

**Pu CONCENTRATION AND ISOTOPIIC COMPOSITION ANALYSIS  
OF CONTAMINATED SOILS FROM SAVANNAH RIVER SITE, USA AND  
FUKUSHIMA PREFECTURE, JAPAN BY A THERMO XSERIES 2  
QUADRUPOLE ICP-MS AND ALPHA SPECTROSCOPY**

An Undergraduate Research Scholars Thesis

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ISAAC JOHNSTON

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Research Advisor:

Dr. Peter Santschi

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## ABSTRACT

Pu Concentration and Isotopic Composition Analysis of Contaminated Soils from Savannah River Site, USA and Fukushima Prefecture, Japan by a Thermo XSeries 2 Quadrupole ICP-MS and Alpha Spectroscopy. (May 2014)

Isaac Johnston  
Marine Science Department  
Texas A&M University

Research Advisor: Dr. Peter Santschi  
Marine Science Department  
Texas A&M University

Inductively coupled plasma mass spectrometry (ICP-MS) and alpha spectroscopy were used to measure Plutonium (Pu) concentrations in soil samples from the Savannah River Site (SRS) and Fukushima Prefecture, Japan, the latter of which was collected after the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident. The SRS in the USA contains one-third of the nation's Pu inventory (~40 metric tons) in the contaminated soils, sediments, and groundwater through activities including nuclear materials production and radioactive waste re-processing. Soils sampled from the Fukushima prefecture contain Pu signals contributed both from atomic bomb fallout and the Fukushima Daiichi Nuclear Power Plant accident in 2011. The concentrations and isotopic ratio of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  in a sample can be used to infer the sources of Pu in the environment, thus providing precious information of Pu migration in the local region. . Pu concentrations and isotope ratios ( $^{240}\text{Pu}/^{239}\text{Pu}$ ) in four soil cores collected from the wetland down gradient of the seepage basin in the SRS suggest the Pu source is mainly atmospheric deposition and contaminated groundwater percolation. Three types of soils (urban, paddy and deciduous) all suggest Pu contributed from the FDNPP accident is well within pre-accident background values,

whereas the coniferous soil contains about three times higher concentration of Pu than background concentrations. All samples were processed and determined for Pu using both ICP-MS and alpha counting, for method comparison. Two classical resins for the separations of actinides and lanthanides (i.e., UTEVA and TEVA) were also compared to evaluate their efficiencies in removing  $^{238}\text{U}$ , which can form  $^{238}\text{U}^1\text{H}^+$  to interfere with  $^{239}\text{Pu}^+$ . In the end UTEVA resin, rather than TEVA resin, was chosen because it has an efficient separation of Pu from the high background of  $^{238}\text{U}$  seen in SRS surface soil, which contains abnormally high  $^{238}\text{U}$  released from the seepage basin, based on their different working principles and elution orders.

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## NOMENCLATURE

SRS	Savannah River Site
ICP-MS	Inductively Coupled Plasma Mass Spectrometer
FDNPP	Fukushima Daiichi Nuclear Power Plant
Bq	Becquerel (SI unit for radioactivity)
Pu	Elemental Plutonium
U	Elemental Uranium

# CHAPTER I

## INTRODUCTION

Pu is predominantly an anthropogenic element created during the decay of Uranium-239 in fission reactors. There are a few rare cases of Pu in nature (e.g., Pu<sup>244</sup>, Hoffman et al., 1971), but most of it is created in nuclear reactors or weapons. Pu has been distributed worldwide due to nuclear fallout, nuclear fuel reprocessing, and nuclear accidents primarily from the 1950's and 60's. The distributed Pu is often used for aquatic sediment dating by using the total activities of <sup>239</sup>Pu and <sup>240</sup>Pu (Kuehl et al., 2012). Pu can also be used to find the mixing rate of the sediment based on the vertical distribution of Pu isotopes and the age of the soil.

In another aspect, <sup>240</sup>Pu/<sup>239</sup>Pu ratio is often used to trace the specific Pu source because Pu isotopic ratios can vary with reactor type, nuclear fuel burn-up time, neutron flux and energy, and, for fallout from nuclear detonations, weapon type and yield. For example, weapon-grade Pu has a low <sup>240</sup>Pu/<sup>239</sup>Pu (<0.07), however global weapons testing fallout has an average <sup>240</sup>Pu/<sup>239</sup>Pu of 0.18. High and low irradiation conditions in reactors would result in these ratios ranging from <0.06 to >0.65, respectively (Dai et al., 2002). Each reactor has a slightly different ratio as does every nuclear warhead. As such, the source of Pu at any location can be found based on the <sup>240</sup>Pu/<sup>239</sup>Pu ratio. The isotopic ratio can be measured by an ICP-MS or other precise machine that can detect very low Pu concentrations (often 1x10<sup>-6</sup> g/L or less) and can distinguish between the two isotopes.

Some research has been done before looking at Pu concentrations using alpha counting (Livingston et al., 1975; Vajda et al., 2009); however, there are some limitations to this method. Alpha counting cannot distinguish between  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  because their alpha emission energies are so close that there is only one  $^{239,240}\text{Pu}$  peak. As such, no  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio can be established. It is also cumbersome; as it takes several days (often over a week) to count a sample in order to statistically distinguish the sample counts from the background counts (i.e. to reduce the counting error). In addition only a limited number of samples can be counted at a time due to the available number of alpha detectors. Due to these factors, alpha counting is not an ideal way to process a large number of samples or for the purpose of tracing Pu sources. In contrast, ICP-MS is quick to process a large number of samples with auto-sampler (each sample is done in less than 5 minutes) and one can obtain the  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios simultaneously. However, a basic ICP-MS (e.g. a Thermo XSERIES 2 Quadrupole ICP-MS) has one-tenth the detection limit of an alpha counter, for Pu analysis. Therefore a much larger soil sample is required for the former.

While testing the samples in the ICP-MS, two different resins, TEVA and UTEVA, are also being used to compare their efficiency in removing the  $^{238}\text{U}$  interference from  $^{239}\text{Pu}$  for high  $^{238}\text{U}$  containing surface soil like those seen in the SRS.



## CHAPTER II

### METHODS

Two sampling camps were attempted in March 2012 – collecting seven urban surface soils – and in March of 2013 – collecting three cores from a paddy soil, a deciduous soil and a conifer soil – all near Fukushima Prefecture. The lone point at the bottom right in Fig 1 denotes the location of the FDNNP while the sites northwest of that are the sampling locations. The samples were then shipped to Texas A&M University at Galveston. Duplicates were run for each sample.

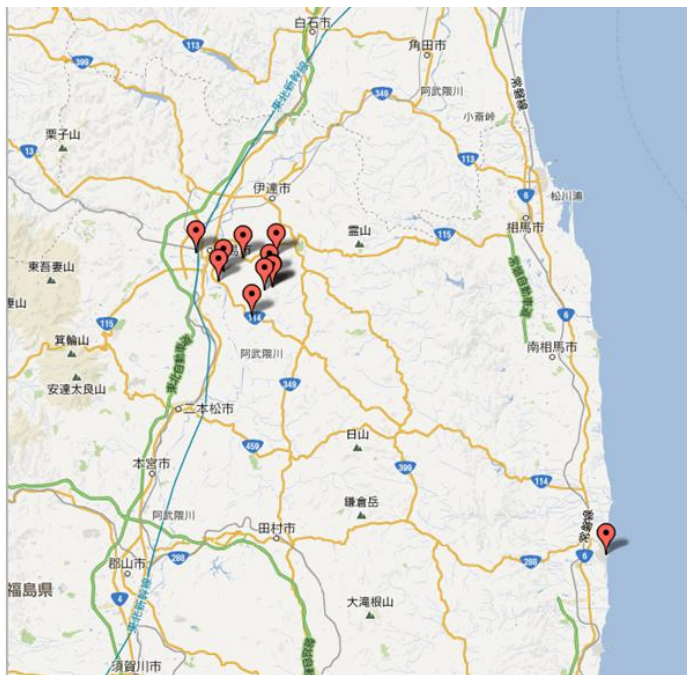


Figure 1 Sampling sites in Fukushima Prefecture, Japan.

The SRS samples were collected from the seep line in the F-area near the O-horizon boundary in the upper middle area of Fig 2. The soil was sampled to a depth of roughly 10-15 inches using a

hand trowel after removing the debris on the surface. The samples were stored in zip lock bags and shipped to Texas A&M University at Galveston where they were immediately placed in a 4°C refrigerator in the lab.

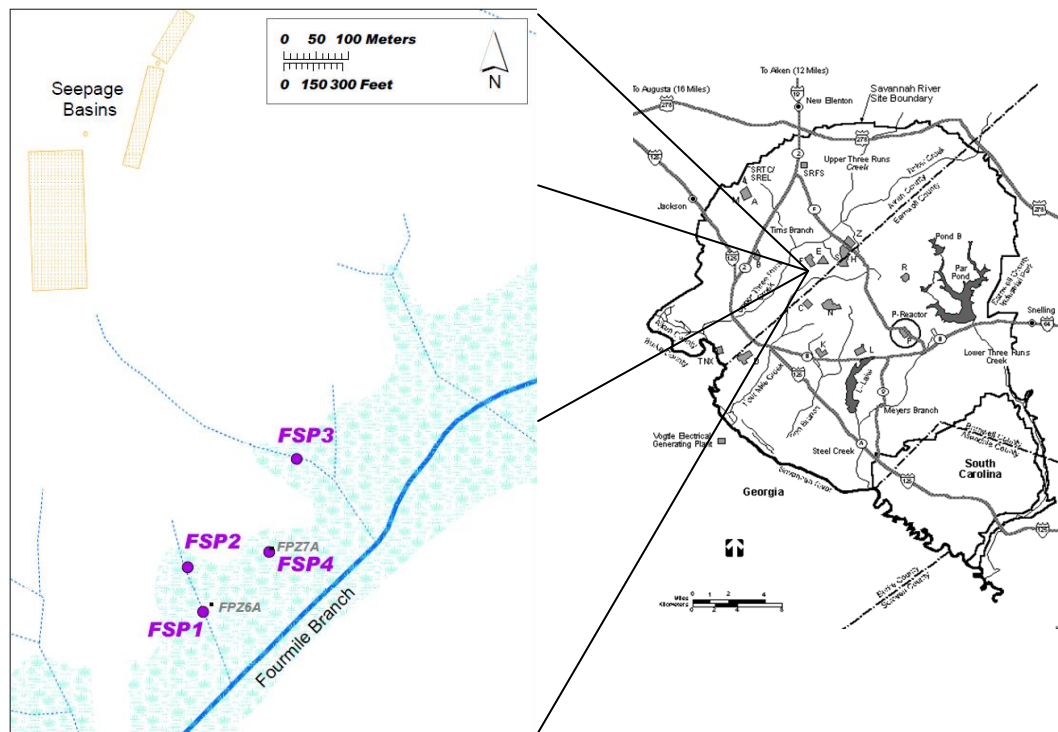


Figure 2 A map of the SRS sampling site with a zoom-in of the F-Area and sampling locations

### ICP-MS Methodology

An XSERIES 2 Quadrupole Thermo inductively coupled plasma mass spectrometer (ICP-MS) was used to measure  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ . Samples were prepared according to Lee *et al* (2011) and Morgenstern *et al* (2002) with some modifications. Ten grams of sediment was weighed out into a crucible. The sample was ashed in a 600 °C degree furnace for upwards of 16 hours. The sample was then transferred to a Teflon tube and 0.001 Bq of  $^{242}\text{Pu}$  tracer was added to the sample. After that, 12 ml of  $\text{HNO}_3$  and 12 ml of  $\text{HCl}$  was added to the sample. The samples were

capped tightly and heated at 85 °C overnight. After it cooled down, the sample was transferred to a centrifuge tube and centrifuged for 15 minutes. The supernatant was decanted and HNO<sub>3</sub> was added to re-suspend the sediment pellet and centrifuged again. All the supernatants were transferred into a glass beaker and evaporated to incipient dryness. After that 3 ml of HNO<sub>3</sub> was added to the beaker and evaporated.

The column pre-condition, sampling loading, elution methodology was as described below.

#### *TEVA*

The sample was treated with 0.5 mL NaNO<sub>2</sub> (0.5 g/ml), to convert all Pu to Pu (IV). Solutions were then processed with columns containing 150 mg of TEVA resin (EiChrom, Lisle, IL, USA). After passage of the entire sample solution through the column, the columns were rinsed with the following sequence: five 2 mL portions of 2M HNO<sub>3</sub>, two 2 mL 8M HCl, and one final 2 mL 2 M HNO<sub>3</sub>. The HNO<sub>3</sub> and HCl rinse steps were meant to remove U and Th (Kuel *et al.*, 2012), as both would otherwise introduce isobaric interferences (<sup>238</sup>U<sup>1</sup>H<sup>+</sup> on <sup>239</sup>Pu<sup>+</sup>) and elevated background contribution from <sup>232</sup>Th or <sup>238</sup>U peak tails. After these rinses, Pu is eluted from the columns with a sequence of 2 mL water, 2 mL of 0.05 M ammonium oxalate, and 2 mL of water, to a Teflon tube. The 6 mL Pu eluent fraction is evaporated to incipient dryness in the heating block at 90 °C. 2 ml 8M HNO<sub>3</sub> was added to it and then evaporated to incipient dryness one more time. Then 2 mL 2% HNO<sub>3</sub> was added and it was ready for ICP-MS analysis.

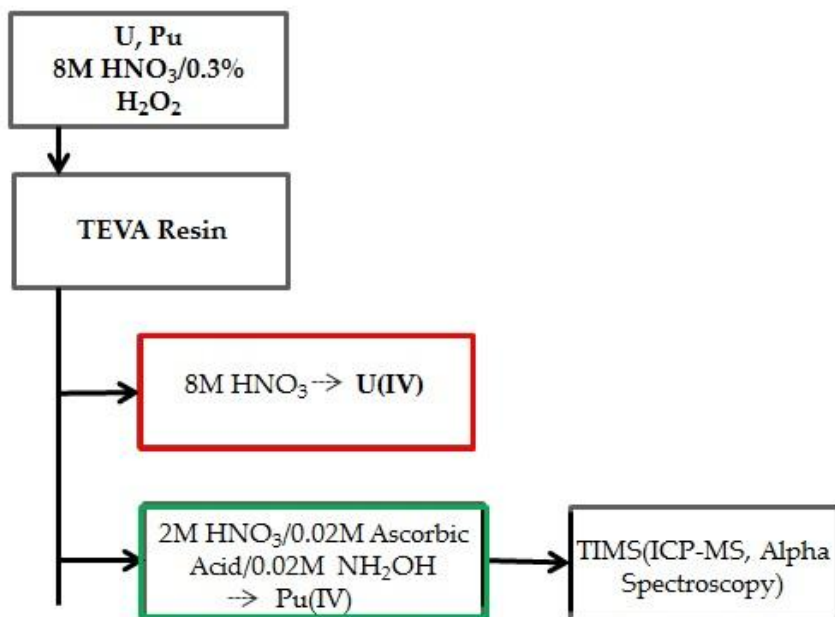


Figure 3 Flow schematic for TEVA resin. Green and red boxes denote the elution of Pu and U fractions, respectively.

### *UTEVA*

A column was set up and rinsed with 2 mL of HNO<sub>3</sub> twice then with 2mL of HNO<sub>3</sub>/0.3% H<sub>2</sub>O five times. Afterwards 2 mL of HNO<sub>3</sub>/0.3% H<sub>2</sub>O<sub>2</sub> was added to the beaker. The solution was then heated to 80 °C and 200 μL of NaNO<sub>3</sub> was added to the beaker after column condition. Sample was loaded into the column and the beaker was rinsed with 2mL HNO<sub>3</sub> and passed through the column. Pu was eluted from the column with 2 mL of HNO<sub>3</sub> containing 0.02 M NH<sub>2</sub>OH.HCL / 0.02 M ascorbic acid. The eluents were collected into a small Teflon tube, evaporated. 2 ml of HNO<sub>3</sub> was next added to glass beaker, and the acid was evaporated again. Then 2 mL 2% HNO<sub>3</sub> was added to re-dissolve the sample, which was then ready for ICP-MS

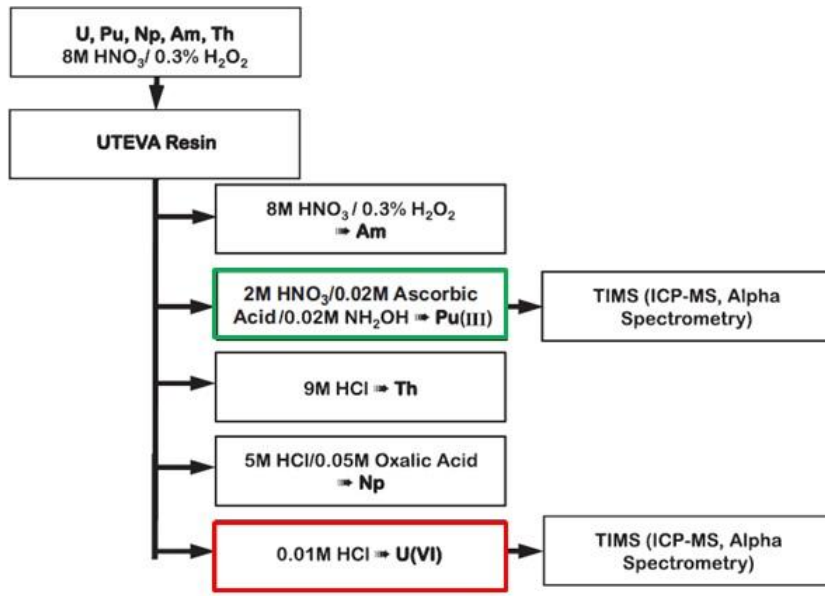


Figure 4 Flow scheme for UTEVA resin. Green and red boxes denote the elutions of Pu and U fractions.

### Alpha Spectroscopy Methodology

Determination of  $^{239,240}\text{Pu}$  total activity by alpha-counting was adopted from Ketterer *et al* (2004) and Santschi *et al* (2002). To prepare each sample for alpha counting, 0.5g of sample was dry-ashed in a 600°C furnace for > 16 hours. 0.05 Bq of  $^{242}\text{Pu}$  tracer was added to the sample. Concentrated  $\text{HNO}_3$  and  $\text{HCl}$  were then added to the sample, which was left at 85°C overnight.

After centrifuging the sample, the supernatant was decanted and  $\text{HNO}_3$  was added to the remaining sediment in the centrifuge tube. The sediment was centrifuged again to get another sample of supernatant. The two samples of supernatant were subsequently added together and evaporated to incipient dryness.

Next HCl and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  were added and left to react for one hour. DOWEX 1x8 100-200 mesh resin was placed in a column and wetted with  $\text{HNO}_3$ .  $\text{NaNO}_2$  was added to the sample; then the sample was carefully added to the column. The column was then successively rinsed with  $\text{HNO}_3$  and HCl to remove any interfering element, e.g.  $\text{U}^{238}$ . Pu fraction was eluted out with an HCl: $\text{NH}_4\text{I}$  solution. The effluent (Pu in HCl: $\text{NH}_4\text{I}$  solution) was evaporated to incipient dryness and was re-dissolved in 4mL 3N  $\text{HNO}_3$ . This evaporation was repeated another time.

Finally, the sample was placed in 5mLs  $\text{NH}_4\text{SO}_4$  and electroplated for two hours. After the two hours  $\text{NH}_4\text{OH}$  was added to the solution and, after one minute, the current was turned off. The electroplating apparatus was disassembled and the planchet, that now has the Pu on it, was placed in the alpha counter. The sample was left in the alpha counter until the counting error for the sample is less than 20%.

## CHAPTER III

### RESULTS AND DISCUSSION

The soil samples from the F-area seepline of the SRS were parallelly processed for the determination of  $^{239,240}\text{Pu}$  on alpha counter and ICP-MS, whereas the Fukushima soil was only processed for the determination of  $^{239,240}\text{Pu}$  on alpha counter, due to time constrains.

#### **Fukushima Prefecture**

Table 1 shows  $^{239,240}\text{Pu}$  concentrations and organic carbon (OC) contents of seven urban surface soils. Figure 5 shows  $^{239,240}\text{Pu}$  concentrations with depth of three types of soil: paddy, deciduous and coniferous soil. Generally, surface Pu concentrations of urban, paddy and deciduous soils are within the typical global fallout  $^{239,240}\text{Pu}$  activity range of 0.15-4.31 Bq/kg observed in Japanese soils before the FDNPP accident. The deciduous forest soil shows a typical surface maximum for  $^{239,240}\text{Pu}$  concentration, suggesting the main source of Pu is atmospheric deposition. The paddy soil has a homogenous  $^{239,240}\text{Pu}$  depth profile due to agricultural disturbances. In contrast, the coniferous forest soil contains elevated  $^{239,240}\text{Pu}$  at 14-17 Bq/kg, over three times the concentration seen in the urban, deciduous and paddy soils. The elevated but homogenous  $^{239,240}\text{Pu}$  depth profile of the conifer forest soil was caused by the slow turnover of biota. Moreover, the litter layer (0 cm) of the conifer forest soil shows no significant amount of  $^{239,240}\text{Pu}$ , which suggests Pu from the FDNPP source should have migrated downward.

Table 1  $^{239,240}\text{Pu}$  concentrations and OC (%,-wt) of seven urban surface soils collected from Fukushima Prefecture in 3/20/2012.

ID	$^{239,240}\text{Pu}$ (Bq/kg)	OC (%,-wt)
1	0.22 ±0.05	2.89
2	0.21 ±0.07	3.25
3	0.06 ±0.06	4.40
4	0.01 ±0.00	12.63
5	0.03 ±0.00	8.88
6	0.10 ±0.00	4.69
7	0.12 ±0.06	4.36

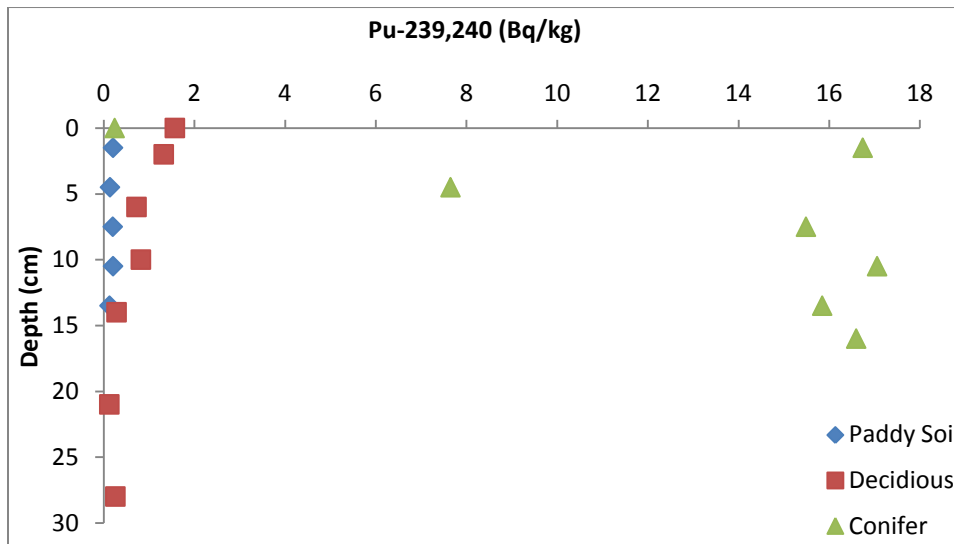


Figure 5 Depth profile of  $^{239,240}\text{Pu}$  in soil from the SRS. 4 locations total were measured however all of them are near the F-Area seepline

### F-Area in Savannah River Site (SRS)

All four of the SRS soils show slightly elevated Pu in the surface soil (ranging from 4Bq/kg to almost 12Bq/kg) which originates from site reprocessing. The Pu concentration decreases with depth for all four samples to below 1Bq/kg. (Fig. 6).  $^{239,240}\text{Pu}$  concentrations were significantly



correlated with organic carbon contents (wt-%), indicating it is mainly complexed with organic matter.

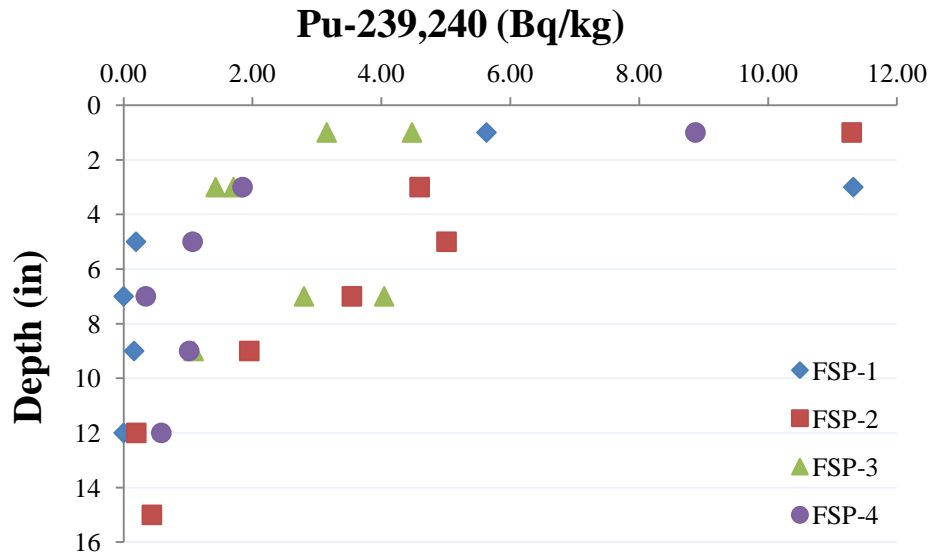


Figure 6 Depth profile of  $^{239,240}\text{Pu}$  in soil from the SRS. 4 locations total were measured however all of them are near the F-Area seepage line

The average  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios for the SRS soils was  $1.25 \pm 0.07$  (Table 2) which is seven times higher than the global average of  $0.180 \pm 0.007$ , suggesting the main source of Pu from SRS is reprocessing of radioactive material hence depleted  $^{239}\text{Pu}$  concentrations.

Only the surface soils that contain high  $^{239,240}\text{Pu}$  were processed for ICP-MS. Additionally, a seepage line soil, which was collected close to the four soil cores, was also included for method comparisons (ICP-MS vs. alpha-counting). The sample  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios ranged from  $0.56 \pm 0.02$  to  $1.99 \pm 0.08$ .

Table 2  $^{239,240}\text{Pu}$  activity concentration (from alpha counting) and isotopic ratios (from ICP-MS) in FSP cores

			$^{239,240}\text{Pu}$	$^{239}\text{Pu}/^{240}\text{Pu}$
	core	core depth(cm)	Bq/kg	
1	FSP1	1	5.63±0.58	
2		3	11.32±0.63	
3		5	0.19±0.10	
4		7	0.00±0.00	
5		9	0.16±0.11	
6		12	0.00±0.00	
1	FSP2	1	11.30±1.39	1.99±0.08
2		3	4.59±0.80	0.78±0.06
3		5	5.01±0.56	1.03±0.01
4		7	3.54±0.47	1.09±0.22
5		9	1.95±0.23	
6		12	0.20±0.11	
7		15	0.44±0.20	
8	FSP3	1	4.47±0.58	0.56±0.02
9		1	3.15±0.00	
9		3	1.70±0.25	1.62±0.25
11		3	1.43±0.00	
10		7	4.04±0.62	
13		7	2.80±0.00	
11	9	1.09±0.17		
13	FSP4	1	8.87±0.49	
14		3	1.84±0.28	1.72
15		5	1.07±0.24	
16		7	0.34±0.21	
17		9	1.02±0.24	
18		12	0.58±0.10	

Samples were run through the methodology for ICP-MS using both resins with 66±4% recovery for  $^{242}\text{Pu}$  when using the UTEVA resin and 60% recovery when using the TEVA resin. The

TEVA resin showed ~33ppt of  $^{239}\text{Pu}$  signal from  $^{238}\text{U}^1\text{H}^+$  interference while the UTEVA resin had a lower  $^{238}\text{U}^1\text{H}^+$  interference.

#### **Resin comparison (TEVA vs. UTEVA)**

Comparing the efficiency of TEVA to UTEVA resin, the recovery rate of  $^{242}\text{Pu}$  for both resins were comparable:  $66\pm 4\%$  for UTEVA and 60% for TEVA. However the TEVA resin did not efficiently remove  $^{238}\text{U}$  from the sample; its presence contributed to ~33ppt of  $^{239}\text{Pu}$  signal by ICP-MS, due to the formation of the  $^{238}\text{U}^1\text{H}^+$  ion. The same interference occurs for samples run through the UTEVA resin however the contributed  $^{239}\text{Pu}$  signal is much lower. Therefore, for high  $^{238}\text{U}$  containing samples, TEVA cannot be used to accurately measure for Pu.

#### **Detection method comparison (ICP-MS vs. alpha counting)**

Comparing ICP-MS results to alpha spectroscopy results for the SRS soil samples: When converting the  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  mass concentrations obtained from ICP-MS to activity concentration acquired from alpha spectroscopy, the result for F-Area seepline soil is  $(0.65 \pm 0.18)$  Bq/kg (n=2). Alpha-counting yields  $(0.92 \pm 0.12)$  Bq/kg (n=4). Thus, results from ICP-MS are about 70% of those by alpha-counting, which was expected. Alpha counting is known to be a more precise, though labor intensive, method.

## CHAPTER IV

### CONCLUSIONS

Therefore there are elevated  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios in the SRS F-Area top soil, which is caused by high  $^{240}\text{Pu}/^{239}\text{Pu}$  groundwater exfiltration and the decay of transplutonium isotopes like  $^{244}\text{Cm}$ . The SRS soil has a total Pu activity in the expected range (4-12Bq/kg in the surface soil) given its proximity to a running nuclear reactor. Three types of Fukushima soil (urban, paddy and deciduous forest soils) contain Pu concentrations within the typical global fallout activity range for that area, yet conifer forest soil shows elevated  $^{239,240}\text{Pu}$  concentrations which is likely contributed by the FDNPP accident.

Future studies of the Fukushima soil should examine the  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio to get a more complete picture of the Pu sources and possible reactor contamination. Future work on the SRS soil should focus on the main organic carrier that is complexing and fixing Pu in the particulate phase.

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