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**TO:** LeRoy Moore, PhD, Rocky Mountain Peace and Justice Center

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**INTERIM REPORT: PuO<sub>2</sub> PARTICLES IN THE INDIANA ST. CORRIDOR**

**Summary:** This report describes the analysis of a soil sample collected from the Indiana Street Corridor, undertaken with the specific objectives of identifying the possible presence of “hot particles” of PuO<sub>2</sub> (s). The sample, Composite #3, was collected along the Jefferson County right-of-way west of Indiana Street, in the proximity of the former east gate of the Rocky Flats plutonium pit production facility. Two hundred milligram nominal mass aliquots (n=12) of the dried, -200 mesh sieved fraction of the soil were analyzed by fusion with potassium hydroxide in the presence of a <sup>242</sup>Pu tracer. Pu fractions were separated using solid-phase extraction, and inductively coupled plasma mass spectrometry was employed to determine <sup>240</sup>Pu/<sup>239</sup>Pu atom ratios and <sup>239+240</sup>Pu activities. The atom ratios revealed that the Pu was essentially of 100% Rocky Flats origin.

A consistent baseline <sup>239+240</sup>Pu activity of (4.76 ± 0.23) pCi/gram was found for a subset of six of the twelve sub-samples. However, six additional sub-samples revealed significantly higher <sup>239+240</sup>Pu activities, an effect which arises from the presence of “hot particles” of pure PuO<sub>2</sub> in these aliquots. The results enabled the detection of PuO<sub>2</sub> (s) particles ranging from 3.2 to 109 pg, having equivalent diameters of 0.82 to 2.62 micrometers.

Respectfully submitted:



Michael E. Ketterer, Ph.D.

## PART I

### SOIL COLLECTION AND DETERMINATION OF BULK $^{239+240}\text{Pu}$ ACTIVITIES

**Soil collection.** A permit was obtained from Jefferson County's Transportation and Engineering Division to access a County-controlled portion of the Indiana Street corridor, in order to obtain soil samples for a Roddenberry Foundation-funded study of uptake of Rocky Flats Pu from soils into hemp plants. On July 6, 2019, I conducted a sampling excursion, with assistance from Tiffany Hansen and Sasha Stiles. The team collected six composite samples, each consisting of one full five-gallon bucket (~ 25 kg soil each). The study site was accessed on foot from our vehicles parked alongside the western shoulder of Indiana St. near the location of the former east gate of the operating Rocky Flats plant.

Composite samples were obtained by combining 25 to 30 individual soil increments (taken to a 5 cm depth with lateral insertion of a shovel into the top soil horizon, **Figure 1**). An area of ~ 15 meters x 15 meters was demarcated for each composite sample, and the composite was obtained by shoveling increments from randomly selected locations onto a tarp placed at the center of the 15 m x 15 m sampled area (**Figure 2**). All material was blended on the tarp and split in the field. Locations were all to the west of Indiana Street, as shown in **Figure 3**. Five gallon plastic buckets and lids were obtained locally. Samples are identified as Composite #1, Composite #2, Composite #3, Composite #4, Composite #5, and Composite #6. A one-quart (~ 1 kg) bag of sample was removed from each Composite sample. Composites #1-5 were transferred to Tiffany Hansen for the plant study; I retained the ~ 1 kg plastic bags, along with Composite #6 (the latter is a field duplicate of Composite #5).

**Sample processing and analytical sub-sampling.** The six ~ 1 kg plastic bag splits of Composites #1 – 6 were oven-dried (120° C, 3-4 hours). The material was de-agglomerated and sieved through a 10 mesh (~ 2 mm opening) brass sieve to obtain “soil” as it is customarily defined operationally. A ~ 30 gram sub-sample was removed from each -10 mesh soil composite; these sub-samples were hand-ground with a porcelain mortar/pestle.

The ground material was of suitable, fine particle size for laboratory analytical sub-sampling. Note that these specific aliquots contain all soil particles (< 10 mesh size), and are useful in estimating the bulk  $^{239+240}\text{Pu}$  activities in the soils.

**Chemical procedures for bulk activity determinations.** Two different treatments were used to prepare the samples for analysis: A) a nitric acid leach procedure and B) a potassium hydroxide molten salt fusion procedure.

**A. Nitric acid leach procedure.** Aliquots of  $2.0 \pm 0.1$  grams of ground sample were weighed into 40 mL Pyrex VOA bottles, each labeled with a high-temperature marker. The samples were dry-ashed at 450° C for three hours in a temperature-controlled muffle furnace to remove organic matter. Thereafter, 0.006932 Bq of Pu-242 tracer (0.061394 Bq per gram in 5 M nitric acid aqueous solution) was added to each sample, along with 10 mL of 16 M nitric acid. In addition to the six composite samples (Composite #1 through 6), various quality control samples were included in the batch:

- \* Composite Sample #6 was prepared/analyzed in duplicate;
- \* Five aliquots of Pu-devoid pulverized rock were prepared and analyzed;
- \* Two ~ 50 mg aliquots of a control sample with known  $^{239+240}\text{Pu}$  activity (IAEA 384, Fangataufu sediment) were mixed with ~ 2 g of inactive powdered rock; these mixtures were prepared and analyzed.

The mixtures were heated overnight (~ 16 hours) at 80° C in a convection oven, with occasional agitation of the bottles' contents. Thereafter, 10 mL of H<sub>2</sub>O were added to each sample; the mixtures were agitated again, and heated to 90° C in a convection oven, cooled, and permitted to sediment. The aqueous phases were decanted and filtered through pipet tips equipped with cotton wool plugs. The filter cakes were rinsed with 3 mL of additional H<sub>2</sub>O and collected in 50 mL polypropylene centrifuge tubes. 100 mg of FeSO<sub>4</sub> \* 7 H<sub>2</sub>O and 0.40 g of NaNO<sub>2</sub> were added to each sample; the solutions were mixed and heated without caps at 90° C for one hour in a convection oven to convert Pu to Pu(IV) and to expel excess NO<sub>2</sub> (g). A Pu-selective resin (TEVA, Eichrom, Lisle, IL) was used to separate and pre-concentrate Pu(IV); 50 mg of this resin was added to a 10 mL pipet tip equipped with glass wool plug; an additional 50 mg of TEVA was added to each sample; the sample-resin slurries were agitated for 30 minutes on an orbital shaker, and the sample-resin mixture was filtered through the columns containing the 50 mg of pre-loaded TEVA resin. After all of the sample solution had drained, each column was rinsed with the following sequence: i) 16.6 mL of 2 M aqueous HNO<sub>3</sub>; ii) 10 mL of 9 M aqueous HCl; and iii) 8.3 mL of 2 M aqueous HNO<sub>3</sub>. The column pass-through and rinses were discarded. Pu was eluted with the following sequence: i) 0.5 mL H<sub>2</sub>O; ii) 0.5 mL of 0.05 M aqueous ammonium oxalate; and iii) 0.5 mL H<sub>2</sub>O. These solutions were collected as one combined fraction in a 5 mL polypropylene test tube, and were suited for ICPMS analysis.

**B. Potassium hydroxide fusion procedure.** Aliquots of 1.0 ± 0.1 grams of ground sample were weighed into 20 mL glass vials, and the samples were ashed at 450° C for three hours in a muffle furnace to remove organic material. The ashed residues were transferred to 50 mL PTFE (Teflon) beakers. Thereafter, 0.006932 Bq of Pu-242 tracer (0.061394 Bq per gram in 5 M nitric acid aqueous solution) was added to each sample, along with 10 g of solid potassium hydroxide. The beakers were covered with a Teflon watch glass, and were heated for 15 hours at 150° C in a muffle furnace. Thereafter, the samples were agitated and then heated for an additional six hours at 235° C. The mixtures were removed from the furnace, cooled, and 5 mL of water was added to each beaker. The solids, consisting of precipitated/decomposed sample, were quantitatively transferred to 50 mL polypropylene centrifuge tubes, using additional deionized water, to achieve a final volume of 30-35 mL. The mixtures were agitated, and then heated at 80° C for one hour in a convection oven. The mixtures were centrifuged and the basic aqueous phases were decanted and discarded. Fifteen mL of warm 4 M HNO<sub>3</sub> (aq) were added to each pellet; the mixtures were again heated at 80° C for one hour in a convection oven. The solutions were filtered to remove any un-dissolved solids (a few milligrams of sand-size, un-ground mineral phases). The filtered solids were rinsed with 2 mL of 8 M HNO<sub>3</sub> (aq), and these rinses were added to the sample solution. 100 mg of FeSO<sub>4</sub> \* 7 H<sub>2</sub>O and 0.40 g of NaNO<sub>2</sub> were added to each sample; the solutions were mixed and heated without caps at 90° C for one hour in a

convection oven to convert Pu to Pu(IV) and to expel excess NO<sub>2</sub> (g). A Pu-selective resin (TEVA, EICrom, Lisle, IL) was used to separate and pre-concentrate Pu(IV); 50 mg of this resin was added to a 10 mL pipet tip equipped with glass wool plug; an additional 50 mg of TEVA was added to each sample; the sample-resin slurries were agitated for 30 minutes on an orbital shaker, and the sample-resin mixture was filtered through the columns containing the 50 mg of pre-loaded TEVA resin. After all of the sample solution had drained, each column was rinsed with the following sequence: i) 10 mL of 2 M aqueous HNO<sub>3</sub>; ii) 10 mL of 9 M aqueous HCl; and iii) 6.6 mL of 2 M aqueous HNO<sub>3</sub>. The column pass-through and rinses were discarded. Pu was eluted with the following sequence: i) 0.5 mL H<sub>2</sub>O; ii) 0.5 mL of 0.05 M aqueous ammonium oxalate; and iii) 0.5 mL H<sub>2</sub>O. These solutions were collected as one combined fraction in a 5 mL polypropylene test tube, and were suited for ICPMS analysis.

In addition to the six composite samples (Composite #1 through 6), various quality control samples were included in the batch:

- \* Composite Sample #6 was prepared/analyzed in duplicate;
- \* Three aliquots of Pu-devoid pulverized rock were prepared and analyzed;
- \* Two ~ 50 mg aliquots of a control sample with known <sup>239+240</sup>Pu activity (IAEA 384, Fangataufu sediment) were mixed with ~ 1 g of inactive powdered rock; these mixtures were prepared and analyzed.

**Mass spectrometry.** Analysis was performed using a Thermo X2 quadrupole ICPMS system located at Northern Arizona University; the instrument was used with a ESI Scientific Apex HF sample introduction system with FEP Teflon concentric nebulizer, self-aspirating at an uptake rate of 0.15 mL/minute. The instrument was tuned with a solution of 0.5 µg/L uranium; a sensitivity of ~ 500,000 cps for <sup>238</sup>U was achieved under these conditions, along with background count rates of < 1 cps at m/z 239 and 240. The <sup>238</sup>U<sup>1</sup>H<sup>+</sup>/<sup>238</sup>U<sup>+</sup> was measured periodically (by monitoring signals at m/z 238 and 239) throughout the analytical runs using the U tuning solutions as well as U-spiked sample fractions for samples devoid of detectable Pu, and was found to be 0.000032. The Q-ICPMS exhibits a mass bias factor of 1.007 per m/z, favoring light masses, and this factor was used in correcting raw ratio data. For the analysis, a “peak-jump” routine was utilized with a 10 ms dwell time at m/z 238, 239, 240, and 242. An individual 46 s integration consisted of 1000 sweeps through these four masses; three sequential integrations were acquired for each sample solution. A rinse solution consisting of 0.015 M ammonium oxalate dissolved in 0.1 M HNO<sub>3</sub> was used, as needed, to rinse the sample introduction system, and signals at m/z 239 were monitored to ensure adequate de-contamination of the sample introduction system prior to analyzing the next sample.

Based upon the results of signals monitored at m/z 238, it was observed that the Pu extracts prepared from the soil samples contained low levels of U, implying, minimal interference at m/z 239 is present. As the UH<sup>+</sup>/U<sup>+</sup> yield was found to be relatively low and very stable, the determination of <sup>239</sup>Pu was not significantly encumbered by interference from <sup>238</sup>U<sup>1</sup>H<sup>+</sup>, although small corrections were applied at m/z 239.

Based upon the results of the sandstone samples, and a critical examination the signals at m/z 240 (which provide a  $^{238}\text{U}^1\text{H}^+$ - free indication of the presence of Pu), a detection limit of  $\sim 0.2$  Bq/kg  $^{239+240}\text{Pu}$  was estimated for a sample of nominal mass of one gram. All of the Rocky Flats Composite samples contained ample detectable  $^{239+240}\text{Pu}$ .

The analyses of the control sample, IAEA-384, was performed in order to assess the accuracy of the activity data. Two determinations of separate sub-samples of IAEA-384 using the nitric acid leach procedure yielded  $^{239+240}\text{Pu}$  activities of  $124 \pm 1$  and  $117 \pm 4$  Bq/kg (one sd). The KOH fusion preparations yielded  $^{239+240}\text{Pu}$  activities of  $129 \pm 4$  and  $126 \pm 5$  Bq/kg (one sd). These results both indicate a positive bias in the activity measurements, as compared to a certified value of 107 Bq/kg and a 95% confidence interval of 103 – 110 Bq/kg, and imply that the results herein may somewhat over-estimate the actual  $^{239+240}\text{Pu}$  activities in the unknown samples.

Results for the Composite samples are given in **Table 1**. The Pu activities were calculated in the SI units of Becquerels per kilogram (Bq/kg) and were converted to pCi/g; note that 1 Bq/kg = 0.037 pCi/gram. The  $^{239+240}\text{Pu}$  activities in Composites 1 through 6 exhibit relatively good agreement between the two different preparation procedures, with disparities in individual pairs of results for specific composites possibly arising from “hot particle” effects. These effects take place when a specific aliquot contains an individual  $\sim$  micron-sized particle of relatively pure  $\text{PuO}_2$  (s).

It was observed that Composite #3 exhibited the highest  $^{239+240}\text{Pu}$  activities. The results of all six Composites indicate a prevailing trend towards increasing  $^{239+240}\text{Pu}$  in the northern portion of the sampled zone. It would be of interest to collect additional composite samples along this corridor at sites north of the Composite 3 location, to investigate for the possible presence of higher activities in other locations.

The Composite samples of surface soil all indicate activities that are considerably higher than “background” levels in Colorado soils arising from global fallout and/or Nevada Test Site fallout. Krey and Hardy (1970) reported an activity of 0.0110 and 0.0112 decompositions per minute per gram (dpm/g) for a fallout-containing soil collected from Derby, Colorado; this value corresponds to about 0.005 picocuries per gram (pCi/g). Hodge *et al.* (1996) published a more extensive study of  $^{239+240}\text{Pu}$  activities in Colorado Front Range soils; for purposes of comparison, their results are given in **Figure 4**. The Hodge samples, collected in 1994, exhibited fallout-derived  $^{239+240}\text{Pu}$  activities of 0.016 – 0.047 pCi/g (average = 0.027; standard deviation = 0.009 pCi/g). In contrast, our Composite samples exhibit  $^{239+240}\text{Pu}$  activities that are  $\sim 33$  to 100 times elevated above the average value for Front Range soils reported by Hodge *et al.* (1996).

It is readily apparent that the Pu source is not explainable as “stratospheric fallout”. A comparison of the  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratios in the samples vs. the known global fallout ratio (Kelley *et al.*, 1999) of  $0.180 \pm 0.014$  (2-sigma) indicates a prevalence of weapons-grade Pu, as is expected from the local Rocky Flats sources (e.g., Harley, 1980). Our ratios resemble values previously reported in mass spectrometric studies of Rocky Flats contaminated soils (Ketterer and Szechenyi, 2008), which have characteristic  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratios of  $\sim 0.05$  – 0.06. Based upon both the substantially elevated activities, and the weapons-grade  $^{240}\text{Pu}/^{239}\text{Pu}$  signatures, it is apparent that essentially 100% of the plutonium activity in these soils originated from Rocky Flats.

**Table 1.** Reported  $^{239+240}\text{Pu}$  activities and  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratios determined for the six composite samples collected from the Jefferson County portion of the Indiana Street corridor.

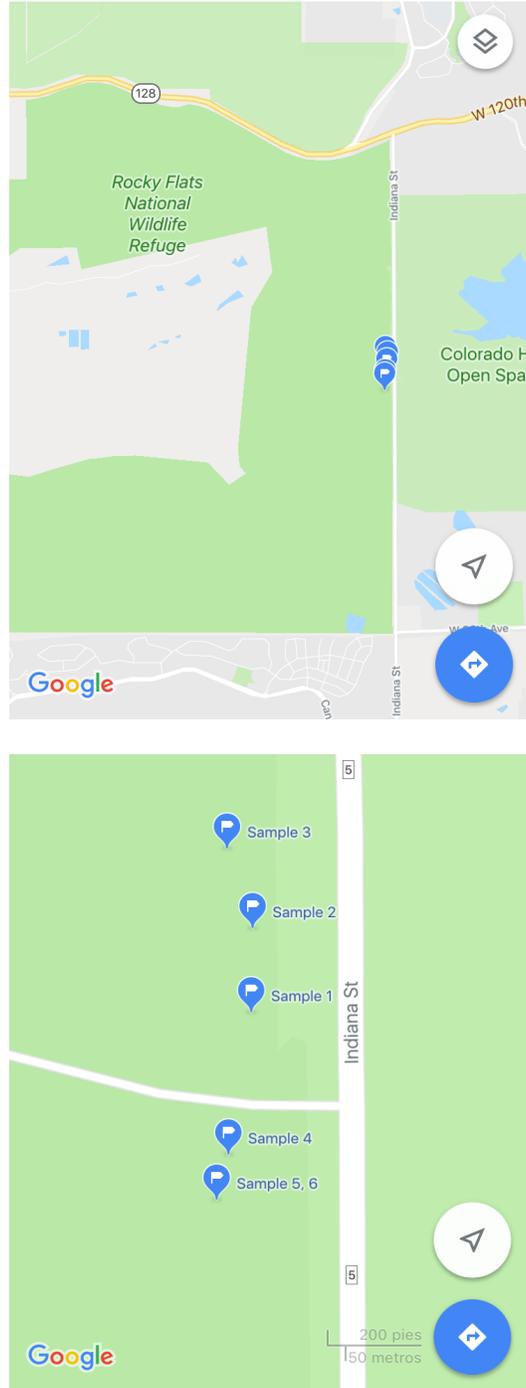
Lab ID	Site	# meas	Treatment	Bq/kg	sd bqkg	pCi/g	sd pCi/g	240/239	240239 sd
56	1	3	HNO3 leach	57.1	0.3	1.54	0.01	0.054	0.002
57	2	3	HNO3 leach	72.8	0.3	1.97	0.01	0.055	0.001
58	3	3	HNO3 leach	97.9	0.6	2.65	0.02	0.055	0.001
59	4	3	HNO3 leach	48.7	0.1	1.32	0.01	0.055	0.001
60	5	3	HNO3 leach	35.4	0.1	0.96	0.01	0.055	0.001
61	6	3	HNO3 leach	35.4	0.4	0.96	0.01	0.054	0.001
62	6 dup	3	HNO3 leach	33.7	0.3	0.91	0.01	0.055	0.001
284	1	3	KOH Fusion	73.0	2.8	1.97	0.07	0.053	0.005
285	2	3	KOH Fusion	63.3	0.5	1.71	0.01	0.051	0.006
286	3	3	KOH Fusion	99.9	2.3	2.70	0.06	0.053	0.002
287	4	3	KOH Fusion	79.2	1.2	2.14	0.03	0.053	0.001
288	5	3	KOH Fusion	34.1	1.1	0.92	0.03	0.057	0.005
289	6	3	KOH Fusion	35.4	1.0	0.96	0.03	0.061	0.006
290	6 dup	3	KOH Fusion	35.1	1.2	0.95	0.03	0.056	0.011



**Figure 1.** Process for collecting individual soil increments to 5 cm depths using a hand shovel.



**Figure 2.** Example of a composite sample, obtained from one of the  $\sim 15 \text{ m} \times 15 \text{ m}$  plots, consisting of 25 – 30 shovels of soil. The material was blended and then a  $\sim 1 \text{ kg}$  analytical aliquot was split in the field.



**Figure 3.** Location of the soil composites collected in this study; details are shown in the lower map. The indicated east-west road in the lower map is no longer present at the site. Each Composite was collected to represent the top 5 cm of soil in a ~ 15 meter x 15 meter square area.

Table I. Sampling Sites (Listed from North to South).

Site	Sample	Latitude N	Longitude W
Dixon Reservoir Area West of Fort Collins	94	40°32'55.72"	105°8'32.27"
Taft Hill Road South of Fort Collins	102	40°30'38.75"	105°6'47.36"
Lon Hagler Reservoir Area SW of Loveland	104	40°21'42.34"	105°9'4.48"
Rabbit Mountain Open Space E of Lyons	131	40°14'55.06"	105°12'20.22"
Antennae Mountain N of Boulder	99	40°7'30.05"	105°14'53.61"
Beech Open Space N of Boulder	130	40°5'16.07"	105°16'35.99"
El Dorado Springs Area NW of Rocky Flats	136	39°56'32.46"	105°15'34.47"
Colorado School of Mines W of Golden	161	39°44'12.31"	105°13'12.53"
Green Mountain Park W of Denver	138	39°42'17.18"	105°10'48.03"
Red Rocks Park N of Morrison	143	39°39'19.07"	105°11'57.99"
Chatfield Reservoir Area SW of Denver	156	39°32'7.92"	105°5'25.60"
Daniels Park NW of Castle Rock	152	39°28'46.21"	104°55'10.64"
Foothills Water Treatment Plant SW of Denver	148	39°28'9.67"	105°3'19.18"
Pine Cliff Ranch S of Sedalia	149	39°23'4.74"	104°59'22.46"
Air Force Academy N of Colorado Springs	158	38°58'36.19"	104°49'42.78"

Table II. Plutonium and Radiocesium in BSCP Soils Collected in the Summer of 1994.

Sample ID	Activity in pCi/g				Activity Ratio Cs/Pu
	Pu-239 + Pu-240 ± 1 S.D.		Cs-137 ± 1 S.D.		
94	0.019	0.001	0.65	0.01	34±2
102	0.027	0.001	0.98	0.03	36±2
104	0.042	0.002	1.52	0.01	36±2
131	0.030	0.001	1.00	0.03	33±2
99	0.037	0.002	1.28	0.03	35±2
130	0.032	0.002	1.22	0.02	38±2
136	0.018	0.001	0.79	0.02	44±3
161	0.024	0.001	0.87	0.02	36±2
138	0.047	0.002	1.76	0.03	37±2
143	0.019	0.001	0.65	0.01	34±2
156	0.016	0.001	0.60	0.02	38±3
152	0.024	0.001	0.98	0.02	41±2
148	0.024	0.001	0.87	0.02	36±2
149	0.022	0.001	0.90	0.02	41±2
158	0.019	0.001	0.92	0.02	48±3
England	0.0059	0.0006	0.23	0.01	39±4
Composite					
Average Ratio (without England)					38±4

**Figure 4.** Data tables from Hodge *et al.* (1996), indicating the locations and results of Colorado soils from their 1994 study of  $^{239+240}\text{Pu}$  and  $^{137}\text{Cs}$  activities. The soils exhibited an average of 0.027 pCi/g with a standard deviation of 0.009 pCi/g.

## PART II

### INVESTIGATION OF $^{239+240}\text{Pu}$ ACTIVITIES IN -200 MESH SOILS INTERROGATION OF SAMPLES FOR “HOT PARTICLES”

A “hot particle” study was specifically conducted on behalf of the Rocky Mountain Peace and Justice Center and the public stakeholder community. In this work, a series of twelve nominal 200 milligram aliquots of -200 mesh-sieved Composite Soil #3 (refer to Part I) were prepared and analyzed. This experiment investigates, operationally, whether a hot particle(s) is present in a small-mass soil aliquot, by comparing the total activities of Pu found among these aliquots.

Soils that *do not* contain hot particles of  $\text{PuO}_2$  (s) or similar refractory phases will normally exhibit a consistent activity with relatively small variance (e.g., < 5% relative) in  $^{239+240}\text{Pu}$  activity. Examples include soils with “global fallout” or other species forms of non-refractory Pu.

In this experiment with Composite #3, it is hypothesized that Rocky Flats-impacted soils will contain a consistent activity of non-refractory,  $\text{HNO}_3$ -soluble  $^{239+240}\text{Pu}$ , along with discrete particles of  $\text{PuO}_2$  (s) that are not attacked by hot  $\text{HNO}_3$  (aq). To chemically resolve the refractory and non-refractory Pu components, there are two basic strategies: i) dissolve the non-refractory Pu by acid leaching, then perform a second dissolution with HF mixtures and/or molten salts on the  $\text{HNO}_3$ -leached residue; and ii) use a total dissolution on all samples, while using a significant number of trials and perform statistical analysis on the pooled results to locate samples deviating from the non-refractory, baseline concentration of bulk-disseminated Pu.

In the present study, the second strategy has been followed, using a KOH fusion performed at  $600^\circ\text{C}$ . Following the dissolution, the samples were worked up and analyzed by ICPMS by similar methods as used in Part I.

**Sample processing and analytical sub-sampling.** A ~ 1 kg oven-dried split of Composite #3 from Part I was used in this work. ~ 100 grams of dry soil were sieved with a 200 mesh stainless steel sieve, having openings of 75 microns. The sieving operation was terminated when approximately 20 grams of -200 mesh material had been recovered.

**KOH fusion procedure.** Nominal aliquots of 200 mg were weighed into 20 mL Pyrex vials, along with  $2.0 \pm 0.2$  g of KOH (s) and 105.6 pg of  $^{242}\text{Pu}$  (NIST 4334j). The contents were melted at  $600^\circ\text{C}$  for 30 minutes; the molten KOH dissolves the sample, also attacking, but not destroying, the integrity of the vial. Thereafter the following workup was used:

- 1) Cool and add 10 mL  $\text{H}_2\text{O}$
- 2) Heat mixtures in glass vials in a boiling water bath for one hour
- 3) Mix; transfer contents to a 15 mL polypropylene centrifuge tube
- 4) Centrifuge/decant; discard aqueous solution phase
- 5) Re-dissolve pellet with 10 mL of 4 M  $\text{HNO}_3$  (aq)
- 6) Filter through a cotton wool plug; recover in a 125 mL polypropylene specimen cup
- 7) Add 100 mg of  $\text{FeSO}_4$  (s) in a concentrated aqueous solution

- 8) Add 400 mg of NaNO<sub>2</sub> (s) in a concentrated aqueous solution
- 9) Heat in a 100° C oven for one hour with lids off to expel NO<sub>2</sub> (g) and complete conversion of Pu to Pu(IV)
- 10) Cool and add 100 mg of TEVA resin in a concentrated aqueous slurry; cap containers and mix occasionally over a ~ 30 minute interval; recover resin on a 7 mL transfer pipet lab-fabricated column with glass wool plug (Globe Scientific)
- 11) Rinse columns with the following sequence: i) 10 mL of 2 M HNO<sub>3</sub> (aq); ii) 5 mL of 9 M HCl (aq) and iii) 5 mL of 2 M HNO<sub>3</sub> (aq); discard rinses
- 12) Elute and collect Pu from the columns via the following sequence: i) 0.5 mL of water; ii) 0.5 mL of 0.05 M aqueous ammonium oxalate; and iii) 0.5 mL of water.

**Mass spectrometry.** Analysis was performed using a Thermo X2 quadrupole ICPMS system located at Northern Arizona University; the instrument was used with a ESI Scientific Apex HF sample introduction system with FEP Teflon concentric nebulizer, self-aspirating at an uptake rate of 0.15 mL/minute. The instrument was tuned with a solution of 0.5 µg/L uranium; a sensitivity of ~ 450,000 cps for <sup>238</sup>U was achieved under these conditions, along with background count rates of < 1 cps at m/z 239 and 240. The <sup>238</sup>U<sup>1</sup>H<sup>+</sup>/<sup>238</sup>U<sup>+</sup> was measured periodically (by monitoring signals at m/z 238 and 239) throughout the analytical runs using the U tuning solutions as well as U-spiked sample fractions for samples devoid of detectable Pu, and was found to be 0.000015. The Q-ICPMS exhibits a mass bias factor of 1.007 per m/z, favoring light masses, and this factor was used in correcting raw ratio data. For the analysis, a “peak-jump” routine was utilized with a 10 ms dwell time at m/z 238, 239, 240, and 242. An individual 46 s integration consisted of 1000 sweeps through these four masses; three sequential integrations were acquired for each sample solution. A rinse solution consisting of 0.015 M ammonium oxalate dissolved in 0.1 M HNO<sub>3</sub> was used, as needed, to rinse the sample introduction system, and signals at m/z 239 were monitored to ensure adequate de-contamination of the sample introduction system prior to analyzing the next sample.

Based upon the results of signals monitored at m/z 238, it was observed that the Pu extracts prepared from the soil samples contained low levels of U, implying, minimal interference at m/z 239 is present. As the UH<sup>+</sup>/U<sup>+</sup> yield was found to be relatively low and very stable, the determination of <sup>239</sup>Pu was not significantly encumbered by interference from <sup>238</sup>U<sup>1</sup>H<sup>+</sup>, although small corrections were applied at m/z 239.

**Results.** The activities of <sup>239+240</sup>Pu, <sup>240</sup>Pu/<sup>239</sup>Pu atom ratios, and the mass concentrations of <sup>239+240</sup>Pu in pg/g are reported in **Table 2**. The Pu activities were calculated in the SI units of Becquerels per kilogram (Bq/kg) and were converted to pCi/g; note that 37 Bq/kg = 1 pCi/gram. The specific activities used in the calculations were: <sup>239</sup>Pu, 2.30 x 10<sup>9</sup> Bq/g; <sup>240</sup>Pu, 8.42 x 10<sup>9</sup> Bq/g, and <sup>242</sup>Pu, 1.46 x 10<sup>8</sup> Bq/g. It is observed that the <sup>239+240</sup>Pu activities of six of the samples form a tight distribution having 4.76 ± 0.23 pCi/g (average ± standard deviation). Note that the minus 200 mesh soil fraction exhibits higher <sup>239+240</sup>Pu activity in comparison to the bulk (-10 mesh) samples analyzed in Part I of the study. Six of the subsamples contain higher <sup>239+240</sup>Pu activities ranging up to 41.9 pCi/g; the results are interpreted as revealing the presence of “hot particles” in the latter six subsamples.

**Sources of Pu.** Besides speed and ease of analysis, a significant advantage of ICPMS in this study is the ability to measure  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratios alongside the  $^{239+240}\text{Pu}$  activities. These atom ratio results are also given in Table 2. It is apparent that all samples are fully congruent with the anticipated  $^{240}\text{Pu}/^{239}\text{Pu}$  isotope composition of Rocky Flats Pu, although significant isotopic differences may exist between the most elevated sample and the baseline group. While it is beyond the scope of this report, it may be feasible to discriminate among different Rocky Flats-related Pu sources (e.g., specific fires or time events, vs. 903 Pad) and chronologies by more refined isotope measurements involving an analysis of the  $^{241}\text{Pu}$ - $^{241}\text{Am}$  parent-daughter pair (Pöllänen *et al.*, 2006). This analysis could reveal interesting information about the relative timing of hot particle releases from various episodic fires vs. the composite emissions of non-refractory Pu from the 903 Pad.

**Threshold for hot particle detection.** The assembled data of Table 2 may be used to determine a “detection threshold” for the presence of a hot particle in a specific sample, when compared to the baseline activity of the non-refractory Pu. The data are expressed in pg Pu per gram soil for purposes of this calculation; the non-refractory Pu group (Lab ID’s 1, 3, 5, 6, 14, 15) contained an average of 67.4 pg/g Pu (summed mass of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ ) with a standard deviation of 3.1 pg/g Pu. If one uses a criterion that a hot particle is present when the measured pg/g of Pu exceeds  $(67.4 + 3 \times 3.1)$  or 76.7 pg/g Pu, the difference in mass concentration (found – 67.4) is used to compute the excess pg/g for the detectable samples. For six samples (Lab ID’s 2, 4, 10, 11, 12, 13) excess pg/g has been used to calculate the excess mass of Pu (pg) present in that aliquot. The mass of elemental Pu is converted into the stoichiometrically equivalent mass of  $\text{PuO}_2$  (s). Based on the  $\text{PuO}_2$  density of  $11.5 \text{ g/cm}^3$ , a corresponding volume, radius and diameter of the particle are computed.

**Size characteristics of Rocky Flats  $\text{PuO}_2$  (s) particles.** The results, as shown in **Table 3** and **Figure 5**, reveal the presence of particles of respirable size, with calculated diameters ranging between 0.82 and 2.62 microns. The propensity for  $\text{PuO}_2$  (s) particles to become airborne from soils must be evaluated under various scenarios representing human use and contact with the surface soils, under different environmental and meteorological conditions.

Additional studies, with greatly expanded sets of samples, are warranted in order to address the following questions: A) what is the geospatial distribution of the  $\text{PuO}_2$  (s) particles; B) what is their size distribution, as a function of distance and direction from the former plant, and C) what scenarios might exist for humans inhaling  $\text{PuO}_2$  (s) particles, either as a result of natural aeolian transport, and/or exacerbated dispersion of the particles during construction activities.

Refinements of the current experiments presented in Part II of the report are envisioned, in order to extend the  $\text{PuO}_2$  (s) detection thresholds to smaller sizes. Detection of smaller particles is more facile in soils having lower baseline, non-refractory  $^{239+240}\text{Pu}$  activities; however, it may also be less likely that lower baseline soils actually contain  $\text{PuO}_2$  (s) particles.

The results further demonstrate that having a reported soil activity of  $< 50 \text{ pCi/g}$   $^{239+240}\text{Pu}$  does not guarantee an absence of  $\text{PuO}_2$  (s) particles, and therefore, the 50 pCi/g soil standard cannot be considered to prevent human inhalation of particles on the Rocky Flats national Wildlife Refuge and surrounding areas. The presence or absence of hot particles needs to be routinely

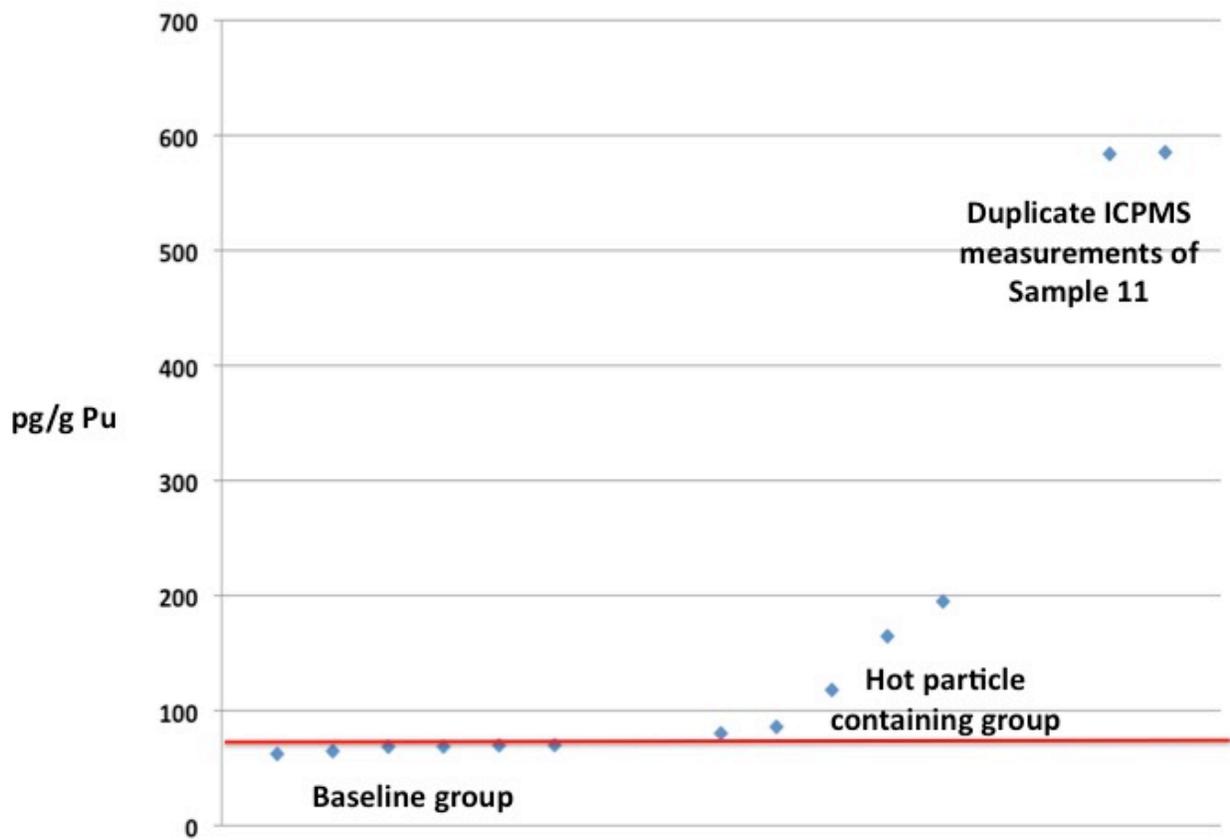
investigated, independently of a simplistic comparison of  $^{239+240}\text{Pu}$  activities vs. a 50 pCi/gram standard in assessing the true risk represented by possible  $\text{PuO}_2$  (s) particles.

Lab ID	# meas	240/239	240239 sd	pCi/g	pCi/g sd
1	3	0.054	0.002	4.85	0.03
2	3	0.057	0.003	11.70	0.02
3	3	0.055	0.004	4.41	0.03
4	3	0.053	0.005	8.31	0.15
5	3	0.050	0.002	4.54	0.02
6	3	0.052	0.004	4.84	0.21
10	3	0.053	0.002	6.06	0.09
11	3	0.062	0.000	41.94	0.26
12	3	0.054	0.002	13.76	0.05
13	3	0.058	0.003	5.71	0.13
14	3	0.054	0.002	4.95	0.02
15	3	0.056	0.001	4.95	0.01
11 duplicate measurement	3	0.060	0.002	41.92	0.44

**Table 2.** Results for the activities of  $^{239+240}\text{Pu}$  and  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratios in a series of 200 mg nominal mass subsamples of Composite Soil #3 from the Indiana St. corridor. The horizontal axis labels correspond to the Laboratory ID's of each specific subsample.

Lab ID	pg/g Pu	Excess pg/g	Excess pg Pu	pg PuO <sub>2</sub>	cm <sup>3</sup> PuO <sub>2</sub>	r, μm	d, μm
13	80.2	12.8	2.85	3.23	2.80E-13	0.41	0.82
10	85.8	18.4	5.12	5.81	5.05E-13	0.49	0.98
4	117.9	50.5	11.2	12.7	1.10E-12	0.64	1.28
2	164.6	97.2	20.8	23.6	2.05E-12	0.78	1.56
12	194.9	128	27.4	31.1	2.70E-12	0.87	1.74
11 avg	584.6	517	96.2	109	9.48E-12	1.31	2.62

**Table 3.** Results for the masses of Pu detected in a series of 200 mg nominal mass subsamples of Composite Soil #3 from the Indiana St. corridor. The results herein are used to determine the equivalent masses of PuO<sub>2</sub> (s), the volume of PuO<sub>2</sub> (s), the radius and diameter of the respective particle (refer to text).



**Figure 5.** Plot of the mass concentrations, in picograms per gram, for the samples analyzed in the experiments of Part II. The horizontal red line corresponds to the detection threshold between “baseline” samples and samples exhibiting hot particles, at a decision threshold of 76.7 pg/g Pu (refer to text).

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