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**Technique development for the extraction of
environmental levels of iodide from groundwaters at the
Nevada Test Site for the purpose of $^{129}\text{I}/^{127}\text{I}$ analyses**

A Report by the Hydrologic Resources Management Program
of the Nuclear Chemistry Division
Lawrence Livermore National Laboratory

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ABSTRACT:

A technique was developed to extract iodine from groundwaters with very low concentrations of iodine (on the order of $\mu\text{g/L}$ or ppb). Sufficient iodine was necessary (approximately 5 mg AgI) for analysis of the $^{129}\text{I}/^{127}\text{I}$ on the Tandem Accelerator Mass Spectrometer (AMS). The technique for separating iodine from groundwater was developed for the field to eliminate shipping of thousands of liters of water back to the laboratory. The technique was field tested on several springs and wells at the Nevada Test Site (NTS). Preliminary isotope ratios are presented along with total iodine concentrations of the waters. A table including 31 selected well and spring samples throughout the NTS presents a previously unknown range of iodine concentrations in groundwaters at the NTS.

INTRODUCTION:

The halogens (Cl, Br and I) are considered to be highly conservative aqueous species and as such have been used as tracers in vadose and phreatic zone groundwater studies (Fabryka-Martin et. al., 1991, Fabryka-Martin et. al., 1985, Phillips et. al., 1988, Sheppard and Thibault, 1992, Wilson and Long, 1993). Although a great deal is still not understood concerning the behavior of the halogens, they do help in the determination of the origin, flow paths and geochemical evolution of groundwater. Iodine, with its long-lived radionuclide ^{129}I ($t_{1/2} = 15.9$ Ma), may have the potential to date very old groundwaters, under special circumstances, up to 100 Ma. Due to the young age of most groundwaters, using the long lived radionuclide ^{129}I to date most groundwaters is not feasible. However, a discussion of the dating method is instructive as some of the problems involved in the dating method are also present when one attempts to use iodine as an environmental tracer. Further clarification of these issues is necessary to better understand the environmental systematics of iodine.

Age dating of groundwaters, using ^{129}I , exploits the decay of ^{129}I to stable ^{129}Xe through a weak β -emission, thus, reducing the initial $^{129}\text{I}/^{127}\text{I}$. This technique either requires the assumption of a closed system with no net iodine flux, or the ability to predict and quantify perturbations to the system that changes the $^{129}\text{I}/^{127}\text{I}$ ratio. Such perturbations may be a vadose zone iodine sink in the form of micro- or macro-organisms utilizing iodine in their bodily functions or a phreatic zone iodine source such as iodine present in a soluble form within the rocks that is leached into the groundwater. Another significant source of subsurface iodine may be spontaneous fission of ^{238}U (Fabryka-Martin, et. al., 1985). While sinks of iodine are usually considered negligible, quantification of the subsurface sources of iodine presents the greatest challenge to researchers attempting to date old basinal waters with ^{129}I (Fabryka-Martin, et. al., 1985).

Most of the natural ^{129}I in the atmosphere is produced by spallation of stable Xe in the upper atmosphere. The dominant natural source of ^{129}I in the subsurface is fission of heavy elements, chiefly spontaneous fission of ^{238}U . Anthropogenic sources of ^{129}I include effluent from nuclear reactors as well as atmospheric and underground testing of nuclear weapons. Thermonuclear weapons testing elevated the concentration of ^{129}I in the atmosphere and in the subsurface. While the subsurface contribution is confined to the very localized area of the Nevada Test Site (NTS), the atmospheric contribution was distributed globally.

The residence time for iodine in the atmosphere ranges from several days to two years (NCRP, 1983), consequently, the $^{129}\text{I}/^{127}\text{I}$ ratio has been decreasing since it peaked at 10^{-6} to 10^{-4} in the early 1960's (Brauer and Strebin, 1982). The present-day ratio is estimated at 10^{-10} to 10^{-12} depending on geographical location and season (Fabryka-Martin, et. al., 1989). Biological samples analyzed for the $^{129}\text{I}/^{127}\text{I}$ ratios in the 1960's and 1970's had ratios as high as 10^{-7} and water samples from Germany and Israel had ratios of 10^{-10} after the Chernobyl accident in 1986 (Fabryka-Martin, J, et. al., 1989). The large reservoir of terrestrial and oceanic stable ^{127}I acts as a dilutant for the atmospheric $^{129}\text{I}/^{127}\text{I}$ ratio and therefore the $^{129}\text{I}/^{127}\text{I}$ ratio is expected to be relatively constant for surface waters (Fabryka-Martin, et. al., 1989).

The residual ^{129}I from underground nuclear testing, however, is such an enormous quantity of ^{129}I in a highly localized area that it swamps the diluting effect of any ^{127}I present underground. Indeed, water extracted from a satellite hole associated with an underground nuclear test contained 10^7 to 10^8 times the number of ^{129}I atoms per liter (Marsh, 1992) than very old groundwater extracted from the Milk River Aquifer, Alberta, Canada (Fabryka-Martin, et. al., 1991) and the Great Artesian Basin, Australia (Fabryka-Martin, et. al., 1985).

By characterizing the ^{129}I in the groundwater at the NTS, iodine's highly conservative behavior in aqueous solutions may be exploited to provide an early detector of radionuclide movement from shot cavities with radioactive melt glass very near or beneath the water table. To quantify low-level ^{129}I migration from shot cavities, a complete characterization of the natural ^{129}I variabilities in the NTS groundwater is necessary. The latter may also help delineate groundwater origins, movement and geochemical evolution. For example, in the Great Artesian Basin of Australia, $^{129}\text{I}/^{127}\text{I}$ ratios indicated the presence of two different water bodies with

separate origins: a basement crystalline rock component and an infiltrated surface precipitation component (Fabryka-Martin, et. al., 1985). Furthermore, in the Milk River Aquifer, the halogens were used to support the hypothesis that subsurface leakage of altered sea water from geologic units with low permeability to units with higher permeability act as a source for stable chlorine and iodine (Fabryka-Martin, et. al., 1991). Thus, iodine may potentially be used as both an early detector for radionuclide movement and a natural hydrologic tracer.

RESIN CLEANING PROCEDURE:

The resin used was Bio-Rad AG 1X8 100-200 mesh, chloride form, analytical grade anion exchange resin. The procedure used to clean the resin followed that used by June Fabryka-Martin (personal. comm.) in her work in the Great Artesian Basin of Australia (Fabryka-Martin, et. al., 1985).

The resin was soaked in Millipore water for about 5 days and the water was changed at least once a day. A 1:1 volume ratio of resin and 5-12% NaOCl (household bleach) was heated to about 35°C for one hour with constant stirring. The resin was then rinsed with Millipore water until the effluent pH approximately equaled 5.

In a column, approximately 25 bed-volumes of 1M $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$ were eluted through the resin. (Note: To reduce the total volume of 1M $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$ required, the initial solution was split into smaller volumes and eluted several times. However, the final aliquot was eluted only once to eliminate any contamination of the resin.) When the 1M $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$ elution was complete, the resin was rinsed with Millipore water until the effluent pH was about 5.

The final stage of purification involved eluting about 15 bed-volumes of a $\text{MeOH} : \text{H}_2\text{SO}_4 : \text{H}_2\text{O}$ (75:1:24) solution. Again, the splitting and recycling method from above was used, and the final aliquot was only eluted once to ensure the integrity of the resin. The resin was then rinsed with Millipore water until the pH was about 5 and stored in a clean vessel under Millipore water until ready for use.

EXTRACTION TECHNIQUE:

Iodine concentrations in surface waters and groundwaters of the arid southwest, including the NTS, are generally low (Hansen, 1936). With the approximation that total iodine concentrations in groundwaters are 1 mg per liter, at least 5400 liters are required to obtain, without using a carrier, the 10 mg of AgI necessary for analysis on the Tandem Accelerator Mass Spectrometer (AMS). Since the iodine concentration for most fresh waters is low, with low $^{129}\text{I}/^{127}\text{I}$ ratios, it is extremely important that the extraction method have a low procedural blank. A low procedural blank will increase the ability to quantify small natural variations in the $^{129}\text{I}/^{127}\text{I}$.

FIELD PROCEDURE:

Iodine's reactive and volatile nature requires rigorous sample preservation. To maintain the integrity of the sample, exposure to light, both sunlight and indoor lighting, should be kept to a minimum, as ultra-violet light promotes the photochemical oxidation of iodide to iodine (Mitake and Tsunogai, 1963). The kinetics involved are, under normal conditions, usually slow, however, the small sample size utilized necessitates the use of extreme care.

In its reduced state, iodide can easily be extracted from large volumes of water with low total iodine concentrations via sorption onto an ion exchange resin. 8-10ml of specially cleaned (Fabryka-Martin, pers. comm.) AG 1X8 Bio-Rad anion exchange resin were placed in a 20ml disposable polyethylene column. Approximately 5ml of Millipore water were added to keep the resin moist until used in the field. Immediately prior to sampling, the Millipore water was allowed to drain from the resin.

Two types of collection techniques were employed in the field because of the dissimilar discharge conditions between pumped wells and springs. Only results from the springs are

reported because the well samples were inadvertently exposed to direct sunlight and high temperatures. Thus, the little iodine present was probably volatilized. As explained later, the sample for ER-12-1 was not a field extraction technique.

The sampling technique for pumped wells involved the use of a hose arrangement, similar to a garden hose, made entirely of tygon tubing. This allowed an in-line sampling system which eliminated the potential for added contaminants from the atmosphere. An in-line field filter removed any large ($> 0.45\text{mm}$) particulate matter that may clog the column or contaminate the sample. Once attached to the pump, the hose and filter were purged for approximately 3-5 min before the column was secured to the hose with hose clamps. The pressure from the pump then forced water over the resin capturing the iodine sample. Flow rates were approximately 500ml/min.

The second sampling method, developed for spring sampling, required a portable peristaltic pump instead of the tygon tubing that attached to the water well pumps. An in-line 0.45 mm filtration sampling system was employed to remove the potential for external contamination, however, the springs are in cave-like settings which are open to the atmosphere and may contain atmospheric input. The flow over the column averaged 200-300 ml/min. The slow flow may be attributed to fine particles clogging the filter which elevated the water pressure inside the system past the point of breaking.

All columns were then rinsed with 40-50ml of Millipore water. 5-10 mls of Millipore water were used to slurry the resin into a teflon vial. The Millipore water kept the resin wet for transportation back to the laboratory.

LABORATORY PROCEDURES:

Relatively small volumes of reagents are used during the purification of iodine to prevent the addition of any contamination into the sample and minimize waste production. This particular method follows that of Kleinberg and Cowan (1960; procedure 15).

If, at the time of sampling, it is believed that a sufficient volume of water did not flow through the resin to provide enough iodine for analysis (roughly 5mg I-), carrier iodide must be added prior to draining the Millipore water from the resin column. The most common carrier iodide solution is dissolved Woodward iodine crystals derived from brines associated with natural gas deposits in Oklahoma.

The iodide was stripped from the column as periodate using 20-30 mls of a 5-12% aqueous solution of NaOCl (household bleach). The resin was then discarded. To the NaOCl solution, approximately 6 mls of concentrated HNO_3 were added dropwise with continual swirling of the reaction vessel. 3 ml of 1M $\text{NH}_2\text{OH} \cdot \text{HCl}$ were slowly added to reduce the periodate to the molecular and very volatile state. The iodine was extracted into an equal volume of diethyl ether, about 30-40 mls, and the aqueous layer was discarded.

4 drops of 2M NaHSO_3 were added to 30 mls of Millipore water and the iodine was extracted into the aqueous phase. The organic phase was subsequently discarded. To the aqueous phase, 1.5 mls of concentrated HNO_3 and 8 drops 1M NaNO_2 were added. The reduced iodine was subsequently extracted into 30 mls of diethyl ether followed by the proper disposal of the aqueous layer. A solution containing 5 drops 2M NaHSO_3 and 20ml Millipore water was added to the separatory funnel containing the organic phase. The iodide was extracted into the aqueous phase which was then transferred to a polyethylene centrifuge tube. The final organic solvent layer was discarded.

0.5ml concentrated HNO_3 and 1 drop of 5% AgNO_3 were quickly added to the centrifuge tube. The resulting yellow precipitate was centrifuged and washed several times with Millipore water and once with a volatile organic solvent to speed the drying process. Following the final rinse, the centrifuge tube was placed in an approximately 70°C oven to dry and subsequently packed in an aluminum target for analysis on the AMS.

RESULTS:

Laboratory experiments involving a carrier source of iodine and Millipore water were executed to establish a chemical isolation and purification protocol. The carrier iodine used in all isotopic analyses was Woodward iodine, a "dead" iodine source derived from Pennsylvanian brines in Woodward and Harper counties of Oklahoma. Carrier and chemical procedure samples were analyzed simultaneously with each sample to ensure quantification of the added ^{129}I during sample preparation and determine the instrumental blank during the developmental stages of running ^{129}I on the AMS. Table 1 presents the $^{129}\text{I}/^{127}\text{I}$ ratios from the carrier and procedural blanks.

Table 1. Carrier, chemical procedure and field blank results.

Sample	$^{129}\text{I}/^{127}\text{I}$ ($\times 10^{-15}$)	Date Analyzed	Date prepared
Woodward Iodine	761	1/27/93	1/21/93
	75	2/25/93	2/25/93
	at detection limit	6/3/93	2/25/93
Procedural blank #1*	124	12/22/93	12/15/92
#2*	1184	1/27/93	1/26/93
#1*	447	1/27/93	12/15/92
#3*	300	2/25/93	2/25/93

NOTE: Numbers reported with *s are background corrected. The unstarred numbers are the different instrumental backgrounds for that day.

Successful laboratory extraction of iodide from low-iodine concentration ultra-pure Millipore water led to extraction attempts from fresh water samples to determine if the complex matrix would interfere with the extraction process. Table 2 indicates the sites sampled and subsequent AMS results. Three liters of ER-12-1 well water were shipped from the NTS to Livermore following a 24 hour pumping test of the well. Carrier iodide was added to the three liter sample to provide sufficient sample mass for analysis. Since all manipulations of ER-12-1 were completed in a laboratory, the potential for contamination after sampling is very low.

The springs sampled are open to the atmosphere. The springs generally occur on the sides of hills and in small caves that extend back into the hillside. It should be noted that the samples were taken at the mouth of the pools created by the springs, not at the point where the water entered the pool which, in some cases, was approximately 30 feet back into the cave.

The two spring samples were collected in the field with the in-line filtration and ionic selective column system described above. The water at Tippihah Spring was clear and required only one filter for the entire sample, however, the water from Tub Spring was slightly murky and required several filters to collect the sample. The field blank sample in Table 2 was collected at the Tub Spring site. 10 mls of resin were placed in a column, 20 mls of Millipore water rinsed the column and the column was sealed for shipping. Subsequent treatment of the field blank was undifferentiated from the spring samples.

Table 2. Initial field sampling results.

Sample	[Iodine] ug/L	$^{129}\text{I}/^{127}\text{I}$ $\times 10^{-10}$	Volume (L)	Date analyzed
Tippihah Spring	5	3.27	38	6/3/93
Tub Spring	7	9.28	19	6/3/93
ER-12-1	2	28.4	3	6/3/93
	2	7.98	3	2/25/93
Field blank	-----	0.034	-----	2/25/93

All results listed in Table 2 have been background corrected.

No previous studies of iodine concentrations in groundwaters or rocks on the NTS are known. Since the LLNL HRMP Isotope Hydrology Group was involved in the geochemical

characterization of NTS groundwaters during FY92-93, iodine was included as an analyte for each of the samples collected in FY93. The iodine concentration was determined using an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). Table 3 presents the iodine concentrations found in the groundwaters sampled by LLNL during FY93. Some of the samples are from water supply wells which were purged at least 30 min. prior to sampling, whereas, the remaining samples are from open boreholes that were sampled using a wireline truck and evacuated stainless steel bailers.

Table 3. Iodine concentrations of wells (pumped and bailed) and springs sampled during FY93.

Sample	[Iodine] $\mu\text{g/L}$	Sample	[Iodine] $\mu\text{g/L}$	Sample	[Iodine] $\mu\text{g/L}$
WW-C	6	UE5n	7	UE17a-831	15
WW-C1	5	PW-1	2	UE17a-992	26
WW-4	3	PW-2	4	UE17a-1085	280
WW UE5c	4	PW-3	3	UE1h-1979	8
WW-5c	7	UE10j	6	UE1h-2137	6
J-13	3	ER-12-1	2	UE20bh-1	2
J-12	4	Tub Spring	7	U12s	3
WW-8	4	Tippipah Spring	5	UE16f	2
WW UE16d	12	Topopah Spring	3	TW-B	13
Army well #1	3	White Rock Spring	7	TW-D	8
		Cane Spring	12		

DISCUSSION:

Initially, the $^{129}\text{I}/^{127}\text{I}$ ratios for the field samples appear to be quite high, however, the $^{129}\text{I}/^{127}\text{I}$ ratios fall within the upper range anticipated for atmospheric ratios (10^{-10} to 10^{-12} , Fabryka-Martin, 1989). As stated previously, the range in the anticipated $^{129}\text{I}/^{127}\text{I}$ ratio is dependent on the geographical location of the sampling site and the season. The total iodine concentration and $^{129}\text{I}/^{127}\text{I}$ precipitation ratio are presently unknown for the NTS which prevent a more quantitative description of the amount of mixing between precipitation and formation waters.

If one assumes the spring samples are indicative of atmospheric precipitation, two hypotheses arise to explain the signals. The first is atmospheric precipitation is collecting in the small associated reservoirs with minimal iodine input from the spring and the second argument is that the spring discharge is in contact with the surrounding lithology for a very short period and consequently does not acquire the $^{129}\text{I}/^{127}\text{I}$ ratio of the rocks.

A point concerning the springs that needs to be addressed is that the samples were collected at the mouth of these springs. This is important because biological activity within the pools could have captured some of the iodine and subsequently been removed from the water via the in-line field filtration system utilized. This would decrease the iodine concentration in the sample but should have no effect on the $^{129}\text{I}/^{127}\text{I}$ ratio.

Any interpretation involving the data from well ER-12-1 must be cautiously considered because the water sampled is known to have contained at least some drilling fluid. The drilling fluid was "tagged" with a LiBr tracer during drilling activities. Anomalous concentrations of these two species in the water sample act as evidence for this claim. The first indication that formation fluid was not sampled is the extremely high concentration of lithium in ER-12-1 (2560ng/ml) when compared to other wells at the NTS like nearby TW-1 (20ng/ml). Lithium concentrations from the other wells at the NTS range from around 20 to 100 ng/ml. The second indication of drilling fluid contamination was the bromide concentration in the water. Generally bromide concentrations in uncontaminated groundwaters at the NTS are not detectable with an ion specific probe, however, the bromide concentration of the ER-12-1 fluid was around 2 ppm (Dave Gillespi, personal

communication). The similarity between the $^{129}\text{I}/^{127}\text{I}$ ratios of ER-12-1 and the springs may indicate that the iodine sampled from ER-12-1 represents more of an atmospheric than formation ratio.

Most of the total iodine concentrations were close to that expected for rainwater (<1-15 mg/L, Kocher 1981) with one notable exception: well UE17a. The unusual iodine concentrations in UE17a may be directly linked to the lithology of the well. UE17a is completed within a shale unit of the Mississippian aged Eleana Formation. The increase in dissolved iodine concentration with depth is probably due to the longer contact time the water has with the shale unit. The well is cased to a depth 1210 feet below surface level (bsl) which indicates that all three samples in Table 3 were taken from a cased well bore. Samples below 1085 feet bsl were not available due to formation particles clogging the inlet needles of the bailers. The samples were field filtered to 0.45mm which effectively removed the visible suspended material and decreased the potential for iodine dissolution from suspended particles.

Since iodine is a known biophilic species and shales commonly contain a great deal of remnant organic material, it is possible that the shales have a very high iodine concentration relative to the surrounding lithology. Therefore, by using only iodine concentration it is possible to detect water that has "seen" the Eleana Formation and is now moving through other units. This process will be complicated by dilution and possibly diffusion. However, if the Eleana Formation has a diagnostic $^{129}\text{I}/^{127}\text{I}$ ratio, determination of that ratio in down-gradient sites will allow a much more sensitive indicator of groundwater movement and evolution.

As the Eleana Formation is Paleozoic in age, the ^{129}I trapped during deposition should have decayed to undetectable limits. One is prevented from concluding that the $^{129}\text{I}/^{127}\text{I}$ ratio derived from the Eleana Formation is effectively zero, and therefore, an easily identifiable point source for a conservative hydrologic tracer, however, because the fissionable heavy element concentration of the shale is unknown at present. Thus, a source of ^{129}I may exist within the shale and raise the $^{129}\text{I}/^{127}\text{I}$ ratio.

Regardless of the processes within the shale, it is possible that the Eleana formation has a diagnostic, and therefore, traceable $^{129}\text{I}/^{127}\text{I}$ ratio. Because of the difference in fissionable element concentrations and deposition ages, all of the units within the NTS may have a diagnostic $^{129}\text{I}/^{127}\text{I}$ ratio. The $^{129}\text{I}/^{127}\text{I}$ ratio of the formation can be determined through analyses of core from various holes.

From Table 1, acceptable low laboratory procedural blank levels were achieved. The near order of magnitude variation in ratios between Procedural Blank #1 measured on 12/22/92 and 1/27/93 indicates either a contamination control problem during storage of the sample or more probably the unusual circumstances at the AMS on 1/27/93 which led to a higher background and a higher ^{129}I count.

SUGGESTIONS:

Groundwater geochemical evolution indicator and tracer

Since we now have the ability to extract iodide from very dilute groundwaters, we can now focus our efforts on some of the more fundamental questions concerning the iodine geochemical cycle in an effort to use ^{129}I as a valuable tracer tool.

As noted in the introduction, a great deal is unknown about iodine sinks, sources and/or behavior. Of some interest is quantification of iodine's movement through the vadose zone toward the phreatic zone. To use iodine as a groundwater tracer, its path to the saturated zone must be studied to allow a more thorough interpretation of groundwater origins, particularly in relatively young waters. A rigorous study of the iodine flux across the root zone is needed to determine the biogeochemical and inorganic behavior of iodine and what role, if any, micro-organisms play in redistributing iodine in the subsurface.

Of primary interest is the question of ^{129}I concentration in the atmospheric precipitation that falls on the NTS. An accurate account of fallout ^{129}I atoms is a vital first step required to quantitatively relate mixing bodies of water and evolution of that water. Similarly, the precipitation

around the NTS should be analyzed to ensure characterization of all possible end-member sources of water.

Finally, to use iodine for tracking and interpreting phases of groundwater movement and evolution, the iodine concentration in the rocks potentially available for leaching must be measured. This is particularly true of the NTS because one of the proposed uses of iodine analyses is to track groundwater movement from one aquifer to another, if possible, using the $^{129}\text{I}/^{127}\text{I}$ and/or iodine concentration signatures. Therefore, each unit should be carefully scrutinized. This includes the laterally-extensive smaller and potentially iodine-rich units, such as the shales and quartzite within the Eleana formation, as well as the limestone units. In addition to the iodine concentration, the uranium concentration would be extremely useful, because the spontaneous fission of ^{238}U yields ^{129}I . Estimates have been made (Fabryka-Martin, et. al., 1984) to determine the ^{129}I yield, but measurements are lacking.

Hydrologic tracer for detecting radionuclide movement from cavities:

^{129}I may also provide us with an invaluable tool for early detection of radionuclide movement from a shot cavity. Experiments involving meltglass (actual and simulated) and leaching have determined that iodine is one of the more labile species created during a nuclear weapons testing event (Smith, 1993). Observations from an induced radionuclide migration study at the NTS indicate that ^{36}Cl atoms and possibly ^{129}I anions migrated faster than tritium (Buddemeier, et. al., 1991). The ^{129}I data is not as definitive as the ^{36}Cl data and this may be linked to difficulties in handling iodine samples.

Accurate knowledge of the background $^{129}\text{I}/^{127}\text{I}$ ratios at the NTS are necessary to detect early migration of ^{129}I from cavities. Samples from each of the representative lithologies must be analyzed because $^{129}\text{I}/^{127}\text{I}$ variabilities within the natural system may span several orders of magnitude as dictated by the surrounding lithology. Additionally, the precipitation $^{129}\text{I}/^{127}\text{I}$ ratios for the NTS and potential recharge areas should be characterized.

An important aspect of the migration of ^{129}I from a shot cavity is the manner in which iodine is introduced into the environment from the cavity. Smith (1993) reports that the more volatile species, which includes iodine, migrate up the chimney immediately following a shot. If the device was fired below the water table, subsequent filling of the cavity will probably introduce iodine into the groundwater. If the device was fired above the water table, groundwater infiltration is no longer a problem, but potential for infiltrating precipitation is reportedly increased (Tyler et. al., 1986). It has been suggested (Tyler et. al., 1986) that the increased permeability in the rubble chimney and a collapsed crater structure created by a nuclear device detonation increases the potential for infiltration through the chimney.

SUMMARY:

A technique has been successfully developed to extract environmental levels of iodide from groundwater in the field, thus avoiding the logistical problems associated with shipping and disposing of large volumes of sample. Additionally, with the sensitivity of the AMS facility at LLNL, samples with very low $^{129}\text{I}/^{127}\text{I}$ ratios can be analyzed.

The $^{129}\text{I}/^{127}\text{I}$ ratio can potentially be useful as an environmental level hydrologic tracer and as a tool for early detection of radionuclide migration from a cavity. The first step to accomplish either, or both, of these objectives is a laterally extensive $^{129}\text{I}/^{127}\text{I}$ characterization of the uncontaminated groundwater at the NTS.

To use iodine as an environmental hydrologic tracer, the prominent and laterally extensive lithologies need to be analyzed for iodine concentrations and isotopic ratios. Similar analyses for uranium would also be very helpful, but are a secondary priority at this time. Constraints on the potential lithologic input of iodine into the groundwater system will allow a better understanding of the migration and evolution of the groundwater at the NTS. As an often overlooked part of the groundwater system at the NTS, precipitation and infiltration should also be analyzed as initial endmembers of an evolving groundwater system. A key point to be made here is that the groundwater beneath the NTS may not be recharged at the NTS, and therefore,

precipitation and groundwater samples of the entire area surrounding the NTS should be analyzed.

In addition to background levels of ^{129}I , the migration mechanisms and paths must be recognized to use iodine as an early radionuclide migration tool. The rate and mechanism by which iodine is introduced into the groundwater system is a topic that deserves more consideration. Migration in the saturated and unsaturated zones should be addressed because radionuclide source terms are present in both media.

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