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REPORT FOR CONSULTING SERVICES
FOR HANSEN RODDENBERRY CATALYST GRANT AWARD
HEMP UPTAKE OF PLUTONIUM STUDY

Introduction. A study has been conducted of the uptake of plutonium (Pu, $^{239+240}$Pu) in commercial *Cannabis sativa* soil-grown hemp plants, in order to investigate the potential uptake of $^{239+240}$Pu from soils. Plants were cultivated indoors at a commercial hemp-growing facility, Rubi Hemp Solutions, under the direction of Zackary Guignardi. The soils investigated were obtained from surface soil in the proximity of the Rocky Flats site (refer to my report of 02 August 2019). A negative control soil was used by Rubi Hemp Solutions, along with five different soils containing Rocky Flats-originating $^{239+240}$Pu at levels ranging from 33 to 100 Bq/kg. The hemp plants were harvested; the flower and leaves were analyzed in this study, while the roots and the stems were not analyzed. Two different plant strains, referred to as "Wife" and "Cherry", were used in the study.

Experimental Procedures. Plant material was air-dried at Rubi Hemp Solutions and transferred to my custody on November 11, 2019. The entire quantity of leaf/flower material obtained from each plant was ground using a household-type coffee bean grinder, which was de-contaminated by wiping and removing all adhering material in between samples. Nominal five gram samples of ground plant material were taken for analysis, and were weighed into 40 mL borosilicate glass vials. The plant material was subsequently dry-ashed at 450^{o} C in a muffle furnace for ~ 16 hours to ensure complete conversion to inorganic residue.

The ashed plant materials were each spiked with a Pu-242 tracer (NIST 4334i, 4.487 mBq, 30.73 picograms); thereafter, each sample was mixed with 5 mL of 2 molar aqueous nitric acid to ensure reaction of carbonates present in the plant ashes. After standing overnight, 10 mL of 16 M nitric acid was added, and the vials were capped; mixtures were heated in a convection oven at 95^{o} C for six hours. Thereafter, 15 mL of deionized water was added, and the mixtures were heated overnight at 75^{o} C. The sample mixtures contained small quantities of un-dissolved residue, which was removed by filtration with a 23 mL transfer pipet equipped with a cotton wool plug.

The filtered sample solutions were collected in 50 mL polypropylene centrifuge tubes, and were each treated with 100 mg of $FeSO_4*7H_2O$ and 600 mg of $NaNO_2$, both added in the form of a

concentrated aqueous solution. This operation was conducted in the fume hood to remove NO_2 (g) generated in the ensuing chemical reaction. The combination of Fe(II) and nitrite converts the Pu to the Pu(IV) oxidation state; to complete the reaction, the treated solutions were geated for 2 hours (uncapped) in a convection oven. After cooling, 150 mg of EIChrom TEVA resin (TES062717, TE-B200-S, 50-100 micron particle size) was added to each sample solution, and the tubes were capped. The sample solution – resin mixtures were shaken on an orbital platform shaker for 30 minutes to permit solution-resin equilibration and uptake of Pu. The resin was subsequently collected on lab-fabricated 23 mL columns (prepared from Globe Scientific "jumbo" transfer pipets, 139050B) equipped with a glas wool plug. The solutions passing through the resin were discarded, and the columns were rinsed with the following sequence to remove uranium (a critical contaminant in the measurement of $^{239+240}Pu$ by mass spectrometry): 2 x 10 mL 2 M HNO_3 + 1 x 10 mL 9 M HCl + 1 x 5 mL 2 M HNO_3. The rinses were discarded, and Pu was eluted with 0.5 mL H_2O + 0.5 mL 0.05 M ammonium oxalate + 1.0 mL H_2O.

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 ~ 600,000 cps for ^{238}U was achieved under these conditions, along with background count rates of < 1 cps at m/z 239 and 240. The $^{238}U^1H^+/^{238}U^+$ 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 0.000018. 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 or five sequential integrations were acquired for each sample solution. A rinse solution consisting of 0.015 M ammonium oxalate dissolved in 0.1 M HNO_3 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 very low levels of U, implying, minimal interference at m/z 239 is present. As the UH^+/U^+ yield was found to be relatively low and very stable, the determination of ^{239}Pu was not significantly encumbered by interference from $^{238}U^1H^+$, although small corrections were applied at m/z 239.

A critical examination of the results yielded a detection limit of 0.05 Bq/kg $^{239+240}Pu$ was estimated for a sample of nominal mass of one gram. Three aliquots of a "control" hemp plant material (grown in non-Rocky Flats soil) were spiked with 50-100 mg quantities of a control sample (IAEA-384, Fangataufu sediment) to evaluate the $^{239+240}Pu$ measurements. The IAEA-384 preparations yielded $^{239+240}Pu$ activities of 104 ± 6, 111 ± 4, and 115 ± 4, which indicate good agreement with a certified value of 107 Bq/kg and a 95% confidence interval of 103 – 110 Bq/kg. The IAEA-384 results thus imply relatively little bias in the measured $^{239+240}Pu$ activities.

Findings. The results obtained are presented in Table 1. The following summarizes the findings:

* Plutonium is detected in the majority of the hemp plant samples, at a detection limit of 0.05 Bq/kg $^{239+240}$Pu.

* The "control" group of samples had the greatest frequency of "not detected" results. However, one of the hemp samples from plant material grown in the "control" soil exhibited relatively high $^{239+240}$Pu activity (Cherry strain, Plant 16, 0.466 Bq/kg).

* Nearly all of the samples of plant material grown in Rocky Flats-contaminated soils exhibited detectable $^{239+240}$Pu, and the three highest plant $^{239+240}$Pu activities were found therein.

* The plutonium measured in the plant samples is of Rocky Flats origin, based upon a ^{240}Pu/^{239}Pu atom ratio that is ~ 0.05-0.06, characteristic of weapons-grade Pu.

* The results appear to suggest that Pu from the soils is being uptaken into the plants, although the findings of a high $^{239+240}$Pu activity in one of the "control" soils is difficult to conflate with soil plant uptake, and may stem from external contamination.

Respectfully submitted:

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My Lab ID	# meas	Strain	Plant #	Soil	Bq/kg	Bq/kg SD	240Pu/239Pu	240/239 sd
4	3	Wife	4	Control	**< 0.05**			
8	3	Wife	8	Control	0.053	0.009		
9	3	Wife	9	Control	**< 0.05**			
13	3	Wife	13	Control	**< 0.05**			
17	3	Wife	17	Control	**< 0.05**			
22	5	Wife	22	Control	**< 0.05**			
38	5	Cherry	16	Control	0.466	0.050	0.042	0.010
39	5	Cherry	17	Control	0.050	0.013		
40	5	Cherry	18	Control	0.071	0.015		
41	5	Cherry	19	Control	**< 0.05**			
42	5	Cherry	20	Control	0.197	0.009		
43	5	Cherry	21	Control	0.073	0.017		
44	5	Cherry	21 dup	Control	0.078	0.003		
45	3	Cherry	21 dup	Control	0.057	0.001		
1	3	Wife	1	1	0.067	0.010		
11	3	Wife	11	1	0.133	0.014		
19	3	Wife	19	1	0.114	0.012		
35	3	Cherry	13	1	0.106	0.022		
36	3	Cherry	14	1	0.055	0.006		
37	3	Cherry	15	1	0.145	0.013		
58	3	Cherry	13 dup	1	0.079	0.007		
5	3	Wife	5	2	0.102	0.015		
16	3	Wife	16	2	0.092	0.019		
20	5	Wife	20	2	0.545	0.018	0.051	0.010
21	5	Wife	21	2	0.260	0.017		

32	5	Cherry	10	2	0.073	0.012		
33	5	Cherry	11	2	0.065	0.016		
34	5	Cherry	12	2	0.323	0.019		
57	5	Cherry	10 dup	2	0.120	0.010		
2	3	Wife	2	3	0.108	0.025		
10	3	Wife	10	3	0.105	0.013		
12	3	Wife	12	3	0.162	0.008		
24	5	Cherry	2	3	0.140	0.011		
26	5	Cherry	4	3	0.902	0.026	0.059	0.003
30	3	Cherry	8	3	0.195	0.015		
59	5	Wife	12 dup	3	0.153	0.025		
6	3	Wife	6	4	**< 0.05**			
7	3	Wife	7	4	0.146	0.004		
15	3	Wife	15	4	0.042	0.009		
28	3	Cherry	6	4	0.085	0.020		
29	3	Cherry	7	4	0.230	0.016		
60	5	Wife	6 dup	4	**< 0.05**			
3	3	Wife	3	5	0.129	0.012		
14	3	Wife	14	5	0.220	0.006		
18	3	Wife	18	5	0.110	0.007		
23	5	Cherry	1	5	0.210	0.006		
25	5	Cherry	3	5	0.773	0.024	0.059	0.005
27	3	Cherry	5	5	0.155	0.025		