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Ultra-Sensitive Nuclear Measurements Initiative

Opportunities for Decay Counting of Environmental Radioisotopes Using Ultra- low-background Detection Systems

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August 2012



Pacific Northwest
NATIONAL LABORATORY

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Executive Summary

We present results from a scoping study whose intent was to define challenge measurements to be pursued on the Ultra-Sensitive Nuclear Measurements Initiative. Potential challenge measurements using new radiation detection technology in the shallow underground laboratory that would have substantial impact in environmental science were the focus of this study. Table 1 summarizes the results for each isotope.

Table 1. Summary of Findings and Recommendations for Challenge Measurements

Isotope	Application	Potential Impact	Recommendation
³⁹ Ar	Age dating of subsurface water in the timeframe from 50 to 1000 years	Proportional counters offer the capability to measure reasonable sample sizes for ocean waters but not ice cores. This isotope is not currently a fertile area of investigation in environmental science. There is considerable demand, however, in the fundamental science community for assaying “ancient” argon.	Continue to engage contemporary environmental sampling activities to understand potential opportunities. Support needs of the fundamental science community.
²² Na	Age dating of young ground waters	The CASCADES array presents a near-ideal tool for measuring the dual 511-keV signatures from ²² Na. There are apparently no on-going measurements of this isotope due to the complexities of analyzing young ground water.	Do not pursue.
Dual ¹⁴ C- ³ H	Determination of carbon stability in soils	Deploying a dual age-dating approach on different fractions of organic matter extracted from different soils will provide unparalleled insights into the stability of different soil organic matter and contribute to new foundations for modeling soil carbon cycling processes.	Develop the necessary sample preparation and execute a demonstration measurement.
Fukushima emissions	Determination of environmental pathways for actinides and daughters	Considerable interest will exist in coming years to measure trace concentrations of emissions that possess half-lives in the range of less than 10 years.	Pursue novel detection technologies that have the potential to exploit compound signatures such as coincident emissions of alpha particles and electrons.

Contents

Executive Summary	iv
1 Environmental Radioisotopes.....	1
2 ³⁹ Ar Analysis for Dating Water.....	3
2.1 Ocean Water Dating.....	3
2.2 Concentrations and Specific Activities of ³⁹ Ar in Water Samples.....	4
2.3 Detection Sensitivity for ³⁹ Ar.....	5
3 Ice Core Dating	8
4 ²² Na Analysis for Dating Young Water.....	11
5 Tritium Enhances ¹⁴ C Dating to Understand Carbon Stability in Soils.....	13
6 Measurement of Radioisotopes Released From Fukushima	15
7 References	17

Tables

Table 1. Summary of Findings and Recommendations for Challenge Measurements.....	iv
Table 2. Listing of Primary Tracers Used in Ocean Water Transport Studies, Ordered by Increasing Dating Range. Note that ³⁹ Ar fills a unique age-dating range between ³ H and ¹⁴ C...3	3
Table 3. Concentrations and Specific Activities of Argon for a Range of Water Characteristics. The total extracted argon assumes an extraction efficiency of 50 percent.	5
Table 4. Detector System Parameters Used for ³⁹ Ar Sensitivity Estimates	6
Table 5. Sample Count Rate and Time Required to Age-date Water with 10% Precision from a 700-mL Sample Operating in a Single Gas Proportional Counter.....	7
Table 6. Isotopes Present in Ice Cores	9
Table 7. Times Required to Measure ²² Na Concentration with 10% Precision. The calculation assumes 500 L of water with an initial ²² Na concentration of 30 Bq/L.	12
Table 8. Interpretation of Dual ¹⁴ C and T Dates for Compound Classes.....	14

1 Environmental Radioisotopes

Recent investments produced new measurement capabilities in the shallow underground laboratory. These include a multi-crystal low-background gamma-ray spectrometer and low-background internal-source gas proportional counters. These new measurement capabilities present the opportunity for addressing environmental science questions through measurement of environmental radioisotopes at extremely sensitive levels.

The purpose of this study was to define a set of challenge measurements that would have significant impact in environmental science. We initially examined a large set of radioisotopes but quickly focused on a narrow set of opportunities on which to focus.

Radiotracers in the Hydrosphere – ^{39}Ar

The age-range from 50 to 1,000 years is useful for applications such as understanding deep ocean mixing and the residence time of water in aquifers that are isolated from surface water. This is a difficult age range because it is a timescale that is longer than typically examined in decay counting but shorter than typically examined in mass spectrometry. The ideal target isotope is ^{39}Ar because its half-life most directly maps onto hydrosphere cycles of interest, for example deep ocean transport times from the poles to the equator and the time scale of interest for long-term groundwater supply impacts due to shifting weather patterns. It is, however, a particularly challenging isotope for mass spectrometry because it requires specialized accelerator mass spectrometers like the National Superconducting Cyclotron Laboratory.

^{22}Na Analysis for Dating Young Water

Cosmic rays produce the current level of environmental ^{22}Na in Earth's atmosphere. Specifically, ^{22}Na has origins primarily in the stratosphere by spallation between secondary cosmic rays and atmospheric argon. A large amount of ^{22}Na was created during nuclear weapon testing in the early 1960s although this inventory has now decayed enough (due to ^{22}Na 's short half-life of 2.6 years) so that cosmogenic production dominates. Thus ^{22}Na provides a steady-state tracer, avoiding the dating complications encountered when utilizing bomb-produced tritium for determining the age of young waters. The short half-life and distinct gamma-ray of ^{22}Na makes it an excellent target for decay counting.

Dual Measurements of ^3H and ^{14}C in Biomass

A combined ^3H - ^{14}C signature to link a definable component of soil organic matter to the metabolic products generated by the microbial community has the potential to be a key measurement tool in the exploration of carbon stability in soils. The "clock" offered by biosphere tritium incorporated into soil biota hydrocarbons is suitable for shorter time-scales (10 to 100 years) not accessible with ^{14}C dating. This may provide insight into the decoupling of carbon from the atmosphere over shorter time-scales. A key motivation of using gas

proportional counting for this measurement is the simplicity offered by tracking hydrogen and carbon together in individual pools without chemical fractionation.

Radionuclides Released from Fukushima

Events at the Fukushima nuclear plant present the opportunity to measure trace contaminants of fission daughter products, activation products, and actinides in the ocean environment. A partial list of radioisotopes of interest includes ^{14}C , $^{137}\text{Cs}/^{134}\text{Cs}$, ^{90}Sr , ^{99}Tc , ^{36}Cl , ^{129}I , and $^{103}\text{Ru}/^{106}\text{Ru}$. A large body of scientific work exists studying the transport of nuclear effluents in the environment, and the Pacific Northwest National Laboratory (PNNL) has significant expertise in this area. This task examined the current measurement capability and needs in the environmental science community to understand the potential role for more sensitive radiation detection technology.

The following sections present findings for each of these isotopes.

2 ^{39}Ar Analysis for Dating Water

2.1 Ocean Water Dating

Since the oceans play a major role in Earth's climate, e.g., through the transport of heat or the intake of CO_2 , understanding ocean dynamics is crucial in predicting possible future climate changes. Various radionuclides, stable isotopes, and chemical tracers provide important information on ocean circulation and mixing processes. Table 2 lists the primary tracers currently in use along with two radioactive isotopes, ^{39}Ar and ^{85}Kr , that are potentially useful but have had somewhat limited application because of analytical challenges. We discuss the most challenging of these two, ^{39}Ar , in detail.

Table 2. Listing of Primary Tracers Used in Ocean Water Transport Studies, Ordered by Increasing Dating Range. Note that ^{39}Ar fills a unique age-dating range between ^3H and ^{14}C .

Tracer	Half-life (years)	Source	Dating Range (ybp)
^{18}O	stable	natural	N/A
^2H	stable	natural	N/A
CFC	stable	anthropogenic	0 – 60
SF_6	stable	anthropogenic	0 – 40
^{14}C	5730	anthropogenic	0 – 50
^{85}Kr	10.8	anthropogenic	0 – 100
^3H	12.3	anthropogenic	0 – 100
^{39}Ar	269	cosmogenic	30 – 3000
^{14}C	5730	cosmogenic	>400

Stable isotopes like ^{18}O and ^2H are useful because of their presence in water molecules that consequently undergo kinetic isotope fractionation. For example, because of their smaller mass, water molecules containing ^{16}O evaporate more quickly from the ocean surface than those containing ^{18}O . Similarly, precipitation is enriched in ^{18}O relative to the water vapor from which it condenses. These processes result in downwind waters being enriched in H_2^{16}O , and thus measuring the isotope concentration can help elucidate the history of a given water mass. Since the degree of isotope fractionation is temperature dependent, information is provided about the temperature when the water was at the surface.

Chlorofluorocarbons (CFCs) and sulfur hexafluoride (SF_6) are synthetic tracers with fairly well known atmospheric histories. CFCs entered the atmosphere in the 1930s when industrial coolants, aerosol spray propellants, etc. became prevalent, while SF_6 entered the atmosphere from the electrical industry in the 1960s. CFC concentrations have recently peaked and are slowly decreasing due to the Montreal Protocol of 1987 that aimed to phase out their production after it was recognized that CFCs could destroy the ozone layer. Because of their long lifetimes, CFCs will be present in the atmosphere throughout this century. Unlike CFCs, the SF_6 concentration continues to increase.

The natural decay of certain radionuclides informs how long a water parcel has been isolated from the atmosphere. A radionuclide will effectively date a particular age range, as listed in Table 2, that depends on the radionuclide's half-life and input function. This conceptually simple procedure is sometimes complicated due to mixing of water with various ages, in which case the use of multiple radioactive tracers helps disentangle the measurements.

While dating with ^{14}C or ^3H is firmly established, dating with either ^{39}Ar or ^{85}Kr is more challenging because of the extremely low isotope concentrations and the effort involved in extracting these noble gases with sufficient purity from water. The use of these latter isotopes, however, is well motivated. First, ^{39}Ar is especially appealing since it spans the time window from 100 to 400 years that resides between ^3H and ^{14}C . Second, the overlap of the dating ranges of ^{39}Ar and ^{85}Kr with the other ranges is helpful in dealing with mixed waters, as noted earlier. Third, as noble gases, both isotopes are highly conservative. Conservative radionuclides have no sources or sinks below the surface, and the radionuclide's surface source function is known. Consequently, the law of exponential decay predicts the isotope's concentration in the water mass with limited impact from systematic errors. Because ^{39}Ar fills a particularly notable time window and because it presents both a challenging but attainable target, the exclusive focus of the following sensitivity analysis rests on ^{39}Ar .

Earth's atmosphere contains 0.93% argon by volume, and this argon primarily consists of stable isotopes (for example, 99.6% ^{40}Ar). Trace amounts of ^{39}Ar reside in the atmosphere due to cosmic ray-induced reactions, primarily $^{40}\text{Ar}(n,2n)^{39}\text{Ar}$. These trace concentrations exist at levels of $^{39}\text{Ar}/\text{Ar} = (8.1 \pm 0.3) \times 10^{-16}$ (Collon, Kutschera et al. 2004).

The premise of age dating with ^{39}Ar is that atmospheric argon dissolves in surface water and equilibrates at the atmospheric $^{39}\text{Ar}:\text{Ar}$ isotopic ratio. After a water mass becomes isolated from the surface, the amount of ^{39}Ar , and thus the $^{39}\text{Ar}:\text{Ar}$ isotopic ratio, slowly decreases due to radioactive decay. By measuring the $^{39}\text{Ar}:\text{Ar}$ isotopic ratio and comparing this ratio to the amount expected from the exponential decay law, one can estimate the time at which the water last equilibrated with the atmosphere. This time duration is often termed the water's "age".

Determining the required sensitivity to make these measurements requires knowledge of the age of the water in these systems and the concentration of (total) argon in water. The purpose of the following analysis is to report sensitivity estimates for a range of ages and total argon concentrations.

2.2 Concentrations and Specific Activities of ^{39}Ar in Water Samples

Argon concentration in water can be quantified using the Bunsen solubility coefficient, defined as the volume of dissolved gas (at STP) per volume of liquid under a 1-atm partial pressure of the gas. This solubility of argon in water increases with decreasing temperature. In the hydrosphere, temperatures differ considerably from the surface environment ranging from above 20°C at the surface down to a few degrees Celsius at depths of a few thousand meters.

For ocean studies that focus on global circulation and mixing, waters below the thermocline (below 1000 m) are most relevant. For the purposes of estimation, we consider a water temperature of 0°C. Table 3 provides characteristic values for argon solubility for fresh and ocean water, assuming temperatures of 0°C (deep) and 25°C (surface) (Hamme and Emerson 2004).

Because of the low concentrations, sample collection involves extracting argon from water samples in-situ by first degassing the water. The extraction efficiency stated in a recent review is 50 percent (Collon, Kutschera et al. 2004). We adopt this value for our estimates although preliminary estimates suggest that significantly higher efficiencies are possible (up to 80 percent). The total extracted argon is then the product of the Bunsen solubility coefficients, the partial pressure of argon in the atmosphere (0.0093 atm), and extraction efficiency. Table 3 lists the amount of argon extracted per 1000 L of water for select temperatures and water sources.

Table 3. Concentrations and Specific Activities of Argon for a Range of Water Characteristics. The total extracted argon assumes an extraction efficiency of 50 percent.

Water Type	Temperature	Bunsen Solubility Coefficient	Extracted Argon per 1000 L Water (L at STP)
Fresh Water	0°C	0.055	0.26
	25°C	0.033	0.15
Ocean Water	0°C	0.041	0.19
	25°C	0.025	0.12

2.3 Detection Sensitivity for ³⁹Ar

To gauge the challenge of measuring ³⁹Ar concentrations with ultra-low-background technology developed at PNNL, we present the following sensitivity estimate for a degassed sample of pure argon. Since ³⁹Ar β-decays with a 565-keV endpoint, gas proportional tubes are the appropriate radiation detector for quantifying its concentration. Table 4 lists detector system parameters of PNNL-developed proportional counters. (Note that these gas proportional counters normally operate at 3 atm, but, to increase sample concentration, they can safely be operated up to a pressure of 10 atm.)

In normal operation, the proportional counter fill gas is P-10 (90% argon, 10% methane) formed from modern argon. The measured background of a detector with 3 atm of modern-day P-10 fill gas in the shallow underground lab at PNNL is 230 cpd (after anti-cosmic veto and pulse-shape-discrimination cuts)¹. This background includes a contribution of approximately 30 cpd from

¹ Compare this background to the no-veto, no-PSD, surface background of approximately 86,000 cpd (or the vetoed surface background of approximately 6,000 cpd). After pulse shape discrimination, the vetoed surface background rate drops to around 2,000 cpd.

modern ^{39}Ar present in the P-10 fill gas. When measuring an argon sample, one forms the P-10 gas from the sample argon. After correcting for this, the non-argon detector background is approximately 200 cpd; we assume this value in the following calculations. (Note that this background may change with fill pressure, but experience dictates that any change is small for the pressures considered below.)

Table 4. Detector System Parameters Used for ^{39}Ar Sensitivity Estimates

Parameter	Values
Active Volume	0.1 L
Pressure	
Normal	3 atm
Maximum	10 atm
Background	
Total	230 cpd
w/o Ar	200 cpd
Detector Efficiency (ϵ)	0.8

To gauge expected count rates, we consider a 900-mL (STP) sample of atmospheric argon. A modern sample possesses a specific activity (A_s) of 1.8 mBq/L. (Note that filling a single proportional tube with this sample requires an operating pressure 7.8 atm.) For this sample, the count rate (R_{sample}) is:

$$\text{Equation 1: } R_{\text{sample}} = \text{volume} \times A_s \times \epsilon = 85 \text{ cpd.}$$

With the background and sample count rates, we estimate the time required to measure the sample concentration for a given precision (p). Starting with the formula

$$\text{Equation 2: } \textit{precision} = \frac{\sigma_{R_{Ar}}}{R_{Ar}}$$

where R_{Ar} is decay rate of ^{39}Ar in the sample, we estimate the measurement time under the assumption that the background count rate estimate ($R_{\text{background}}$) results from a measurement time ($t_{\text{background}}$) longer than the sample measurement time (t_{sample}). This yields:

$$\text{Equation 3: } t_{\text{sample}} = \frac{R_{Ar} + R_{\text{background}}}{p^2 R_{Ar}^2 + \frac{R_{\text{background}}}{t_{\text{background}}}}$$

For the aforementioned modern sample, the measurement time required for 10% precision is 4.2 days (100 h). This duration is considerably smaller than the 40 days (960 h) reported in Table 1 of (Collon, Kutschera et al. 2004).

Measurement of older water samples is considerably more challenging due to the reduced concentration of ^{39}Ar from radioactive decay. We consider now measurement of samples with

ages of 250 and 500 years. Such samples could be encountered, for example, when investigating possible over-exploitation and/or contamination of moderately deep aquifers. For these samples, Table 5 lists the reduced sample count rates and increased counting times required for 10% precision.

Table 5. Sample Count Rate and Time Required to Age-date Water with 10% Precision from a 700-mL Sample Operating in a Single Gas Proportional Counter

Water Age (y)	Sample Count Rate (cpd)	Counting Time (d)
0 (surface)	112	2.5
250	59	8
500	31	32

The counting times in Table 5 are reasonable targets for measurements in the shallow underground laboratory, but an initial survey of the environmental science community revealed a dearth of interest in measuring ³⁹Ar at this time. Engagement is ongoing and interest may exist if low-cost measurement options are possible.

3 Ice Core Dating

Ice cores drilled from Earth's ice sheets and glaciers are an indispensable source of paleoclimatic data. These records, depending on location, can extend back in time for hundreds of thousands of years and allow us to expand our knowledge of past climate change from the limited amount provided by direct measurements over the last 150 years. Currently the longest core is from EPICA (European Project for Ice Coring in Antarctica) at 800,000 years (Wolff, Barbante et al. 2010). Such time scales are ideal for studying long-term global trends and oscillations like ice ages. Ice core data continue to produce greater understanding of the extremely complex system that is our planet and enable us to more successfully predict future changes.

A key ingredient in the analysis of ice cores is to determine the age of the ice core as a function of depth. In general, four methods have been developed and refined over time to date ice cores. First, annual layers may be counted down until depths at which the annual signal is degraded, e.g., by pressure or diffusion of isotopic tracers. For example, one of the most commonly used annual layers is caused by the isotopic fractionation between H_2^{18}O and H_2^{16}O that occurs during evaporation and during the formation of precipitation. Since the amount of fractionation is temperature dependent, the seasonal temperature cycle translates into a seasonal isotopic concentration cycle preserved in the ice core. In other words, this method uses annual ice layers that are analogous to tree rings in dendrochronology. This method is sometimes meaningful up to several thousand years.

A second method uses independently dated events that leave distinguishing features in the ice. A large volcanic eruption is the typical example where ash and acidic precipitation create an easily recognizable layer. Obviously, this method critically depends on the reliability of the independent dating of the event. This method is often used as a check on the accuracy of other dating schemes.

Ice flow models also attempt to predict the relationship between depth and age. Since this third method involves relatively large uncertainties, it is typically only used when other methods are insufficient. For deep cores, the uncertainty is especially large due to the highly exponential character of the age-depth relationship caused by the ice's extreme compaction and deformation.

The natural decay of radionuclides trapped in the ice provides a fourth method. Dating with radioisotopes is crucial for establishing well-characterized ages past the dating range provided by counting annual layers (typically applicable for the youngest few millennia). Many isotopes have been investigated for this purpose, each applicable to a different dating range depending on half-life and source term input function. The ages potentially covered vary as a function of isotope from a few years to hundreds of thousands of years before present (ybp). Table 6 lists some of the radionuclides used in ice core dating, along with relevant information for understanding their application. The list is ordered by ybp for which the isotopes are effective.

Table 6. Isotopes Present in Ice Cores

Radionuclide	Half-life (years)	Source	Dating Range (ybp)
¹⁴ C	5730	weapon testing	0 – 50
³ H	12.3	weapon testing/ cosmogenic	0 – 100
²¹⁰ Pb	22	radon progeny	0 – 150
³² Si	144	cosmogenic	20 – 1,000
³⁹ Ar	269	cosmogenic	30 – 3,000
¹⁴ C	5730	cosmogenic	400 – 5 x 10 ⁴
⁸¹ Kr	2.13 x 10 ⁵	cosmogenic	>2 x 10 ⁴
³⁶ Cl	3.01 x 10 ⁵	cosmogenic	>6 x 10 ⁴
²⁶ Al	7.17 x 10 ⁵	cosmogenic	>10 ⁵
¹⁰ Be	1.36 x 10 ⁶	cosmogenic	>2 x 10 ⁵

Tritium and radiocarbon methods are well established. But because of a plateau in the calibration curve for radiocarbon between 50 and 350 ybp, a time gap exists that is potentially filled by the radionuclides ³²Si and ³⁹Ar (Morgenstern and Fifield 2009). Both these isotopes have very small concentrations and thus require special measurement techniques such as low-background decay counting or accelerator mass spectrometry (AMS).

For ice core dating, there is an additional key constraint: a typical sample contains of ~ 1 kg ice. This sample size is a consequence of the targeted elapsed time duration over the sample. In deep cores, a millimeter segment corresponds roughly to a year of accumulation; in shallow cores, a year corresponds to a length closer to a centimeter. Since core diameters are ~ 10 cm, a kilogram of ice covers a time span of 10 to 100 years (depending on the depth of the segment). Larger samples are possible, but only with the concomitant loss of time resolution.

³⁹Ar has been shown to reproduce the correct dates for ice cores with known ages (Loosli 1983), though in this case, the spatial resolution of ~100 m corresponds to a sample size of ~1000 kg. A calculation for the standard 1-kg sample (small enough to provide adequate dating resolution) shows that it is too small to make decay counting feasible within a reasonable amount of time. For example, assuming the ³⁹Ar concentration present is equal to the level in fresh surface water equilibrated with the atmosphere (see previous section), the specific activity of ³⁹Ar is ~ 10⁻⁶ Bq/kg. Therefore, a 1-kg ice sample counted over a month produces an average of 3 decays.

In the case of ³²Si, the specific activity is an order of magnitude larger than that of ³⁹Ar, but decay counting remains infeasible. A kilogram of ice typically has between 10,000 and 50,000 atoms of ³²Si (Morgenstern and Fifield 2009). Assuming the high end of this concentration range, a month of observation produces 20 decays. Measuring this concentration with 10% precision requires at least 10² counts and thus requires more than 5 months of measurement time.

AMS uses small samples and, though challenging, has successfully measured the low concentration ratios, e.g., $^{39}\text{Ar}/\text{Ar} = 10^{-15}$, of both these isotopes (Morgenstern, Keith Fifield et al. 2000) (Collon, Kutschera et al. 2004).

In summary, even for the shorter half-life isotopes, which give a relative advantage to decay counting, the limited amount of sample makes decay counting infeasible. Though difficult to perform, AMS is the default option for measuring radionuclides with such low concentrations in ice cores.

4 ^{22}Na Analysis for Dating Young Water

^{22}Na is a cosmogenic radioisotope that has significant untapped potential for dating young surface or ground water (Leonard, Grinberg et al. 2008). Cosmic rays produce the current level of environmental ^{22}Na in Earth's atmosphere. Specifically, ^{22}Na has origins primarily in the stratosphere by spallation between secondary cosmic rays and atmospheric argon. A large amount of ^{22}Na was created during nuclear weapon testing in the early 1960s although this inventory has now decayed enough (due to ^{22}Na 's short half-life of 2.6 years) so that cosmogenic production dominates. Thus ^{22}Na provides a steady-state tracer, avoiding the dating complications encountered when utilizing bomb-produced tritium for determining the age of young waters.

Atmospheric sodium precipitates onto the terrestrial surface—either with moisture or in dry form—where it can dissolve in surface waters. Because sodium ions are conserved in water solutions, the ^{22}Na concentration of a water parcel may be used to “date” the water, i.e., determine the time since the water has been in contact with the surface.

Fleishman provides a review of various attempts to use ^{22}Na as chronometer for young water ((2008; Fleishman 2008)Fleishman (D.G 2008)2008. In summary, the ^{22}Na dating method was first attempted in the early 1970s during investigations of a number of Northwestern Russian basins. A large amount of bomb-produced ^{22}Na was found to be present although this did not exclude obtaining meaningful results since sufficient knowledge was gained about the relevant atmospheric fallout of ^{22}Na . Next, studies from the 1980s demonstrated that the bomb-produced ^{22}Na , consistent with predictions, had decayed significantly below the cosmogenic concentration by the mid-1980s. Since the steady-state cosmogenic level has been reached, a number of papers reported ^{22}Na dating including results for young water from the largest lake in Europe, Lake Ladoga, as well as for the largest lake in Japan, Lake Biwa (Sakaguchi, Ohtsuka et al. 2005). Most recently, results have been reported for waters in the Caucasus Mountains (Nevinskii, Tsvetkova et al. 2004) and for ground water from Daisen Volcano, Japan (Inoue and Komura 2007).

Water dating with ^{22}Na usually involves low concentrations, on the order of tens of mBq per cubic meter of water. A typical sample preparation involves concentrating the sodium, along with other cations, from a large volume of water, e.g., through the use of an ion exchange column. The concentrate is then evaporated to dryness and the sodium chemically isolated. Most importantly, ^{40}K must be removed to avoid interference with the 1274.5-keV gamma-ray peak that serves as the signature for ^{22}Na . The final sample may then be formed into a shape consistent with the detector's geometry.

To gauge the challenge of measuring ^{22}Na , we present the following sensitivity estimate based on decay counting with one of our high-purity germanium 7-crystal arrays. The detection method sums the individual crystal energies and counts the number of events in a narrow band around the 1274.5-keV gamma ray. We assume the detector's absolute efficiency is 5% for the

full-energy peak at 1274.5 keV after summing events from all seven crystals. This isotope also emits a positron whose subsequent coincident gamma rays could be analyzed, but we do not consider this signature here.

To begin, we calculate the counting time for a sodium sample obtained from a 500-L volume of water with a ^{22}Na concentration of $30 \mu\text{Bq/L}[\text{H}_2\text{O}]$ characteristic of the values recently measured in the Lake Biwa system (Sakaguchi, Ohtsuka et al. 2005). We define the counting time as the time required to measure the sample concentration with 10% precision. Since sodium extraction yields can be close to unity, e.g., 98% in the Lake Biwa study, we will assume a 100% yield. We also calculate counting times for 500-L water samples where the water is 5 or 10 years old with an original ^{22}Na concentration equal to the above value.

As an example, we consider 5-year-old water where the sample count rate (R_{sample}) is:

$$\text{Equation 4: } R_{\text{sample}} = V \times A_{\text{specific}} \times \varepsilon$$

where V is the sample volume, A_{specific} is the sample's specific activity, and ε is the counting efficiency.

For the case of 500 L of water with a ^{22}Na concentration of $30 \mu\text{Bq/L}$, the count rate is approximately 17 cpd. The empirical background rate in the region of interest is 13 cpd. This leads to a counting time of 25 days. Table 7 lists calculated counting times for a variety of ages.

Table 7. Times Required to Measure ^{22}Na Concentration with 10% Precision. The calculation assumes 500 L of water with an initial ^{22}Na concentration of $30 \mu\text{Bq/L}$.

Water Age (y)	Counting Time (days)	
	$\varepsilon = 5 \%$	$\varepsilon = 15 \%$
0	1.9	0.58
5	10	2.9
10	86	21

The ^{22}Na signature is one that is ripe for exploitation by gamma-ray spectrometers in the shallow underground laboratory, but the unique use of ^{22}Na as a natural radiotracer limits its applicability. Potential opportunities to perform ^{22}Na measurements should be explored throughout the course of the initiative, but an initial survey of the environmental science community did not reveal any active work on this isotope.

5 Tritium Enhances ^{14}C Dating to Understand Carbon Stability in Soils

Soil contains a huge pool of organic carbon and an understanding of the carbon in soil is required to assemble a comprehensive functional characterization of global carbon cycling. Despite its importance, large knowledge gaps remain in terms of such fundamental questions revolving around components in soil undergo long-term storage, what components are quickly degraded and released from the systems, and what factors govern fluxes through these two fates. Deploying a dual age-dating approach on different fractions of organic matter extracted from different soils will provide unparalleled insights into the stability of different soil organic matter and contribute to new foundations for modeling soil carbon cycling processes.

Co-measurement of ^{14}C and ^3H in different classes (i.e., lipids, carbohydrates, proteins, fulvics, humics, water soluble, etc.) of soil organic compounds is uniquely situated to address the fundamental roles that chemical structure and physical protection play in organic carbon fate. The soil carbon pools regarded as highly stable can be deceptively dynamic. A number of experiments in which labeled carbon is added to soils consistently show key pools, such as total microbial biomass carbon or seemingly recalcitrant carbon, changing little in size, yet rapidly incorporating fresh carbon. Isotopic analysis can help assess whether the continuity of pool size is sufficient for describing a class of carbon as stable or if there is a greater mechanistic understanding to be gathered by identifying discrete carbon compounds that persist intact in soils for decades to centuries. Thus, a rigorous analysis of soil carbon that reports the size of a carbon pool and also indicates the stability of that pool is greatly needed.

Carbon-14 dating provides one-dimensional data to determine the age of carbon within different compound classes. The ^{14}C date alone, however, records only the carbon's fixation from atmospheric CO_2 and deposition in the soil and may not reveal subsequent degradation or enzymatic turnover of the carbon into another pool; thus on its own ^{14}C dating cannot effectively address absolute stability of different classes of soil carbon. Incorporation of ^3H dating will further elucidate activity of different carbon compounds. Continuous influx of soil water, with associated background ^3H could continuously alter the ^3H age of different labile compounds if those compounds are interacting with the water pool through bond formation. Incorporation of hydrogen from soil water into an organic compound could result from enzymatic or abiogenic hydrolysis and would shift the ^3H age of the compounds towards that of the water. Resulting divergence between ^{14}C and ^3H ages would indicate a carbon pool is actively being cycled versus being completely recalcitrant. However, if a pool, or chemical component were to exhibit synchronous and old ^{14}C and ^3H ages, one could conclude that that carbon pool is indeed chemically very stable. Given that soils are continuously bathed with water, dual dating of ^{14}C and ^3H could identify how dynamic physically protected carbon is, and whether this is physical or chemical protection (i.e., completely controlled by the nature of the chemical structure or more independent of the chemical form and more dependent on impact from location in the soil). ^3H could also be used to identify pool turnover rates in seemingly

persistent carbon pools. This information would powerfully enhance our current understanding of carbon stability in soils and in turn, improve current modeling efforts and our ability to predict the long-term disposition of carbon in soils.

We recommend development of methods for converting specific classes of soil organic matter to chemical species suitable for dual ^{14}C and ^3H measurement by PNNL's ultra-low background proportional counters. Once suitable methods are demonstrated, this capability should be applied to organic matter extracted, separated, and purified from several organic rich soils. Elucidation of the organic matter recalcitrance in these soils will both highlight the utility of dual isotope measurements and provide insight to basic soil function and its impact on global carbon cycling.

Compilation of the dual ^{14}C and ^3H ages of different soil organic carbon components will help establish the nature of each of these pools (recalcitrant versus labile, dynamic versus static, etc.). Expected ages for each class of compounds could fall into the categories outlines in Table 8. Very important will be the synchronous versus divergence between the ^{14}C and ^3H dates. Mutual agreement between the two dates will imply a truly recalcitrant carbon pool with long-term, stable carbon storage. Divergence between the two dates with a younger ^3H age will infer chemical reactivity of the materials in that pool and would indicate a pool vulnerable to enzymatic/microbial exploitation or abiogenic organic matter maturation.

Table 8. Interpretation of Dual ^{14}C and T Dates for Compound Classes

Time Scale	T-Decadal	T-Century	T-Extinguished
C-Decadal	Young pool; compare with the prevailing opinion on the stability of this pool. High organic matter turnover in this pool via biological or abiogenic processes.	A labile C assemblage minimally reacting with new water. One reaction direction (mineralization, not accrual).	Interaction of organic matter with 'ancient' water, i.e., melting permafrost or an isolated reservoir.
C-Century	Recycling of 'old' carbon in the presence of fresh surface water, possible reworking by microbial activity.	Chemical recalcitrance.	Permafrost? Ancient water?
C-Millennial	Stable C that is interacting with T cycling from contemporary water.	Chemical recalcitrance Long-term storage forms.	Ancient system; ancient pool. Very stable.

6 Measurement of Radioisotopes Released From Fukushima

There is a long history of using radioisotopes to study a variety of environmental processes. The recent release of radioisotopes from the nuclear power facilities in Fukushima, Japan, prompted a review of the current measurement practices applied to the measurement of actinides and radioactive fission products in the environment. Our focus rests on actinides and fission products. A full description appears in the manuscript (Warren and Runkle 2012). We summarize the results of this study here.

As a case study, we consider here one isotope that could significantly benefit from radiometric capabilities: ^{238}Pu . One aspect of interest for ^{238}Pu compared to the other Pu isotopes is that its significantly shorter half-life enables age dating. Currently, mass spectrometry is the method of choice for the other plutonium isotopes. With mass spectrometry, ^{238}U , which is often far more abundant than ^{238}Pu , creates an interference. As a result, ^{238}Pu is often assayed using alpha counting techniques. The difference in measurement techniques for ^{238}Pu versus the other Pu isotopes raises issues about systematic consistency across the isotopes. Another challenge is that, to reliably conduct these alpha measurements, ^{241}Am must first be removed from the sample because it has a similar alpha energy as ^{238}Pu (5.578 MeV for ^{241}Am compared to 5.593 MeV for ^{238}Pu). The development of a radiometric system that could both assay ^{238}Pu without first removing ^{241}Am and simultaneously measure other Pu isotopes would be a significant advancement.

There are several observations to be drawn about the plutonium isotopes and ^{241}Am . ^{238}Pu and ^{241}Am generate α particles that are within 15 keV of each other, while ^{239}Pu and ^{240}Pu generate α particles that are within 12 keV of each other. Only ^{241}Am generates a photon with energy greater than 50 keV. The Auger electrons are likely to be as large or larger than the x-ray components, but all of the x-ray/Auger energies are less than 20 keV. While the most intense signature for three of the four isotopes is a single alpha particle, that is not true for ^{241}Am . Each of these signatures has the potential to be used for radiometric assay of these isotopes.

Traditional alpha spectroscopy detectors for measuring ^{238}Pu include proportional counters and silicon detectors. These detectors have a full-width half maximum resolution of 10 to 15 keV, so that they are not able to cleanly differentiate ^{238}Pu from ^{241}Am or ^{239}Pu from ^{240}Pu . As a result, chemical separation of Am is necessary to measure ^{238}Pu , and it is common practice to assay the sum of ^{239}Pu from ^{240}Pu . However, once the Am is separated from the Pu, these detectors have been used to measure ^{238}Pu activity on the scale of ~ 0.1 mBq (9 decays/day) over 7 days. Any new detector technology will need to achieve a similar level of sensitivity but should also be able to discriminate between ^{238}Pu and ^{241}Am . The low activity of the sample forces one to design a detector focused on the most likely signatures and the highest possible detection efficiency.

We conclude that a fairly high level of sophistication is currently used to conduct plutonium isotopic measurements, ranging from various flavors of mass spectrometry to low-background

gamma-ray spectroscopy. However, one remaining weakness is the assay of ^{238}Pu in environmental samples. Two broad concepts have the potential to address this weakness, namely the use of coincident radiometric techniques and higher resolution alpha spectroscopy that is suitable for the high sample volume of environmental measurements. While the detector concepts were focused on the assay of ^{238}Pu , ^{241}Am , ^{239}Pu and ^{240}Pu , it is quite likely that a detector built to address those needs could be applied to other alpha-emitters, such as those in the ^{238}U and ^{232}Th decay chains. The next step is to conduct radiation transport modeling of these concepts.

7 References

- (1960). Woods Hole Oceanographic Institution atlas series. Woods Hole, Mass. :, Woods Hole Oceanographic Institution.
- Collon, P., W. Kutschera, et al. (2004). "Tracing Noble Gas Radionuclides in the Environment*." Annual Review of Nuclear and Particle Science **54**(1): 39-67.
- D.G, F. (2008). "Cosmogenic ^{22}Na as an index of the residence time of water in freshwater basins: a review." Journal of Environmental Radioactivity **99**(8): 1203-1215.
- Fleishman, D. G. (2008). "Cosmogenic ^{22}Na as an index of the residence time of water in freshwater basins: a review." Journal of Environmental Radioactivity **99**(8): 1203-1215.
- Hamme, R. C. and S. R. Emerson (2004). "The solubility of neon, nitrogen and argon in distilled water and seawater." Deep Sea Research Part I: Oceanographic Research Papers **51**(11): 1517-1528.
- Inoue, M. and K. Komura (2007). "Preliminary application of low-background gamma-spectrometry to volcanic ground water." Journal of Radioanalytical and Nuclear Chemistry **273**(1): 177-181.
- Leonard, D. S., P. Grinberg, et al. (2008). "Systematic study of trace radioactive impurities in candidate construction materials for EXO-200." Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment **591**(3): 490-509.
- Loosli, H. H. (1983). "A dating method with ^{39}Ar ." Earth and Planetary Science Letters **63**(1): 51-62.
- Morgenstern, U. and L. K. Fifield (2009). "Silicon-32 as a tool for dating the recent past." Quaternary Geochronology **4**(5): 400-405.
- Morgenstern, U., L. Keith Fifield, et al. (2000). "New frontiers in glacier ice dating: Measurement of natural ^{32}Si by AMS." Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms **172**(1-4): 605-609.
- Nevinskii, I. O., Tsvetkova, T. V., et al. (2004). "Low-Background Measurements of ^{22}Na in Natural Waters of Krasnodar Krai." Atomnaya Énergiya **96**(1): 6.
- Sakaguchi, A., Y. Ohtsuka, et al. (2005). "Cosmogenic radionuclide ^{22}Na in the Lake Biwa system (Japan): residence time, transport and application to the hydrology." Earth and Planetary Science Letters **231**(3-4): 307-316.
- Warren, G. A. and R. Runkle (2012). "New Concepts for Radiometric Measurements of Environmental Samples Containing Fission Products and Actinides." MARC IX Conference
- Wolff, E. W., C. Barbante, et al. (2010). "Changes in environment over the last 800,000 years from chemical analysis of the EPICA Dome C ice core." Quaternary Science Reviews **29**(1-2): 285-295.