MONITORING ^{241}Pu IN UKRAINIAN SOIL

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ABSTRACT. We collected *ca.* 500 soil samples from within the inhabited territory of the Ukraine for ^{241}Pu determination. To cover the expected wide range of contamination levels due to fallout from the Chernobyl Nuclear Power Plant (NPP) accident, we took samples in the following regions: Kiev (170 samples), Gitomir (70 samples), Chernigov (60 samples), Rovno (70 samples), other regions (130 samples). We used 10 g of soil from a 5-cm depth coring cylinder. We ashed the samples for 4 h at 400°C and then used a mixture of HCl and HF followed by HNO_3 to solubilize the plutonium. We stabilized the plutonium with $NaNO_3$ and isolated it using Dowex-1 ion exchange resin. Finally, we deposited the plutonium electrochemically onto stainless steel disks. We determined the activities of the α-emitting isotopes of plutonium, including the ^{242}Pu yield tracer, using traditional α-spectroscopy systems. Our chemical yields were typically 40–80%. We used liquid scintillation counting (LSC) for the determination of the ^{241}Pu activity on each disk. Our method employs an ultra low-level α/β spectrometer (Quantulus 1220™), 7-ml aluminium/Teflon® vials and a high light output, toluene based liquid scintillation cocktail (GS-1). The analytical parameters were: counting efficiency = 15%, background count rate = 0.55 cpm, figure of merit (E^2/B) = 409, minimum detectable activity (MDA) for 120 min count = 2.3 Bq kg^{-1} and the MDA for a 500 min count = 1.0 Bq kg^{-1}. Geometric mean values and standard deviations for ^{241}Pu activities in soil from the inhabited regions which were studied were $20.5^{+35.2}_{-12.9}$ Bq kg^{-1}.

INTRODUCTION

Although ^{241}Pu is a low-energy beta-emitter (E_{max} = 20.8 keV) with a comparatively short half-life (14.4 yr), it is indirectly of considerable radiological significance because it decays to ^{241}Am ($t_{½}$ = 432 yr) which in turn decays to ^{237}Np ($t_{½} = 2.1 \times 10^6$ yr). Both of these daughters are α-emitters and are therefore regarded as being highly radiotoxic while the half-life of ^{237}Np gives it importance in terms of long term repository storage. The main sources of plutonium in the environment are derived from nuclear weapons testing fallout, discharges from nuclear fuel reprocessing plants and accidental releases due to NPP incidents. Releases from Chernobyl of the main long-lived radionuclides are given in Table 1 (Begithsev *et al.* 1990). The ^{241}Am activity released into the environment from Chernobyl is significantly less the activities of the majority of plutonium isotopes; however, ^{241}Pu decay will produce a significant increase in the environmental inventory of ^{241}Am (Fig. 1). Indeed, within 50 yr of the accident, the activity of ^{241}Am in the environment will reach a peak and will exceed the initial activity by a factor of ×40. Therefore, the increasing environmental inventory of ^{241}Am and its radiotoxicity make this study important. Different methods of analysis based on LSC can be used for the determination of ^{241}Pu in different environmental samples (Horrocks and Studies 1959; Miglio and Willis 1988; Parua, Raab and Radoszewski 1993; Ryan *et al.* 1993; Seidel and Volf 1972; Yu-fu *et al.* 1990, 1991). The method that we propose to use is based on a 2π counting geometry where the α- and β-emitting isotopes of plutonium are electrodeposited onto metal disks (Ryan *et al.* 1993). The advantages of this method are high sensitivity, absence of any influence of quenching and preservation of the disks (non destructive analysis). The quality of the ^{241}Pu determinations depends on the degree of chemical separation and subsequently, the quality of the electrodeposition (source thickness).

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TABLE 1. Activities of the Main Long-Lived and Biologically Significant Radionuclides in the "Active Zone" of the Fourth Chernobyl NPP Reactor at the Time of the Accident (Begithsev *et al.* 1990)*

Radionuclide	Activity (Bq)	Radionuclide	Activity (Bq)
^{238}Pu	9.4×10^{14}	^{241}Am	1.37×10^{14}
^{239}Pu	9.6×10^{14}	^{137}Cs	2.60×10^{17}
^{240}Pu	1.5×10^{15}	^{134}Cs	1.50×10^{17}
^{241}Pu	1.9×10^{17}	^{90}Sr	2.20×10^{17}
^{242}Pu	2.0×10^{12}		

*Ratio of ^{241}Pu to sum of $^{238}Pu + ^{239}Pu + ^{240}Pu \approx 59$

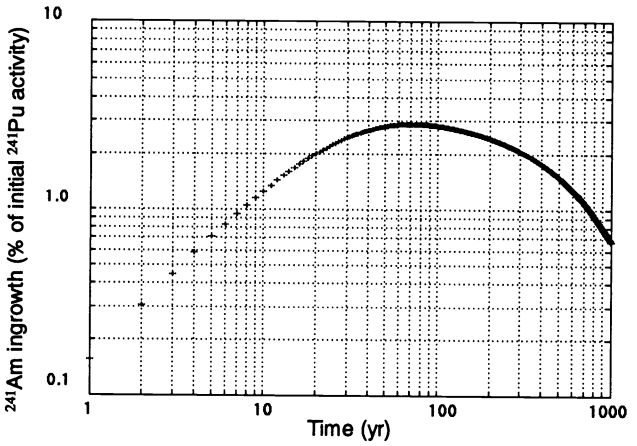

Fig. 1. Ingrowth of ^{241}Am activity from ^{241}Pu

METHODS

To determine the chemical yield, we used calibrated sources of ^{236}Pu and ^{242}Pu. Soil sample size was 10 g, obtained from a 5 cm depth coring cylinder. We ashed the soil samples at 400°C for 4 h and then digested them in a mixture of HCl and HF, followed by HNO_3. Plutonium preconcentration was by neodinium hydroxide precipitation, followed by ion exchange. For hot particles and vegetation, the samples were ashed and plutonium (IV) extracted with trioctylamine (TOA) in 6M HNO_3. Extraction efficiency was at least 85%. Finally, all samples were electrodeposited onto stainless steel disks.

To determine the activity of the α-emitting isotopes, we used semiconductor detectors manufactured by Ortec and Canberra Industries. Summary errors for $^{239,240}Pu$ activities were: *ca.* 20% for activities of 0.03–0.05 Bq kg^{-1}, *ca.* 10% for 0.5–5 Bq kg^{-1} and <6% for 5–50 Bq kg^{-1}. We measured ^{241}Pu activities with the Wallac Quantulus 1220™ liquid scintillation spectrometer. Chemical yield was deduced from the α-spectrometry measurements using either the ^{236}Pu or ^{242}Pu yield tracer. We based the absolute calibration of the ^{241}Pu on the similarity between ^{241}Pu and ^{3}H LSC spectra (Parus, Raab and Radoszewski 1993). We achieved improved energy resolution for samples extracted into an organic (toluene-based) scintillation cocktail in Teflon® vials (Fig. 2). We should point out the need for the determination of activity in the ^{241}Pu window from the α-emitting isotopes (Ryan *et al.* 1993). Beta to α ratios used were 0.11 and 0.39 for ^{236}Pu and ^{242}Pu, respectively.

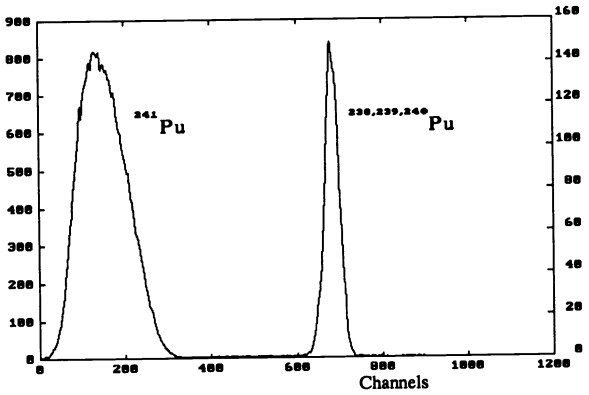

Fig. 2. α and β spectra of chemical separated (extracted) plutonium in hot particle N217506

We used a range of aluminium-Teflon® vials (3, 7, 15 and 20 ml). Counting performances for all vials are given in Table 2. It can be seen that each vial size gives good counting performance, with the 7- ml vials producing the best performance (Figure of Merit = 409). The counting parameters for the 7-ml vials were as follows: For α counting; background = 0.01 cpm, efficiency = 50%. For ^{241}Pu counting; background = 0.55 cpm, efficiency = 15%. MDAs, with a 50% uncertainty, for a 120-min counting period are 0.01 Bq for α emitters and 2.2 Bq for ^{241}Pu. The efficiency for high energy β-emitting radionuclides counted in such a manner is *ca.* 50%, background = 1.5 cpm and MDA (120-min count) = 0.12 Bq. The α and β spectra from ^{242}Pu and ^{241}Pu, electroplated onto a stainless steel disk, and counted in a 7-ml vial, are shown in Figure 3. The metal disk has to be <16 mm in diameter to fit the internal dimensions of the LSC vial.

TABLE 2. ^{241}Pu Counting Performance When Electroplated onto Metal Disks and Placed in Vials of Different Sizes

Vial size (ml)	Efficiency (%) (E)	Background (cpm) (B)	Figure of merit (E^2/B)
3	9.5	0.32	282
7	15	0.55	409
15	16	0.67	382
20	18	0.98	331

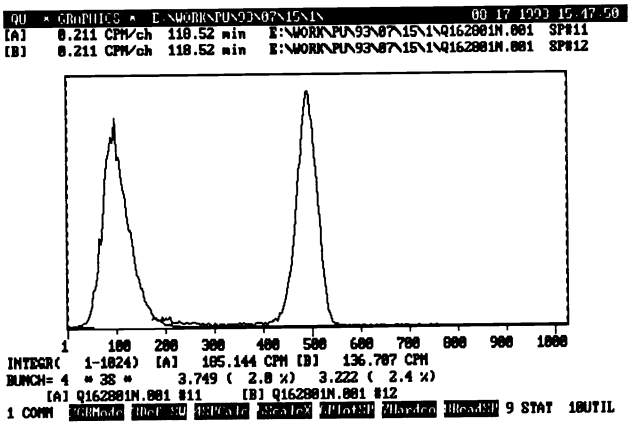

Fig. 3. Spectra obtained from a calibration disk source containing ^{241}Pu and ^{242}Pu and counted in a 7-ml aluminium-Teflon® vial

RESULTS

The results of our study are presented in Tables 3–5. Table 3 lists the results for ^{241}Pu and $^{238,239,240}Pu$ in some of the hot particles that were collected from soil samples. The results were decay corrected to the time of the accident. These demonstrate β/α ratios in the range 54.7 to 73.1, with a mean value of 60.2. This is in good agreement with the data of Begithsev *et al.* (1990) (Table 1) which equate to a ratio of 59. It was noted that the extractive techniques for sample preparation gave better energy resolution and sensitivity for ^{241}Pu determinations (see Fig. 2). The data for plutonium concentrations in vegetation samples from Kiev, collected during 1986, are given in Table 4. Here, the β/α ratios range from 10.2 to 43.6, with a mean value of 28.0.

TABLE 3. Plutonium Isotope Activities (Bq) and Activity Ratios in Some of the Hot Particles Collected from Soil Samples when Decay Corrected to the Time of the Chernobyl Accident (26 April 1986)

Sample	^{241}Pu	$^{238,239,240}Pu$	β/α ratio
1	110.4	2.0	54.7
2	1041.0	18.2	57.0
3	0.85	0.02	56.2
4	484.1	8.4	57.3
5	19.5	0.26	73.1
6	43.8	0.71	61.1
7	183.3	2.9	62.5
Average			60.2

TABLE 4. Plutonium isotope activities in 1986 from ash samples of grown plants (Bq kg^{-1}). Activities recalculated at the time of the accident.

N	Sample	Date	^{241}Pu	$^{238,239,240}Pu$	β/α
435	Leaves	3 May 1986	5312	130.5	40.7
438	Grass	3 May 1986	4585	136.0	33.7
3299	pine	25 July 1986	206	16.1	12.8
3300	Leaves (lime tree)	28 July 1986	1768	40.6	43.6
3306	Grass	28 July 1986	387	10.4	37.3
3476	Pine	11 August 1986	1015	89.5	17.9
3580	Leaves (lime tree)	26 August 1986	2614	255.5	10.2
Average					28.0

Our first measurements of ^{241}Pu concentrations in soils were carried out by washing the electrodeposited plutonium from the disks, following alpha spectroscopy. The measurements were made using Teflon vials and Optiphase Hisafe™ 3 cocktail. These data were in the range 11.9 to 480 Bq kg^{-1}. Further analyses were made by direct counting of the disks in scintillation vials. The results of ^{241}Pu analyses on soils, presented as averages and standard deviations for the most representative sample batches, are given in Table 5. The geometric mean for all the data is 20.5 Bq kg^{-1} of soil. We also predicted the ^{241}Am accumulation levels in soil samples (for the Ukraine as a whole and for representative regions) due to decay of ^{241}Pu. The maximum corresponds to about 3% of the initial ^{241}Pu activity. The geometric mean value for the predicted additional ^{241}Am soil contamination is 0.6 Bq kg^{-1}.

TABLE 5. Average ^{241}Pu Activity in Ukrainian Soil Samples and Predicted Maximum Additionally Accumulated ^{241}Am Levels in Ukrainian Soil Due to ^{241}Pu Decay (Within 50 yr After Chernobyl NPP Accident), Bq kg^{-1}

	^{241}Pu		^{241}Am	
Region	Average	STD	Average	STD
Ukraine	32.7	32.3	0.98	0.97
Vinnitsa	49.6	37.3	1.49	1.12
Kiev	35.2	38.0	1.06	1.14
Gitomir	22.5	15.0	0.68	0.45
Rovno	26.9	23.1	0.81	0.69
Cherkassy	55.2	41.0	1.66	1.23
Chernigov	15.6	17.5	0.47	0.53

CONCLUSION

A high degree of chemical purification is required if samples are to be analyzed for low levels of ^{241}Pu, to avoid contamination by natural β-emitting radionuclides. The solvent extraction technique is preferable for LSC as it gives 2–3 times better energy resolution. 2π α- and β-counting of metal disks with electrodeposited plutonium is a modern nondestructive method that is useful when additional sample measurements may be required at a later stage.

Our average result for β/α ratios of plutonium in hot particles is 60.2 and in close agreement with the result calculated from the inventories of plutonium isotopes that were estimated to have been released during the Chernobyl accident. The β to α ratio range determined for soil samples was rather wide, having a mean value of 49.6. This is attributed to the variable activities of both global weapons testing and Chernobyl fallout that are present in the soils.

The β/α ratios for vegetation samples collected from Kiev are lower than for hot particles (average of 28 *cf.* 60). We have no firm explanation for the difference in the ratios. Our only possible suggestion is that particles deposited where the vegetation samples were collected were much smaller than those deposited close to the plant and may have been released at a different time and been associated with different fuel elements.

Predicted additional accumulations of ^{241}Am due to ^{241}Pu decay will be *ca.* 3% of the ^{241}Pu activity, and for the samples that we studied, this will represent up to 4.6 Bq kg^{-1}. A lognormal distribution of the data gives an average additional level of 0.6 Bq kg^{-1}.

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