Plutonium Isotopes in the Terrestrial Environment at the Savannah River Site, USA: A Long Term Study

Christopher R. Armstrong, Patterson R. Nuessle, Heather A. Brant, Gregory Hall, Justin E. Halverson, and James R. Cadieux*

Nonproliferation Technology Section, Savannah River National Laboratory, Aiken, SC 29808

Abstract. This work presents the findings of a long term plutonium study at Savannah River Site (SRS) conducted between 2003 and 2013. Terrestrial environmental samples were obtained at Savannah River National Laboratory (SRNL) in A-area. Plutonium content and isotopic abundances were measured over this time period by alpha spectrometry and three stage thermal ionization mass spectrometry (3STIMS). Here we detail the complete sample collection, radiochemical separation, and measurement procedure specifically targeted to trace plutonium in bulk environmental samples. Total plutonium activities were determined to be not significantly above atmospheric global fallout. However, the ^{238}Pu/$^{239+240}$Pu activity ratios attributed to SRS are above atmospheric global fallout ranges. The ^{240}Pu/^{239}Pu atom ratios are reasonably consistent from year to year and are lower than fallout, while the ^{242}Pu/^{239}Pu atom ratios are higher than fallout values. Overall, the plutonium signatures obtained in this study reflect a mixture of weapons-grade, higher burn-up, and fallout material. This study provides a blue print for long term low level monitoring of plutonium in the environment.

INTRODUCTION

Background. The Savannah River Site (SRS), formerly Savannah River Plant (SRP) began operation in the early 1950's. The site, located close to the Savannah River in South Carolina (Figure 1), encompasses roughly 310 square miles. The primary function at SRS was to develop materials in support of the US nuclear weapons program and particularly materials required for hydrogen bomb design. Although plutonium was also produced in large quantities, tritium (3H) was the major material produced at SRS. At its peak operation, five nuclear reactors (heavy water cooled and moderated) operated at SRS. Targets placed inside these high-flux reactors contained lithium (7Li) to produce tritium. In addition, the unique versatility of the SRS reactors was exploited as other materials were also placed in these targets to produce novel isotopes. For example the addition of ^{237}Np into targets produced significant quantities of 238Pu. Targets containing ^{242}Pu produced ^{244}Pu, heavier curium isotopes, e.g., $^{246\text{-}248}$Cm, and ^{252}Cf.

As the cold war dissipated, all SRS reactors were gradually decommissioned. The last reactor was shut down in 1988. Today, ongoing operations at SRS include the H-Canyon used nuclear fuel (UNF) reprocessing facility, a tritium facility, and waste storage and stewardship facilities such as the Defense Waste Processing Facility (DWPF).

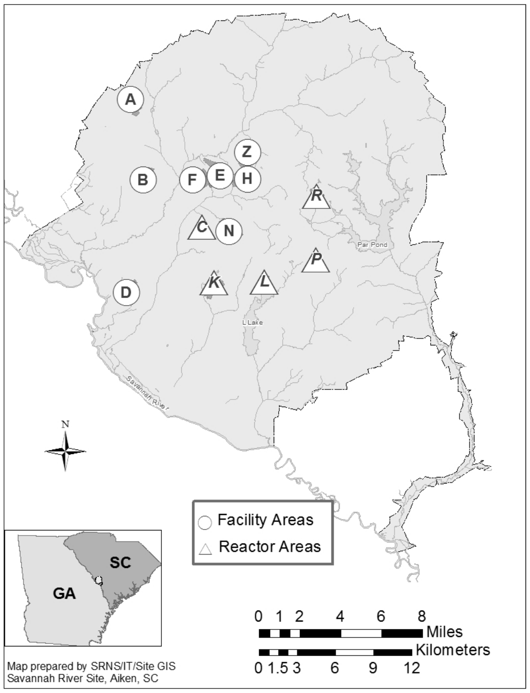

Figure 1. Map of Savannah River Site (SRS) located in South Carolina, USA. Triangles show previous reactor locations (C, K, L, P, and R reactors). Circles show other locations of interest including A: Savannah River National Laboratory (SRNL); M: Fuel Fabrication Facility (decommissioned); H: H-Canyon Reprocessing Facility; K: Plutonium storage facility.

Need for more detailed and long term plutonium studies. Remediation efforts associated with the Fukushima Daiichi Nuclear Power Plant (FDNPP) event require a rigorous assessment of the extent of environmental contamination associated with the accidental release. These investigations must be both long term, e.g., several years, and detailed in terms of the diversity and concentration, i.e., low level monitoring, of possible contaminants [1]. Although detailed investigations have been undertaken for the elements contributing to the majority of the radionuclide release, e.g., ^{131}I, ^{132}Te, ^{134}Cs, ^{136}Cs, ^{137}Cs, ^{133}Xe, ^{85}Kr, etc., to date studies reporting data for the actinides are sparse [2]. Schneider et al. conducted Pu analysis of soils and vegetation in the vicinity of FDNPP [3]. This study confirmed the presence of commercial reactor-grade plutonium attributed to FDNPP, but called for additional investigations, particularly the need for more background data. A critical review by Zheng et al. reported the presence of Pu isotopes released from the damaged reactors, but also highlighted the need for more detailed plutonium investigations [4].

It is clear that to better assess plutonium mobility in the environment, detailed long term monitoring of Pu activity, i.e., involving adequate bulk sample collection, and both alpha spectrometry and mass spectrometry measurements, are required. For example, detailed monitoring before (background), during, and after the release would enable a more complete assessment of the extent of plutonium activity in the terrestrial environment around FDNPP. In the context of an accidental release such as the FDNPP event, long term Pu monitoring according to the methodology described herein would enable assessment of possible releases originating from different sources, e.g., spent fuel pools and/or damaged reactors. Moreover, the complexities of plutonium isotopic signatures in the terrestrial environment make data interpretation and accurate determination of the original source(s) a challenge. Thus, further investigation into plutonium fate and transport, particularly focusing on subtle differences in Pu isotopic behaviors in the environment, is critical from radiological, environmental, and nonproliferation perspectives.

Aim. Owing to its rich history of plutonium production, the Savannah River Site (SRS) provides a unique test bed to investigate plutonium content and isotopic (^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{242}Pu) behavior in a highly complex background. The SRS environment is one of the few locations worldwide where both weapons-grade and reactor-grade (higher burn-up) plutonium signatures abound [5]. This study details a long term investigation of trace level plutonium content and isotopic composition in the SRS environment. Here we report the methodology for plutonium collection in bulk environmental samples, analysis by alpha spectrometry and mass spectrometry, and data interpretation i.e., examining Pu isotopic signatures to gain insights into possible sources of plutonium.

Few studies investigating plutonium in the terrestrial environment provide both alpha spectrometry and mass spectrometry results. A complementary analytical approach using both of these techniques offers both Pu activity data from alpha spectrometry and abundance data from mass spectrometry [6]. The goal of this report is two-fold: 1) to present a complete procedure for the collection, radiochemical processing, and analysis of plutonium in bulk environmental samples, and 2) to determine the sources of Pu particularly in light of the legacy of plutonium production and processing at SRS. The methodology presented herein provides a template for effective low level plutonium collection, processing, and measurement.

EXPERIMENTAL SECTION

Methodology. The environmental samples in this study consist of foot borne solids, e.g., soil, mineral fragments, vegetation debris, etc., removed from the bottom of visitors' footwear via a shoe brush [7] before entering the clean laboratories at Savannah River National Laboratory (SRNL). The shoe brush (Liberty Shoe Brush 2010SC; Liberty Industries Inc., East Berlin, CT, USA) mechanically removes foot borne debris via four rotating brushes that contact the front, sides, and bottom of the footwear in conjunction with a vacuum (suction) system. Material is dislodged from the footwear by the brushes and collected by vacuum into a nearby compartment. Samples are taken periodically when the shoe brush compartment is emptied. Because this is a mixture of materials, this is an ideal method to collect true bulk samples of the nearby environment. Moreover, the amount of sample collected (~ 100 g) ensures an adequate amount of plutonium activity to attain an acceptable uncertainty (generally < 10%), while obtaining plutonium content and isotopic compositions that are representative of the total sample [8, 9]. These solids are dry ashed (to remove organic components), leached, and processed to separate and purify plutonium. Samples are initially electroplated and analyzed by alpha spectrometry. Subsequently, samples undergo additional purification steps and analyzed by mass spectrometry using a three stage thermal ionization mass spectrometer (3STIMS). Complete details are provided in the foregoing sections.

Sample Preparation, alpha spectrometry, and mass spectrometry. All glass, quartz and plastic materials pretreated (leached) by refluxing for several hours at 60 ^{o}C in 8 M nitric acid. Type 1 (18 MΩ) water and high purity acids are used exclusively this study.

Debris is removed from the shoe brush and mixed manually. Approximately 100 grams of material ares initially weighed out. Samples are ashed and digested according to a proven method [10]. Solutions are separated by centrifugation. An aliquot of a known amount of solution is transferred by weight to a leached pyrex beaker and spiked with either ^{236}Pu or ^{242}Pu. The remaining solution is archived. The valence is adjusted in with sodium nitrite and an iron carrier is added to each sample solution. Base (ammonium hydroxide) is added and plutonium precipitates out with the solid fraction. After centrifugation, this solid fraction is then dissolved with 8 M nitric acid and a valence adjustment step is undertaken with sodium nitrite to ensure a Pu(IV) oxidation state. Ion exchange columns are prepared according to an original methodology [11] by loading each column with AG1X8 resin (Eichrom) to a bed height of 8 cm.

Predetermined volumes of 8 M nitric acid are added to the columns and allowed to drain completely before and after the sample solutions are loaded onto the columns. Subsequently, the columns are conditioned with predetermined volumes of 8 M hydrochloric acid and plutonium is eluted from the columns with freshly prepared solution of 8 M hydrochloric acid and 0.1 M ammonium iodide. The eluted sample solutions are evaporated to incipient dryness on a hotplate. The samples are then re-dissolved with 8 M nitric acid and AG1X4 (Eichrom) ion exchange columns are prepared by initial rinsing and loading with 0.1 M hydrochloric acid. After a small addition of sodium nitrite, the sample solutions are then loaded onto the columns and rinsed with 8 M nitric acid and 9 M hydrochloric acid respectively. The samples are eluted with additions of 9 M hydrochloric acid and 0.1 M ammonium iodide. The eluate is treated with 8 M nitric acid and the solutions are heated and evaporated to incipient dryness. The residues are re-dissolved with 0.36 M sodium bisulfate and 8 M nitric acid and the solutions are heated on a hot plate to incipient dryness.

Electrodeposition preparation. The samples are brought into solution with 0.75 M sulfuric acid with a small amount of thymol blue indicator and transferred to an electrodeposition vial containing a platinum disk. The pH is adjusted by dropwise addition of concentrated ammonium hydroxide to slightly acidic and the vials are positioned in the electrodeposition unit. The power is turned on and current is set to 0.75 amps and the electrodeposition reaction is allowed to proceed for one hour. After one hour, 2 mL of concentrated ammonium hydroxide is added to each vial and deposition proceeds for one minute after which power is turned off and anodes are removed from the vials. The electroplated disk is then removed, rinsed with deionized water, and air-dried before alpha spectrometry measurements.

Mass spectrometry sample preparation. The electrodeposited material is dissolved from the platinum discs by gently warming the disks in individual beakers containing 3 mL of 8 M hydrochloric acid. Approximately 10 mg of sodium nitrite is added to the sample solutions while stirring. A 0.5 mL pre-packed column of AG 1X4 anion exchange resin is conditioned by rinsing each column once with 5 mL of 0.1 M hydrochloric acid then twice with 5 mL of 8 M nitric acid. The columns are loaded with the samples and the remainder in the beakers is rinsed with small amounts of 8 M hydrochloric acid. Each column is rinsed successively with 5 mL of 8 M hydrochloric acid, 5 mL of 8 M nitric acid, and 5 mL of 8 M hydrochloric acid. The beakers containing the rinse solutions are removed and replaced with leached 30 mL beakers. The columns are eluted by adding 3 mL of 9 M hydrobromic acid to each column in three 1 mL portions. The samples are evaporated to incipient dryness on a hot plate and allowed to cool. Then 3 mL of 8 M nitric acid is added to each sample while stirring and the samples are transferred to acid-leached Teflon vials with three 1 mL portions of 8 M nitric acid. The vials are capped and submitted for mass spectrometry analysis as described below.

Alpha spectrometry. Alpha-spectrometry was performed using the EG&G Ortec Octête PC Alpha Spectrometer. Passivated implanted planar silicon (PIPS) detectors with an active area of 450 mm^2 were used. The samples were measured for several weeks and the received spectra evaluated using the software program Maestro.

Three stage thermal ionization mass spectrometry (3STIMS). Plutonium measurements were conducted with a 1960's KAPL (Knolls Atomic Power Laboratory) design Three Stage Thermal Ionization Mass Spectrometer (3STIMS) fabricated in house in the 1970's with updated electronics and control systems added over the years and as recently as 2012. The single ETP electron multipler detector instrument has three 90^0 x 30.5 cm sectors in BBE configuration and routinely analyzes picogram to femtogram mass Pu samples. Purified samples are loaded onto anion exchange resin beads, which are then loaded by hand onto high purity rhenium filaments and placed in the source region of the mass spectrometer for thermal ionization.

RESULTS AND DISCUSSION

Laboratory QA/QC: Alpha spectrometry. Quality assurance (QA) and quality control (QC) exercises are conducted routinely in this laboratory. One example is the yearly radiochemical processing and alpha spectrometry analysis of a National Institute of Standards and Technology (NIST) soil sample, standard reference material (SRM 4350B). This standard, comprising Columbia River sediment, is processed using the same procedure discussed herein. Alpha spectrometry data for $^{239+240}$Pu from 2002 to 2013 are shown in **Figure 2**. Data points depict yearly measurements with two-sigma standard deviation error bars included. Multiple data points in the same year represent replicate samples. The solid grey and dashed lines represent the NIST standard reference value with two-sigma standard deviation respectively. In general the data from this laboratory agree well with the reference value.

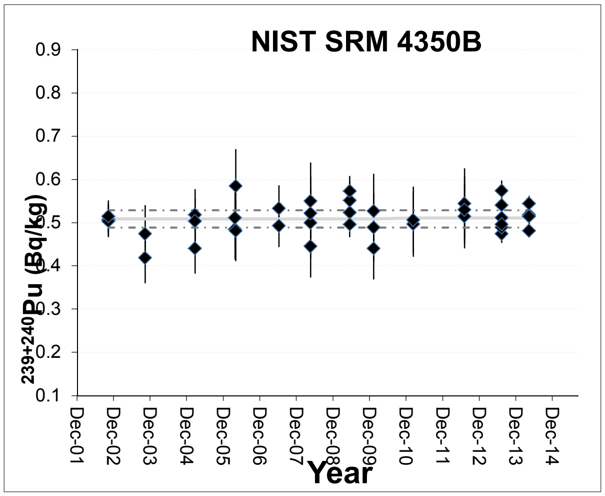

Figure 2. Alpha spectrometry measurements of NIST SRM 4350B at SRNL. The grey and dotted lines denote the certified reference value and two-sigma uncertainty respectively.

Laboratory QA/QC: Mass spectrometry. QA/QC exercises monitoring three stage TIMS (3STIMS) performance are also conducted routinely in this laboratory. For example, in one series of experiments, two NIST standards, SRM 4350B [9] and the Peruvian soil standard, SRM 4355 were processed via the radiochemical procedure mentioned above and measured for plutonium content and isotopic composition (^{239}Pu, ^{240}Pu, and ^{241}Pu) by 3STIMS. These data, shown in **Figure 3**, provide a clear example of the instrumental precision (95% confidence interval) observed with plutonium measurements via the three stage TIMS. In addition, these data show the range over which the 3STIMS can provide meaningful Pu results. Two sample sizes were investigated: 2.5 and 10 grams. Multiple data points are plotted for replicate runs. A broad range of plutonium masses (fg) are reported for isotopes ^{239}Pu, ^{240}Pu, and ^{241}Pu.

Independent of a particular Pu isotope, precision decreases with decreasing Pu content. For Pu concentrations greater than approximately 10 femtograms, a two-sigma relative standard deviation (RSD) of 10 % (or better) is expected.

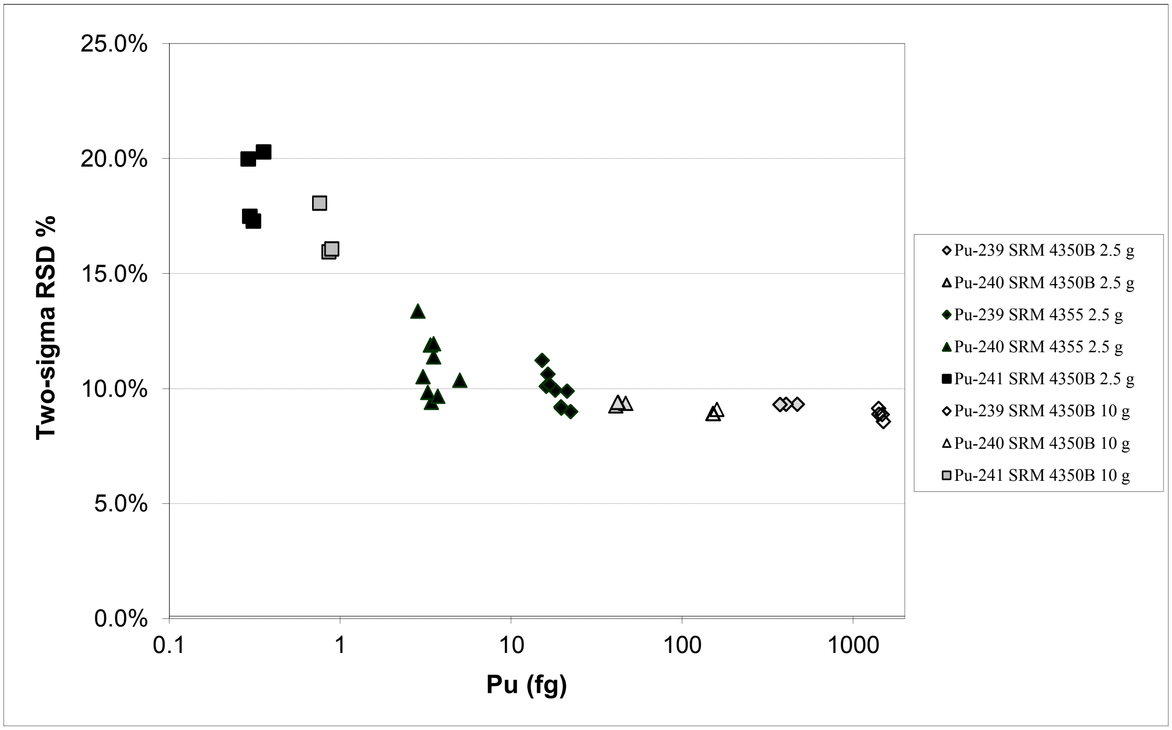

Figure 3. Three stage TIMS (3STIMS) measurements of NIST SRM 4350B and SRM 4355 at SRNL.

Alpha spectrometry results. Alpha spectrometry monitoring ^{238}Pu and $^{239+240}$Pu activities was conducted on all of the environmental samples collected in this study over the 2003 to 2013 time interval. For illustrative purposes, some of the more salient features observed over this period are shown in **Figure 4**. For example, stark differences in the plutonium signatures in 2013, 2009, and 2006 are readily noticeable by qualitatively comparing the ^{238}Pu and $^{239+240}$Pu peaks in the spectra. The alpha spectrum for 2013 (top panel) was chosen because it is a roughly representative spectrum of the SRS environment which typically features higher ^{238}Pu activity than observed for atmospheric global fallout. Conversely, alpha spectra from 2006 (bottom panel) and 2009 (middle panel) are shown because these years feature rather anomalous Pu signatures, namely inordinately high $^{239+240}$Pu and ^{238}Pu observed in 2009 and 2006 respectively, as described in detail below.

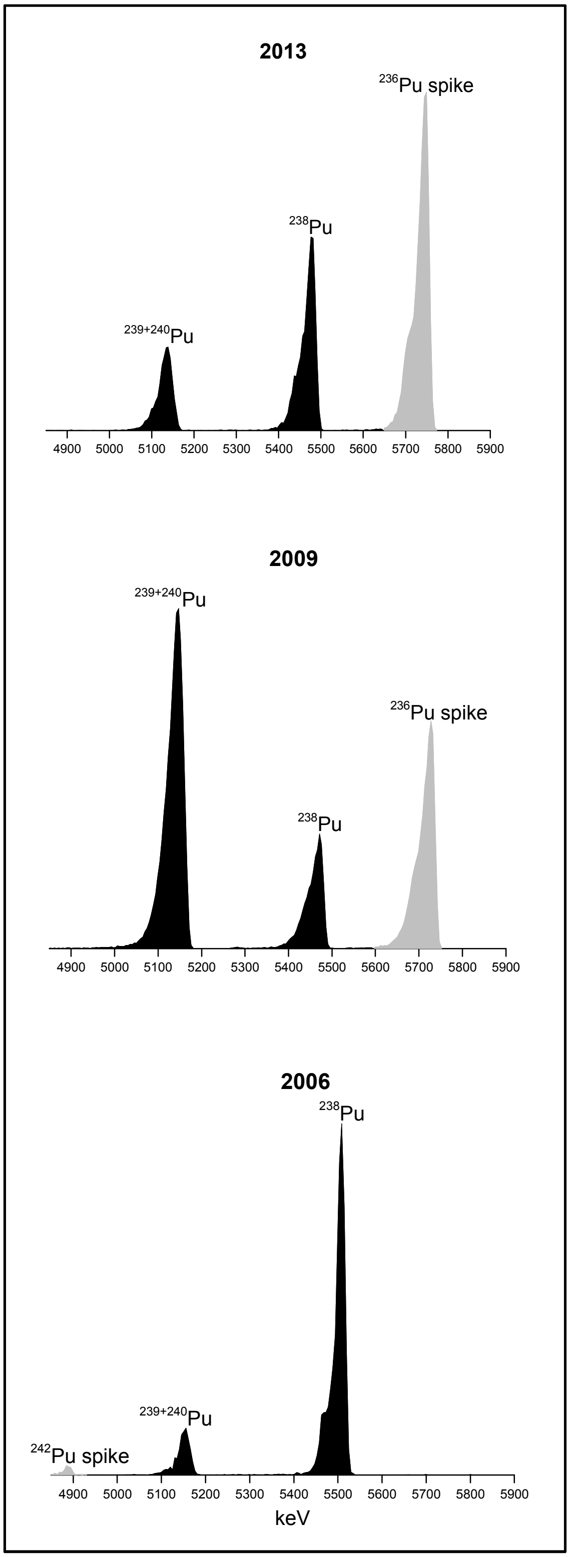

Figure 4. Alpha spectra of terrestrial environmental samples collected at SRS (SRNL A-area) in 2013 (top), 2009 (middle), and 2006 (bottom).

Total Pu alpha activity measured ($^{238+239+240}$Pu) over the ten year span of this study is shown in **Figure 5.** Plutonium activity varies from year to year with notably high activity (10 Bq/kg) featured in 2009. Anomalous Pu isotopic signatures were also observed in 2009 which suggested the presence of higher burn-up Pu (commercial reactor-grade) fuel. Moreover, a laboratory survey and inspection suggested that the anomalously high Pu activity observed in 2009 was likely due to minor contamination in the laboratory from a relatively high activity sample associated with a commercial power reactor, i.e., not an SRS source. Although the Pu activity from SRS sources ranges from approximately 0.3 to 4.9 Bq/kg, these values are not significantly greater than atmospheric global fallout (0.1 – 1 Bq/kg [12]), and therefore are not a concern from a radiological contamination perspective.

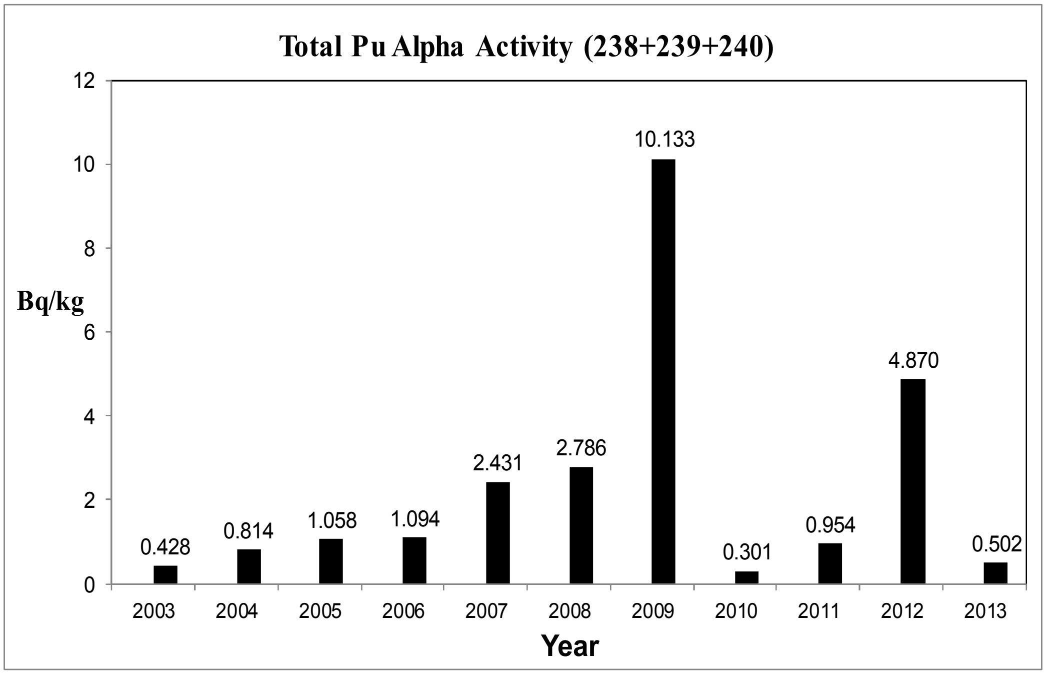

Figure 5. Total Pu activity in terrestrial environmental samples collected at SRS (SRNL A-area) from 2003 to 2013.

The variability in plutonium activity observed from year to year is likely the result of multiple factors including, 1) the amount and diversity of Pu produced at SRS, 2) the wide assortment of debris collected in the samples including vegetation, mineral aerosols and rock fragments, and 3) varying climatic conditions (rainfall, humidity, wind, etc.). For example, wind and rain have competing effects on the amounts of resuspended plutonium-containing material collected [13-15].

The ^{238}Pu/$^{239+240}$Pu alpha activity ratios for the ten year timespan of this study are shown in **Figure 6.** These results are also tabulated in **Table 1.** Notably, all of these values, ranging from 0.3 to 6.4 in 2009 and 2006 respectively, are markedly above the atmospheric global fallout ^{238}Pu/$^{239+240}$Pu activity ratio of 0.02 – 0.04 [12]. These rather high ratios are partly due to the rich legacy of Pu production activities at SRS, in this case, specifically ^{238}Pu. Over one hundred kilograms of ^{238}Pu were produced between approximately 1958 and 1987 at SRS primarily to support the NASA deep space program [16]. In addition to the relatively high plutonium-238 generally observed at SRS, an inordinately high ^{238}Pu is observed in 2006 which is also exhibited in the corresponding alpha spectrum (**Figure 4**, bottom panel). Although significantly more ^{239}Pu was produced at SRS, owing to its relatively high specific activity, ^{238}Pu is particularly sensitive to alpha spectrometry measurement.

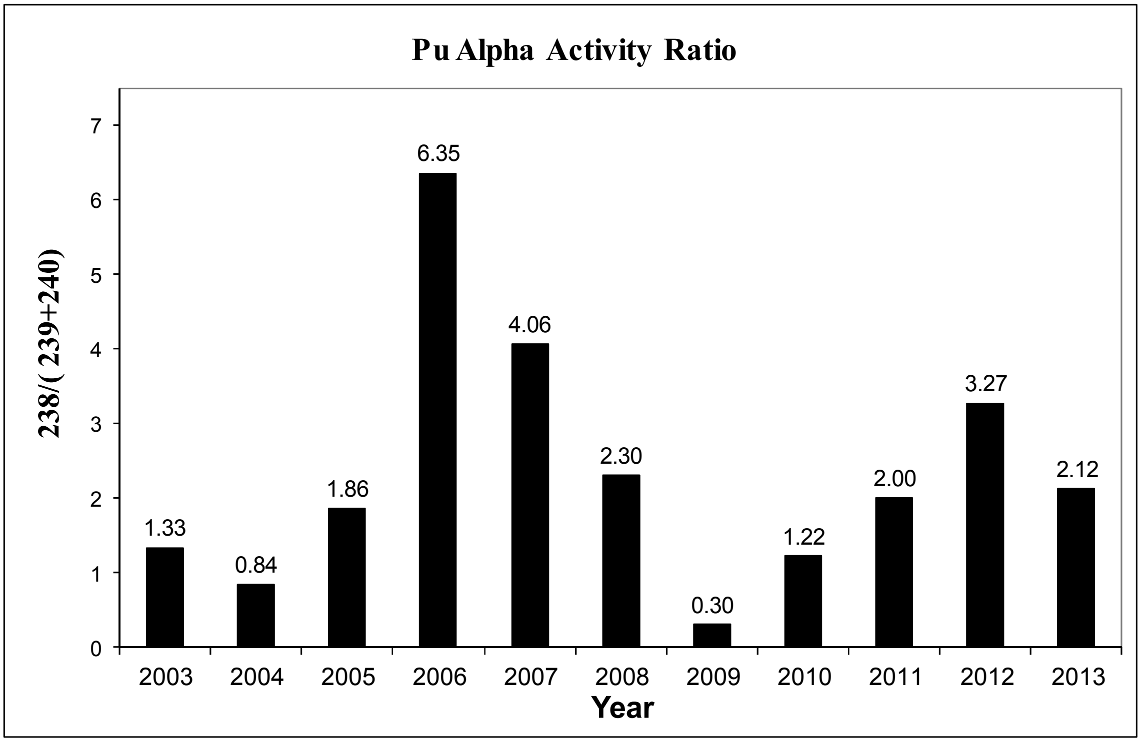

Figure 6. ^{238}Pu/$^{239+240}$Pu alpha activity ratios in terrestrial environmental samples collected at SRS (SRNL A-area) from 2003 to 2013.

As seen in Fig. 4 (top panel) plutonium-238 activity is expected to be relatively high in the SRS background, and the unusually high year (2006) may simply be due to a small number of ^{238}Pu oxide hot particles [17]. Plutonium-238 oxide materials tend to be highly recalcitrant and therefore mobilize freely in biosphere. For example, ^{238}Pu containing particles from SRS have been measured in the Savannah River estuary tens of kilometers downstream of SRS [15]. It is noteworthy that several years (2003, 2005, 2008, 2010, and 2013) are similar to the ^{238}Pu/$^{239+240}$Pu activity ratios measured associated with the FDNPP accident (1.07 - 2.89; Zheng et al., 2013). In addition, years 2003, 2004, and 2010 exhibit activity ratios roughly similar to sediment samples associated with the Mayak Production Association (reservoir 10) in Russia which fall in the 0.5 – 1.5 range [12].

3STIMS results. For all of the samples in this study, quantifiable measurements of ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{242}Pu were obtained by mass spectrometry (3STIMS). Due to isobaric interferences with ^{238}U [18], ^{238}Pu is not measured with this technique. Atom ^{240}Pu/^{239}Pu ratios obtained over the ten year span of this study are shown in **Figure 7**. These data are also reported in **Table 1**. With the exception of 2009 where the highest ratio (0.303) is observed, the ^{240}Pu/^{239}Pu atom ratios are reasonably consistent from year to year, ranging from 0.08 in 2004 to 0.13 in 2013. Notably, all of these years (except 2009) exhibit ^{239}Pu content greater than expected for atmospheric global fallout, e.g., 0.18 [19]. These data generally appear to be representative of a variable admixture of both fallout and weapons-grade plutonium, with several ratios approaching the ^{240}Pu/^{239}Pu atom ratio of weapons-grade Pu, typically in the 0.01 - 0.07 range [20]. These findings are not surprising, given the amount of plutonium that was produced on site (metric tons of weapons-grade Pu from ca. 1956 - 1989).

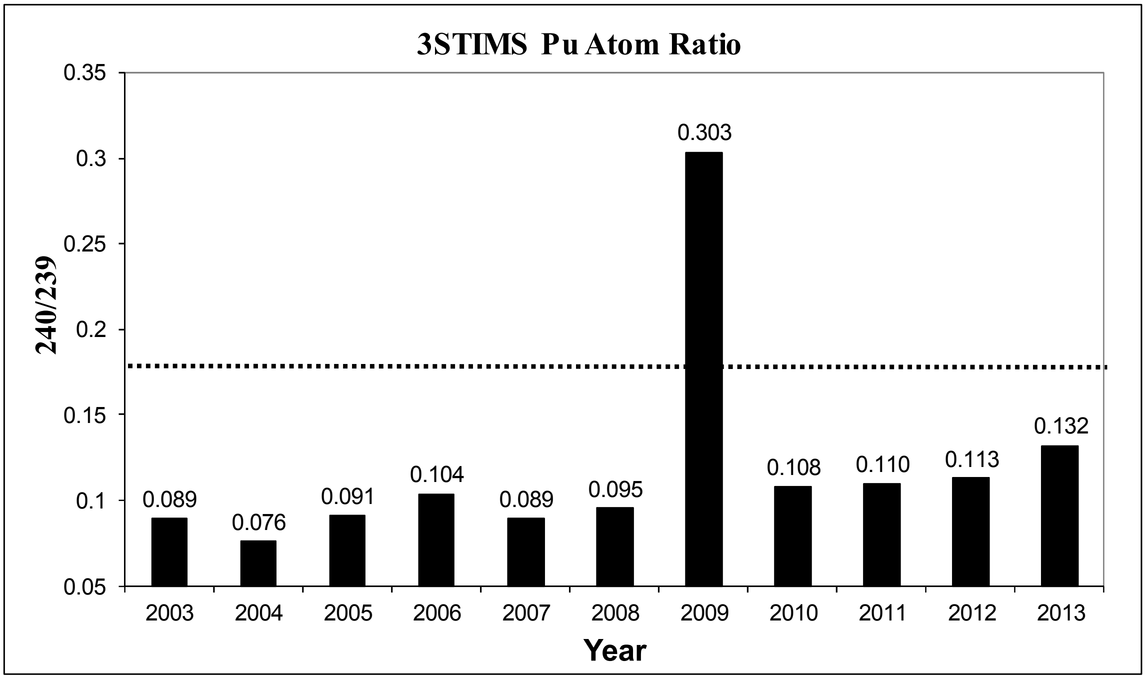

Figure 7. 3STIMS ^{240}Pu/^{239}Pu atom ratios in terrestrial environmental samples collected at SRS (SRNL A-area) from 2003 to 2013. Dotted line denotes atmospheric global fallout ratio [19].

These ^{240}Pu/^{239}Pu atom ratios, together with corresponding alpha spectrometry findings in 2009, **(Figs. 5, 6; Table 1)**, clearly show a significant contribution of ^{240}Pu unique to that year. This perturbation may be explained by the possible presence of a small amount of ^{240}Pu containing hot particles [17] associated with an offsite commercial reactor-grade, i.e., relatively high burn-up fuel, that was processed in this laboratory. It is interesting to note that this value is roughly similar to data obtained from soil collected near Fukushima following the accident (^{240}Pu/^{239}Pu: 0.381 ± 0.046, [3]) which was attributed to release from the damaged reactors.

Table 1. Alpha activity and three stage thermal ionization mass spectrometry (3STIMS) plutonium atom ratios for SRS environmental samples spanning a ten year period. Data from global fallout are cited from [4, 12, 21, 22]. Note: ^{242}Pu data are reported in years when a ^{242}Pu tracer was not used (2008, 2010, 2012, and 2013). NA: Data not available.

	α-spectrometry	**3STIMS (atom ratios)**		
Year	^{238}Pu/$^{239+240}$Pu	^{240}Pu/^{239}Pu	^{241}Pu/^{239}Pu	^{242}Pu/^{239}Pu
2003	1.332 ± 0.320	0.089 ± X.XE-04	NA	NA
2004	0.840 ± 0.052	0.076 ± 4.0E-04	0.002 ± 5.6E-05	NA
2005	1.860 ± 0.110	0.091 ± 5.4E-04	0.002 ± 6.5E-05	NA
2006	6.350 ± 0.224	0.104 ± 4.5E-04	0.002 ± 5.0E-05	NA
2007	4.060 ± 0.143	0.089 ± 6.7E-04	0.002 ± 9.0E-05	NA
2008	2.300 ± 0.081	0.095 ± 2.8E-04	0.002 ± 2.0E-05	0.020 ± 7.9E-05
2009	0.296 ± 0.007	0.303 ± 1.5E-03	0.031 ± 2.4E-04	NA
2010	1.217 ± 0.075	0.108 ± 3.1E-04	0.001 ± 3.1E-05	0.019 ± 1.2E-04
2011	1.997± 0.070	0.110 ± 2.4E-03	0.002 ± 2.6E-04	NA
2012	3.267 ± 0.039	0.113 ± 1.6E-03	0.002 ± 1.1E-04	0.017 ± 5.1E-04
2013	2.124 ± 0.126	0.132 ± 1.1E-03	0.001 ± 9.5E-05	0.043 ± 5.5E-04
Fallout	0.030	0.180	0.002	0.004

The results reported in Table 1 show ^{241}Pu/^{239}Pu atom ratios roughly similar to fallout, largely due to decay of plutonium-241 (T½ = 14.4 a). As such, these data are representative of older, e.g., pre-1970s, SRS material [23], which is consistent with what would be expected at SRS with plutonium production ceasing in the 1980's. Notably, in accordance with the elevated ^{240}Pu/^{239}Pu observed in 2009 (**Fig. 7, Table 1**), an exceptionally high ^{241}Pu/^{239}Pu is also exhibited in 2009. These data further support the likelihood of the 2009 sample containing a contribution of offsite commercial reactor grade, i.e., higher burn-up, fuel.

For years when a plutonium-242 yield tracer was not used, ^{242}Pu was measured by 3STIMS and reported in **Table 1.** These data show markedly higher $^{242/239}$Pu than fallout (0.0041 ± 0.006

[12]), and suggest the presence of a significant contribution of higher burn-up fuel related material in the samples.

CONCLUSIONS

This work presents the results of a ten year study of plutonium in terrestrial environmental samples from the Savannah River Site, USA. This long term study reveals clear examples of where a single Pu source is demonstrable, as well as subtleties in Pu behavior where mixtures of sources are likely. Specifically, the following conclusions are drawn. The SRS environment features total Pu activities that are somewhat higher than atmospheric global fallout. Measured ^{238}Pu/$^{239+240}$Pu activity ratios attributed to SRS are above atmospheric global fallout ranges. The ^{240}Pu/^{239}Pu atom ratios are consistently lower than fallout, while the ^{242}Pu/^{239}Pu atom ratios are higher than fallout values. Overall, the plutonium signatures obtained in this study reflect a mixture of weapons-grade, higher burn-up, and fallout material. This study provides a blue print for long term low level monitoring of plutonium in the environment.

AUTHOR INFORMATION

Corresponding Author

*Phone:803-725-7756.Fax: 803-725-4478.E-mail: christopher.armstrong@srnl.doe.gov.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge Sheila Smalley for her tireless efforts and extraordinary attention to detail in performing the radiochemical separations throughout her many years of service at Savannah River National Laboratory.

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