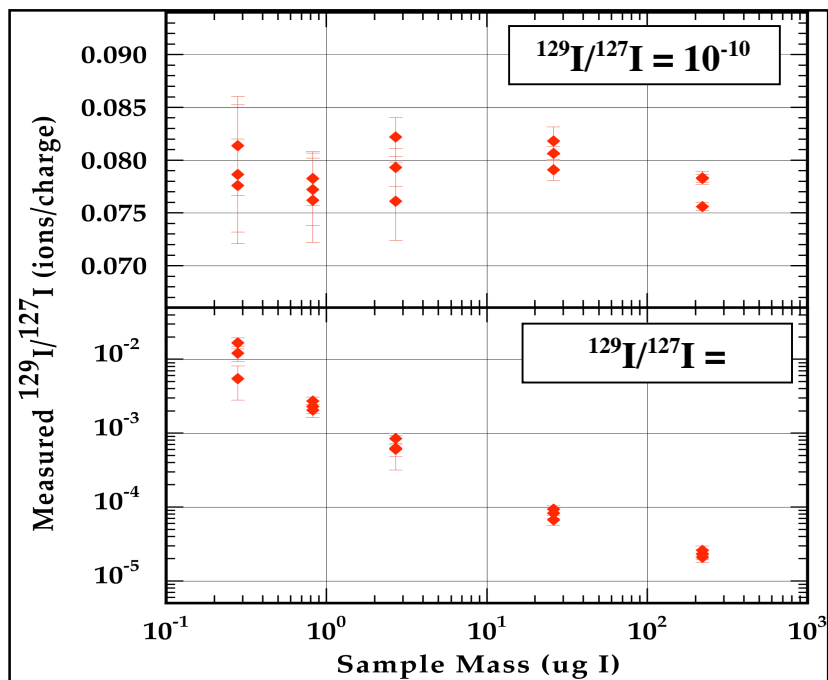
Figure 19. Measured ^{129}I/^{127}I (in ions/charge) in samples with different amounts of iodine (in μg) in the cathode target. Bottom is for Woodward iodine, top is for the NIST SRM4949c standard diluted to 1E-10. These samples have no Br or Cl as bulking material. AgI was diluted with Nb to achieve smaller target masses.
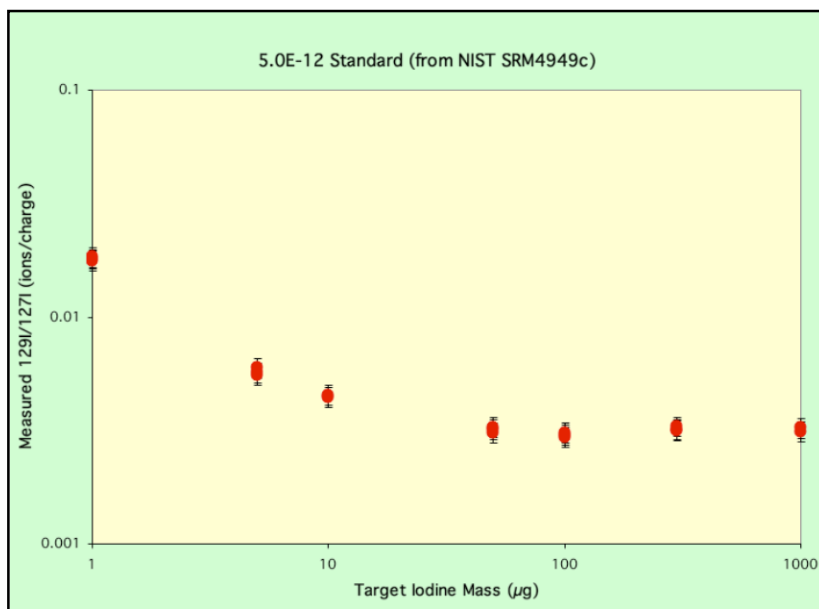

Figure 20. Measured ^{129}I/^{127}I (in ions/charge) in 5E-12 standard samples with different amounts of iodine (in μg) in the cathode target. These samples have AgCl as a bulking agent, using "old" NaCl. As discussed in the text, better results are expected when using newer NaCl.
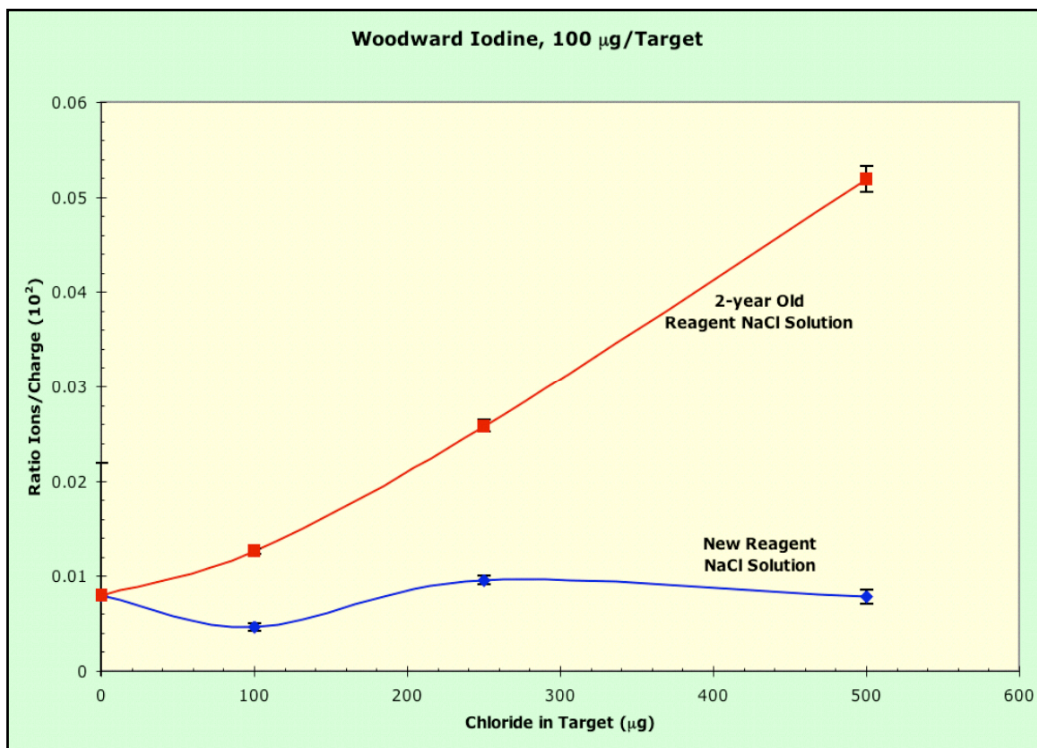
Figure 21. $^{129}I/^{127}I$ measurements of Woodward iodine when using different amounts of Cl as bulking material for the samples. When using our older NaCl for the Cl, there is a positive correlation between the amount of Cl in the sample and the measured $^{129}I/^{127}I$, indicating contamination from the older NaCl. No correlation, and no contamination is observed when using newer NaCl.

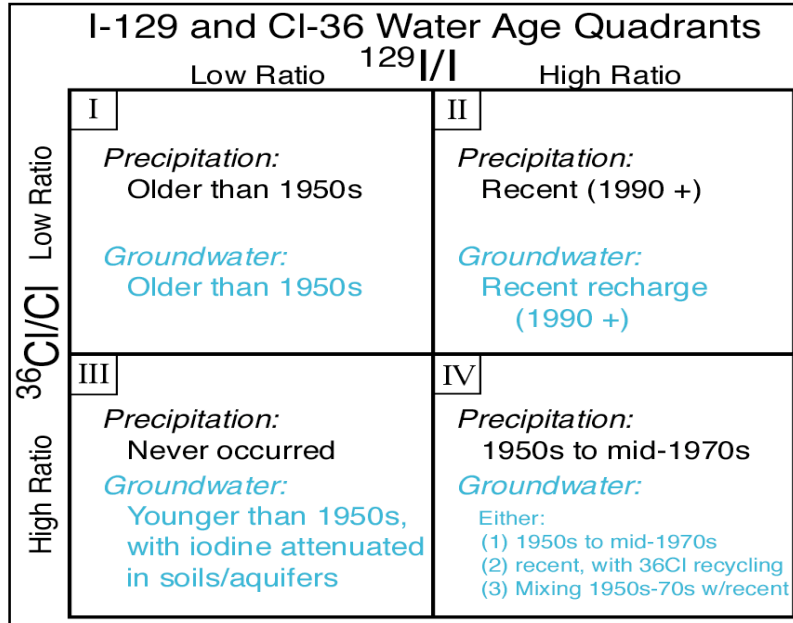**Figure 22**. Theoretical relation between values of $^{36}Cl/Cl$ and $^{129}I/^{127}I$ in groundwaters and the expected recharge age of the waters. Whether or not these relations can be observed in natural samples is being investigated by the Sierra Nevada research project being conducted at UC-Merced.
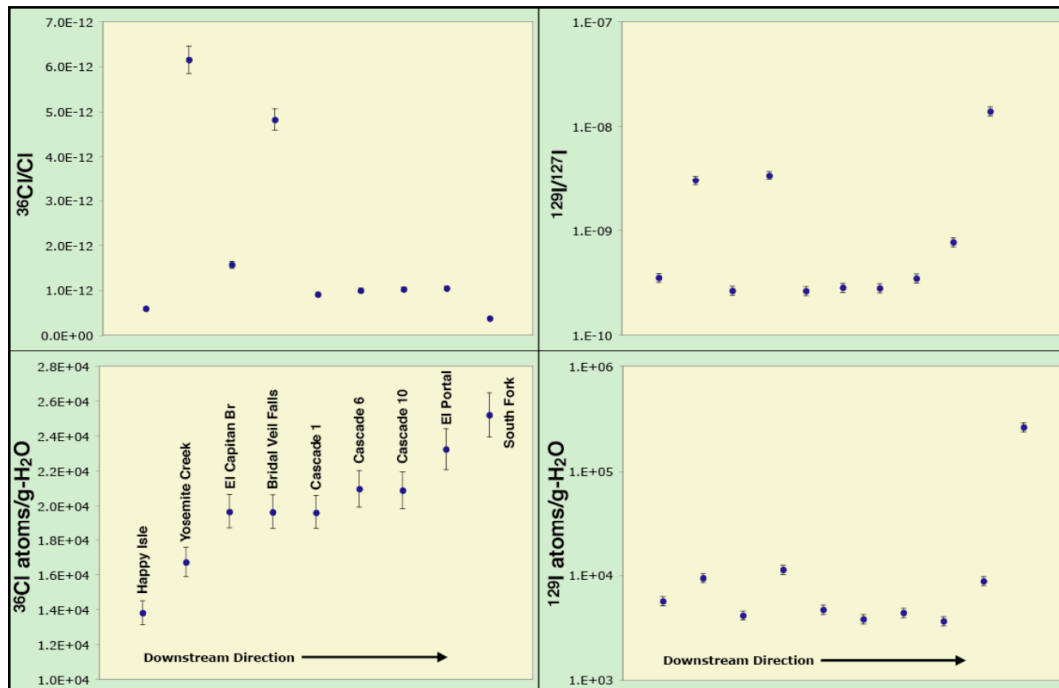

Figure 23. Initial feasibility analyses of $^{129}I/^{127}I$ and $^{36}Cl/Cl$ for waters from the Merced River, and Yosemite and Bridalveil Creeks in Yosemite Valley.