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Title: Comparison of the sensitivity of 236U measurements in environmental samples by MC-ICP-MS and ATONA based high precision U TIMS measurements.

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NA-22 Technical Report

Project Title: **Exploring high-precision uranium isotopic analysis with new, high-sensitivity amplifiers**

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Principal Investigator: Jeremy Inglis

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Report Title: **Comparison of the sensitivity of ^{236}U measurements in environmental samples by MC-ICP-MS and ATONA based high precision U TIMS measurements.**

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Executive Summary

The ATONA project is focused upon exploring the improvements in uranium isotope ratio measurements by thermal ionization mass spectrometry (TIMS) provided by a new, capacitor-based, amplifier technology. These “ATONA” Faraday amplifiers (Isotopx Ltd, UK) promise accurate, low-noise measurements of very small signals (< 1 femto-amp) in a traditional Faraday cup, which was only previously possible using an ion counter. This report outlines a series of experiments that were performed to assess the performance of the system in samples that test our rapid analysis procedures, and then compare the results against other mass spectrometry techniques currently available for environmental analyses. The following major goals were achieved: (1) illustrated the importance of ^{236}U measurements for the screening and analysis of environmental samples; (2) improved sensitivity for ^{236}U, and then identified ^{236}U in the 4350B standard at ultra-trace levels (3) Provided comparison of the ^{236}U sensitivity to multi-collector inductively coupled mass spectrometry techniques (4) Illustrated high TRL for the ATONA based measurement technique. This completes the reporting requirements for task 4 in the project LCP and highlights the utility of the system to make highly sensitive ^{236}U measurements in programmatically relevant sample matrices and at relevant uranium concentrations.

Introduction

Modern international nuclear safeguards, treaty monitoring, and non-proliferation missions largely rely on environmental soil, sediment and air particulate samples to identify and characterize source inputs of nuclear material into the environment. Uranium remains one of the main analytes of interest for these measurements, as the isotopic composition of uranium can provide useful information on the enrichment, fuel composition, reactor type or fission process of the source. Natural sources of uranium contain three main isotopes ^{234}U, ^{235}U & ^{238}U, and display a relatively uniform ^{238}U/^{235}U composition ranging between 137.792 and 137.961[1], ^{234}U is more variable[2], due to its increased mobility in the environment[3, 4]. By contrast U released from nuclear fuel cycle processes can have widely variable ^{238}U/^{235}U ratios resulting from either ^{235}U enrichment processes or due to changes resulting from neutron reaction processes in nuclear reactors. These contrasts in isotope composition between natural and anthropogenic uranium can be exploited to identify and help characterize outputs from nuclear facilities using both bulk and particle analysis methods[5-7].

The identification of the possible source inputs of anthropogenic uranium in bulk environmental samples is complicated by the ubiquitous occurrence of natural uranium in the environment, that can dilute the source's true isotope composition. Relatively small inputs of U from the highly depleted or enriched isotopic end members of the nuclear fuel cycle can easily perturb the ^{238}U/^{235}U isotope composition of natural uranium in soils and sediments[8-10]. When, however, the uranium released from a site closely matches the natural isotope composition, as is the case with some spent fuels, then the major isotopes may be perturbed to a such a low degree that it may not be possible to identify the input. To illustrate this problem, in Fig.1 we model two scenarios that mix anthropogenic U input with a soil sediment. In the first scenario (Fig. 1A), we model the rather extreme case of mixing weapons test fall-out with the natural uranium contained in soil sediments. Using data from Eppich et al.[11], we model first-order estimates on the amount of fall-out required to produce a 5% deviation in a natural ^{235}U/^{238}U ratio. We assume uranium a concentration of 2.5 ug/g (2.5 ppm)in the soil, the average concentration of continental sediments, and then estimate a range of possible fallout end members with enriched uranium, noting that our range spans the average from Eppich et al.[11] for glassy fallout from a uranium-fueled device of 20 ug/g (20 ppm) with a ^{235}U/^{238}U ratio of 3 (values in the middle of the range of concentration and isotopic composition described in Eppich et al.[11]). The model results indicate that only a minor amount of fallout—0.006%—is required to produce a 5% deviation. To understand this input more broadly, this amount would equate to ~ 60 mg of fallout per kg of sediment. For the second scenario (Fig. 1B), we model input of a uranium source associated with release of spent VVER-400 reactor fuel, using data from the SFCOMPO 2.0 database[12] for fuel from the Novovoronezh-4 reactor (assembly 13602496)[13]. Inputs were modelled for air particulate 'fallout' with U concentrations ranging from 5-50ppm and an average ^{235}U/^{238}U fuel composition of 0.00853. Even when considering a relatively high U particulate concentration of 50 ppm, 10s of grams of input per kg of soil are required to perturb the natural ^{235}U/^{238}U signal to any degree and would be unlikely to occur in all but the most serious of release events.

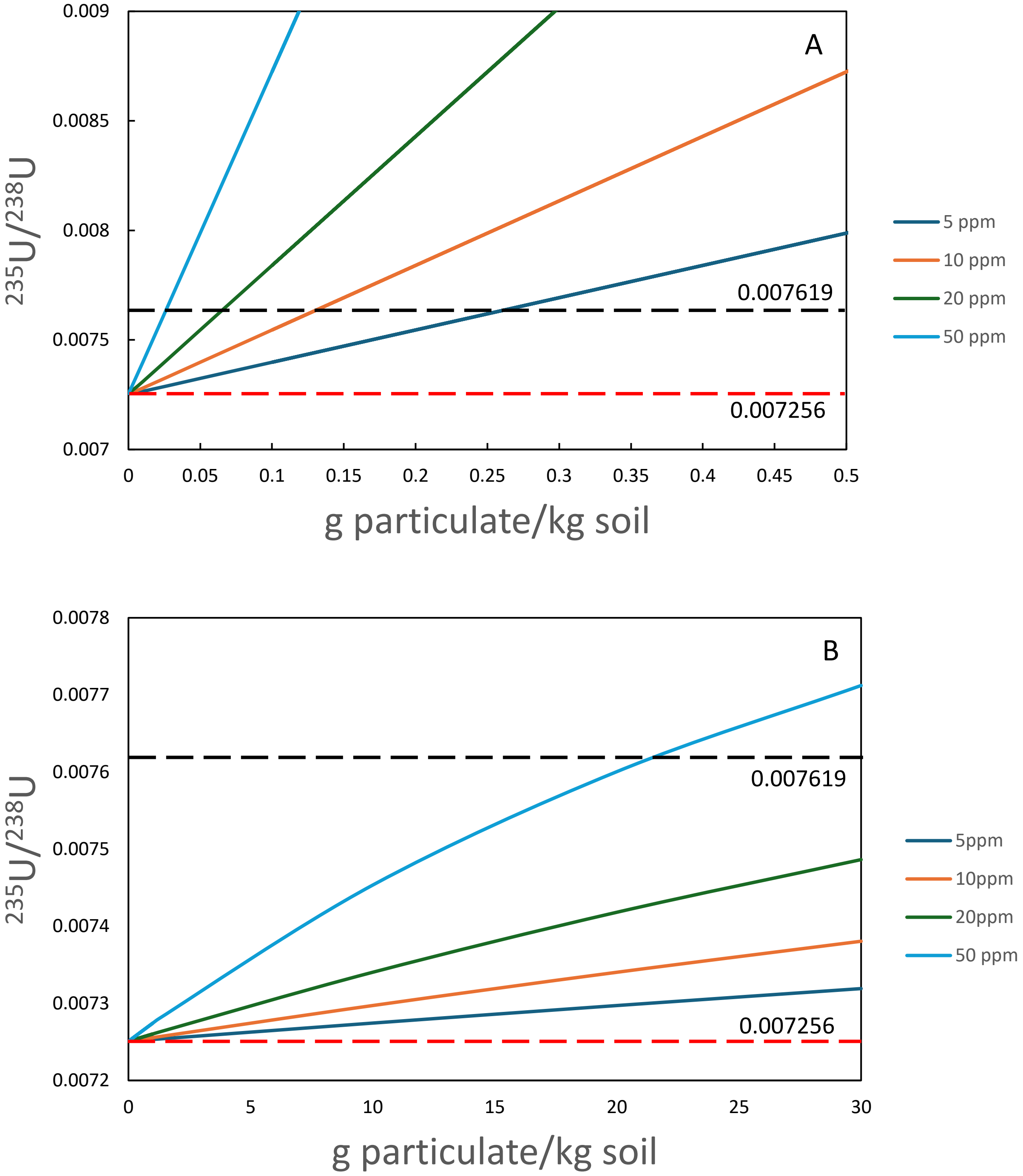

Figure 1. Mixing curve model showing the variation in the resulting $^{235}U/^{238}U$ isotopic composition in an environmental sample post-mixing between a natural uranium end member ($^{235}U/^{238}U = 0.00725$ and [U] = 2.5 ppm) and an anthropogenic end member. ***Panel A*** *shows mixing of enriched fallout particulate ($^{235}U/^{238}U = 3$) plotted as a function of the grams of the fallout material per kg of soil.* ***Panel B*** *estimates mixing from the slight enriched fallout ($^{235}U/^{238}U = 0.00853$) associated with the release of spent fuel particles. Each curve represents a different first-order model calculation with the uranium concentrations in the fallout material varying between 5, 10, 20, and 50 ppm*

Importance of ^{236}U: An obvious solution to the dilution of anthropogenic uranium in the natural environment is the identification of non-natural ^{236}U[14-17] . Only extremely small amounts of ^{236}U form naturally, such that natural $^{236}U/^{238}U$ ratios are typically in the range of 10^{-10}– 10^{-14}, representing a ^{236}U concentration of only a few tenths of a fg per g in environmental samples[17]. However, significant amounts of ^{236}U can be produced anthropogenically by thermal neutron activation of ^{235}U during nuclear fission, and a lesser amount by the $^{238}U(n/3n)^{236}U$ nuclear reaction. When input into the environment any anthropogenic U that contains appreciable ^{236}U can easily override the low $^{236}U/^{238}U$ of natural U and can provide a clear indicator of non-natural input, even when no $^{235}U/^{238}U$ perturbation is observed. Such ^{236}U signatures in bulk sample aliquots could be used to help identify samples for further characterization and isolation of their potential anthropogenic signatures, by techniques other than bulk analyses. For example, in fig. 2 we consider examples of input of UO_2 spent fuel particles with different amounts burnup into an environmental sediment sample and use the measured $^{236}U/^{238}U$ ratio of the bulk sample to estimate the number of UO2 particles contained per gram of sediment. In both these cases no perturbation in the $^{235}U/^{238}U$ of the sample would be observable, but 100s-1000s of particles could be present. Modelled estimates, such as these, can be used to identify potential samples for particle pre-concentration from the bulk sample. In addition, U in its oxidized form is quite soluble in alkaline solutions [18]. As a result, loosely bound UO_2, has the potential to be removed by partial leaching methods and could provide a further pathway to characterize the isotopic signature of the particulate, especially in situations where the particulate is difficult to isolate or measure because either (1) on the sub-micron scale, and therefore difficult to measure on a particle-by-particle based scale or (2) loosely bound to the soil or sediment matrix.

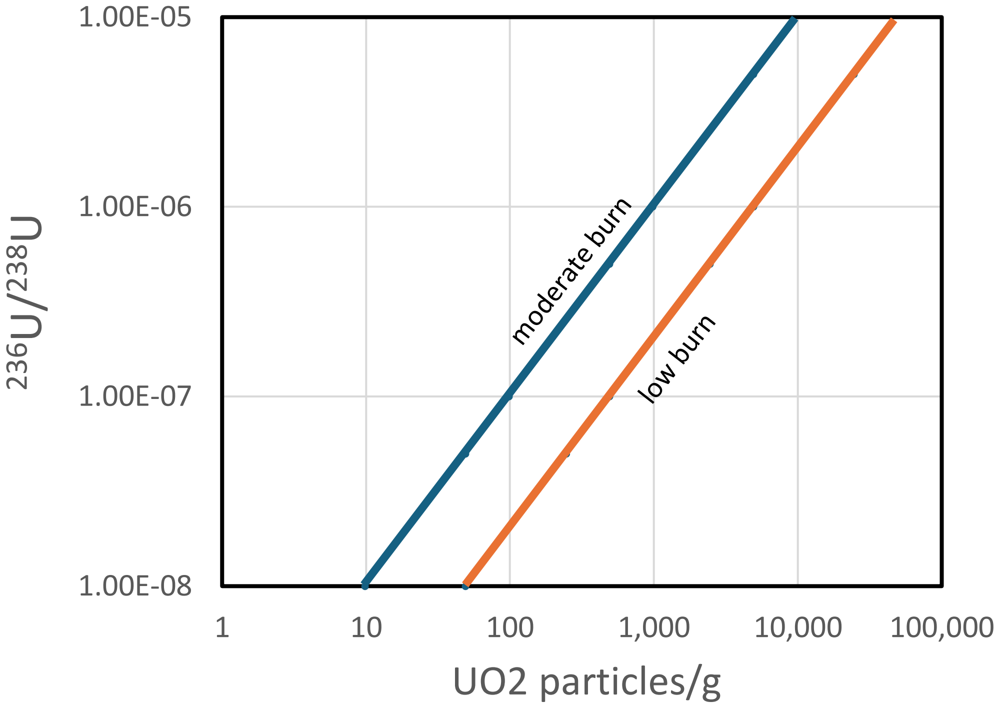

Figure 2. Model estimates of the number of UO_2 spent fuel particles expected within a gram of sediment for a given $^{236}U/^{238}U$ soil ratio. Blue line represents a moderate-burn scenario (^{236}U abundance = 0.05%). Orange line represents a low-burn scenario (^{236}U abundance = 0.01%). For the model the sediment was assumed to have a natural uranium isotope composition and uranium concentration of 2.5 ug/g. Particles were assumed to have a UO_2 composition with diameter of 1 µm.

Measurement of ^{236}U: Detection of ^{236}U in environmental samples represents a significant technical challenge to the mass spectrometry methods currently used in uranium isotope analyses in environmental samples, including accelerator mass spectrometry (AMS), inductively coupled plasma mass spectrometry (ICP-MS) and thermal ionization mass spectrometry (TIMS). Accelerator mass spectrometry (AMS) remains the benchmark for highly sensitive ^{236}U measurements[14, 17] but remains a highly specialized technique with limited sample throughput. More recently, highly sensitive triple quadrupole inductively coupled based (QQQ – ICP MS) techniques have been developed[15, 16], that promise rapid analyses of U with $^{236}U/^{238}U$ detection limits on the order of 10^{-11}. An important drawback of these current QQQ-ICP-MS based measurements is that they are limited by a need for to introduce high concentrations of U into the instrument. This limits the technique to samples where either (1) the samples contain sufficiently high concentrations of U to liberate several micrograms of U for analysis or (2) or in the case of sample types with low U concentrations, there is sufficient quantity of material to liberate and purify enough uranium for an accurate measurement. Likewise, although TIMS measurements can yield detection limits on the order of 10^{-10}[19], this level of sensitivity has only been achieved using filament loads > 1ug, limiting the sample concentrations that can be analyzed.

Clearly, any enhancements in our ability to measure ^{236}U at lower sample concentrations could aid in our capacity to fully characterize the uranium isotope composition in materials with low uranium concentration, or in materials where the bulk sample size limited. Increased uranium measurement sensitivity could also be useful when there is a desire to minimize the aliquot size of the uranium fraction in a bulk sample, providing the option to perform other analyses from the sample. One recent technological advance that can be applied to uranium isotope measurements by thermal ionization mass spectrometry is the ATONA capacitive transimpedance amplifier developed by Isotopx Ltd.[20-23]. We have previously reported on the ability of ATONA system to make rapid and precise measurements of the major isotopes of uranium (^{234}U, ^{235}U, ^{238}U)[1]. Here we focus on the use of the ATONA based TIMS measurements on environmental samples to achieve improved ^{236}U measurement sensitivity at concentrations not previously achievable by traditional TIMS based measurement techniques[24]. We then compare the sensitivity of the ATONA TIMS measurements against what can be achieved using current multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) instrumentation.

Materials and Methods:

Standards: This study presents data from test standards and environmental reference materials. Most of the data presented are for the assessment of ^{236}U measurement precision, using certified reference materials CRM 112A, C129A, and NIST 4350B. CRM 112A (originally NBS U960) is a natural uranium

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[1] See ATONA project technical reports for tasks 1 & 2 and Reinhard et al. 23. Reinhard, A.A., et al., *Application of ATONA Amplifiers to the Measurement of Uranium Isotopic Ratios by Thermal Ionization Mass Spectrometry.* Analytical Chemistry, 2024.

standard with no measurable ^{236}U, and therefore provides a test of the detection limit of the instrument. CRM 129-A is a uranium oxide assay and isotopic standard prepared in 1984. It has a natural uranium composition, with exception of ^{236}U which is slightly elevated with a $^{236}U/^{238}U$ ratio of 0.000000097 ±0.000000012, it provides a test of measurement precision and accuracy at low abundances of ^{236}U. NIST SRM 4350B, Columbia River Sediment, is an environmental standard originally certified by NIST in 1981 as an environmental radioactivity standard. NIST records and personal recollections from the sampling team[2] indicate that the standard was most likely collected in 1977 from Columbia River ~25 km upstream of the McNary Dam, near Juniper cliffs. This is ~100 km downstream of the Hanford reactor site, which is known to have released large amounts of radionuclides from 1944 to the early 1970's. The 4350B sediment standard represents an interesting sample to study for non-proliferation uranium measurements as ^{236}U has thus far not been identified in the standard, but previous studies indicate evidence for transuranic input from either ruptured fuels or neutron activated cooling water[25]. It is therefore likely that at least some ^{236}U was input into the environment along with these other transuranic nuclides, although at relatively low concentrations, such that the standard provides a significant challenge to ^{236}U measurement sensitivity in programmatically relevant sample matrices.

Dissolution and uranium purification of 4350B: Powder aliquots of the standard were weighed, dried at low temperature (typically 40 °C) following instructions on the certificates as necessary, and re-weighed. Then the samples were dry-ashed in a muffle furnace to 550 °C to remove organic matter. These materials were dissolved using standard hotplate-open Teflon beaker $HCl–HNO_3–HF–HClO_4$ methods employed in our laboratory [26]. After adding 0.5 ml HClO4 to each aliquot, they were dried at 200 °C and then 1-2 ml 7.5M HNO3 was added and dried at 110 °C. Samples were then redissolved in 1-2 ml of 7.5M HNO3 for column chemistry purification. The entire protocol consists of three separate anion exchange columns (AG1 × 4, 100-200 mesh) made from disposable transfer pipettes and 1 ml pipette tips packed with quartz wool. The following description is for samples containing < 20 ng of U. For samples with > 20 ng U, the separation uses the same steps but with the volumes of the resin and reagents doubled for the first two columns; the third column is the same for all sample sizes. The first column (1 ml of resin) is cleaned and conditioned with 2.5 ml Milli-Q water then 5 ml 7.5M HNO3. After sample loading, the column is washed with an additional 2 ml 7.5M HNO3. The U is eluted into a clean vial with 2 ml Milli-Q water, followed by 3 ml 1M HBr. Samples are taken to dryness under a lamp, dried in 4-6 drops of HCl at 100 °C, and redissolved in 0.5 ml HCl-H2O2 (≈ 0.1% H2O2) for loading onto column 2. The second column (0.5 ml of resin) is cleaned and conditioned with 1.5 ml Milli-Q water then 1 ml HCl-H2O2. After sample loading, the column is washed with 1 ml 8M HCl-H2O2, 0.5 ml 8M HCl-3M H2SO4, 1.5 ml 0.1M H2SO4, and 1.5 ml 6M HCl-H2O2. The U is eluted into a clean vial with 1 ml Milli-Q water, followed by 1.5 ml 1M HBr. Samples are taken to dryness under a lamp, and the residual H2SO4 is driven off at 250 °C. Next, samples are dried in 0.25 ml 7.5M HNO3 at 130 °C and redissolved in 0.25 ml 7.5M HNO3 for loading onto the final column. The third column (0.5 ml resin) is cleaned and conditioned with 1.25 ml Milli-Q water then 2.5 ml 7.5M HNO3. After sample loading, the column is washed with an additional 1 ml 7.5M HNO3. The U is eluted into a clean vial with 1 ml Milli-Q water, followed by 1.5 ml 1M HBr. The final U fractions are taken to dryness under a lamp, fluxed overnight in 1 ml 7.5M HNO3 at ≈ 50 °C, and dried a final time under a lamp. At this point, the samples are ready for TIMS analysis.

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[2] Kenneth Inn (NIST, retired) provided original notes on sampling location and year for the 4350B sediment [personal communication, Sept' 2024].

TIMS analysis: All uranium isotopic measurements presented in this study were performed on either an IsotopX Iso-probeT (LANL TIMS 1) or IsotopX Phoenix (LANL TIMS 2). Both instruments have been upgraded with new collector blocks and ATONA amplifier systems consisting of 9 moveable Faraday cups. Each instrument also features a rear secondary electron multiplier and rear Daly ion-counter positioned behind a wide aperture retarding potential (WARP) energy filter. The WARP acts as a filter for ions with disturbed energy, such as those resulting from the tailing from higher mass peaks. Energy filters such as the WARP can improve the abundance sensitivity of the TIMS instrument by over 2 orders of magnitude to < 0.1 ppm, measured at 1 amu either side of ^{238}U. In addition, both instruments have been outfitted with a 300L^{-s} turbo pump in the collector vacuum region to further improve the analyzer vacuum and abundance sensitivity. All filaments used in this study were made using zone refined Re ribbon (99.999% H. Cross Company). The samples were analyzed using a single center filament configuration and were loaded using a "graphite sandwich" technique, in which 1 µL of colloidal carbon (suspended in 18.2 MΩ water) is dried on the filament at 0.8 A, the 1 µL of sample solution is loaded and dried down at 0.8 A, then an additional 1 µL of colloidal carbon is loaded on top of the sample and dried down at 1.4 A prior to analysis.

Analyses were performed using our '^{236}U' static total evaporation technique[23] in which ^{234}U, ^{235}U and ^{238}U were measured on the ATONA detectors and ^{236}U was measured on the center SEM (**table. 1**). All samples were measured using the "total evaporation" technique (TE) in which the sample is run to exhaustion and the total number of counts collected at each mass is used to calculate U isotopic ratios. The total evaporation method corrects for mass fractionation by using time integrated isotopic ratios and assuming that the entire sample is volatilized from the filament. Ramping of the filament current was controlled using the TE control function built into the IsotopX Isolinx software, this feature ramps the filament(s) current up or down to maintain the ion beam intensity selected by the user for a particular mass (e.g. a 2 V ion beam on mass 238). For large samples (200 ng) a target intensity for the largest ion beam was between 1 V and 2 V based on the observed ion beam behavior during an analysis. The smaller (10 & 20 ng) samples were analyzed using the same TE technique however the target intensity for the largest ion beam (mass 238) was set to between 0.5 V and 1 V. This intensity was chosen to balance achieving a measurable ^{234}U signal (> 1500 counts per second [cps]) and extending analysis time to yield more measured ratios. Based on the modeling performed by LLNL an integration time of 30 seconds and baseline analysis time of 300 seconds were chosen to optimize detector noise and the total number of cycles collected.

Table 1. ATONA Collector Configuration used for measurements.

Collector	**Low 2**	**Low 1**	**Rear IC**	**High 1**	**High 2**
Isotope	233U	234U	236U	235U	238U
Collector type	ATONA	ATONA	SEM	ATONA	ATONA

MC-ICP-MS analysis: Sample solutions were analyzed by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) using either a Thermo Scientific Neptune Plus instrument (LANL) or Nu Plasma 3 instrument. Uranium samples, standards, and washes were introduced as 2% HNO3 solutions into the mass spectrometer. Uranium isotopic measurements were made using static multi-collection analysis routines. Acid blanks were measured before each sample using a 2% HNO3 wash solution (all samples and standards were blank-corrected). The mass bias corrections for sample measurements were performed using bracketing standards of CRM U010, a New Brunswick Laboratory (NBL) certified reference material. Detector gain calculations were made using NBL CRM U010 or SRM 960 (also named CRM 112-A). Energy filters (RPQs) were used to decrease the contribution of low mass tailing from 238U and 235U on 236U and 234U peaks, respectively. Tail calculations and corrections were performed by measuring four off-peak masses (-0.5, -0.35, +0.35, +0.5 amu away from peak center), fitting the points to an exponential curve, and subtracting the tail contribution from the measured signal.

Results:

CRM 112A: CRM 112A, believed to have a ^{236}U abundance considerably lower than TIMS detection limits, was used to the determined ^{236}U measurement sensitivity of the ATONA system (Fig. 3). Replicate analyses of CRM 112A, using aliquot sizes between 10-200ng, provided an average $^{236}U/^{238}U$ background ratio of $5.68\times10^{-9} \pm 1.3\times10^{-9}$ (K=1). This background ratio is believed to be primarily a function of the dark noise on the SEM detector, which remained stable throughout the analysis period. In addition, no appreciable difference in the $^{236}U/^{238}U$ background noise level was observed across the sample load sizes analyzed. A statistical detection limit for ^{236}U can be calculated from all the measurements using **Eqn 1,** adapted from McCroan and Keller 2006[27].

Eqn 1

$$L_D = 3\times\ L_C = t_{1-\alpha}(n-1)\times s(B_i)\times\sqrt{1+\frac{1}{n}}$$

In this equation $t_{1-\alpha}$(n-1) denotes the (1 – α) quantile of the student's t-distribution with n – 1 degrees of freedom for a 99% confidence level and s(B_i) is the standard deviation of the repeated background tests. 22 replicate background tests of the $^{236}U/^{238}U$ provide a standard deviation of 1.3×10^{-9}. This equates to a $^{236}U/^{238}U$ L_D of 4.04×10^{-9}.

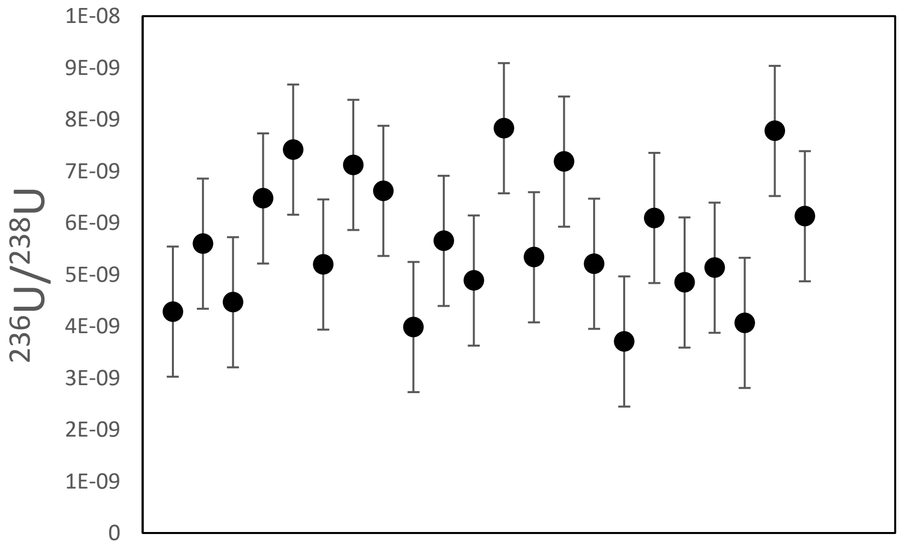

Figure 3. Replicate analyses of $^{236}U/^{238}U$ *ratio in CRM112-A measured on using the ATONA amplifiers, provides lower detection limit for* ^{236}U *measurements.*

CRM 129A: To provide a direct comparison of the ^{236}U sensitivity of the ATONA TIMS against MC-ICP-MS measurements, the team at Lawrence Livermore National Laboratory (LLNL) analyzed a series of 20 ng aliquots of CRM 129-A on their Nu Plasma 3 multi collector inductively coupled plasma mass spectrometer (MC-ICP-MS). In addition, further MC-ICP-MS measurements of CRM 129-A were performed at LANL, using a Thermo Scientific Neptune Plus instrument. These two instruments represent the current ICP-MS standard for environmental analyses of uranium at both LANL and LLNL. A 20ng aliquot was chosen to mimic the size of a reasonably representative environmental analysis sample. A 20ng sample size represents the lower end of the concentrations seen in many operational samples and could prove useful in minimizing uranium aliquot sizes from larger bulk samples. At these concentrations MC-ICP-MS instruments have a much higher ionization efficiency for uranium than thermal ionization mass spectrometers (TIMS). This results in the ICP-MS having an apparent advantage for measuring uranium, because more ions can be measured from a given sample size. However, ICP-MS instruments suffer from several disadvantages when it comes to measuring samples that have extreme differences in relative isotope abundances like the $^{236}U/^{238}U$ in CRM 129-A. MC-ICP-MS have relatively poor vacuum compared to a TIMS which results in significant peak-tailing from large ion-beams like ^{238}U tailing onto mass 236 and the plasma ionization source generates more poly-atomic interferences than a thermal ionization source. These limitations are evident in Figs. 4 & 5, where we compare TIMS ATONA measurements of 129-A to those run by MC-ICPS-MS. In Fig. 4 we compare LLNL data, note the nearly 2 orders of magnitude higher estimated limit of detection (LOD) for the MC-ICP-MS relative to the TIMS equipped with ATONA amplifiers. In addition, note how the ATONA $^{236}U/^{238}U$ data plotted in Fig. 4 are in excellent agreement with the certificate value. Interestingly, Fig. 4 shows that the LLNL MC-ICP-MS data all overlap within uncertainty with the certificate value, however the uncertainties reported are as large as 66% (2 RSD). More importantly all the CRM 129-A data measured by MC-ICP-MS fall below the calculated limit of detection (LOD) of the LLNL MC-ICP-MS technique. This means that if measured by MC-ICP-MS these samples would be reported as non-detects for ^{236}U rather than having a very small but measurable $^{236}U/^{238}U$ ratio if the sample were analyzed using the ATONA TIMS method. In Fig. 5 we compare ATONA data against similar MC-ICP-MS measurements performed on a Thermo Neptune at LANL. Interestingly, the Neptune data clusters quite tightly around an average value of $3.3x10^{-7}$, but shows a significant positive bias relative to the certificate value. We interpret this bias to be a measurement of the detection limit of the instrument, indicating that the Thermo Neptune does not have the required sensitivity to detect ^{236}U at level below $3x10^{-7}$.

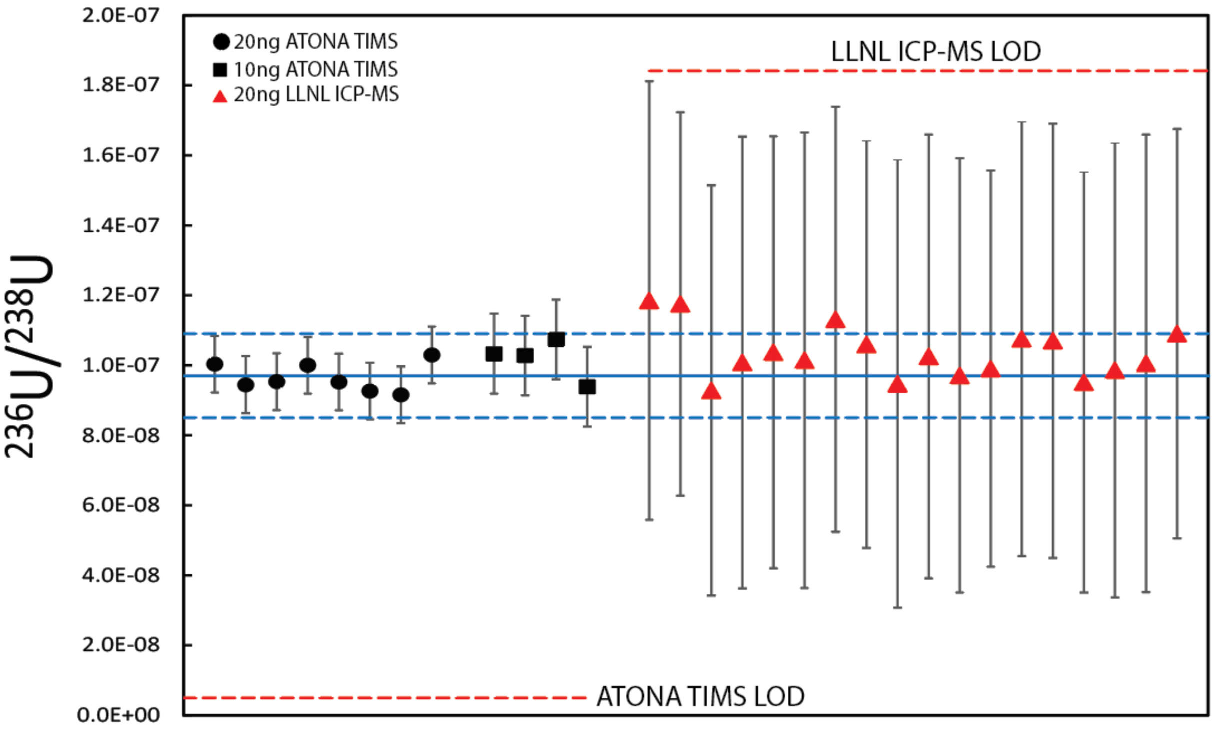

Figure 4. Comparison of 236U/238U measurements made by TIMS with ATONA amplifiers and Nu instruments Plasma 3 MC-ICP-MS analyses from LLNL. Blue lines represent the certificate $^{236}U/^{238}U$ value for CRM-129A and associated uncertainty. Note that both the 20ng and 10ng data fall within the certificate uncertainty.

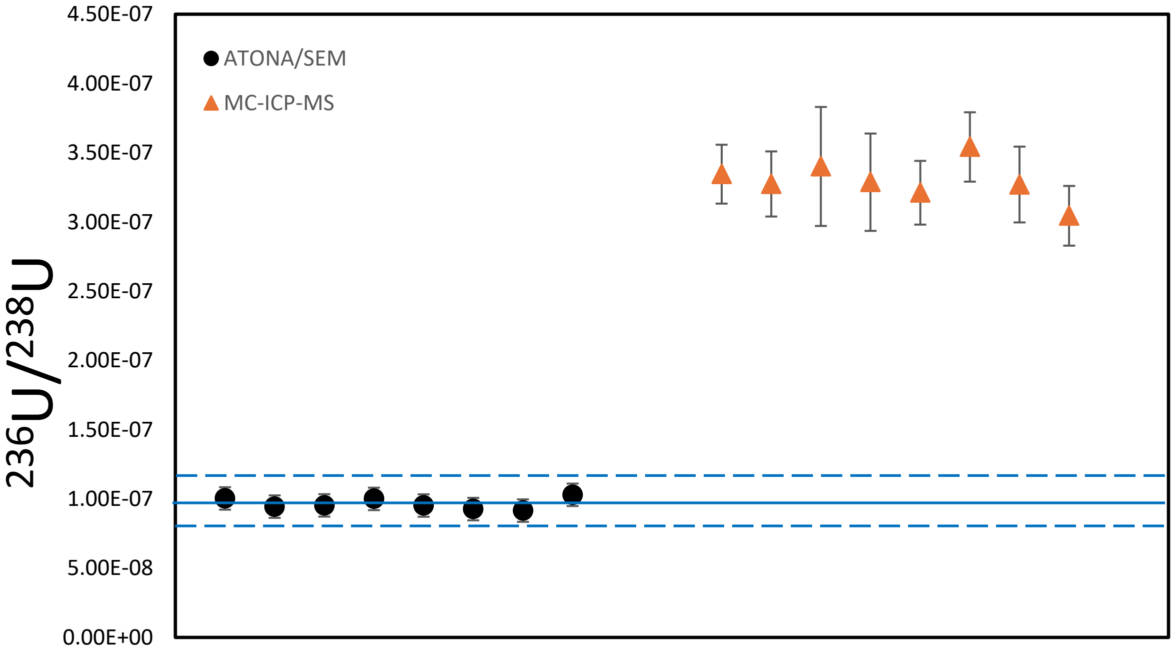

Figure 5. Comparison of ^{236}U/^{238}U measurements made by TIMS with ATONA amplifiers and Thermo Scientific Neptune Plus MC-ICP-MS analyses at LANL, using 20ng aliquots of CRM 129-A. Orange triangles are data from the Neptune MC-ICP-MS, black circles are from ATONA TIMS instrument. Blue lines represent the certificate ^{236}U/^{238}U value for CRM-129A.

NIST 4350b: Results of the ATONA based measurements of ^{236}U in the 4350B standard are summarized Fig. 6, where they are compared against the calculated detection limits of both traditional TIMS peak hopping method and MC-ICP-MS instruments at LANL and LLNL. These more established methods have, to date, not accurately detected ^{236}U in such a challenging standard like 4350B, this is most likely the result of the ^{236}U/^{238}U ratio being below their established detection capabilities (i.e. Figs. 4& 5). Indeed, to our knowledge, the ^{236}U/^{238}U results presented here represent the first time that ^{236}U has been measured within the 4350B sediment standard. It is important to note that the ATONA measurements were made of the course of several analytical sessions, used two separate sample dissolutions, and included load sizes varying from 10-200 ng. Consequently, we believe the average ^{236}U/^{238}U ratio of $7.12 \times 10^{-8} \pm 1.50 \times 10^{-8}$ (21.0% 2RSD) for all the data represents a reasonable first order estimate of the ^{236}U abundance in the standard. Additional confidence in the measured value is provided by the observation that a consistent ^{236}U/^{238}U value is seen across all the load sizes measured (Fig. 6). The external reproducibility is expectedly higher for the smaller load sizes (~25% 2 RSD for 10ng loads), however at the 200-ng level the external reproducibility is 6.5% and this may suggest that the overall ^{236}U/^{238}U value will be closer to 6.5×10^{-8}. Further analyses of the standard at either higher concentrations or on other high sensitivity instrument platforms may provide additional confidence in the value we have currently determined and in turn may (1) aid in determining the level heterogeneity in the standard, and (2) help establish 4350B as a ultra-low level environmental standard for ^{236}U measurements.

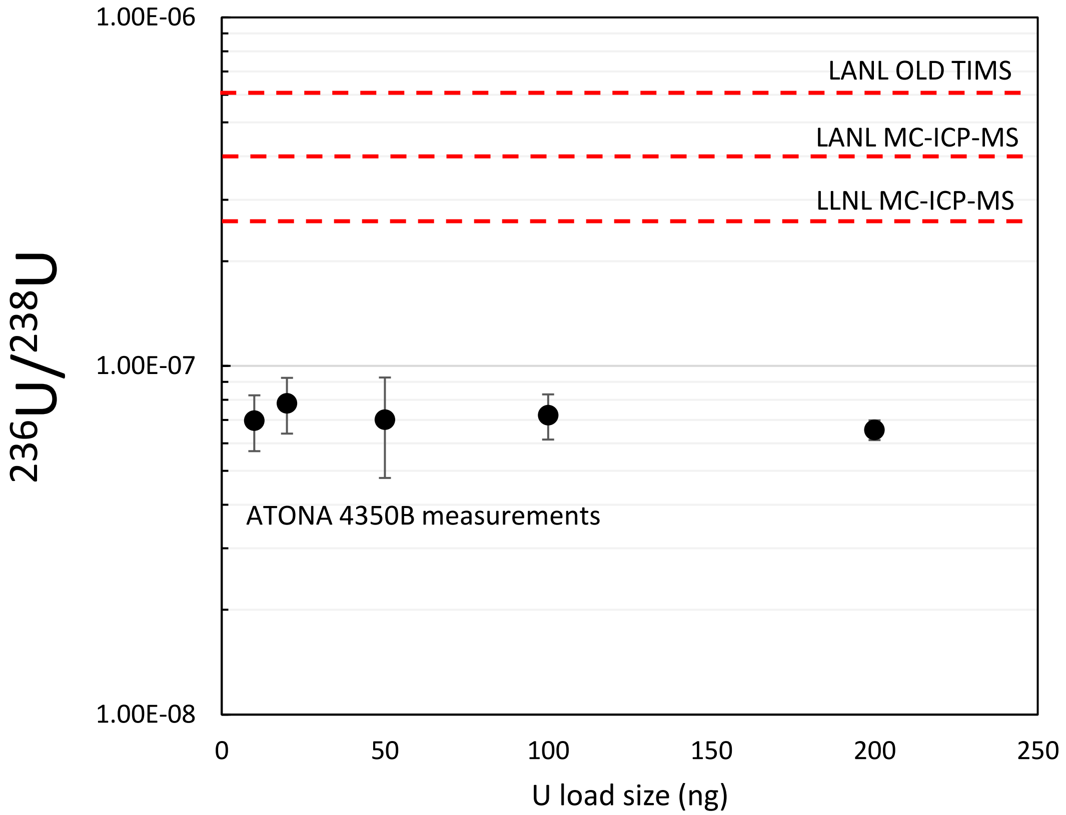

Figure 6. *Plots of replicate analyses of NIST 4350B analyzed with the ATONA amplifiers. The x-axis is the aliquot of total U processed through chemistry and loaded on the filament for TIMS analysis. Black data points are the average value of the replicates, and the error bars are the 2RSD of the replicate analyses.*

This first identification of ^{236}U within 4350B provides the opportunity to comment upon the possible source terms of the anthropogenic signatures within the standard. We note that the measured ^{236}U concentrations within 4350B are several orders of magnitude higher than ^{236}U concentrations in global fallout. In addition, combining the data presented in this study with previous estimates for the concentration of ^{239}Pu in the 4350B standard from Goldstein et al. [24] yields a ^{236}U/^{239}Pu atom ratio of ~0.83. We note that this value is considerably higher than the 0.1 – 0.5 ^{236}U/^{239}Pu range of values observed in global fallout [14, 28, 29], including a value of 0.19 ± 0.04 for global fallout observed in soils from Washington State [28]. This implies that greater than 90% of the ^{236}U measured in 4350B was derived from a local source. This appears to support previous studies of Columbia River sediment that determined the presence of a significant reactor derived signature downstream of the Hanford Site [24, 25]. While these previous studies primarily focused on plutonium, our ability to measure ^{236}U may help provide further insight into the Hanford reactor signatures that have been captured in the Columbia River sediments.

Summary

This study illustrates the potential utility of ^{236}U measurements in environmental samples for purposes of non-proliferation and treaty monitoring. Using the results from repeated analysis of Columbia River sediment (NIST 4350B), we demonstrate the effectiveness of the rapid ATONA based uranium methods to make highly sensitive ^{236}U measurements at operationally relevant sample sizes and to rapidly identify inputs of anthropogenic into the environment. This increased uranium measurement sensitivity could be useful in rapid screening of environmental samples or in cases when there is a desire to minimize the aliquot size of the uranium fraction in a bulk sample, providing the option to perform other analyses from the sample.

References

1. Brennecka, G.A., et al., *Natural variations in uranium isotope ratios of uranium ore concentrates: Understanding the 238U/235U fractionation mechanism.* Earth and Planetary Science Letters, 2010. **291**(1): p. 228-233.
2. Keatley, A.C., et al., *Uranium isotope variation within vein-type uranium ore deposits.* Applied Geochemistry, 2021. **131**: p. 104977.
3. Kronfeld, J., *Uranium deposition and Th-234 alpha-recoil: An explanation for extreme U-234/U-238 fractionation within the trinity aquifer.* Earth and Planetary Science Letters, 1974. **21**(3): p. 327-330.
4. Neymark, L.A., *Potential effects of alpha-recoil on uranium-series dating of calcrete.* Chemical Geology, 2011. **282**(3): p. 98-112.
5. Donohue, D.L., *Strengthening IAEA safeguards through environmental sampling and analysis.* Journal of Alloys and Compounds, 1998. **271-273**: p. 11-18.
6. Donohue, D.L., *Peer Reviewed: Strengthened Nuclear Safeguards.* Analytical Chemistry, 2002. **74**(1): p. 28 A-35 A.
7. Inglis, J.D., et al., *An introduction to the significance of sample size in particle analyses for nuclear forensics and radiological investigations.* Journal of Radioanalytical and Nuclear Chemistry, 2023. **332**(8): p. 3371-3381.
8. Conrad, C., et al., *Anthropogenic uranium signatures in turtles, tortoises, and sea turtles from nuclear sites.* PNAS Nexus, 2023. **2**(8).
9. Yoshida, S., et al., *Concentrations of uranium and 235U/238U ratios in soil and plant samples collected around the uranium conversion building in the JCO campus.* Journal of Environmental Radioactivity, 2000. **50**(1): p. 161-172.
10. Lloyd, N.S., S.R.N. Chenery, and R.R. Parrish, *The distribution of depleted uranium contamination in Colonie, NY, USA.* Science of The Total Environment, 2009. **408**(2): p. 397-407.
11. Eppich, G.R., et al., *Constraints on fallout melt glass formation from a near-surface nuclear test.* Journal of Radioanalytical and Nuclear Chemistry, 2014. **302**(1): p. 593-609.
12. Michel-Sendis, F., et al., *SFCOMPO-2.0: An OECD NEA database of spent nuclear fuel isotopic assays, reactor design specifications, and operating data.* Annals of Nuclear Energy, 2017. **110**: p. 779-788.

13. Makarova, T.P., B.A. Bibichev, and V.D. Domkin, *Destructive analysis of the nuclide composition of spent fuel of WWER-440, WWER-1000, and RBMK-1000 reactors.* Radiochemistry, 2008. **50**(4): p. 414-426.
14. Tims, S.G., et al., *236U and 239,240Pu ratios from soils around an Australian nuclear weapons test site.* Journal of Environmental Radioactivity, 2016. **151**: p. 563-567.
15. Wang, Y., et al., *Determination of ultra-low 236U in environment samples using ICP-MS/MS measurement and chemical separation.* Talanta, 2021. **224**: p. 121882.
16. Diez-Fernández, S., et al., *A new method for determining 236U/238U isotope ratios in environmental samples by means OF ICP-MS/MS.* Talanta, 2020. **206**: p. 120221.
17. Steier, P., et al., *Natural and anthropogenic 236U in environmental samples.* Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 2008. **266**(10): p. 2246-2250.
18. Kertes, A.S. and R. Guillaumont, *Solubility of UO2. A comparative review.* Nuclear and Chemical Waste Management, 1985. **5**(3): p. 215-219.
19. Richter, S., et al., *Isotopic "fingerprints" for natural uranium ore samples.* International Journal of Mass Spectrometry, 1999. **193**(1): p. 9-14.
20. Cox, S.E., S.R. Hemming, and D. Tootell, *The Isotopx NGX and ATONA Faraday amplifiers.* Geochronology, 2020. **2**(2): p. 231-243.
21. Mixon, E.E., et al., *Optimizing 40Ar/39Ar analyses using an Isotopx NGX-600 mass spectrometer.* Chemical Geology, 2022. **593**: p. 120753.
22. Reinhard, A., et al., *Isotopic analysis of sub-nanogram neodymium loads using new ATONA™ amplifiers.* Rapid Communications in Mass Spectrometry, 2021. **35**(7): p. e9032.
23. Reinhard, A.A., et al., *Application of ATONA Amplifiers to the Measurement of Uranium Isotopic Ratios by Thermal Ionization Mass Spectrometry.* Analytical Chemistry, 2024.
24. Goldstein, S.J., et al., *High-precision measurement of U-Pu-Np-Am concentrations and isotope ratios in environmental reference materials by mass spectrometry.* Journal of Environmental Radioactivity, 2021. **237**: p. 106689.
25. Beasley, T.M., et al., *Hanford-Derived Plutonium in Columbia River Sediments.* Science, 1981. **214**(4523): p. 913-915.
26. Goldstein, S.J., M.T. Murrell, and D.R. Janecky, *Th and U isotopic systematics of basalts from the Juan de Fuca and Gorda Ridges by mass spectrometry.* Earth and Planetary Science Letters, 1989. **96**(1): p. 134-146.
27. McCroan, K.D. and J.M. Keller, *Data Calculation, Analysis, and Reporting*, in *Radioanalytical Chemistry*, B. Kahn, Editor. 2007, Springer New York: New York, NY. p. 189-219.
28. Ketterer, M.E., et al., *Deposition of 236U from atmospheric nuclear testing in Washington state (USA) and the Pechora region (Russian Arctic).* Journal of Environmental Radioactivity, 2013. **118**: p. 143-149.
29. Sakaguchi, A., et al., *First results on 236U levels in global fallout.* Science of The Total Environment, 2009. **407**(14): p. 4238-4242.